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***“Corrosion inhibition of carbon steel in aqueous
solutions using some organic phosphorus compounds
and inorganic additives”***

A Thesis submitted

To

Faculty of Science

Cairo University

By

***Waleed Samy Abd El-Latif Hassan
(M.Sc.)***

For

***The Degree of Ph. D. of Science
(Chemistry)***

2008

CPAT
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Approval sheet for submission

Title of Ph. D. thesis: Corrosion inhibition of carbon steel in aqueous solutions using some organic phosphorus compounds and inorganic additives.

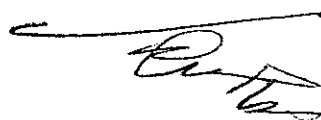
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ABSTRACT

Name: Waleed Samy Abd El-Latif Hassan

Title of Thesis: "Corrosion inhibition of carbon steel in aqueous solutions using some organic phosphorus compounds and inorganic additives"

Submitted by: Waleed Samy Abd El-Latif Hassan

For the Ph.D., Faculty of Science Cairo University 2008

The present work aimed to study the corrosion behavior of carbon steel in HCl solutions and its inhibition by using organo-phosphorus compounds and inorganic additives. The phosphorus compounds included Tri-n-Butyl Phosphonate (TBP) and Tri-n-Octyl Phosphine Oxide (TOPO). The inorganic additives were Zn^{+2} and Mg^{+2} ions.

The techniques of measurements used in this study were: weight loss, linear polarization, electrochemical impedance spectroscopy, corrosion penetration and potentiostatic polarization. The results indicated that the rate of corrosion of carbon steel increases with the increase of HCl concentration and with the increase of temperature. The inhibition efficiency (I.E %) was calculated from the data of the different techniques of measurements. The value of I.E% increases gradually with the increase of inhibitor concentration (TBP) or (TOPO) reaching a limiting value at higher concentrations of inhibitor. The combinations (TBP + Zn^{+2} ions up to 71.42 ppm) and (TBP + Mg^{+2} ions) have higher inhibition efficiency than TBP alone. Also, the combinations (TOPO + Zn^{+2} ions up to 71.42 ppm) and (TOPO + Mg^{+2} ions) have higher inhibition efficiency than TOPO alone.

The inhibitors adsorbed on the surface of the carbon steel according to Frumkin's adsorption isotherm. The adsorption of the inhibitors on the metallic surface could be physically or chemically. The presence of inhibitors in 2M HCl solution increases the value of the activation energy of corrosion process. The negative value of the free energy of adsorption (ΔG^*) indicates the spontaneous occurrence of adsorption on the metallic surface. The inhibitors TBP and TOPO acted as anodic inhibitors by the formation of Fe^{+2} -TBP and Fe^{+2} -TOPO complexes, respectively. The combinations (TBP + Zn^{+2} ions),

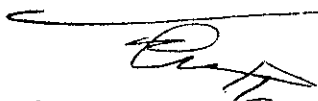
(TBP + Mg^{+2} ions), (TOPO + Zn^{+2} ions) and (TOPO + Mg^{+2} ions) acted as mixed inhibitors.

Key words: corrosion, corrosion inhibition, carbon steel, inhibitors and organo-phosphorus compounds.

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Waleed Samy Abd El-Latif Hassan

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Chapter One

Aim and scope of the present work

The carbon steel is used as essential parts in the manufacturing of installation used in the petroleum industry. These installations may be subjected to corrosion in different media. The use of inhibitors is one of the most practical methods for the protection against metallic corrosion, especially in acidic media. Hydrochloric acid is often used in pickling of steel and ferrous alloys. Inhibitors find application in pickling, cleaning of boilers, acidification of oil wells, ...etc. Organic compounds containing both phosphorus and oxygen atoms are of particular interest as they give good inhibition efficiencies.

The present work is devoted to the study of the corrosion behavior of carbon steel in hydrochloric acid solutions and its inhibition by organ-phosphorus compounds and some inorganic additives in combination with these organo- phosphorus compounds.

The organ-phosphorus compounds are: Tri-n-Butyl Phosphonate (TBP) with molecular formula $[\text{CH}_3(\text{CH}_2)_3\text{O}]_3\text{P}(\text{O})$ and Tri-n-Octyl Phosphine Oxide (TOPO) with molecular formula $[\text{CH}_3(\text{CH}_2)_7]_3\text{P}(\text{O})$. The inorganic additives are: Zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$).

The techniques of measurements used in this study are: 1- weight loss measurements, where the weight loss of the carbon steel coupons was determined in absence and in presence of different concentrations of inhibitors (TBP) or (TOPO) and the combination with Zn^{+2} or Mg^{+2} ions at different temperatures. From these measurements the corrosion rate (R_w , mpy) is determined. From the

values of R_w the inhibition efficiencies (I.E %) and surface coverage (θ) are calculated. 2- Linear polarization measurements which carried out in the range of -20 mV to +20 mV. From the plots of E versus i, the linear polarization resistances (R_p) are determined. The values of inhibition efficiency (I.E %) was also determined for the different inhibitor and their combinations. 3-Electrochemical impedance spectroscopy which are shown as Nyquist plots. From these measurements the values of charge transfer (R_t) and the capacity of the double layer (C_{dl}) are calculated for the carbon steel electrodes in different operating conditions. From the values of R_t the values of inhibition efficiency are calculated for the investigated inhibitors. 4- Corrosion penetration (CP) and parabolic rate constant (k) for the carbon steel coupons are calculated under the different operating conditions. The values of inhibitions efficiencies (I.E %) calculated from the values of CP and k for the different inhibitors and their combinations with Zn^{+2} and Mg^{+2} ions.

From the above mentioned measurements the type of adsorption isotherm is elucidated. This is done from the experimental relationship of the surface coverage (θ) and concentration (C).

From the results of weight loss measurements the values of activation energy of corrosion (E_{corr}^*) of carbon steel in 2M HCl solution in absence and in presence of different inhibitors (TBP) or (TOPO) and their combinations with Zn^{+2} and Mg^{+2} ions. Also, from these measurements, the values of enthalpy of adsorption, ΔH^* , are calculated to elucidate the type of adsorption (physical or chemical) of the inhibitors on the carbon

steel. Also, the values of ΔG^* are calculated to elucidate the spontaneity of the adsorption process. The values of ΔS^* are calculated from weight loss measurements.

The potentiostatic polarization measurements were carried out to elucidate the action of the inhibitors and their combination on the corrosion process of the carbon steel in 2M HCl solution.