

EFFECT OF URACIL ON THE CORROSION OF SEVERAL METALS IN ACID MEDIUM

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ABSTRACT

The inhibitive properties of uracil have been investigated against steel, zinc and lead in acidic solutions (1 M HCl). The efficiency is attributed mainly to the presence of N and O atoms as active centers for adsorption of the organic molecule onto the metallic surfaces. The efficiency of uracil increase in the order lead < steel < zinc. On lead, steel and zinc the inhibitive effect is due to the adsorption of uracil molecule. Measurements of the corrosion rates of the three metals with and without uracil (10^{-3} – 10^{-5} M) were performed. The desorption of uracil was elucidated. Thermodynamic parameters for adsorption process (ΔG_{ads} and f) of uracil were calculated using the Frumkin adsorption isotherm.

INTRODUCTION

Organic substance have been known as efficient inhibitors. This efficiency is attributed mainly to the presence of one or several N, S, or O atoms in the molecule as active centers for adsorption of the organic molecule onto the metallic surfaces [1-6]. Heterocyclic compounds containing nitrogen or oxygen have been proved to be effective inhibitors for the corrosion of many metals in aqueous solutions. Compounds such as benzimidazoles [7, 8] and 1, 2, 3- triazole derivatives [9, 10] were reported to effectively inhibit the corrosion of copper and its alloys. In previous work, some organic compounds containing nitrogen atoms were found to be effective inhibitors for the corrosion of copper in acid chloride solutions [11]. These considerations made interesting to investigate, from a theoretical and practical point of view, the behaviour of uracil against the corrosion of different metals.

EXPERIMENTAL

Pure metallic materials were used (Johnson-Matthey Gd) mild steel, zinc and lead. The samples were machined in cylindrical form 3 cm in length and 0.5 cm² cross sectional area. It was inserted in teflon tube so that only the flat surfaces were in contact with solutions. The surface preparation procedure [12] was shown to give reproducible polarisation curves, with an error in corrosion current density of less than 0.1 %.

Reagent grade chemicals were used and solutions were made up with bi-distilled water. A stock solution from uracile was prepared and diluted to the required concentrations (10^{-5} M to 10^{-3} M) with 1 N HCl acid solution. Before each measurements, the solution was purged with nitrogen gas for 6 hours. Measurements were carried out in presence of N₂ gas in order to avoid oxygen entrance into the electrolyte. The sample was allowed to reach a stable open-circuit potential, which was attained in about 30 minutes.

Afterward, cathodic and anodic polarisation measurements were performed at scan rate of 1 mV/sec.

The cell used for polarisation measurements was composed of two compartments separated by a fritted glass disc to prevent mixing of anolyte and catholyte. The cell with a double wall water jacket, and provide with two opening in the outer wall for inlet and outled and can be connected to the external closed-loop water circulating system (Haakn West Germany) for the accurate temperature control. A conversion three electrodes were used, the auxiliary electrode was a platinum sheet, the working electrode was a lead, steel or zinc anode, and the reference electrode was a saturated calomel electrode (SCE) with a Luggin capillary.

Potentiokinetic studies were performed using a corrosion measurement system, a model (273 soft) corrosion software potentiostat/galvanostat. The cathodic polarisation measurements were obtained at a scan rate of 1 mV/sec and the potential ranging from -500 to + 100 mV.

The electrochemical parameters of uracil, which were obtained from the potentiokinetic polarisation curves at 30 °C are listed in Table 1. These include; the corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafel slopes B_c and B_a respectively) and corrosion rate. An average of five independent runs were made.

Table 1. Influence of uracil on the main Electrochemical Parameters Obtained For Zinc, Steel and Lead in 1 M Hydrochloric Acid.

Metal Uracil Conc.	-E corr. mV/SCE	i_p corr. $\mu\text{A}/\text{cm}$	b_c mV	b_a mV	Corrosion Rate. (MPY)	θ	Protection efficiency P %
Steel Blank	513	218	-117.5	66.6	226.6	—	—
1 x 10 ⁻⁵	506	147	-113.5	97.8	153	0.3250	32.50
5 x 10 ⁻⁵	505	124	-111.5	116.5	129	0.4309	43.09
1 x 10 ⁻⁴	504	104	-112.5	121	125.8	0.5228	52.28
5 x 10 ⁻⁴	505	86	-111.2	128	89.4	0.6056	60.56
1 x 10 ⁻³	506	70	-112.7	132	72.8	0.6806	68.06
Zinc Blank	1045	5541	-195	70	7204	—	—
1 x 10 ⁻³	1046	4540	-160	68	5903	0.1805	18.05
5 x 10 ⁻³	1057	4317	-142	70	5170	0.2823	28.23
1 x 10 ⁻⁴	1065	1231	-140	75	1475	0.7952	79.52
5 x 10 ⁻⁴	1070	11053	-293	195	13236	—	—
1 x 10 ⁻³	1067	9514	-335	215	11066	—	—
Lead Blank	541	118	-420	34	289	—	—
1 x 10 ⁻⁵	447	26	-109	27	60	0.7923	79.23
5 x 10 ⁻⁵	554	16	-157	26	40	0.8615	86.15
1 x 10 ⁻⁴	555	14	-126	26	33	0.8858	88.58
5 x 10 ⁻⁴	555	12	-113	26	29	0.8996	89.96
1 x 10 ⁻³	452	8.6	-75	25	20	0.9307	93.07

RESULTS

Table 1. compares the polarisation curves parameters measured under steady state conditions for the three tested metals in deaerated 1 M HCl solutions (uninhibited acid solution). Figs. 1-3 shows the polarisation-current curves for the three tested metals. It can be seen that in case of lead (Fig. 3) there is a large shift in the cathodic branch of the polarisation curve. This can be attributed to the high hydrogen overvoltage on lead metal [13]. It can also be observed that in spite of such shift, the cathodic Tafel slopes b_c have different values which means that the mechanism of the hydrogen evolution reaction is changed. The main parameters calculated from polarisation curves (Figs 1-3), given in Table 1, indicate that uracil is an effective inhibitor for the corrosion of steel and lead, but in case of zinc at lower concentration only uracil have an inhibitive effect, at higher concentration (conc. > 10) uracil has an acceleration effect in 1 M HCl solution. The increasing order of efficiency being zinc < steel < lead. It must be pointed out that these results have been obtained for 2h contact time between uracil and the metallic surface. Chloride ions have great tendency to adsorb on the metals surface [14]. Chloride ions has slight effect on the corrosion of zinc in acid solution [15].

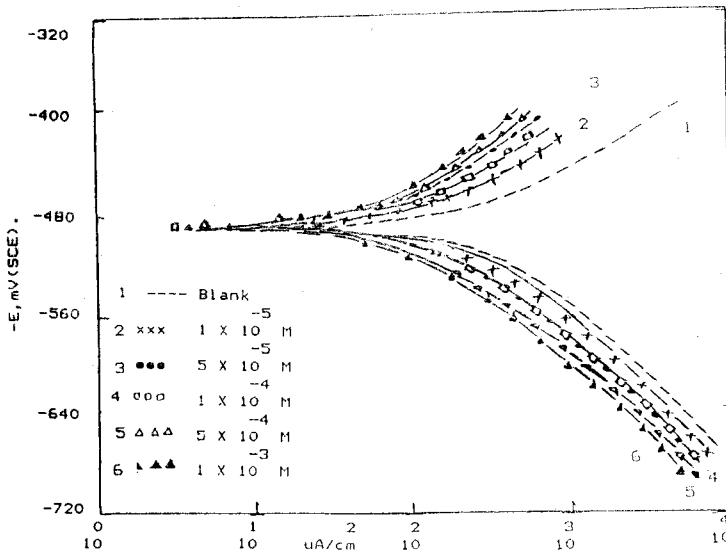


Fig. 1. Polarisation curves of steel at different concentrations of uracil in 1 M HCl.

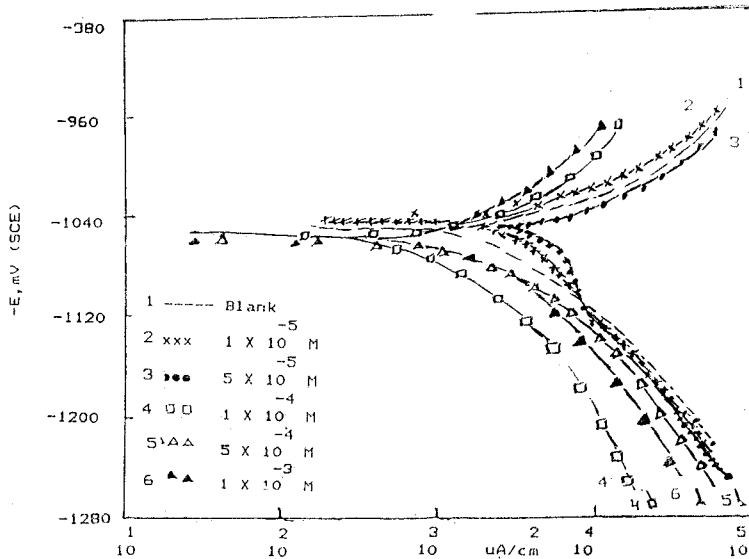


Fig. 2. Polarisation curves of zinc at different concentrations of uracil in 1 M HCl.

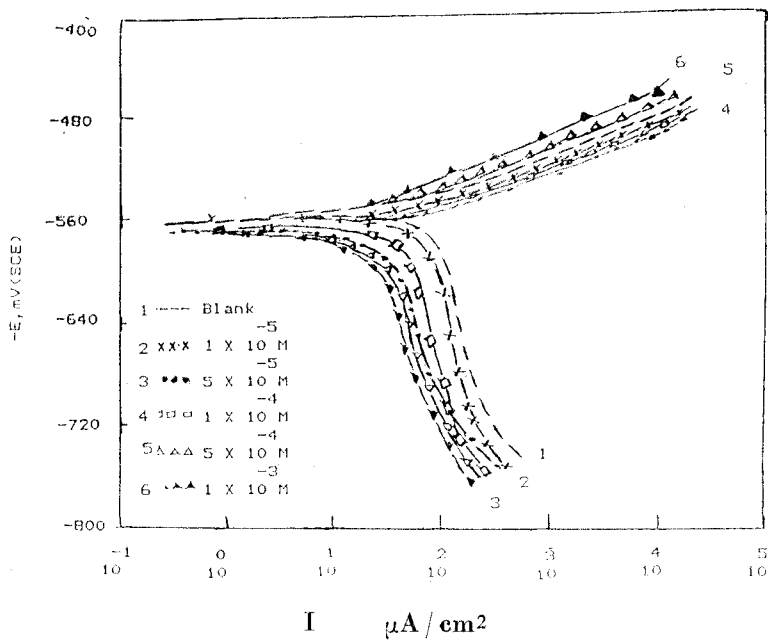


Fig. 3 Polarisation curves of lead at different concentration of uracil in 1 M HCl.

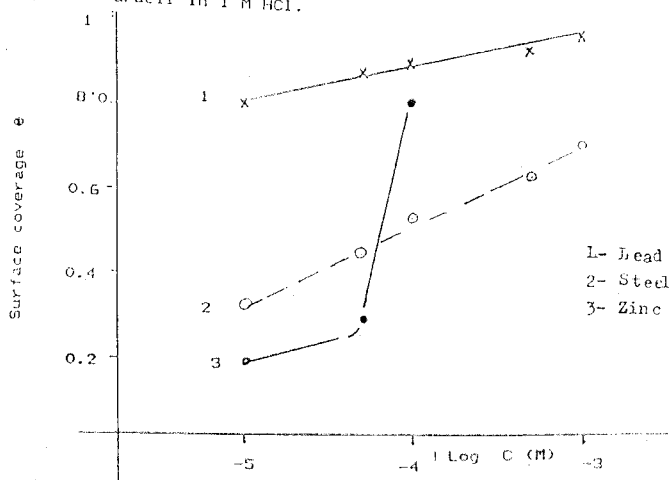


Fig. 4 Variation of surface coverage θ with logarithm of inhibitive concentrations in 1 M HCl.

From anodic and cathodic Tafel slopes (Table 1), it could be concluded that uracil affect both the anodic and cathodic reactions i.e. mixed inhibitor, and the inhibition increases as the inhibitor concentration increases with the exception of Zn.

The inhibition efficiency, P % was calculated using Equation 1

$$P \% = \left(1 - \frac{i_{inh.}}{i_0}\right) \times 100 \quad (1)$$

where i_0 and i_{inh} are the corrosion current in absence and presence of inhibitor and the results are summarized in Table 1. The higher efficiency is for lead, while the lower efficiency is for steel at lower concentrations. The inhibition efficiencies follow the order lead > steel > zinc at constant concentration assuming that the inhibition occurs through chemisorption of the uracil molecules Adsorption isotherms of the inhibitor for the corrosion process have been discussed [16]. The Frumkin isotherm [17] has the formula.

$$KC = \theta / 1 - \theta \exp (-f\theta) \quad (2)$$

where C is the concentration of the adsorbed substance in the bulk of the solution and θ is the degree of coverage of the metal surface by the inhibitor. K is the modified equilibrium constant of the adsorption process, which is related to the standard free energy of adsorption according to the following equation.

$$K = 1 / 55.5 \exp (-\Delta^\circ G_{ads} / RT) \quad (3)$$

In equation 2 (f) is a constant depending on intermolecular interaction in the adsorption layer and on the heterogeneity of the surface. This parameter can either be positive or negative, but cannot have arbitrary large positive values.

The degree of coverage of the investigated surfaces by the adsorbed uracil was calculated from the equation

$$\theta = 1 - i_1 / i_2$$

where i_1 and i_2 are the corrosion currents in absence and in presence of uracil respectively.

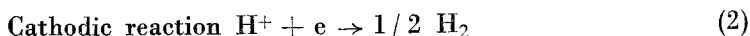
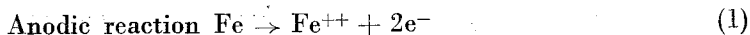
The present investigation examined the adsorption of uracil on steel, zinc and lead surfaces from HCl solution.

DISCUSSION

Uracil, obviously presents noticeable difference in its behaviour between the three metals, showing an inhibiting effect for Pb, Zn (at low concentration $< 10^{-4}$ M), and steel. For Fe, uracil behaves as mixed inhibitor (very slight positive displacement of the open-circuit potential).

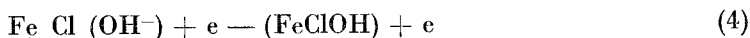
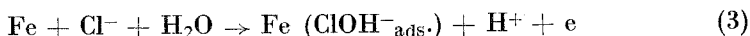
Steel

The cathodic Tafel slopes remain unchanged (112 mV) in presence of uracil. The inhibition process is assumed to occur via the adsorption of the inhibitor through the lone pair of electrons of the nitrogen atom. According to Jofa [18], chemisorbed halide ions create dipoles oriented to the surface. This increases the possibility of attachment of the protonated uracil to the electrode surface through the resulting dipoles. The corrosion of steel in acidic solution is the sum of the following reactions [19].

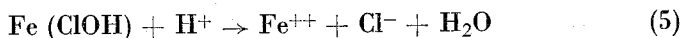


However, each of the reactions proceed with many consecutive steps depending on pH of the solution and the type of anions present in the solution.

Anodic dissolution of Fe in acidic solution could be written as



Adsorption of uracil on the electrode surface in acidic solution affects the kinetics of anodic dissolution of Fe.



The fractional order of the corrosion reactions with respect to $[\text{H}^+]$ and $[\text{Cl}^-]$ ions and the decrease of these orders in the presence of inhibitors indicate the complex nature of the corrosion and inhibition of mild steel in HCl [20].

Zinc

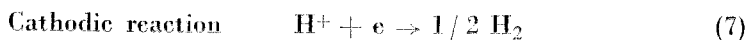
On zinc, the change in cathodic Tafel slope in presence of uracil shows that a change in the kinetics of the reduction of H^+ must occur.

This change leads to an acceleration of hydrogen evolution reaction (HER) and was attributed to the intervention of the protonated form of uracil into the cathodic process.

The high Tafel slope measured on zinc in the absence of uracil is probably due to the presence of some layers at the surface in which H_{ads} plays a determining role. The protonated uracil may be more easily reduced at the zinc surface, without H_{ads} being a reaction intermediate. The effect resulting from the adsorption of the protonated uracil in the outer Helmholtz plane would account for the change in Tafel slope. In our results, it seems more likely that a partial blocking of the cathodic zones by uracil occurs, which results in an increase of the overpotential on the unoccupied cathodic sites, the protonated uracil contributes to the partial increase of the hydrogen evolution reaction.

Lead

The conjugate anodic and cathodic reactions underlying the corrosion of lead in 1 M HCl may be represented by.



It is known that Cl^- ion act as anodic inhibitor and the inhibitive function may associated with its ability to become adsorbed on lead surface, thus chemisorbed ions create dipoles oriented to the surface [18]. This increases the possibility of attachment of uracil to the electrode surface through the resulting dipoles and thus retard the entry of Pb^{++} ions into the solution at the anodes. The decrease in the corrosion rate and i_{corr} with increase of uracil concentrations suggests that uracil act as anodic inhibitor (The anodic Tafel slope slightly changed). The higher cathodic Tafel slope in absence of uracil is mainly due to that the cathodic hydrogen evolution reaction is slow on lead, i.e. the H_2 overpotential is higher on lead [21]. The mechanism of hydrogen evolution reaction is not the same because of the change in the values of cathodic Tafel slope in presence of uracil, this change leads to an acceleration of the hydrogen evolution (HER) and was attributed as in case of zinc to the interaction of the protonated form of uracil into the cathodic process. From results in Table 1, it could be concluded that uracil has an inhibitive property and the corrosion rate decreases at higher concentration of uracil.

Table 1 shows that the values of degree of coverage (θ) for the three tested metals increased by increasing the concentrations of uracil except for zinc at high concentration (Fig. 4).

Using of K and f values obtained from Eqs (2) and (3) it was possible to calculate some of thermodynamical data concerning the adsorption process. The experimental data were collected in Table 2. They indicate that the adsorption of uracil on zinc metal has the lowest standard free energy of adsorption. The other two metals steel and lead have higher standard free energy of adsorption values. Fig. 5 showing the relation between the protective efficiency ($P\%$) and the standard free energy of adsorption (ΔG)^o_{ads}.

Table 2. Thermodynamic data calculated from experimental isotherm of adsorption of uracil on lead, zinc and steel metals in 1 N HCl at 30 C° at 10⁻⁵ M of inhibitor concentration.

Metals	f	K	-G kcal/mol
zinc	4.06	4000	3.2
steel	2.10	10000	3.4
lead	0.70	111111	4.1

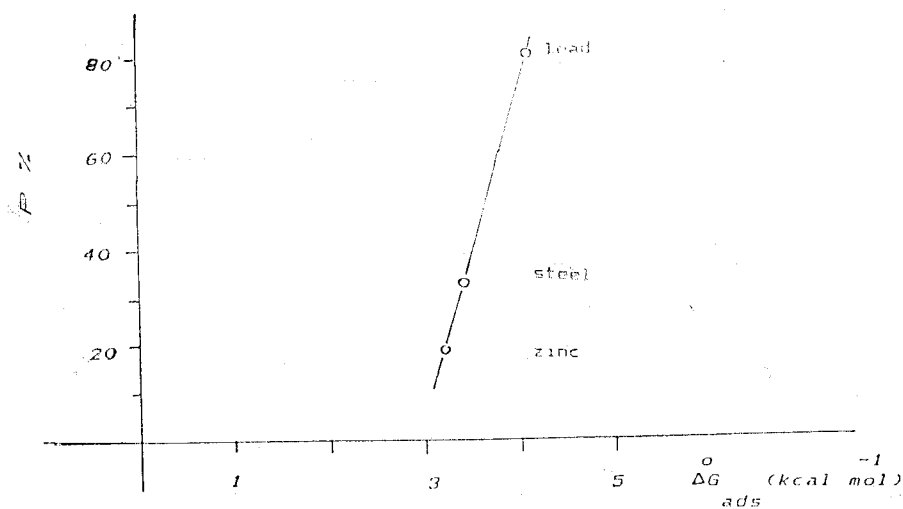


Fig. 5. The dependance of the protective effectiveness of the examined metals on their standard free energy of adsorption (ΔG), inhibitor concentration 0.00001 m/l.

The standard free energies of adsorption values of uracil for the three metals are within the limits of 3–4 kcal/mol which have been observed for the majority of organic inhibitors in aqueous media [22]. The positive values of f (Table 2) indicate that adsorption of uracil is accompanied by mutual attraction of the molecules.

The variation of ΔG°_{ads} with θ (Fig. 6) indicates the change in the mechanism of inhibitor action with inhibitor concentration. The negative values ΔG°_{ads} indicate that the adsorption of inhibitor on the metals surface is a spontaneous process. Also the increase in the negative values of ΔG°_{ads} with θ indicates that there is a lateral interaction between adsorbed inhibitor molecules on the surface [23].

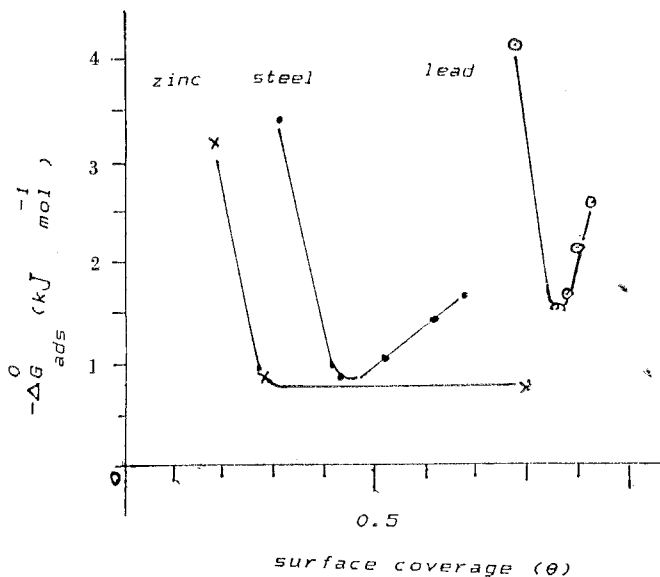


Fig. 6. Standard free energy for uracil on zinc, steel and lead metals as a function of surface.

CONCLUSION

1- Uracil is an effective inhibitor of the corrosion of lead, steel and zinc (at low concentration) in deaerated 1 M HCl.

2- It acts through a non-reactive coverage of the molecule in the case of Pb, Fe and Zn. For Zn and Pb, both protonated form of uracil

and adsorbed hydrogen play a role in the inhibition, the first one by accelerating the H.E.R., the second one by raising the inhibition rate of uracil.

REFERENCES

1. ABDEL-WAHAAB, S.M. and GOMMA, G.K. (1986). *J. Chem. Tech. Biotech.* 36, 185.
2. ABDEL-WAHAAB, S.M., GOMMA, G.K. and El-BARRADIE, H.Y. (1986). *J. Tech. Biotechnol.* 36, 435.
3. GOMMA, G.K. and El-BARADI, H.Y., SEPT. 24-26. (1986). *Proc. 1st Chem. Cong., Fac. Sci., Mans. Univ.*
4. GOMMA, G.K. (1988) *B. Electrochem.* 4 (11) November, 941.
5. GOMMA, G.K. (1993) *Indian Chemical Society*, Vol. 70, February, p. 132.
6. GOMMA, G.K. (1993) *Asian Journal of Chemistry*, Vol. 5 (3) 189.
7. LEWIS, G. (1982) *Ibid.* 22, 579.
8. PATEL, N.K., MAKWANA, S.G. and PATEL, M.M. (1974). 14, 91.
9. FOX, P.G. and BRADLEY. P.A. (1980) *ibid.* 20, 43.
10. SCHULTZE, J.W. and WIPPER MANN, K. (1987). *Electrochem. Acta*, 32, 823.
11. GOMMA, G.K. and WAHDAAN, M.H., *The First International Conference in Chemistry and its Applications, Doha-Qatar (1993).*
12. GOMMA, G.K. (1993) *Asian Journal of Chemistry*, Vol. 5 (2) 404.
13. BAUGH, L.M. (1979). *Electrochim. Acta* 24, 669.
14. KOLOTYRKIN. Ka. M. (1961). *J. Electrochem. Soci.* 108, 209.
15. HURLEN, T. (1962) *Acta Chem. Scand.*, 16, 1337, 1346.
16. MAYANNA, S.M., *J. Electrochem. Soc.* 122 (1975) 251.
17. FRUMKIN, A.N. (1925). *Phys. Chem.*, 116, (1926) 35, 792, 466.
18. JOFA, Z.A. (1966). *Annali. Univ. Ferrara, N.S. Sez V, suppl. No. 4*, p. 93.
19. WILLARS, H. and HAMPSON, N.A. (1976). *Surface Technology*, 4, 465.
20. JAYARAM, B. and MAYANNA, S.M. (1983). *Tetrahedron*, 39, 2271.
21. NIŞANCIOĞLU, K. and HOLTAN, H. (1979). *Corrosion Sci.* 19, 537.
22. DAMASKIN, W.W., PIETRIJ, O.A., BATRAKOW, W.W. (1968). *Adsorpcija Organicheskih Sojedinenijna Electroдах. Moskow.*
23. BOCKRIS, J.O.M., GREEN, M., SWINKELS, D.A.J. (1964). *J. Electrochem. Soc.* 111: 736.