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Corrosion Inhibition of Brass in Industrial Cooling Water Systems

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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Original Research Article

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ABSTRACT

The inhibitory effect of PASAC1, PASAC 11 and PASAC13 on the corrosion behavior of brass in cooling water system at temperature of 25° C was studied by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), FTIR spectroscopy and metallurgical microscopy techniques. In the present paper, three types of organic inhibitors obtained by radicalic polymerization, i.e., PASAC1 (urea and maleic anhydride at molar rapport 1:1.5 at temperature of 140°C), PASAC 11 (polyaspartic acid and H₃PO₄ molar ratio 1:0.05 at temperature of 170°C), PASAC13 (polyaspartic acid 0.07 M and H₃PO₄, gravimetric ratio 1/1.5 with trisodium citrate at temperature of 200°C) was selected. The result of these polymers concentration on inhibition efficiency, the corrosion rate and surface coverage is investigated. Results show that these organic inhibitors exert a strong inhibiting effect on brass corrosion and acts as a mix-type inhibitor. The inhibition efficiency of organic polymers may be due to either the adsorption of inhibitor molecules

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building a protective film or the formation of an insoluble complex of the inhibitor adsorption obeys the Langmuir model. Further, characterization using FT-IR demonstrates the adsorption of organic inhibitors and the development of corrosion compounds at brass surface. EIS results confirm its corrosion inhibition ability.

Keywords: Organic inhibitor; brass; cooling water; electrochemical techniques; EIS and FT-IR.

1. INTRODUCTION

Adding of an inhibitor to the electrolyte is known as one method of inhibiting corrosion. Many studies on the addition of inhibitors have been done in the field of copper and brass corrosion inhibition in the different environments. Some researches [1-5] have reported the inhibiting effects of alkyl amines, phenyl-alkyl amines, imines derivatives and polymer inhibitors. Among all the inhibitors the most important are the organic ones, also called adsorption inhibitors. They check the corrosion action on the cathodic or anodic response or both of them. When they are presenting sufficient concentration, they usually affect the whole metal surface and therefore they cannot be called anodic or cathodic inhibitors. Therefore, the interaction of polymer and metal surface can be proved by adsorption isotherm and in general, inhibitors can function either by physical adsorption or chemisorptions with the metal [5-9].

Wet corrosion is a manifestation of the significance of electrochemistry and electrochemical adsorption in environmental degradation of industrial materials [6-10]. Electric field-assisted mechanisms of corrosion initiation processes involve a local penetration or degradation of passive films by activating ions and/or a coordination of surface metal sites by such ions. These interfacial events facilitate dissolution of metals, ultimately leading to corrosion. Conversely, adsorption/incorporation of corrosion inhibitors may prevent environmental corrosive attacks on the surface sites.

Metals corrosion in water –conveying system such as cooling water circuits is of major concern in industrial applications. In order to decrease corrosion of pipes, heat exchangers corrosion inhibitors are widely applied [9-15]. It is well known that, in all the cases of cooling water systems at the metal/water interface contact appear frequent corrosion processes which determine deposition of corrosion products, like scales. Due to the scales formation the heat exchange becomes more difficult, that disturbs the normal function of industrial installation

[10-18]. The use of inhibitors is one method to reduce corrosion and to protect metals and alloys in the aggressive medium. Recently, research in corrosion prevention is oriented to the development of green compounds with good inhibition efficiency, non-toxicity but low risk of environmental pollution. The ability of an inhibitor to provide corrosion protection therefore depends to a large extent upon the interaction between the inhibitor and the metal surface under corrosion conditions. Generally, it is assumed that strong adsorption of the inhibitors is a prerequisite [15-20].

Brass materials are relatively noble for which brass possesses attractive properties, namely, good corrosion resistance, high thermal and electrical conductivity and better resistance to bio fouling. It has been widely used in water distribution systems, water treatment units, condensers. desalination. power plant condensers and petrochemical heat exchangers. shipboard condensers, and many other applications [4-25]. Brass with 65% Cu and 35% Zn is prone to corrosion attack when exposed to a corrosive media because of the brass α -phase. Increasing the zinc content in the alloy changes α -phase to β -phase and accelerates the corrosion damage [12-23]. Dezincification of brass is one of the well-known and common processes by means of which brass loses its valuable physical and mechanical properties leading to failure of structure [9-25]. Therefore, the corrosion mechanism and the corrosion protection of brass in different aggressive media have attracted the attention of a number of investigators. Several researchers have investigated brass in view of resistance to corrosion [12-33]. Many techniques are used to improve the corrosion resistance of the brass used as mechanical parts in industry. The use of inhibitors, applying organic, metallic or inorganic coatings, cathodic and anodic protection, technique, galvanostatic polymerization nanostructurated coating methods are (techniques) for metal corrosion protection.

In our study, the corrosion inhibition of brass in industrial cooling waters system of inhibitors has been studied by electrochemical studies, electrochemical impedance spectroscopy FT-IR and metallography measurements. analysis. Electrochemical measurements are used to evaluate the anticorrosive properties of these new inhibitors. This work is a continuation of previous work [15-19] on the evaluation of some organic polymers that have been synthesized by radical polymerization using the microwaves energy. Well as development of new corrosion inhibitors for cooling water systems, as green inhibitors.

2. EXPERIMENTAL

Electrochemical polarization curves and electrochemical impedance spectroscopy measurements were performed out by using a single -compartment cell with the conventional three electrode set up at temperature 25°C. The cell was connected to a VoltaLab potentiostat coupled to a PC running Volta Master software. A saturated calomel electrode (SCE) was employed as the reference electrode and a bright platinum gauze as an auxiliary electrode. The working electrode was a brass with a surface area 0.5 cm². The electrochemical techniques employed were corrosion potential monitoring, anodic and cathodic polarization curves. Experimental methods were described previously [15-19]. The determinations were repeated with each solution until a good reproducibility of the results was obtained.

The inhibiting action has been studied from the polarization curves obtained usina the galvanostatic and potentiodynamic method and calculation of the potentiodynamic polarization parameters for corrosion of carbon steel OL 37 in presence and absence of different concentration of inhibitors. The electrochemical impedance spectroscopy (EIS) experiments were performed VolaLab PGZ 301 instrument using Potentiostat/Galvanostat (Radiometer Analytical, France) at open circuit potential disturbed with amplitude of 10mV ac sine wave and over a frequency range of 100 kHz to 40 MHz The working electrode made of brass had a surface area of 0.5 cm². The investigated inhibitors have been some polymers: PASAC1 (urea and maleic anhydride molar rapport 1:1.5 at temperature of 1400 C), microwave power 400 W, reaction time of 120 minutes, PASAC11-(polyaspartic acid and H3PO4 molar ratio 1:0.05 in propylene carbonate with sodium tart rate at temperature of 1700 C), microwave power 600 W, reaction time of 180 minutes, and PASAC-13 (polyaspartic acid 0.07

M and H3PO4, in ethylene carbonate/propylene carbonate, gravimetric ratio 1/1.5 with trisodium citrate at temperature of 2000 C), microwave power 600 W, reaction time of 90 minutes, that have been synthesized by radical polymerization using the microwaves energy at frequencies of 2450 MHz. Some properties of these new polymers are: PASAC 1: active substance 43%, pH=8.5, reduced viscosity of 0.17 dLg-1 and antiscale properties for 5pp =48% and for 10 ppm=65%; PASAC11: active substance 37%, pH=9.4, reduced viscosity of 0.21 dLg-1 and antiscale properties at 5pp =68% and for 10 ppm=88%; PASAC13: Active substance 45%, pH=9.6, reduced viscosity of 0.19 dLg-1 and antiscale properties at 5pp =79% and for 10 ppm=95%;

The aggressive medium has been industrial cooling water type S1 with the composition shows in Table 1.

Table 1. The composition of S₁

| Indicators | UM | Water type |
|--|--------|----------------------------|
| | | S ₁ , values of |
| | | parameters |
| PH | | 8.42 |
| Conductivity | µs/cm | 1061 |
| Alcalinity p | mval/L | 0.1 |
| Alcalinity m | mval/L | 3.3 |
| Total Hardness | mval/L | 8.3 |
| Calcium Hardness | mval/L | 3.0 |
| Chloride, Cl⁻ | mg/L | 117.01 |
| Sulfate | mg/L | 155 |
| Solid substances | mg/L | 2.75 |
| Organic | mg/L | 11.37 |
| compounds | | |
| Iron | mg/L | 0.073 |
| Aluminum, | mg/L | 0.0175 |
| Nitrite, NO ₂ ⁻ | mg/L | <0.1 |
| Nitrate, NO ₃ | mg/L | 10 |
| Phosphate, PO ₄ ³⁻ | mg/L | 0.046 |
| Copper, Cu ²⁺ | mg/L | <0.015 |
| Zinc, Zn ²⁺ | mg/L | <0.1 |

The structure of the brass is: Fe% 0.29. Cu% 65.60, Zn% 34, Si% 0.060, Pb% 0.059. Brass was obtained from MISUMI. Japan. The working electrode was brass in the form cylindrical with a surface area of 0.5 cm². The cylindrical form is favorite, as it ensures a higher surface and without edges. The brass electrode has been polished with emery papers of varied granulation (600, 1200, 2600, 4000 grid) up to mirror-luster. Then, the brass electrode was washed with bidistilled water and introduced in the electrochemical cell. The preparation of working

electrode before measurements is the same as described before [15-19]. Each experiment there was carried out at temperature of 25°C under atmospheric condition. Surface analysis on the brass sample of the adsorbed film has been examined by FTIR spectroscopy (FTIR spectrometer Tensor 37 Bruker optik GmbH, Germany) and metallographic micrographies (Microscope Hund H660, WETZLAR Germany).

3. RESULTS AND DISCUSSION

The treatment of the aggressive media can be performed by eliminating the active chemical agents or by means of inhibitors, what check the corrosive attack on the anodic or cathodic process or both. In this study, the anticorrosion protection is the result of the adsorption of these inhibitors on the electrode surface by formation an unseen film of some molecular thickness. The inhibition activity analysis of these inhibitors has been made by assuming that the mechanism of inhibition by organic molecules is chemisorption. [17-23].

The typical potentiodynamic polarization curves of the brass in cooling water S1 at various concentrations of PASAC1, PASAC11 and PASAC13 are presented in Figs. 1-3. Electrochemical corrosion kinetics parameters, i.e. corrosion potential, cathodic and anodic Tafel slopes and corrosion current density obtained from the Tafel extrapolation of the polarization curves, were given in Tables 2-4, where the inhibition efficiency were calculate. The presence of inhibitor causes a significant decrease in corrosion rate; change the anodic curves to more positive potentials and the cathodic curves to more negative potentials. This may be ascribed to adsorption of inhibitor over the surface.

Analyzing the cathodic potential curves from Figs 1-3 one can see that on the each cathodic curve there is a potential range where the cathodic current density decreases or is constant. It can see that, in this potential interval the brass surface is passivated. We assume that, in this potential interval the cathodic process is prevented by the passive film. In this potential interval occurs the oxygen reduction cathodic reaction by to equation:

$$\frac{1}{2}O_2 + H_2O + 2e \to 2HO^-$$
 (1)

This suggest that addition of these inhibitors of type PASAC gives rise to the formation of the passive film on the brass surface and further inhibits the corrosion.

As it can be seen, both cathodic and anodic reactions of brass electrode were inhibited with the increase of organic inhibitor concentration in cooling water system. The addition of PASAC 13, PASAC 11 and PASAC 1 decreases the corrosion current density (icorr) values significantly for all the studied concentrations due to increase in blocked fraction of the electrode surface by adsorption. This confirms that these inhibitors behave as a mixed inhibitor.



Fig. 1. Potentiodynamic polarization curves of brass in S₁+X ppm PASAC 1 at temperature of 25° C



Fig. 2. Potentiodynamic polarization curves of brass in S $_1$ +X ppm PASAC 11 at temperature of 25°C



Fig. 3 Potentiodynamic polarization curves of brass in S1 +X ppm PASAC 13 at temperature of 25°C

The electrochemical parameters derived from the polarization curves at different concentrations are given in Tables 2-4. From Figs. 1-3 and Tables 2-4, one can see that the addition of all three organic inhibitors led in all cases to a decrease of the corrosion rate and to increase of the inhibitor efficiency. The results obtained in this study could be explained by the effects of organic inhibitors on the electrochemical properties of the working electrode (brass). All the studied of organic inhibitors (PASAC11, PASAC13 and PASAC1) showed a very good inhibition properties for the corrosion of brass in cooling water system type S1 and the corrosion current

density decreased and the inhibitor efficiency increasing increased with inhibitors concentrations. By examining in comparison the inhibition efficiency and the corrosion rate (R_{mpy}, in mil per year; P, in mm per year and Kg, in gm ²h⁻¹) of all three inhibitors, in the identical condition, one can observe as, the PASAC13 and PASAC11 have a very good efficiency for anticorrosion protection of brass in S1 and PASAC1 had aood inhibition efficiency. Sometimes on the anodic curves appears oxidation peaks followed by the narrow passive range and a decrease of the current density (this behavior can be explained due to formation of oxo-hydroxo-complexes of Cu). The maximum efficiency is obtained at the inhibitor concentration for PASAC 13 is 20 ppm and 100 ppm, for PASAC11 is 50 ppm and 100 ppm and for PASAC1 is 50 ppm. These dates demonstrate as these polymers can be classified as mixed type corrosion inhibitors.

The variation of inhibition efficiency and current density with inhibitor concentrations is shown in Fig. 4. The inhibition efficiency increased with increase in concentration and current density decreased with increase in concentration and from Fig. 4, it can observe more the effect of these corrosion parameters on the electrochemical behavior of the brass in cooling water system (see Fig. 4). It is obvious from the figures. that all these compounds inhibit the corrosion of brass in cooling water system at all concentrations used in this study.

Adsorption isotherm is very important in determining the mechanism of organoelectrochemical reactions. Also, the greater inhibitor efficiency is an effect of the adsorption process. The adsorption isotherm can give important information on the interaction of inhibitor and metal surface. To measure the influence of organic inhibitor concentration on the corrosion rate, it is used to match the rate data to equilibrium adsorption expressions, as Langmuir equation: θ / (1- θ) =KC, [15-20] where θ is the degree of the coverage on the electrode surface by the inhibitor and K is the equilibrium constant of the adsorption process, θ is determined by: θ = (icorr-i.inh)/icorr where iinh and icorr are the corrosion current density in S1 with and without inhibitor.[14-19]. All correlation coefficient (R2) 0.99 (PASAC13-R2=0.99939: exceeded PASAC11- R2=0.99879; PASAC1- R2=0.99338) indicates that the inhibition was attributed to adsorption of these compounds on the metal surface.

Utilization of the Langmuir behavior is frequently justified with the argument that inhibition shall include adsorption.

In this study, straight lines were obtained when concentration Cinh/ θ were plotted against Cinh. with a slope of unity. The linear relationship suggests that the adsorption of inhibitors obeys the Langmuir adsorption isotherm (Fig. 5). The high value of the adsorption equilibrium constant reflects the high adsorption ability of this inhibitor on brass surface. The equilibrium constant of the adsorption process (Kads) is related to the standard adsorption free energy (ΔG_{ads}^{o}) obtained by the relation: [14-20].

The deduced value of ΔG_{ads}° obtained is negative and means that the adsorption of organic inhibitor is a spontaneous process, and furthermore the negative values of ΔG_{ads}° also show the strong interaction of the inhibitor molecule with the surface.

The obtained values ΔG_{ads}° around -20Kjmol-1 or lower indicates the electrostatic interaction between charged metal surface and charged in the bulk of the solution while those around -40KJmol-1or higher involve charge sharing or charge transfer between the metal surface and organic molecules (see Table 5) [28-31].

Mechanism of inhibition - From the results obtained, it was concluded that all the three organic inhibitors (PASAC 1, 11 and 13) inhibit the corrosion of brass in cooling water systems by adsorption of inhibitors at metal/solution interface. Adsorption of organic compounds can be described by physical adsorption process. This process is influenced by the nature and charge of the metal, the chemical structure of the inhibitor and the type of electrolyte. The inhibition efficiency of organic inhibitors (PASAC 1, 11 and 13) against the corrosion of brass in cooling water systems can be explained on the basis of the number of adsorption sites, molecular size and mode of interaction with the metal surface. Physical adsorption requires presence of both electrically charged surface of the metal and charged species in the bulk of the solution.

The corrosion behavior of brass in cooling water system at the various concentrations of PASAC 1, PASAC 11 and PASAC13 at temperature of 25° C was investigated by electrochemical impedance spectroscopy (EIS). Impedance measurements were performed at open circuit potential on the frequency range between 100 kHz and 40 mHz with an AC wave of \pm 10 mV (peak-to-peak) and the impedance data were obtained at a rate of 10 points per decade change in frequency.

Fig. 6 showed a typical set of Nyquist plots for brass in cooling water system in absence and presence of various concentrations of organic inhibitors. The impedance spectra of brass electrode show one capacitive loop. In all cases, it is found that the diameter of the capacitive loop increases with increase in PASAC1, PASAC11, PASAC13 resulting that the formed protective film has been accomplished by the addition of organic inhibitors. But, these capacitive loops are not perfect semicircles and this fact is attributed to frequency dispersion, largely attributed to roughness and inhomogeneities of the solid surface. Fig. 6 as well shows that the diameters of these semicircles in the presence of 50 ppm PASAC1+Brass-S1, 50 ppm and 100 ppm PASAC11+Brass-S1 and for 50 ppm PASAC13+Brass-S1 are much higher than those in the absence of organic compounds, resulting that has good anticorrosion protection on the brass in S1.



Fig. 4. Variation of current density and inhibition efficiency of the inhibitors: PASAC11, PASAC13 and PASAC1 at various concentrations for brass in S1 at 25°C

| Concentration | i _{corr} | R_p | R _{mpy} | | Kg | E (%) | -E _{corr} | ba | -b _c | θ |
|---------------|-------------------|--------------------|------------------|----------------------|--------|-------|--------------------|------------------------|------------------------|------|
| (ppm) | (µAcm⁻²) | KΩcm ⁻² | | P _{mm/year} | g/m²h | | (mV) | (mVdec ⁻¹) | (mVdec ^{⁻1}) | |
| 0 | 5.31 | 2.92 | 2.60 | 0.066 | 0.064 | - | 207 | 186 | 76 | |
| 20 | 1.225 | 20.93 | 0.65 | 0.0164 | 0.016 | 77 | 160 | 193 | 296 | 0.77 |
| 50 | 0.915 | 34.17 | 0.45 | 0.0113 | 0.011 | 83 | 157 | 134 | 291 | 0.83 |
| 100 | 1.16 | 19.95 | 0.567 | 0.0144 | 0.014 | 78 | 155 | 147 | 305 | 0.78 |
| 250 | 2.662 | 6.97 | 1.301 | 0.033 | 0.032 | 50 | 167 | 135 | 196 | 0.50 |
| 500 | 2.59 | 9.86 | 1.267 | 0.032 | 0.031 | 51 | 175 | 189 | 293 | 0.51 |
| 800 | 2.03 | 10.05 | 0.9584 | 0.025 | 0.0246 | 62 | 174 | 187 | 206 | 0.62 |

Table 2. Potentiodynamic polarization parameters of brass in S₁ at various concentrations of PASAC1 at temperature of 25°C

Table 3. Potentiodynamic polarization parameters of brass in S₁ at various concentrations of PASAC11 at temperature of 25°C

| Concentration | i _{corr} | R _p | R _{mpy} | | K _g | E (%) | E _{corr} | b _a | b _c | θ |
|---------------|-------------------|--------------------|------------------|----------------------|----------------|-------|-------------------|----------------|------------------------|------|
| (ppm) | (µAcm⁻²) | KΩcm ⁻² | | P _{mm/year} | g/m²h | | (mV) | (mVdec⁻¹) | (mVdec ^{⁻1}) | |
| 0 | 5.31 | 2.92 | 2.60 | 0.066 | 0.064 | - | 207 | 186 | 76 | |
| 20 | 0.151 | 89.92 | 0.074 | 0.0018 | 0.0018 | 96 | 151 | 117 | 196 | 0.96 |
| 50 | 0.126 | 181.26 | 0.061 | 0.0016 | 0.0015 | 97 | 168 | 127 | 186 | 0.97 |
| 100 | 0.116 | 170.25 | 0.056 | 0.0014 | 0.0014 | 98 | 162 | 89 | 183 | 0.98 |
| 250 | 0.449 | 43.88 | 0.219 | 0.0055 | 0.0054 | 91 | 197 | 87 | 184 | 0.91 |
| 500 | 1.158 | 17.52 | 0.567 | 0.0144 | 0.014 | 78 | 172 | 111 | 172 | 0.78 |
| 800 | 0.296 | 62.19 | 0.145 | 0.0037 | 0.0036 | 94 | 163 | 113 | 142 | 0.94 |

Table 4. Potentiodynamic polarization parameters of brass in S₁ at various concentrations of PASAC13 at temperature of 25°C

| Concentration | İ _{corr} | R _p | R _{mpy} | | Kg | E (%) | -E _{corr} | b _a | -b _c | θ |
|---------------|-----------------------|--------------------|------------------|----------------------|--------|-------|--------------------|----------------|-----------------|--------|
| (ppm) | (µAcm ⁻²) | KΩcm ⁻² | | P _{mm/year} | g/m²h | | (mV) | (mVdec⁻¹) | (mVdec⁻¹) | |
| 0 | 5.31 | 2.92 | 2.60 | 0.066 | 0.064 | - | 207 | 186 | 76 | |
| 20 | 0.167 | 106 | 0.081 | 0.002 | 0.002 | 97 | 199 | 92 | 137 | 0.97 |
| 50 | 0.194 | 96 | 0.091 | 0.0023 | 0.0022 | 96 | 198 | 95 | 145 | 0.96 |
| 100 | 0.185 | 98 | 0.09 | 0.0022 | 0.0022 | 96.5 | 195 | 96 | 146 | 0.96.5 |
| 250 | 0.280 | 78.6 | 0.137 | 0.0034 | 0.0033 | 95 | 172 | 136 | 224 | 0.95 |
| 500 | 0.462 | 47.38 | 0.226 | 0.0057 | 0.0056 | 91 | 166 | 109 | 205 | 0.91 |
| 800 | 0.330 | 51.36 | 0.161 | 0.0041 | 0.0039 | 94 | 167 | 87 | 180 | 0.94 |







In this paper of all the PASAC in the studied concentration interval, the electrochemical impedance spectra are characterized by one depressed semicircle, with a high frequency capacity loop and low frequency inductive loop. Deviation from perfect circular shape, often known as frequency dispersion was attributed to surface roughness and inhomogeneities of the metal surface.

Bode diagrams presented in Figs. 7-9 are in accordance with Nyquist diagrams. It can see that without of inhibitor the brass shows one time constant according to a phase angle of 30° at medium and low frequencies, this shows an inductive comportment with low diffusive predisposition. From Figs. 7-9 it can see that with the inhibitor, to seem a top corresponding to a phase angle of 75° which means that where the electrode has a strong capacitive behaviour, in according with the results obtained by electrochemical polarization and in concordance with the Nyquist diagrams [14-19]. Similar results were reported in several studies [13-20].

In this study of all three organic inhibitors in the studied concentration interval, the electrochemical impedance spectra are characterized by one semicircle and they were fitted using one time constant equivalent model with capacitance (C), the charge transfer resistance (R_t) and Rs solution resistance were obtained using the Nyquist diagrams [15-23].

The equivalent circuit used in this paper is shown in Fig. 10. The lower capacitance values for systems: Cooling water system -S1+Brass with PASAC-11, PASAC-13 and PASAC-1, indicate the inhomogeneity of the metal surface roughened due to corrosion. The double layer capacitance (Cdl) values decreases on increasing of the inhibitor concentration and reaches very low values for the optimum concentrations of inhibitors for all the studied systems indicating that the reduction of charges accumulated in the double layer due to the formation of adsorbed inhibition film. This behaviour has been described and discussed by many authors [15-27].

Several researchers have confirmed that FT-IR spectrometry is a powerful tool that can be used to determine the type of bonding for organic inhibitors adsorbed on the metal surface [37-42].

In this study, FT-IR spectra revealed that the new organic inhibitors were adsorbed on the brass

surface. All spectra in this paper were obtained at a resolution 4 cm⁻¹ in the range 4000-500 cm⁻¹. [15-19] In order to evaluate the protective layer formed on the metal surface in presence of inhibitor on the brass surface was analyzed by FT-IR spectra.

Transmission spectra of polymer PASAC11 is show in Fig. 11a. FT-IR transmittance spectrum of protective film adsorbed on the brass surface in S1 containing of 100 ppm PASAC11 is presented in Fig. 11b. From Fig. 11b it can be observed all important peaks of polymer PASAC11 appeared in the protective film. A broad band in the range from 3500-3300 cm⁻¹ is attributed to O-H stretching, which indicates that the protective film contains H2O. [15-20,37-42] The band in the region 3000-2700 cm-1 are attributed to C-H stretching vibration, the band at 1650 and 1540 cm⁻¹ corresponds to the C=O and N-H. The presence of C-N and C-O is indicates stretching at 1100-1000 and 900-800 cm⁻¹. [15-19,38-42] Comparing Figs. 11a and b, it can be suggested that PASAC11 is adsorbed on the brass surface.

Transmission vibrational spectra of polymer PASAC 13 is depicted in Fig. 12a. From fig. 12a, a broad peak at 3200 cm⁻¹ shows the existence of the C-H. The N-H and C=O stretching frequencies are manifest in the region 1642 cm and 1491 cm⁻¹. The weak band at 1325 to 1210 cm⁻¹ respectively is attributed to C-H bending. The FT-IR spectra obtained for the brass with 20 ppm PASAC13 inhibitor organic is presented in Fig. 12b. This shows the characteristic band for the adsorbed PASAC 13 on the metal surface. A broad band in the range from 3340 cm⁻¹ is assigned to C-H. In region 1520 cm⁻¹, the appearance of the peak is assigned to N-H. The presence of C-N is indicates stretching at 1436 cm⁻¹. The C-O bends are shown around at 1150-1000 cm⁻¹.

The transmission FT-IR spectra obtained of PASAC 1 and for 50 ppm PASAC1 inhibitor organic is presented in Figs.13a and 13b. From Figs. 13b it can be observed all important peaks for the adsorbed inhibitor PASAC1 on the brass surface. A medium band in the region at 3500-3200 cm⁻¹ is attributed to C-H. The band at 1600-1550 cm⁻¹ is assigned to N-H stretching vibration. The peaks for C-N stretching modes can be attributed in the range at 1400-1350 cm⁻¹. The bands 1200-1100 cm⁻¹ and 900-780 cm⁻¹ are assigned to C-O and C-N [15-19,37-42].



Fig. 6. The Nyquist plot for brass in S1 at various concentrations inhibitor

| The system | Type of metallic material | Values of K _{ads} , M ⁻¹ | Values of ΔG°_{ads} KJmol ⁻¹ | Type of adsorption |
|--|---------------------------|---|--|-----------------------|
| Cooling water type S ₁ +PASAC 1 | Brass | 1.088x10 ² | -12.447 | Physical adsorption |
| Cooling water type S ₁ +PASAC 11 | Brass | 1.171 x10 ³ | -17.497 | Physical adsorption |
| Cooling water type S₁+PASAC 13 | Brass | 7.366 x10 ³ | -22.051 | Physical adsorption |

Table 5. The values of K_{ads} and ΔG°_{ads} for PASAC-brass- cooling water systems



Fig. 7. The Bode plot for brass in S1 at various concentrations inhibitor PASAC-1



Fig. 8. The Bode plot for brass in S1 at various concentrations inhibitor PASAC-11



Fig. 9. The Bode plot for brass in S1 at various concentrations inhibitor PASAC-13



'W Transmittance [%] 70 80 Wavenumber cm-1 a) Transmittance [%] 5 90 95 Wavenumber cm-1 b)

Fig. 10. Equivalent circuit

Fig. 11. FT-IR transmittance spectrum of (a) PASAC11and (b) Brass+100 ppm PASAC11



Fig. 12. FT-IR transmittance spectrum of (a) PASAC13 and (b) Brass+20 ppm PASAC13

Comparing Figs. 11a-b, 12a-b and 13a-b it can be suggested that these organic inhibitors (PASAC11, PASAC13 and PASAC1) are adsorbed on the brass surface.

The formation of the protective surface film of organic inhibitor on the electrode surface was confirmed by metallurgical research microscope observation on the electrode surface. Fig. 14 shows some micrographies were analyzed for our systems: brass +S1 before and after a certain immersion in S1 in presence and absence organic inhibitor of type PASAC. [17-19] From Figs. 14b-j it is evident that the inhibited brass surface is smoother than the uninhibited surface where showing protective layers are formed of adsorbed films of inhibitor and corrosion products. These films act as a barrier between aggressive medium and metal surface and as a result the corrosion process is protected [15-19,41-43].

From Figs. 14(a-j), it can see that, the corrosive attack is much more accentuated in absence of these inhibitors than in presence of all the organic inhibitors. Hence, the protective nature of the film formed on the brass surface is confirmed by metallurgical microscopy techniques examination in very good concordance with the results obtained from electrochemical and FT-IR technique (see Tables 2-4 and Figs. 1-3).



Fig. 13. FT-IR transmittance spectrum of (a) PASAC1 and (b) Brass+50 ppm PASAC1



a) Brass polished

b) Brass+S1



c) Brass+50 ppm PASAC-11+S1

d) Brass+100 ppm PASAC-11+S1



E) Brass+20 ppm PASAC-13+S1



f) Brass+50 ppm PASAC-1+S1



g) Brass+50ppm PASAC-11+S1



h) Brass+100 ppm PASAC-11+S1



i) Brass+20 ppm PASAC-13+S1

j) Brass+50 ppm PASAC-1+S1

Fig. 14. Micrographies of the brass in s1 in presence and absence of organic inhibitor pasac-11, pasac13 and pasac-1

4. CONCLUSIONS

All the studied of these organic inhibitors (PASAC11, PASAC13 and PASAC1) showed a very good inhibition properties for the corrosion of brass in cooling water system type S1 and the corrosion current density decreased and the inhibitor efficiency increased with increasing inhibitors concentrations.

The adsorption of all organic inhibitors studied on the brass electrode obeyed the Langmuir adsorption isotherm model.

The results of FTIR, also reveals the adsorption of inhibitor molecule on the electrode surface and blocking the active sites.

PASAC11, PASAC13 and PASAC1 acted as mixed type corrosion inhibitor.

In all of the studies, the inhibitor type PASAC-13 and PASAC11 had a very good efficiency; PASAC-1 had a good efficiency.

The inhibition efficiency follows the order: PASAC13>PASAC11>PASAC1 because the presence of these inhibitors causes a significant decrease in corrosion rate.

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COMPETING INTERSTS

Both authors have declared that no competing interests exist.

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