June 2009 Volume 4 Issue 1
CHEMICAL TECHNOLOGY
An Indian Journal
Trade Science Inc.
Full Paper
CTAIJ 4(1) 2009 [20-26]

New study for protection of carbon steel of petroleum equipment by Al/ Zn epoxide

Osama M.Abo-Elenine, Olfat E.Elazabawy, Nahed M.Amer*
Egyptian Petroleum Research Institute, Nasr City, Cairo 11727, (EGYPT)
E-mail : nahedamer56@yahoo.com
Received: 12th May, 2009 ; Accepted: 17th May, 2009

ABSTRACT

The epoxy compound; Kema POX RL 671 X 75; Chemicals and Technologies Company; is used as a resin material. It is formulated at ratio 100 parts with inorganic filler as 25 parts of aluminum past, 15 parts Talc, 10 parts Silica gel, 10 parts of TiO_2 and different ratios of Zinc dust 0, 5, 10,15, 20, 25 parts. These formulas are cured with Kema POX HF 115 70 at 10, 20 and 30 parts of toluene di-isocyanate (TDI). The visual inspection, physical, mechanical and chemical properties such as Wet Film Thickness (WFT), Dry Film Thickness (DFT), adhesion force, bending, impact, and hardness were studied. Sea water effect at period time of two weeks for the formed dry films was studied in salt spray test. The surfaces of the films were visually inspected by magnification power after all tests. The results indicated that the corrosion spots did not be detected on the surface of the formed dry films. Potentiodynamic polarization and electrochemical impedance spectroscopic studies were performed for the formed dry films. These results approved that; these films can be used as protecting agents for the surfaces of petroleum equipment against corrosion.

KEYWORDS

Coating carbon steel;
Physical;
Mechanical and chemical properties corrosion protection.

INTRODUCTION

The carbon steel is used in large scale for production and manufacture of petroleum, petrochemical equipments and different industries[1-4]. Corrosion problems may occur in numerous systems within the petroleum industry[5-11]. Organic coatings may be used to protect metallic materials against physical and chemical environments. Generally, inhibitive inorganic pigments are introduced into organic coatings as the main substance for corrosion inhibition. These pigments are played an important factor in the performance of a coating and act as anticorrosive resistance of metals[6,7]. For this purpose, the zinc is commonly used in the corrosion process of coatings and improves the barrier properties of the coating. It can also inhibit the cathodic process at the interface. However, also the zinc either acted in compliance with electrochemical mechanism or improved the barrier function of the binder[11]. Our knowledge was insufficient for better understanding of the role of zinc pigment on the corrosion of the coatings. Therefore, to clearly understand the action mechanism of zinc pigment, further studies on this topic were really of necessary.

Electrochemical impedance spectroscopy (EIS) is a well-known electrochemical means to evaluate the performance of organic coatings, and has proven to be a powerful tool for acquiring specific parameters of systems of organic coatings/metals mechanism information[12-16].

The aim of this work depends on the formulation of 100 parts epoxy compound with inorganic filler as 25 parts of Al paste, 15parts Talc, 10 parts Silica and 10 TiO_2 parts and different ratio of Zn dust 0.0, 5, 10, 20 and 25 parts to produce formulas Y_0 - Y_5. In order to study the effect of different Zn dust ratio in organic coating and to evaluate the performance of the coatings in presence of Al The visual inspection, physical, mechanical and chemical properties of the formed dry films are evaluated and discussed. Also electrochemical impedance spectroscopic studies were also performed on the formulas Y_0 - Y_5 in salt water as electrolyte media.

EXPERIMENTAL

Preparation of painting formula

100 parts of the epoxy compound Kema POX RLX 75from chemicals and technologies company were mixed with 25 parts of Al paste 15parts Talc, 10parts silica gel, 10 parts of TiO_2 and different parts of Zn dust 0, 5, 10, 15, 20, 25 parts respectively. The Kema POX HF 115 × 70 was used at three concentrated ratio 10, 20 and 30 parts as a curing agent, to obtain various formulation designated from Y_0-Y_5. These formulations were applied on the prepared surfaces of carbon steel specimens by brushing method.

Preparation of the surface metal specimen

Each specimen was cleaned, polished with different grade emery paper 150, 400 and 600. Rinsed with distilled water, degreased with acetone, weight and finally stored under vacuum. These formulations were applied by brushing method[17]. A set of specimens were coated with these formulas Y_0-Y_5 and cured under static air, ambient pressure and temperature.

Evaluation of the physical, mechanical and chemical properties

The coating films were examined by measuring the WFT, DFT, adhesion force, impact test, bending, hardness, pull off, chemical test (Salt Spray) and electrochemical test. The evaluation of the physical and mechanical properties of the formed coating films were carried out thought the following characterization techniques:

Physical properties

Visual inspection

The coating films on the surface of specimens were visually inspected after application to determine sealing, sagging, fish eyes, shrinking, coagulation, smoothes and homogeneity[18] were inspected and Tabulated.

Measuring the (WFT) of coating according to ASTM (D-1212-91)

The WFT Gauge type elcometer is used for assessing the thickness of freshly applied coating films for all formulations Y_0-Y_5 at ambient temperature. The obtained result was recorded after coating immediately.

Measuring the (DFT) of coating according to ASTM (D-1186 and D 1005)

The DFT of the formed films Y_0-Y_5 after cured, were measured by using Posit-Ector, model 6000-FT_2, coating thickness with probe gauge 6000-FT_2.

Mechanical properties. Adhesion technique according to ASTM (D 3359)

These test methods cover procedures for assessing the adhesion force of coating dry films to metallic surfaces by cross hatch cutting tool, X cut tape test are made in the film of the substrate surface, and pressure sensitive tape is applied over the cut and then removed. The data of adhesive forces for the formed films from the formula Y_0-Y_5 were recorded.

Impact test according to ASTM (G 14-88)

This test method cover the determination of the energy required to rupture coating films under specified conditions of impact from a falling weight, at varying heights. (Impact apparatus sheen instrument LTD). Visual inspection to detect the resultant breaks in the coating surface. (Maintain a constant height 1 meter then reduce the height by 50cm).

Bending test according to ASTM (D522)

These test method cover the determination of resistance to cracking (flexibility) using Conical Mandrel Test Apparatus.

Pull off strength of coating film by dolly test according to ASTM (D-4541)

The general pull off test is performed by securing a loading fixture (dolly) perpendicular to the surface of the dry coating film with an adhesive. After the adhesive is cured, a testing apparatus is attached to the loading fixture and aligned to apply tension normal to the test surface. The Elcometer 108 is a Hydraulic adhesion tester, the value of the force applied is displayed on a digital display .load is applied through the center of the dolly by hydraulic piston and pin. The pressure reacted by the dolly is the same as the pressure in the bore and is transmitted directly to the pressure slowly by turning the handle clockwise. The tester is available in the working range 0-3000psi (0to20MPa), Units of Psi (MPa=1N\mm^2)

Chemical properties

The corrosion resistance of the formed films is evaluated by Salt Spray test, potentiodynamic polarization and electrochemical impedance spectroscopic studies[19].

Salt Spray Cabinet Model Sf \ 450

Salt Spray Cabinet Model Sf \ 450was used for evaluating the corrosion resistance of the formed films was according to ASTM B117-03) and the test was conducted using 5.5% sodium chloride solution (PH 6.5-7). The corrosion resistance of the formed film was evaluated and recorded. The edges of the specimen were sealed with paraffin wax to avoid the excessive corrosion at the edges. Blank (without Zn dust) and the formed films were scribed to the base metal with a sharp needle so that the base metal is exposed to the salt mist. The spreading of corrosion from the X scribe, after 2 weeks of exposure were assessed and photographed.

Electrochemical measurements

Electrochemical experiments were carried out by means of impedance equipment (Tacussel- Radiometer PGZ 301) and controlled with Tacussel corrosion analysis soft ware (Volta master 4), connected to a personal computer. Measurements were obtained using the electrochemical cell containing five openings: three of them were used for the electrodes and two for nitrogen bubbling during all the experiments .The formed films are the working electrode. The counter electrode was a platinum electrode and the reference electrode was a saturated calomel electrode (SCE). All potentials in the test are quoted versus this electrode. The surface area of working electrode was 1cm^2 and mounted in a glass tube with araldite epoxy[20]

Potentiodynamic polarization technique according to ASTM G5-94[21]

The polarization measurements were carried out and the anodic/cathodic polarization curves were recorded under a constant sweep rate of 20 mvs^{-1}, initial potential -1000 mV and final potential 0 mV. The corrosion potential (E_{corr}) and corrosion current ensity (i_{corr}) were calculated using computer program method (Volta Lab master 4).

Electrochemical impedance (EIS) according to ASTM - G106-89

The EIS measurements were performed at open circuit potential in the frequency range from 100 kHz to 10 mHz, with an alternating current amplitude of 10 mV. Each measurement was taken after 2 hr of immersion in corresponding solution[22].

RESULTS AND DISCUSSION

TABLE 1 illustrates the chemical formula Y_0-Y_5 and curing agent percentages, which were applied on the prepared surface of specimens to optimize the condition of curing agent at 20 parts.

TABLE 1 : The chemical composition of the paintings formula Y_0-Y_5

Formula composition / parts	Y_0	Y_1	Y_2	Y_3	Y_4	Y_5
Epoxy Kema POX	100	100	100	100	100	100
Zn dust	0	5	10	15	20	25
TiO_2	10	10	10	10	10	10
Silica gel	10	10	10	10	10	10
Solvent	10	10	10	10	10	10
Al paste	25	25	25	25	25	25
	10	10	10	10	10	10
Curing agent ratio	20	20	20	20	20	20
	30	30	30	30	30	30

TABLE 2 data indicated that the time of touch dry for formula Y_0-Y_5 were decrease by increasing organic additives. Results indicated the compatibility of the binder with the inorganic filler and complete reaction with the

TABLE 2 : Data of the optimum condition for the curing agent with respect to time for the formula at ambient temp

Ratio of the curing agent	Touch dry time for each formed films from the formula (min.)					
	Y_0	Y_1	Y_2	Y_3	Y_4	Y_5
10	30	24	21	15	7	5
20	26	21-22	18-19	10	5	3
30	17	13	10	6	3	2

TABLE 5 : The mechanical properties of dry films formed from Epoxy compound

Formula	Bending	Adhesion	Impact		Pull off
			50 cm	100cm	
Y_0	Pass	fail	Pass	fail	4 MPa
Y_1	Pass	Pass	Pass	Pass	4 MPa
Y_2	Pass	Pass	Pass	Pass	4 MPa
Y_3	Pass	Pass	Pass	Pass	3 MPa
Y_4	Pass	Pass	Pass	Pass	3 MPa
Y_5	Pass	Pass	Pass	Pass	3 MPa

TABLE 3 : Data of the visual inspection after application of the painting films formed by the formula Y_0-Y_5 of epoxy compounds

Formula	Sealing	Sagging	Fisheyes	Shrinking	Coagulation	Smoothes	Homogeneity
Y_0	No sealed	Not sagging	No fish eyes appeared	No shrinking	No	High	Homogeneity of the formed films
Y_1	No sealed				No	Smooth	
Y_2	No sealed				No	Smooth	
Y_3	No sealed				Few	Smooth	
Y_4	No sealed				Few	Rough	
Y_5	No sealed				Few	Rough	

TABLE 4 : the physical measurements of the formed films from Epoxy, WFT, DFT films thickness and touch dry at ambient temp.

Formula	Wet films thickness	Dry films thickness	Touch dry	Curing temp.	Relative humidity	Optimum curing ratio
Y_0	200 µm	180 µm	30 min	20°C	50 %	20
Y_1	200 µm	180 µm	28 min.	20°C	50 %	20
Y_2	200µm	185µm	25 min.	20°C	50%	20
Y_3	200µm	185 µm	20 min.	20°C	50 %	20
Y_4	200 µm	190µm	18 min.	20°C	50 %	20
Y_5	200 µm	190 µm	12 min.	20°C	50%	20

curing agent.

The films formed from formula Y_0-Y_5 at optimize condition were visually inspected and listed in TABLE 3.

Physical and mechanical measurements

Data of WFT, DFT were given in TABLE 4. These data indicating the DFT were increased with increasing the inorganic additives.

Mechanical properties data were given in TABLE 5 and showed that the dry films formed from Y_0-Y_5 were improved with increasing the amount of fillers and inorganic additives. The adhesive force of the formula Y_0 was failed ,while adhesive force from the formula Y_1-Y_5 were passed .These data showed that the adhesion forces was increased by increasing the Zn ratio of the inorganic additives. The bending and impact test for the formed dry films were improved with increasing the inorganic additives

Chemical properties; salt spray

Figure 1: The corrosion behavior of the formed dry films subjected to salt spray by 5.5 % NaCL for 2 weeks

Figure 1 illustrate evaluation of corrosion resistance of Zn coatings by Salt Spray test assumes significance. The ability to prevent under film corrosion is best measured by assessing the spreading of corrosion from the X-scribed made on the dry films formed. After 2 weeks of Salt Spray test, the type of corrosion product formed in the scribed region it self is quite different from that dry film Y_0 (without zinc). Visual observation of the corrosion product on the surface of the dry films (Y_0-Y_5) indicates the formation of red rust film appeared after 7 dyes in Y_0, after 10 days in Y_1, after 12 days in Y_2, Y_3 while in case Y_4, Y_5 no spots appeared until 15 days. This exposes the base metal for further corrosion. Salt Spray test convincingly proves the white rust formation on the scribed region of the painted dry film and in most parts of the surface after 10 days. The corrosion behavior of dry films formed exhibits the stability of this coating films which lasts for 12 days with no red rust formation. Results were indicated that the films formed from the formula Y_2-Y_5 were valid for protecting the surface of carbon steel against aggressive media. Generally, due to the ratio of spots to the total sur-

TABLE 6 : Visual inspection for the effect of synthetic sea water 5.5%NACL on the surface of the formed dry films for 2 weeks

Period time (days)	Y_0	Y_1	Y_2	Y_3	Y_4	Y_5
1	No spots	No spots	No spots	No spots	No spots	No spots
2	No spots	No spots	No spots	No spots	No spots	No spots
3	No spots	No spots	No spots	No spots	No spots	No spots
5	No spots	No spots	No spots	No spots	No spots	No spots
7	No spots	No spots	No spots	No spots	No spots	No spots
8	Few corrosion spots on scribe line	No spots	No spots	No spots	No spots	No spots
10	Few corrosion spots on scribe line	No spots	No spots	No spots	No spots	No spots
12	Few corrosion spots on scribe line	Few corrosion spots on scribe line	No spots	No spots	No spots	No spots
15	Few corrosion spots on scribe line	Few corrosion spots on scribe line	Few corrosion spots on scribe line	Few corrosion spots on scribe line	No spots	No spots

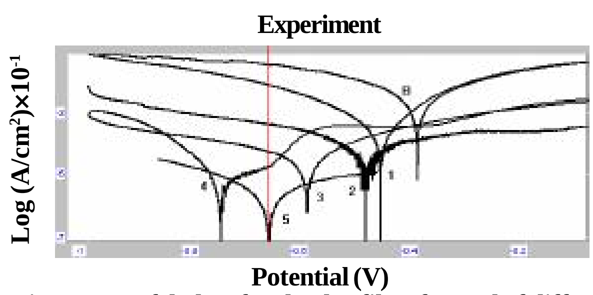

Figure 2 : Tafel plots for the dry films formed of different formulaY_0-Y_5 B: Y_0 = 0 Zn dust, 1-5 :(Y_1 - Y_5) respectively measured in sea water

face area was less than 0.1%.

Polarization measurements

Figure 2 shows the cathodic and anodic polarization curves of the formed dry filmes (y_0-y_5).

Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafle slops (ba and bc) and polarization resistance (R_p) were calculated and listed in TABLE 7.

The efficiency (I %) was calculated using the following equation:

$$I\,\% = (1 - i/i_0)\,100 \quad (1)$$

Where i_0 and i are the corrosion current densities in the absence and presence of the different zn dust ratio respectively. The values of polarization resistance (R_p) were calculated from the well- Known stern - geary equation

$$R_p = ba\,bc / 2.303\ i_{corr}\,(ba + bc) \quad (2)$$

It is evident from the above figure and TABLE that the E_{corr} shifts towards more negative (higher cathodic values) compared to that film without Zn dust Y_0. The shift in corrosion potential towards more cathodic value

TABLE 7 : Relation of the composition of different Zn dust ratio of coating with the -E_{corr}, I_{corr}, RP, and E% measured by potentiodynamic method measured in sea water

Formula	Zn ratio%	-E_{corr}, mV	I_{corr}, mA/Cm^2	R_P, ΩCm^2	I %
Y_0	0	-399.3	3.76	12.83	-
Y_1	5	-466.4	0.63	87.95	83
Y_2	10	-492.5	0.12	379.39	96.8
Y_3	15	-602.2	0.09	1000.09	97.6
Y_4	20	-759.9	0.06	2000.79	98.4
Y_5	25	-571	0.04	12000.74	98.9

is due to the increase of metallic zinc dust ratio in the formed film. The increase in Zn dust ratio leads to the increase in R_p (polarization resistance) and I % (efficiency) while i_{corr} is decreased.

Electrochemical impedance spectroscopic study (EIS)

Electrochemical impedance spectroscopy (EIS) is used to examine the activity difference between the formed films in absent of Zn dust and presence of different ratios of Zn dust. Impedance is a totally complex resistance when a current flows through a circuit made of capacitors, resistors, or insulators, or any combination of these[23]. EIS measurement results in currents over a wide range in frequency. Corrosion metals are modeled with an equivalent circuit (called a Randles circuit) as illustrated in figure 3a, which is made of a double layer capacitor in parallel with a charge transfer resistor and connected in series with a electrolyte solution resistor. The impedance (Z) depends on the charge transfer resistance (Rct), the solution resistance (Rs), the capacitance of the electrical double layer, and the

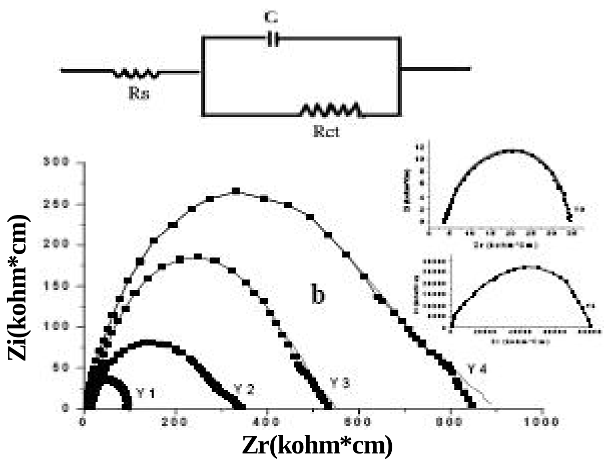

Figure 3: (a): Randles equivalent circuit, (b): Typical Nyquist diagrams of the formed films in sea water solution in the absence and presence of various ratio of Zn dust

TABLE 8 : Impedance measurements and inhibition efficiencies for the formed films in see water solution in the absence and presence of various ratio of Zn dust

Sample no.	R_t Ohmcm^2	N`	C_{dl} µF cm^{-2}	I%
Y_0	35	0.82	16.5	-
Y_1	105	0.85	0.00058	66
Y_2	350	0.79	0.00036	90
Y_3	555	0.76	0.000174	39.6
Y_4	850	0.83	0.00017	95.8
Y_5	8000	0.84	0.00015	99.5

frequency of the AC signal (ω).

The high-frequency intercept is equal to the solution resistance, and the low-frequency intercept is equal to the sum of the solution and charge transfer resistances [24].

Typical Nyquist diagrams are shown in figure 3b. It is clear that the diagrams display non-perfect semicircles of the formed films in see water solution in the absence and presence of various ratio of Zn dust. This behavior can be attributed to frequency dispersion[25].

The equivalent circuit model for electrochemical impedance measurements[26], where Rs is the solution resistance, Rt the charge transfer resistance and Cdl is the electrochemical double layer capacitance given in figure 3a. Various electrochemical parameters derived from Nyquist plots are calculated and listed in TABLE 8. The values of Rt were given by subtracting the high frequency impedance from the low frequency one as follow[27]

Rt = Zre (at low frequency) - Zre (at high frequency) (3)

The values of electrochemical double layer capacitance Cdl were Calculated at the frequency fmax, at which the imaginary component of the impedance is maximal (-Zmax) by the following equation[28]

$$Cdl = 1/ 2\pi f_{max} \times 1/Rt \quad (4)$$

The values of percentage inhibition efficiency (I %) were calculated from the values of Rt according to the following equation[29]

$$I\% = Rt(Zn{=}y_1\text{-}y_5) - Rt(Zn{=}y_0) \;/\; Rt(Zn{=}y_1\text{-}y_5)) \times 100 \quad (5)$$

where $Rt(Zn{=}y_0)$ and $Rt(Zn{=}y_1\text{-}y_5))$ are the values of the charge transfer resistance in the absence and presence of different ratios f Zn dust, respectively. The impedance data listed in TABLE 3 indicate that the values of both Rt and I % are found to increase by increasing the Zn ratio Concentration, while the values of Cdl are found to decrease. This behavior can be attributed to increase in the thickness of the electrical double layer, suggests that the Zn molecules act by adsorption on the surface of carbon steel (steel / epoxy interface)[30].

CONCLUSIONS

The main conclusion of the present study could be summarized in the following points:

1. Formula of the formed filmes y_0- y_5 was compatibility of the binder with the inorganic filler and complete reaction with the curing agent.
2. The DFT were increased with increasing the inorganic additives
3. The adhesion, bending and impact techniques for the formed dry films were improved with increasing the inorganic additives
4. Results from chemical test were indicated that the films formed from the formula Y_2-Y_5 were valid for protecting the surface of carbon steel against aggressive media. Generally, due to the ratio of spots to the total surface area was less than 0.1%.
5. The shift in corrosion potential towards more cathodic value is due to the increase of metallic zinc dust ratio in the formed film. The increase in Zn dust ratio leads to the increase in R_p (polarization resistance) and I% (efficiency) while i_{corr} is decreased.
6. The values of both Rt and I % are found to increase by increasing the Zn ratio Concentration, while the values of Cdl are found to decrease. This behavior can be attributed to increase in the thickness of the electrical double layer.
7. The net result indicating the validity of the formed dry films for protection of carbon steel in petroleum equipments.

REFERANCES

[1] N.J.Bjerrum, E.Christensen, T.Steenberg; U.S. patent, 6,346, 168 **(2002)**.
[2] H.E.Townsend; Corrosion, **54(7)**, 561-565 **(1998)**.
[3] N.U.Yanik, H.Yaleinkaya, Nkizlcan; Surf. Coatinte.PartB:Coatings Transactions, **84(B4)**, 243-336 **(2001)**.
[4] A.J.Fream, S.E.Magent; Surf.Coat.Intern, **9447-9454**, 35,311-313 **(2002)**.
[5] M.A.Migahed, I.F.Nassarb; Electrochimica Acta, **53**, 2877-2882 **(2008)**.
[6] Ming-Ren Tarng, Mao Chen, J.Edward; Journal of Coatings Technology, **74(935)**, 2002 **(2002)**.
[7] G.Blusteina, A.R.Di Sarlia, J.A.Jaenb, R. Romagnolia, B.Del Amoa; Corrosion Science, **49**, 4202-4231 **(2007)**.
[8] B.Rossenbeck, P.Ebbinghaus, M.Stratmann, G. Grundmeier; Corros.Sci., **48**, 3703-3715 **(2006)**.
[9] G.Grundmeier, B.Rossenbeck, K.J.Roschmann, P. Ebbinghaus, M.Stratmann; Corros.Sci., **48**, 3716-3730 **(2006)**.
[10] M.Zubielewicz, W.Gnot; Prog.Org.Coat., **49**, 358 **(2004)**.
[11] A.C.Bastos, M.G.Ferreira, A.M.Simes; Corros.Sci., **48**, 1500 **(2006)**.
[12] J.M.McIntyre, H.Q.Pham; Prog.Org.Coat., **27**, 201 **(1996)**.
[13] S.Gonzlez, I.C.Mirza Rosca, R.M.Souto; Prog. Org. Coat., **43**, 282 **(2001)**.
[14] H.Marchebois, S.Joiret, C.Savall, J.Bernard, S. Touzain; Surf.Coat.Technol., **157**, 151 **(2002)**.
[15] J.T.Zhang, J.M.Hu, J.Q.Zhang, C.N.Cao; Prog.Org. Coat., **51**, 145 **(2004)**.
[16] Yawei Shaoab, Cao Jia, Guozhe Mengab, Tao Zhangab, Fuhui Wangab; Corrosion Science, **51**, 371-379 **(2009)**.
[17] O.M.Abo-Elenien, H.M.Abu Elainien; Egypt.J. Petral, **9**, 13-18 **(2000)**.
[18] A.M.MAbd ELRahman, H.M.Abu Alanein; O.M. Abo-Elenien; Egypt, APPl, Sci., **19(8)**,196-211 **(2004)**.
[19] A.Hugot-Le Goff, C.Bernad, N.phillips, H. Takenouti; Mater.Sci.Forum, **192-194**, 779 **(1995)**.
[20] P.Bommersbach, C.D.alemany, J.P.Milletand, B. Normand; Electrochemical Acta, **51**, 1076 **(2005)**.
[21] E.Mc Coerty; Corrosion Science, **47**, 3202 **(2005)**.
[22] Jui-Mingyeh Tai Hung Kuo, Hou, Ju Huang, Kung Chin Chang, Mai Jingchang, Jen ChangYang; European Polymer Journal, **43**, 1624 **(2007)**.
[23] S.M.Park, J.S.Yoo; Anal.Chem.A, **75**, 455A **(2003)**.
[24] A.Amirudin; Thierry D.Prog.Org.Coat., **26**, 1 **(1995)**.
[25] F.Mansfeld, M.W.Kending, S.Tsai; Corrosion, **37**, 301 **(1981)**.
[26] F.Mansfeld, M.W.Kending, S.Tsai; Corrosion, **38**, 570 **(1982)**.
[27] A.P.Yadav, A.Nishikata, T.Tsuru; Corros.Sci., **46**, 169 **(2004)**.
[28] A.Galal, N.F.Atta, M.H.S.Al-Hassan; Mater.Chem. Phys., **89**, 38 **(2005)**.
[29] M.A.Ajmal, J.Rawat, M.A.Quarishi; Br.Corros.J., **24**, 220 **(1999)**.
[30] K.F.Khaled; Appl.Surf.Sci., **252**, 4120 **(2006)**.