# Novel Corrosion Inhibition for Carbon Steel Alloy: Synthesis and Characterization

**O. M. Abo- Elenien**
*Egyptian Petroleum Research Institute (EPRI). Petrol.. Appl. Dept.*
*Nasr City, Al-Zhor Region, P.O. 11727. Cairo, A.R.E.*

E. mail. drossamaa12@yahoo.com        drossama@material.tohoku.ac.jp    Tel: +2025083797;  +202 0122725626

**H. M. Abu-Alainin**
*Dept. Prod. Eng., Design Faculty Eng., Elminia Univ. (61111) Elminia, A.R.E.*

## Abstract:

The inhibitor effect of Tri-ethoxysilyl-di-ethylphosphate (TEOSDEOP) on the corrosion resistance of carbon steel alloy A36 in distilled water, tap water, sea water and 1 M hydrochloric acid were investigated by weight loss and electrochemical methods. The results suggest that TEOSDEOP inhibition efficiencies provides 99.19% for 10 ppm, 98.35% for 20 ppm in distilled, tap and seawater, respectively. While 97.65% for 30 and 40ppm in acid media. The corrosion potential in open circuit and electrochemical at low inhibitor concentrations were shifted towards positive direction (i.e. cathodic protection). On the other hand at high inhibitor concentrations, the potentials were shifted towards negative direction (i.e. anodic protection). Also, the electrochemical impedance results indicated that the inhibition efficiency increased with increasing the inhibitor concentrations. The graphical SEM images of coupons immersed 3hs in 1MHCl were investigated.

*Keywords: Carbon steel alloy A36; TEOSDEOP; corrosion inhibitor*

## Introduction:

Corrosion is the most localized problem encountered in petroleum, petrochemical and many industries. The extent of these problems was depended on the fluid composition (1-19). Inorganic compounds such as chromate, dichromate and nitrate are widely used as corrosion inhibitors in several media and for different metals and alloys (2). Its non-environmental-friendly (3, 4). Among alternative corrosion inhibitors, organic products containing one or more polar functions (with N, O and S atoms) have π electrons and showed to be quite efficient to prevent corrosion (5,6 ). The inhibiting action of those organic compounds is usually attributed to interactions with metallic surfaces by adsorption. The polar function is frequently regarded as the reaction center for the adsorption process establishment (7), wherein being the adsorption bond strength determined by the electron density and polarizability of the functional group (8). The corrosion inhibition of carbon steel alloy in acidic aqueous solutions by different types of organic compounds has been studied widely (1-17). Existing data show that most organic inhibitors act by adsorption on the metal surface (19-22).

This phenomenon is influenced by the nature and surface charge of metal, the type of aggressive electrolyte, and the chemical structure of inhibitors (1-27).

The dissolution and passivity of iron in aqueous solutions have been studied extensively during the last decades owing to their scientific and technological importance particularly to corrosion and protection of materials in presence of electrolytes (1 -18).

In certain field's activity, the use of inhibitors for mitigation of corrosion is the method of choice. The evaluation of the effectiveness of corrosion inhibitors is an important research and development activity among both users and the manufactures of these products. Techniques for controlling corrosion are subdivided into design, materials selection use of coating, electrochemical protection and chemical inhibition by additives known as corrosion inhibitors (1-30).

In this work, the behavior of TEOSDEOP compound as corrosion inhibitor for carbon steel alloy A36 in aqueous and HCl acid medium were studied by weight loss and electrochemical (open circuit potential, potentiodynamic polarization and electrochemical impedance spectroscopy) techniques. The coupons surfaces were also analyzed employing scanning electron microscopy (SEM) to evaluate its condition after been located in the aggressive media without and with inhibitor.

## Experimental

The coupons and bar of unused petroleum carbon steel alloy A36 were used for experiments. Surface of specimens were mechanically polished on wet silicon carbide paper grades 120, 320 400, 600, 800,100 and 1200, then rinsed with double- distilled water, degreased in ethanol before use, and dried at room temperature.

The TEOSDEOP was prepared according to three steps. First, 1.0 mol of phosphoric acid was reacted with 3.0 mol of dry ethanol in presence of water a zoetrope and 0.5 ml HCl as catalyst to form tri-ethyl phosphate (TEPO). It was purified by vacuum distillation and its structure was confirmed by FT.IR. Second, 1.0 mol of tetra-chlorosilane was reacted with 4.0 mol of dry ethanol under inert media and triethylamine as acid acceptor. Then, the product tetra-ethoxysilane (TEOS) was purified by vacuum distillation and confirmed by FT.IR. Finally, 1.0 mol of TEPO was treated with 1.0 mol of TEOS in presence 0.5ml HCl as catalyst to form TEOSDEOP. This product was distilled under vacuum and confirmed by FT.IR.

The IR spectrum of the synthesized TEPO, TEOS and TEOSDEOP are measured by using FT.IR. Spectrometer model 550 Nicollet Magnet.

The experimental work was carried out in the absence and presence at different concentrations (10, 20,……..100ppm) of the corrosion inhibitor TEOSDEOP, in distilled, tap and sea water (D.W, T.W, S.W) at ambient temperature for 90 days. These tests were carried out in a glass container 500 ml. using closed system. The same steps were carried out in 1 M HCl for

7 days. The weight loss for each specimen was calculated from the weight before and after immersion. The efficiency of inhibitor was evaluated and visually inspected. Weight loss experiments were carried out according to ASTM G31 [22].

For electrochemical measurements, the cell contained five openings: three of them were used for the electrodes and two for air free. The counter electrode (CE) was a platinum wire, the reference electrode was a saturated calomel electrode (SCE) and working electrode (WE) was a carbon steel rod.

Open Circuit potentional of carbon steel alloy electrode was measured against time with respect to saturated calomel electrode (SCE) in 1 M HCl solution. These measurements were performed in presence or absence of different concentrations of the inhibitor TEOSDEOP compound using a Volta lab Radiometer PGZ 301 potentiostate/galvanostat interfaced with Volta Master 4. All potentials in the text are quoted versus this electrode. The working electrode (WE) was a 0.867 $cm^2$ carbon steel rod mounted in a glass tube with Araldite epoxy. The working electrode surface was polished with 600, 800, 1000 and 1200 emery paper. Subsequently, the electrode was cleaned, degreased with acetone, rinsed with deionized water and air dried. The potentiodynamic polarization curves were accomplished in agreement with the ASTM G5 [22].

For potentiodynamic measurements, the cell was used a conventional three electrodes SCE, CE and WE. The potentiodynamic current – potential curves recorded by varying the electrode potential automatically from – 1000 to + 2000 mV with scan rate 20mVs$^{-1}$. The Volta Master 4/Voltalab PC Software were used.

Electrochemical impedance spectra were obtained in the frequency range 100kHz to 10mHz and a sine wave with 10 mV amplitude was obtained using a Volta lab PGZ 301 Radiometer Copenhagen potentiostat interfaced with a microcomputer running Volta Master 4.0 software for data acquisition and analysis. A Hitachi- Amray 1810 scanning electron microscope, and suitable visual images were recorded photographically.

## Results and discussion
### FT-IR Characterization

Fig.1-a illustrates the FT.IR spectrum of TEOS compound, the characteristic band of the -SiOCH$_3$ group appeared at 1190 cm$^{-1}$ indicating the formation of alkoxysilane. The bands at 1000-1400 and 3560 cm$^{-1}$ illustrate the stretching vibration of C-O-Si groups and the bands at 2870-3050 cm$^{-1}$ illustrate the – CH$_3$ aliphatic groups. Also, the disappearance of the bands at 3000-3300 cm$^{-1}$ indicates the reaction completion. On the other hand Fig.(1-b) shows characteristic bands of TEOP compound at 1090 cm$^{-1}$ for -POCH$_3$ group, indicating the formation of alkoxyphosphate and 1150 cm$^{-1}$ indicating the P=O group. Also, a band 2870-3050 cm$^{-1}$ was observed assigned for the stretching of – CH$_3$ aliphatic groups. Characteristic bands at 879and 3200 cm$^{-1}$ indicate the formation of Si – O – P bonds for TEOSDEOP Fig. (1-c).
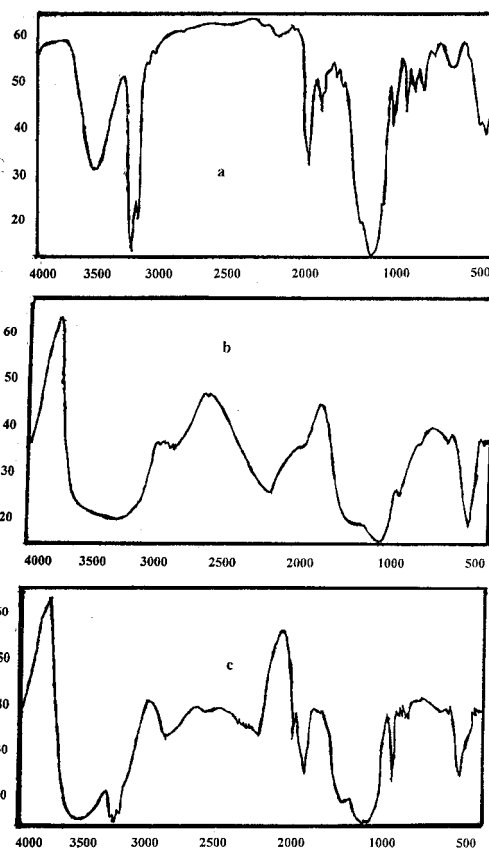


Fig (1) I.R spectrum of a) TEOS, b) TEOP, c) TEOS- DEOP compounds.

## Weight loss

Fig. 2 illustrates the relation between the inhibition efficiency (E %) and concentration of TEOSDEOP (10 to 100 ppm). It also shows the E dependence on the immersion time. E was calculated by the following equation [23]:
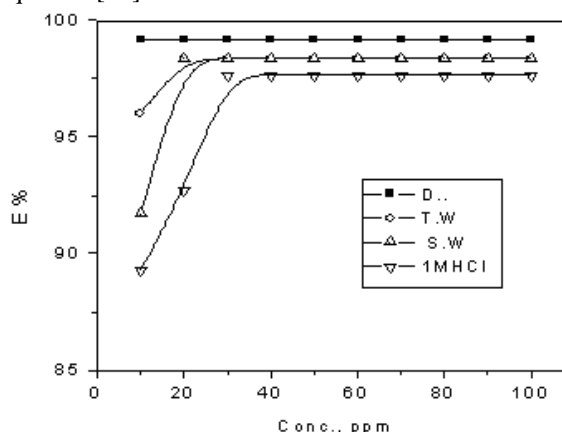


Fig .(2) Effeciency of the inhbitor TEOSDEOP in different media

$$E \% = \frac{W_0 - W}{W_0} \times 100$$

where W and $W_0$ are the corrosion rates calculated in presence and absence of TEOSDEOP, respectively.

From these data, one may conclude that, the efficiency of TEOSDEOP as corrosion inhibitor can be optimized at 99.15% (10 ppm.), 98.35% (20 ppm.) for distilled, tap, and sea water, respectively, while 97.65% (30-40ppm) for 1 M HCl. Visual inspection of the specimen surfaces after duration tests in distilled, tap, sea water and 1M HCl in absence and presence of TEOSDEOP were

carried out by using glass power magnifier for determining the corrosion spots (dust / pitting). From this inspection, it is clear that, in absence of the inhibitor, the surfaces of specimen were covered by bale brownish to dark brownish color in distilled, tap and sea water. While in presence of corrosion inhibitor TEOSDEOP, the surfaces of specimen are free from any spots/pitting at concentration from 20 to 100 ppm for all of the distilled, tap and sea water. On the other hand in acidic media the corrosion spots were not appeared upon using concept ratios 30 ppm. These results indicate that the amount of corrosion was decreased by increasing the concentration of corrosion inhibitor. Regarding weight loss results, it's obvious that, the efficiency of inhibitor results is in agreement with visual inspection data.

## Electrochemical results

Figs. 3 and 4 shows the open circuit potential (OCP) and the potentiodynamic polarization curves for carbon steel alloy in 1 M HCl solution without and with different concentrations of corrosion inhibitor TEOSDEOP (10 to 100ppm). In Fig. 3, OCP displaced towards positive potentials at concentrations 10 to 50 ppm, while at concentration from 60 to 100 ppm the OCP displaced towards negative potentials. This behavior suggests a possible spontaneous film formation onto the metallic surface, which might control and reduce the alloy dissolution. The reached OCP after 80 min of immersion is TEOSDEOP concentration-dependent, being more positive at lower TEOSDEOP concentrations and negative at higher concentrations. According to Riggs [6], the classification of a compound as an anodic or cathodic type inhibitor is feasible when the OCP displacement is measured for the blank solution. Here, the inhibitor action was found in both anodic and cathodic parts of potentiodynarnic polarization curves, it has been perceived that both the anodic current density $(b_a)$ and the cathodic current density $(b_c)$ in presence of any TEOSDEOP concentration was changed from in its absence. This means that TEOSDEOP ion decreases both the anodic and cathodic dissolution of carbon steel and the hydrogen evolution reaction. The results clearly shows that TEOSDEOP is mixed-type corrosion inhibitor.
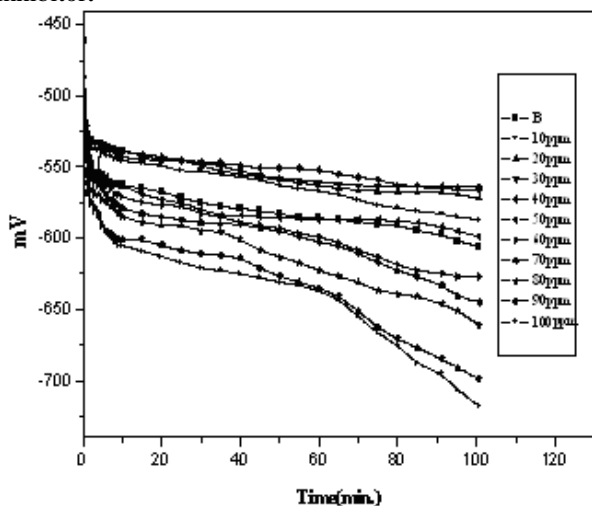


Fig. 3 Potentional-time (OCP) curves of carbon steel alloy in the 1MHCl in absence and presence of different concentration of the TEOSDEOP inhibitor.
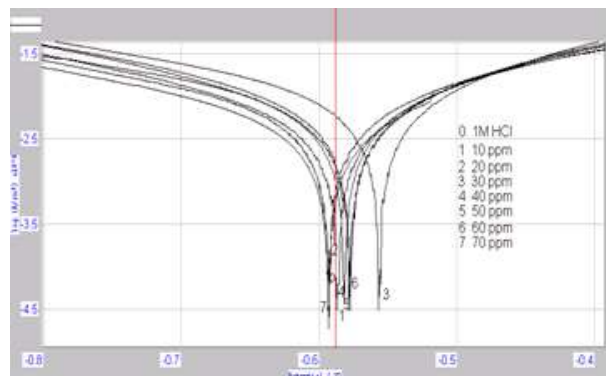


Fig. 4 Galvanic polarization curves for carbon steel alloy in 1M HCl in absence and presence of different concentration of inhibitor TEOSDEOP

These results are more confirmed by galvanostatic polarization measurements (Table 1).

Table (1) Galvanostatic polarization data of carbon steel alloy in 1 M HCl with and without inhibitor TEOSDEOP concentrations

| E% | CR mm/y | bc mv/ decade | ba mv/ decade | i corr. mA/cm$^2$ | E corr. mv(SCE) | Conc. (ppm) |
|---|---|---|---|---|---|---|
| - | 49 | - 166 | 145 | 4.2446 | - 581 | Blank |
| 83 | 8 | - 170 | 139 | 0.7013 | - 587 | 10 |
| 87 | 6 | - 180 | 148 | 0.5707 | - 593 | 20 |
| 90 | 5 | - 180 | 141 | 0.4317 | - 557 | 30 |
| 91 | 4 | - 181 | 150 | 0.3971 | - 582 | 40 |
| 91 | 3 | - 168 | 140 | 0.3893 | - 578 | 50 |
| 92 | 3 | - 157 | 141 | 0.3551 | - 577 | 60 |
| 92 | 1 | - 172 | 137 | 0.3427 | - 594 | 70 |

Figure 4 shows the typical galvanostatic polarization curves for carbon steel in 1M HCl solutions in absence and presence of the various concentration of TEOSDEOP. The Tafel lines are shifted to more negative and more positive for cathodic and anodic processes, respectively, relative to the blank curve. This means that, influence mixed type corrosion inhibitor (TEOSDEOP).

The following electrochemical parameters; cathodic and anodic tafel slopes ($b_c$ and $b_a$ respectively), free corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), and the percentage inhibition efficiency (E %) were obtained from the polarization curves and listed in Table 2. The E % was calculated according to the following equation [24]:

$$E\% = \frac{I_0 - I}{I_0} \times 100$$

Where $I_0$ and $I$ are the corrosion current density measured in blank and TEOSDEOP containing solution, respectively. The inhibition mechanism for the TEOSDEOP molecule involves a simple reaction site blocking. The corrosion potential values ($E_{corr}$) are displaced towards more positive potential with concentration 30 ppm then increase in the inhibitor concentrations causes displacement towards more negative potential i.e. cathodic/anodic protection. The order of inhibition efficiency of TEOSDEOP different further concentrations are derived by galvanostatic polarization measurements and listed in Table 2. which shows agreement with the above results.

Table (2) Parameters obtained by fitting the Nyquist plots shown in Fig. 5  with the equivalent circuit shown in Fig.6.

| TEOSDEOP Conc. Ppm | $R_S$ ($\Omega$) | Q ($\mu F/CM^{-2}$) | n | $R_p$ ($k\Omega$) | W | E (%) |
|---|---|---|---|---|---|---|
| 0.0 | 575 | 16.46 | 0.8 | 2.25 | $8.85 \times 10^{15}$ | - |
| 10 | 232 | 14.6 | 0.8 | 5.79 | $1.3 \times 10^{-1}$ | 57.26 |
| 20 | 230 | 12.3 | 0.8 | 7.81 | $3.2 \times 10^{-5}$ | 61.38 |
| 30 | 122 | 9.91 | 0.8 | 9.79 | $2.1 \times 10^{-4}$ | 79.16 |
| 40 | 122 | 9.89 | 0.8 | 11.83 | $1.5 \times 10^{-3}$ | 79.76 |
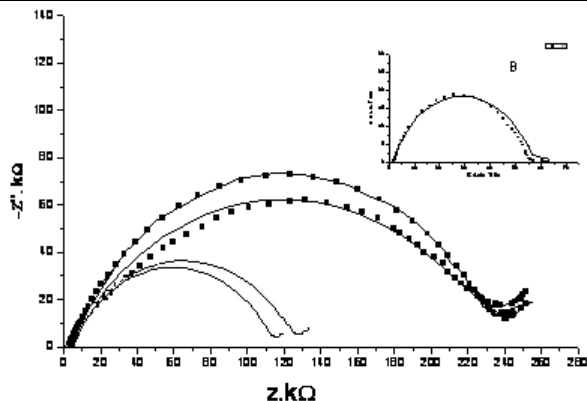


Fig.5 Nyquist diagrams for the carbon steel alloy electrode A36 after 24 hrs immersion in 1M HCl solution in the absence (B) and presence of 10,20,30 and 50ppm TEOSDEOP.
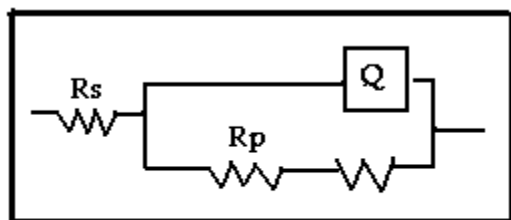


Figure 6 The equivalent circuit used to fit experimental data prisinted in Fig. 5.

The mechanism of protection carbon steel alloy in aqueous media D.W, T.W, S.W  and acidic media suggested the formation of protection film on the surface of specimens as shown in the following schematic diagram(1). Since the inhibitor has  8  polar groups it acts as a chelating agent i.e. the compound is more polar than water. In other words it has surface activity more than water. So that, the inhibitor compound reduces the surface tension of the aqueous media ($37mN/n^2$) more than the water ($72.29mN/n^2$) at 30°C. Finally, results show that the inhibitor covered the surface of specimen to form a protective film and agreed with elsewhere works [12].



Schematic digram(1) for formation protection film
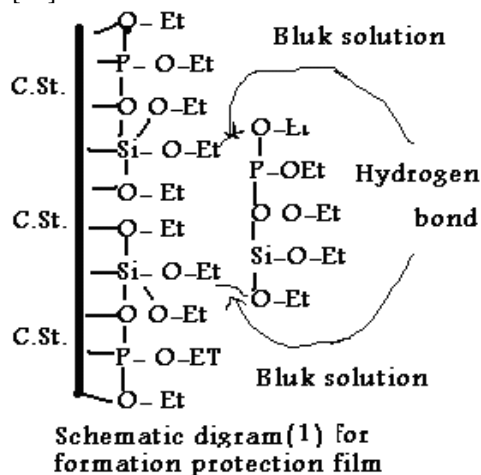
## EIS measurements

Typical Nyquist impedance plots obtained for carbon steel alloy electrode at an open circuit potential after 3hrs immersion in 1M HCl in absence and presence of 10,20. 30 and 40 ppm of TEOSDEOP are shown in Fig. 5. The dots in Fig. 5  represent the actual data and solid lines represent the best fit using the equivalent circuit shown in Fig. 6. The parameters obtained by fitting the equivalent circuit are listed in Table 2. Figure 6 and Table 2 indicate that the increase in TEOSDEOP concentrations raises the polarization resistance,Rp. The constant phase elements(Q) with  their n values close to 1.0 represent double-layer capacitors with some pores; the Q decrease upon of  TEOSDEOP and upon increase in its concentration, which are expected to cover the charged surfaces reducing the capacitive effects. It has been reported that, the semicircles at high frequencies are generally associated with the relaxation of electrical double –layer capacitors, and the diameters of the high – frequency capacitive loops can be considered as the charge – transfer resistance. This suggests that the electron- transfer reaction corresponding to the second semicircle takes place through the surface layer, which limits mass transport (Warburg) or acts just like another resistor. The presence of the Warburg (W) impedance indicates that the mass transport is limited by the surface covered with TEOSDEOP layer.

The inhibition efficiency, E%, of TEOSDEOP for the carbon steel alloy A36 electrode can then be calculated from the following equation [25]:

$$E\% = \frac{Rp - Rs}{Rs} \, x \, 100$$

Where Rs and Rp are the charge transfer resistance in blank and in presence of organic TEOSDEOP corrosion inhibitor, respectively. The attained results are shown in Table 2. The increasing of *Rs* value verified for 1MHCl in presence of TEOSDEOP pointed out a reduction in the alloy corrosion tendency, resulting in an E  of 79.76 %. A slightly decrease of Cdi values has also been detected, which corroborates the above proposal that TEOSDEOP acts as corrosion inhibitor by adsorption onto the metallic surface [26-30].

## SEM

Figs. 7 and 8 shows the graphical SEM images of coupons immersed 3hs in 1MHCl without and with 30ppm inhibitor respectively, the image in Fig. 7 show dark surface of specimens with some pitting, while the image in Fig. 8 show white surface and appear as coverlet chaps it's indicate the thin film of inhibitor was promoted by the adsorption onto the surface of carbon steel alloy Specimens.
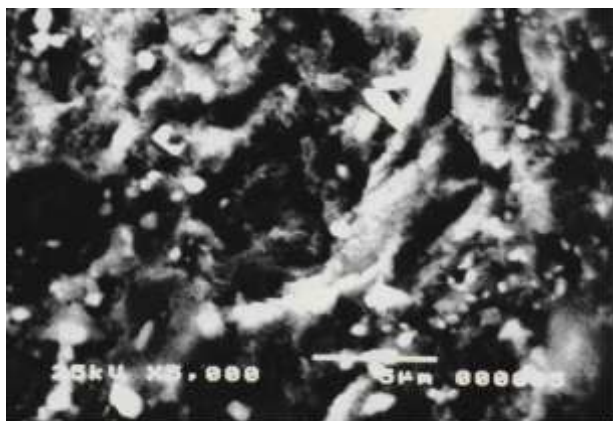
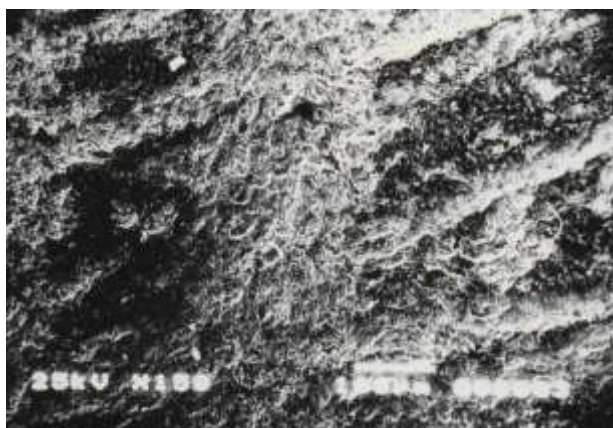Figure 7 SEM images of coupons immersed 3hr in 1MHCl without inhibitor



Figure 8 SEM images of coupons immersed 3hr in 1MHCl with 30 ppm of TEOSDEP inhibitor

## Conclusion:

The results obtained from weight loss and electrochemical data showed that TEOSDEOP inhibits the corrosion of carbon steel alloy A 36 in 1 M HCl solution. The OCP curves showed clear characterize of TEOSDEOP as cathodic and anodic type inhibitor. In most of the carried out experiments, the OCP displacement was found to be toward anodic at low concentration and at high concentrations toward cathodic. Therefore, TEOSDEOP has been proposed to be a mixed – type inhibitor. The maximum inhibition efficiency was 92 % for 1M HCl solution with 60 ppm. The corrosion inhibition process in 1M HCl was promoted by the adsorption of TEOSDEOP molecules onto the carbon steel alloy electrode surface.

## References:

[1] Bentiss,F. Lagrenee, M. Traisnel M. and Hornez, J. C. (1999) Corros. 55(10),p 968.

[2] M.G. Fontana. Corrosion Engineering, 3rd cd., McGraw-Hill, Singapore, 1986.

[3] J. Sinko, Prog. Org. Coat. 42 (2001) 267.

[4] S.E. Manahan, Environmental Chemistry, 6th cd., Lewis, Boca Raton, 1994.

[5] S.W. Dean Jr., R. Derby, G.T. Vondembusschc, Mater. Perform. 20 (1981) 47.

[6] O.L. Riggs Jr., Corrosion Inhibitors, 2nd cd., C.C. Nathan, Houston, TX, 1973.

[7] M.G. Fontana, K.W. Staehle, Advances in Corrosion Science and Technology, vol. 1, Plenum Press, New York, 1970.

[8] S. Sankarapapavinasam, F. Pushpanadcn, M.F. Ahmed, B. Elctrochcm. 5 (1989) 319.

[9] Yurt, A. Balaban, S. Ustun Kandemir, G. Bereket, B. Erk, Materials Chemistry and Physics 85 (2004) 420.

[10] F. C. Giacomeli, C. Giacomeli, M. F. Amadori, V. Schmidt, A. Spinelli, Materials Chemistry and Physics 83 (2004) 124.

[11] F. Bentiss; M. Lagrenee; and M. Traisnel Corrosion, 56(7) (2000) 733.

[12] O.M. Abo-Elenien, 14th Petroleum Conference, Control, Pipelines, Corrosion & Scales, Cairo, Egypt, 2 (1998) 106.

[13] R. Hariharaputhran; A.Subramanian; A. A. Antony; P.M. Sankar; A. Gopalan, T. Venkatakrishnaiyer , British Corrosion Journal 33(3) (1998) 214.

[14] E. S. Ferreira; C. Giacomelli, F. C. Giacomelli; A.Spinelli, Materials Chemistry and Physics 82 (2004] 129.

[15] F. Li; D. H. Bremner; Aa. E. Burgess , Corrosion Science 41 (1999) 2317.

[16] F. C. Giacomelli; C. Giacomelli; M. F. Amadori; V. Schmidt and A. Spinelli Materials Chemistry and Physics 83 (20004) 124.

[17] A. G. Zelinsky; B. Ya. Pirogov; O. A. Yurjev, Corrosion Science 46 (20004) 1083.

[18] K. Bouzek; H. Bergmann, Corrosion Science 41 (1999) 2113.

[19] A. Barbucci; G. Farne; P. Matteazzi; R. Riccieri, Corrosion Science 41 (1999) 463.

[20] S. Bilgic, Materials Chemistry and Physics 76 (2002) 52.

[21] H. Ashassi-Sorkhabi; M.R. Majidi; K.Seyyedi, Applied Surface Science, 225 (2004) 176.

[22] American Society for Testing and Materials, Annual Book of ASTM Standard, ASTM, Philadelphia, PA, 1978, p. 817.

[23] S.S.A.E. Rchim, M.A.M. Ibrahim, K.F. Khalid, Mater. Chcm. Phys. 70(2001)268.

[24] D.A. Skoog, D.M. West, F.J. Holler, Fundamentals of Analytical Chemistry, 6th cd., Saunders, New York, 1992.

[25] M. Ajmal, J. Rawat, M.A. Quraishi, Br. Corros. J. 34 (1999) 220.

[26] M.A. Quraishi, J. Rawat, Mater. Chcm. Phys. 77 (2002) 43.

[27] B.E. Mehdi, B. Mernari, M. Traisncl, F. Bcntiss, M. Lagrcnee, Mater. Chcm. Phys. 77 (2002) 489.

[28] l.L. Roscnfcld, Corrosion Inhibitors, McGraw-Hill, New York, 1981.

[29] M.A. Quraishi, J. Rawat, Mater. Chem. Phys. 70 (2001) 95.

[30] F. Bcntis, M. Traisne, L. Gcngembrc, M. Lagrencc, Appl. Surf. Sci. 161 (2000) 194.

# مانع تاكل جديد لسبيكة الكاربون ستيل. التركيب والمواصفات

**اسامة محمود ابو العينين**

**معهد بحوث البترول المصري، حي الزهور، مدينة نصر، 1 شارع احمد الزمر، القاهرة، جمهورية مصر العربية**

**حامد محمود ابو العينين**

**قسم هندسة الانتاج، كلية الهندسة، جامعة المنيا، (61111)، المنيا، جمهورية مصر العربية**

**الملخص:**

درست قابلية تثبيط التاكل لثلاثي– ايثوكسي سلايل– ثنائي– ايثايل فوسفيت(TEGSDEOP) على مقاومة التاكل لسبيكة الكاربون ستيل A36 في الماء المقطر و ماء الاسالة ومياه البحر ومحلول حامض الهيدروكلوريك 1M بطريقتي فقدان الوزن والالكتروكيميائية.

بينت النتائج ان كفاءة تثبيط التاكل الـ TEGSDEOP تصل الى 99.19% عند 10 ppm و 98.35% عند 20 ppm في الماء المقطر وماء الاسالة وماء البحر على التوالي. بينما تصل الى 97.65% عند 30

ppm و 40 ppm في الوسط الحامضي. ان جهد التاكل في حالتي الدائرة المفتوحة والالكتروكيميائية في تراكيز مثبط التاكل الواطئة تميل الى الاتجاه الموجب( حماية القطب الموجب). وبعبارة اخرى، في حالة تراكيز المثبط العالية يميل الجهد الى الاتجاه السالب( حماية القطب السالب). كما بينت نتائج الطريقة الكيميائية الكهربائية ان كفاءة التثبيط تزداد مع زيادة تركيز المثبط.