Condensed Waters in Oil Industry

Inhibition of Corrosion Processes

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Some aspects of corrosion phenomena in condensed water have been reported. One Refining Installation from Lukoil - Ploiesti has been studied.OL37 steel has been used and INCOR107, as corrosion inhibitor has been tested. Polarization curves, EIS measurements, metallographic analysis have been reported. With 300 ppm of INCOR107 an % 85,60 IE has been obtained. A protective film on the metallic surface has been formed.

Keywords: corrosion rate, condensed water, corrosion inhibitors, protective film

This paper approaches a very important and current problem and is a part of an ample study regarding corrosion which takes place in aqueous media from oil industry and also the anticorrosive protection of the metallic materials used in petroleum industry [1-4].

Condensed water used as corrosive medium (representing a separate condense of gasoline) has been sampled from the reflux vessel V_1 of the oil atmospheric distillation column, from Lukoil Refinery of Ploiesti.

Experimental part

Experimental determinations established the corrosion behavior of OL37 steel in condensed waters, in presence and absence of INCOR107. This water soluble inhibitor , is formed of quaternary ammonium salts type, elaborated by INCERP S.A. Ploiesti.

The metallic electrodes have been polished with an abrasive paper of different granulations, to obtain a glossy and perfect homogenous surface. Then,they have been degreased in benzene, at boiling, cleaned in 5% HCl solution with inhibitor, washed with acetone and dried at room temperature.

The electrochemical studies have been performed with a VoltaLab 40 apparatus, which is a modern laboratory device, an assembly of potentiostat/galvanostat, with multiple functions and data processing software.

For the polarization curves drawing, it has been used the potentiodynamic technique. The electrode potential scanning has been performed at 2 mV/s rate and the working electrode potential has been measured in any moment with respect to the reference electrode, the saturated calomel electrode. As an auxiliary electrode, it has been used a platinum electrode.

By using Evans method (Tafel tangents extrapolation method), it has been determined the corrosion process rate, the corrosion current density, i_{cor}, as well as other kinetic corrosion parameters like polarization resistance (R_p), corrosion potential (stationary potential E_{cor} (i=0)), penetration index (P), cover degree (θ) and inhibitors efficiency (E.I.).

There have been performed electrochemical impedance spectroscopy measurements (EIS) and Nyquist and Bode diagrams were drawn. The corresponding parameters for Nyquist diagrams: R1 – electrolyte resistance, R2- polarization resistance of metal, and C- capacity of the double layer from the interface metal-solution have been determined.

By means of HUND H 600 metallographic/ metallurgic microscope, there has been achieved the metallographic analysis of the metallic electrodes surface, before and after the corrosion tests and the corresponding micrographics are presented .

Results and discussion

The chemical composition of OL37 steel and the condensed water characterization are presented in tables 1 and 2.

Using INCOR107 as corrosion inhibitor have been obtained the polarization curves of OL37 steel at 25°C, in

Table 1
CHEMICAL COMPOSITION OF THE OL37 STEEL

Chemical composition, (%)						
C	Si	Mn	P	S	Al	Fe
0,150	0,090	0,400	0,023	0,020	0,022	99,293

Table 2
CONDENSED WATER CHARACTERIZATION

pH	HCO_3 mg / l	D_T mval Ca^{2+}/l	TDS ppm	Resistibility kohm	Conductivity $\mu S.cm^{-1}$	Salinity ppt
5,1	73,2	4	232,5	2,582	380	0,187

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Table 3
CORROSION KINETIC PARAMETRS DETERMINED FROM THE POLARIZATION CURVES OL 37 STEEL IN CONDENSED WATER, IN PRESENCE OF INCOR 107 INHIBITOR

Inhib. conc. (ppm)	i_{cor} ($\mu A/cm^2$)	E_{cor} (mV)	βa (mV)	-βc (mV)	Rp ($ohm \cdot cm^2$)	P (mm/year)	I.E. (%)
-	7,906	- 721,5	116,0	139,6	2540	0,083	-
50 INC107	3,331	- 501,0	127,7	147,0	6500	0,035	57,86
100 INC107	1,334	- 431,6	91,6	97,9	11290	0,014	83,13
300 INC107	1,139	- 410,5	112,8	112,6	15690	0,012	85,60
500 INC107	2,175	- 452,9	104,6	120,4	8340	0,023	72,48
800 INC107	6,825	- 432,0	72,3	129,9	3290	0,072	13,67

condensed water, in absence and presence of different quantities of inhibitor.

In table 3 the kinetic parameters are synthetically presented and in figure 1 some characteristic polarization curves.

Analyzing the polarization curves from figure 1 there can be observed that, at reduced over voltages in condensed water, the corrosion process of OL37 steel is controlled by activation. There can be also observed that at high over voltages, on the anodic curve, the process is controlled diffusely and at very high over voltages, there is achieved a limit value of the diffusion current.

By comparative analysis of the cathodic and anodic curves, the potential domain where the process is controlled by activation is smaller than that on the anodic curve and the diffusion current density which appears faster on the cathodic curve has a smaller value than in case of the anodic process and it covers a large potential domain. We assume that, on this domain of potential, depolarization is produced by oxygen reducing, this process being controlled by diffusion.

From the allure of cathodic polarization curves, it can be observed that after the potential domain where the cathodic process is diffusely controlled, a sudden increasing of current takes place, which corresponds to hydrogen evolution (depolarization with hydrogen reducing).

A maximum efficiency (I.E. = 85,60%) of the corrosion process inhibition is noticed when it is used 300 ppm INC107. Over this value of the inhibitor concentration it is observed that it takes place an increasing of the domain which is controlled by activation on the polarization curve and thus, an increasing of the corrosion rate.

In all cases, it has been observed the formation of a black suspension in the electrolytic cell, probably because of the reaction between metal and sulphur compounds from condensed waters.

The electrochemical impedance spectroscopy measurements were performed for OL37 steel in condensed waters with and without adding INC107 corrosion inhibitor, at potential in open circuit. The obtained results are presented in Nyquist diagrams from figure 2 and Bode from figures 3-5 and the characteristic parameters for these are presented in table 4.

By analyzing Nyquist diagrams from figure 2 there can be observed in all studied cases, both in condensed water with and without INCOR107 inhibitor, the appearance of a capacitive loop which is very well defined in the domain of very high and medium frequencies.

Table 4
CHARACTERISTICS PARAMETERS FOR NYQUIST FOR OL37 STEEL IN CONDENSED WATER, IN PRESENCE OF INCOR 107 INHIBITOR

Inhibitor conc. (ppm)	R1 ($ohm \cdot cm^2$)	R2 ($ohm \cdot cm^2$)	C ($\mu F/cm^2$)
-	1398	525	1516,0
50 INC107	1630	2177	584,70
100 INC107	1362	4033	88,38
300 INC107	1116	5411	37,05
500 INC107	623	4454	80,04
800 INC107	675	1200	296,80

There can be also observed in the domain of small and very small frequencies the appearance of some inductive zones which evidence the adsorption of some reactive species on the electrode surface, followed by relaxing phenomena, evidencing reactions of these reactive species on the electrode surface.

The capacitive loops which appear at high and medium frequencies, evidence the formation on the electrode surface of some oxide films or other compounds which are opposed to charge transfer reaction, the diameter of these capacitive loops being a measure of polarization resistance. A larger and better drawn capacitive loop assumes the formation of a protective film (of oxide, salt, inhibitor), more stable, which is opposite to the charge transfer reaction and leads to a higher polarization resistance and to a smaller corrosion rate, too.

From the figure 2 there can be observed that the best capacitive loop is obtained in case of an inhibitor concentration of 300 ppm INCOR107 in condensed water, which means that in this case the protective film is the most stable, the polarization resistance in the highest and the corrosion rate is the smallest . This corresponds to the results obtained by potentiodynamic and electrochemical polarization measurements (fig. 1).

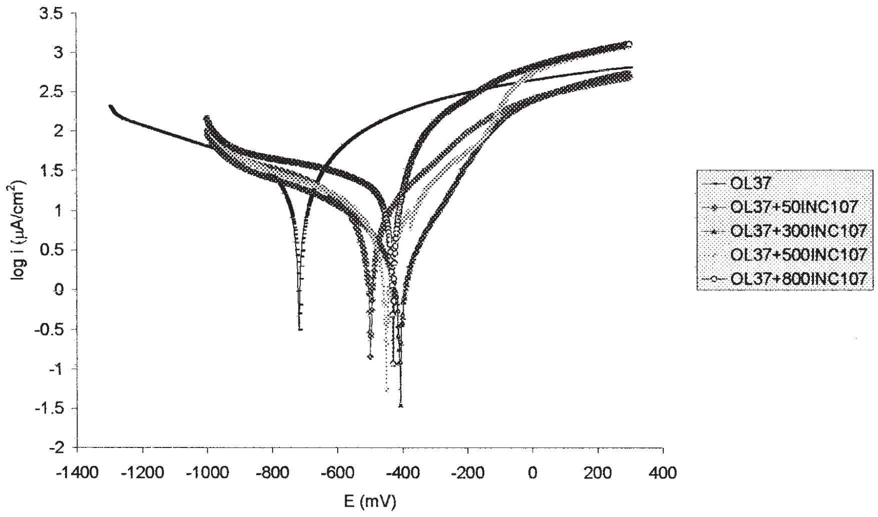

Fig. 1. Polarization curves for OL37 steel in condensed water with and without inhibitor INCOR107

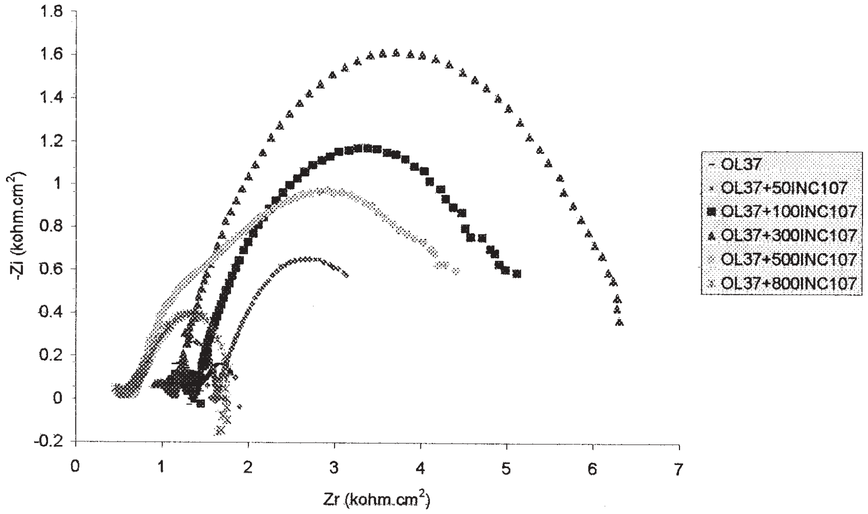

Fig. 2. Nyquist diagram for OL37 steel in condensed water with and without inhibitor INCOR107, at potential in open circuit

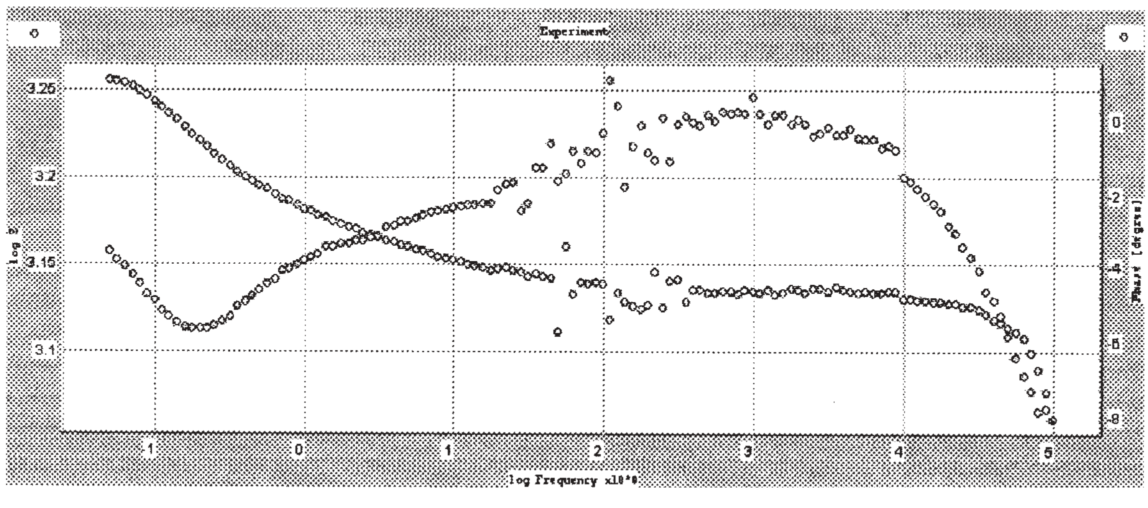

Fig. 3. Bode diagram for OL37 steel in condensed water

It can be observed (fig. 2) that the smallest capacitive loop and the smallest polarization resistance is obtained in condensed water without inhibitor, which means that in this case, the corrosion rate is the highest one.

The addition of INCOR107 inhibitor, in different concentrations, in all cases has lead to the capacitive loop increasing, of its diameter, thus , to the increasing of the polarization resistance, which means an inhibition of the charge transfer reaction, an increasing of the double layer and an inhibition of the OL37 steel corrosion in condensed water. This aspect can be observed from the Nyquist diagrams (fig. 2, table 4).

Some Bode diagrams for the OL37 steel in condensed water, with and without INCOR107 inhibitor are presented in figures 3-5. From the comparative study of these diagrams with Nyquist (fig. 2) it can be observed a concordance between the results obtained the two diagrams.

By analyzing diagrams from figures 4-5, there is observed that Bode diagrams from the condensed water with an inhibitor presents on the curve $\varphi = f(\log\omega)$, (phase angle function of frequency logarithm) a maximum very well defined, which corresponds to a single time constant and to the formation of a protective film (of oxide, salt, inhibitor), this aspect being also evidenced by the Nyquist diagrams by those well defined capacitive loops (fig. 2).

In this case also in the condensed water without inhibitor, on the curve $\varphi = f(\log\omega)$ it appears a maximum

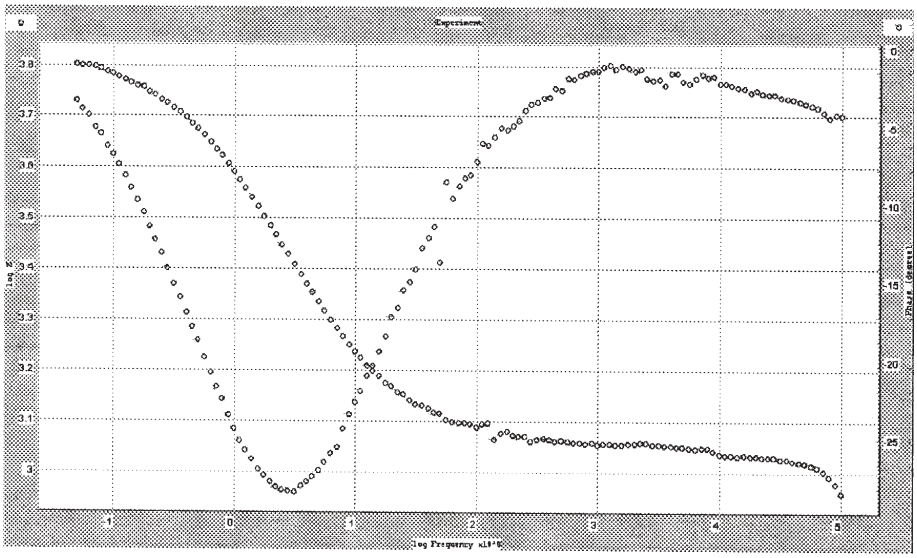

Fig. 4. Bode diagram for OL37 steel in condensed water with 100 ppm INC107

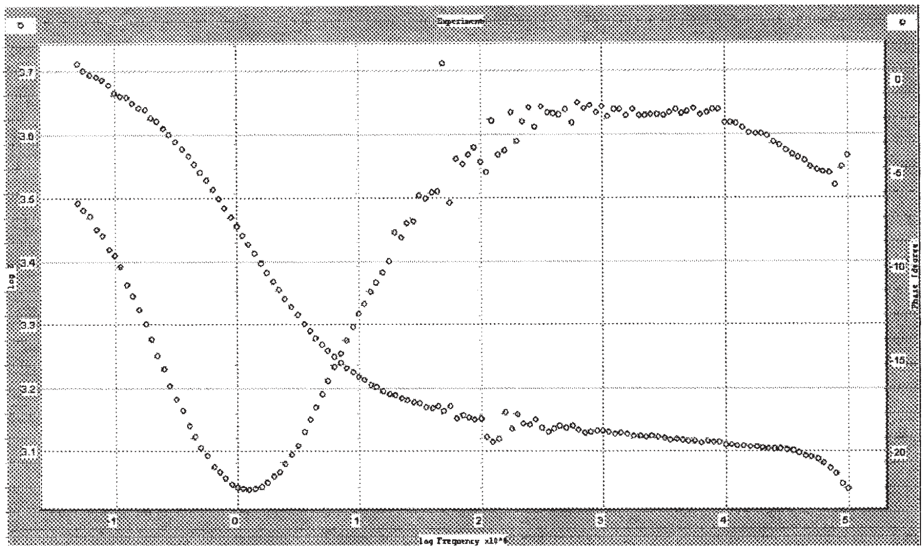

Fig. 5. Bode diagram for OL37 steel in condensed water with 300 ppm INC107

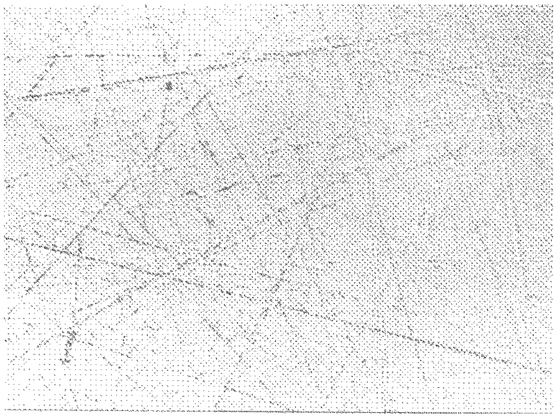

Fig. 6. Micrograph for OL37 not corroded- 200x

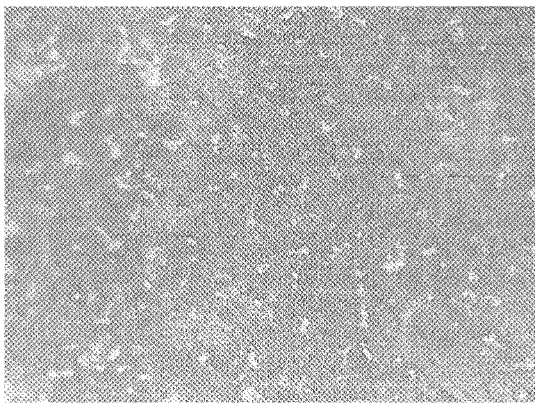

Fig. 7. Micrograph for OL37 in condensed water- 200x

less defined which corresponds to Nyquist diagram for the condensed water without inhibitor, when the capacitive loop and the diameter have been very small, so, polarization resistance has been small, what means that the protective film is not well formed, it is not stable and adherent and thus, corrosion rate is higher comparing to cases when INCOR107 corrosion inhibitor has been used.

It has also been performed the metallographic analysis of OL37 working electrode, before and after immersing in condensed water and there have been made the electrochemical polarizations.

In figures 6-8 are presented the structural micrographs of metallic electrode surfaces. From the analysis of surfaces structural micrographs there can be observed that corrosion processes are reduced when INCOR107 of 300 ppm is used in condensed water, this concentration corresponding to a maximum efficiency of the inhibition of corrosion processes while, for OL37 in condensed water

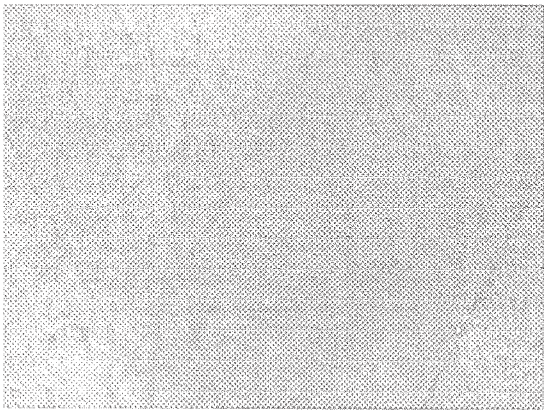

Fig. 8. Micrograph for OL37 in condensed water with 300 ppm INC107, after 72 h - 200x

without inhibitor, the micrograph (fig. 7) evidences an advanced corrosion.

Conclusions

Some corrosion phenomena in condensed waters, in oil industry, has been analyzed;

There has been tested the corrosion behavior of steel OL37 in condensed waters in presence of anticorrosive inhibitor INCOR107.

All the results obtained both by potentiodynamic method (polarization curves), by electrochemical impedance spectroscopy (EIS) and metallographic analysis lead to the conclusion that corrosion processes of OL37 steel in condensed water can be inhibited efficiently by means of INCOR107 inhibitor, at a concentration of 300 ppm, when there is obtained a maximum efficiency inhibition of 85,60%.

The inhibition of corrosion processes is explained by formation of a film (of oxide, salt, inhibitor) on the metal surface, which consists of a protective barrier at the separation surface metal/ condensed water.

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