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Blending of some organic resin with inorganic material to applied as corrosion protection of petroleum equipments

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ABSTRACT

Some organic resins novolac,furan and epoxy were blended with inorganic additives Ti O_2, $CaCO_3$, Talc, Zn dust and Sintered glass. These materials were formulated to produce ten formula designated from F_{10}-F_{100}. The toluene diisocyanate (TDI) was used as curing agent at different ratios 5, 10, 15 and 20 parts. The carbon steel alloy specimens were provided from unused petroleum pipelines. The surfaces of specimens were prepared by polishing with different grade emery paper. The visual inspection, physical, mechanical and chemical properties such as, wet film thickness (WFT), dry film thickness (DFT), adhesion forces, bending, impact, hardness and thermal stability at 50 - 500 ºC at intervals of 50 ºC were studied and discuses. Effect of organic solvent for 72 days, methylethylketon, chloroform, acid effect (10% H_2SO_4) at period time of 50 days and salt spray tests effect at period time of 21 days for the formed dry films were studied. The surfaces of films were visual inspected by magnification power after chemical tests. Electrochemical for formed dry films were studied and indicated. The surface morphology of formed dry films before and after electrochemical tests were exanimate by scanning electron microscope (SEM). The results indicated that the corrosion spots did not detect on the surface of the formed dry films. These films approved to be a protections agent for the surface of petroleum equipments against corrosion.

KEYWORDS

Novolac;
Furan;
Epoxy;
Talc;
TiO_2;
ZnO_2;
Sintered glasses;
TDI and unused petroleum carbon steel;
Electrochemical corrosion;
SEM.

INTRODUCTION

The carbon steel alloys are used at high temperatures in large scale for production and maunfacture of petroleum, petrochemical equipments and different industries. The carbon steel alloys are corroded quickly when subjected to both chemical and physical environmetal conditions[1-8].

The types of protective coatings must be compate the metal surfaces without any change. The formation films are provided a barrier between the metallic surfaces and the surrounding corrosive medium. These include paints, varnishes, enamels, plastics and metals which were applied by brushing, electroplating, hot dipping flame spraying, etc.[5-14].

Paintings are one of the most suitable, less expensive, and more efficient method for corrosion and wear control, which could be more suitable binders source and high efficiency as protective compounds.[11-18].

The aim of this work depends on the blending of furan, novolac and epoxy resins and is formulated inorganic additives Ti O_2, $CaCO_3$, Talc, Zn dust and Sintered glas. The different ratio of curing agent TDI is used. The preparation surface of carbon steel alloy specimens AG-15 are coated by these formula. The visual inspection, physical, mechanical and chemical properties of the formed dry films are evaluated and discussed.

EXPERIMENTAL WORK

Preparation of the painting formula F_{10}-F_{100}

TABLE 1 illustrates the formation of painting formula F_{10}-F_{100} as following different parts (10, 20, 30, 40, 50, 60, 70, 80, 90, 100) of furan were mixed with 10 parts of Novolac, 10 parts of epoxy resin, 10 parts of Zinc dust, 20 parts of TiO_2, 20 parts of $CaCO_3$, 20 parts of talc, 10 parts of sintered glass and 15 parts of methyl ethyl ketone (MEK) as solvent.

Optimum condition of the curing agent

The toluene diisocyanate (TDI) was used in different ratios (5, 10, 15, and 20) parts as curing agent; which were mixed with each formula to form various painting formulation. Each formulation was applied on the surface of carbon steel specimens by brushed and spray method and cured at room temperature, to determine the optimum condition.

Preparation of the surface metal specimens

Unused carbon steel alloy type AG-15 were provided from petroleum pipelines of Belayim Petroleum Company at Port -Fouad station to be used as specimens supplier. The specimens were cut as regular edged cuboids with dimensions ≈ 8, 15, 0.1 cm average. Each specimen was cleaned, polished with150, 400, 600 emery papers, rinsed with distilled water, degreased with acetone, weight and finally stored under vacuum after wrapping with adhesive thin paper into sets. Each set includes specimens having nearly similar weight and surface area.

The optimization steps

To obtain the optimum coatings were carried out under static air,at ambient pressure and temperature within a selection formula. A set of specimens were coated with these formula and cured by curing agent TDI at ambient condition. The coating specimens were gradually inspected to recorded the optimization conditions for each formula. The coating films over the surface of specimens were examinateed by measuring the WFT, DFT, adhesion, thermal stability, impact, bending, hardness and chemical tests. The formation of the best coating was achieved in steps and kept constant through the optimization procedure.

The characterization techniques

Visual inspection.

The visual inspection for the formation coating as sealing, sagging, fish eyes, shirinking, cogulastion, smoothes and homogeneity were inspected and tabulated.

Physical properties

Measuring and calculation of Wet film thickness(WFT), dry film thickness(DFT), adhesion, thermal cycling test, Electrical conductivity, and Pinhole test of the formed coatings were carried out according to ASTM (D-1212-91), ASTM (D-1186 and 1005-95). ASTM (D-1212), (D-1186 and 1005), (D 3359), BS-6670 Part 5 BS-6670 Part 5, ASTM (D-4399) and (D-5162), respectively

Mechanical properties

Bending, adhesion forces, hardness, and impact tests were carried out according to ASTM (D-522), (D- 3363) and ASTM (D-2794 and G14-88), respectivily.

Chemical properties

The effect of organic solvents, 10% H_2SO_4 and synthetic sea water by salt spray tests 3.5% NaCl were carried out according to ASTM D-44, 4752, 468, 610, G-31, BS-6670, and ASTM B117 respectively. The data of results were recorded and investigated.

Electrochemical polarization

Electrochemical polarization measurements were carried out in a Pyrex cell with three electrodes. A working carbon steel electrode has 1cm^2 surface areas, was embedded in glass tube sealed by Araldite steel epoxy, surface of electrode was prepared as above method. A saturated calomel electrode (SCE) was used as reference and platinum wire as counter electrode. Experiments were obtained using an potentiostate

VoltalabMaster PGZ 301 connected to an Voltamaster 4 and function generator. The open circuit potential was measured at potential -540 mV versus time for coated and noncoated specimens in electrolyte synthesis sea water for 2hrs. The potential was scanned from the negative to positive direction at scan rate $10mVs^{-1}$. The cyclic voltametry polarization for uncoated and formed films from formula F10- F100 were measured by at potential range ± 1000 mv and scanning rate $10mvs^{-1}$ in synthesis sea water. The potentiodynamic polarization for formed films from formula F_{10}- F_{100} were measured at potential range ± 1000 mv and scanning rate $10mvs^{-1}$ in synthesis sea water. The electrochemical impedance (EIS) was carried out at 100 KHz to 10Hz at scan rate $10mVs^{-1}$. The obtained data from EIS were analyzed by Fitting Z Simpwin computer program.

The metallurgical surface morphology for the some dry films before and after electrochemical evaluation were measured by A Jeol (840X Japan) scanning electron microscope (SEM) equipped with an Olympus Camera.

RESULTS AND DISCUSSION

Studies the optimization concentration for curing agent (TDI) with formula F_{10}-F_{100}

TABLE 2 illustrates the optimize ratios of the curing agent (toluene diisocyanate TDI) for each formula of F_{10}–F_{100} at room temperature respectively. The touch curing time was the main factor for determine the TDI concentration of the formation films. The furan ratios (10-100gm) were affected in curing time for each formula from F_{10}–F_{100}.. From the optimization studies of the touch curing time were observed that the time increases with increasing the furan ratio and decreased with increased the TDI ratio. The duration times / or complete drying were recorded at room temperature was 3-5 day's for formula F10-F100, these results were computed for 15gm of TDI. On the other hand, the inorganic materials ratios were affected on touch dry time.

Visual inspection for formula F_{10}-F_{100}

TABLE 3 shows the visually inspection data during painting processing and after drying (dry film). Firstly, the results data from films were observed that, they were free from sealing, shrinkable and coagulation not appeared for the formulation films for formula F_{10}-F_{100}. From these data one should be concluded that the validity of the application these formula through the brush and spray methods. The formation films during and after curing on the surface of carbon steel specimens were showed as one layer compatible with each other, compact and adhesion as well as stable on the surface of carbon steel specimens.

Measuring and calculating of the wet and dry films thickness (WFT and DFT) formed from formula F_{10}-F_{100} on the surface of carbon steel specimen's

TABLE 4 indicates the measuring and calculating data of the WFT and DFT formed from the formula F_{10}-F_{100} on the surface of carbon steel specimens at room temperature. From these results the weights of formed films were increased by increasing the furan ratio. Also the weights of dry films formed films were increased by increasing the furan ratio.

From these data one observed that the weights and the normalized weights of formed wetting films were matched with these of drying films formation on carbon steel specimens.; and also, the weights and the normalized weight per unit area data for wetting and drying films were confirmed the optimization condition of curing agent TDI.

Adhesive forcing of the formed dry films on the surface of carbon steel specimens

TABLE 5 illustrates the measuring and calculating

TABLE 1 : Different ratio of chemical painting formula containing furan resin.

Formula Component	F_{10}	F_{20}	F_{30}	F_{40}	F_{50}	F_{60}	F_{70}	F_{80}	F_{90}	F_{100}
Furan	10	20	30	40	50	60	70	70	90	100
Epoxy	10	10	10	10	10	10	10	10	10	10
Novolac	10	10	10	10	10	10	10	10	10	10
Calcium carbonate	20	20	20	20	20	20	20	20	20	20
Talc	20	20	20	20	20	20	20	20	20	20
TiO_2	20	20	20	20	20	20	20	20	20	20
Zn dust	10	10	10	10	10	10	10	10	10	10
Sintered glass	10	10	10	10	10	10	10	10	10	10
	5	5	5	5	5	5	5	5	5	5
Curing agent%	10	10	10	10	10	10	10	10	10	10
	15	15	15	15	15	15	15	15	15	15
	20	20	20	20	20	20	20	20	20	20

TABLE 2 : Data of optimum condition for the curing agent TDI against curing time for F10-F100 formula at ambient condition

R.C.A (TDI)	Touch dry time for each formula (hr)									
	F_{10}	F_{20}	F_{30}	F_{40}	F_{50}	F_{60}	F_{70}	F_{80}	F_{90}	F_{100}
5	4-5	4-6	4-7	4-8	5-7	5-8	5-9	6-10	6-11	6-12
10	3-5	3-5	3-6	3-6	4-6	4-6	5-7	5-7	5-8	5-8
15	2-3	2-3	2-4	2-4	3-4	3-5	3-5	4-6	4-6	5-6
20	1-2	1-3	2-4	2-4	3-4	3-4	3-4	3-4	3-4	4-5

TABLE 3 : Data of the visual inspection after application of the painting wet and dry films for formed from formula F_{10}-F_{100}.

Test Formula	Sealing	Sagging	Fish eyes	Shrinking	Coagulation	Smoothes	Homogeneity
F10							
F20							
F30							
F40							
F50							
F60	-ve	-ve	-ve	-ve	-ve	+ve	+ve
F70							
F80							
F90							
F100							

data of the adhesion forces of drying films formed from the formula F_{10}-F_{100} on the surface of carbon steel specimens at room temperature. From these data, the adhesion forces of the formation dry films were excellent. The rate of adhesion forces of the formation dry films were depended on the both techniques X-cut tape and cross-cut tape according to ASTM (D3359) were 5A and 5B, respectively. These data were indicated that the effect of resin compounds on the adhesion forces for formed dry film with steel surface. These films were no peeling or removal and the edges of the cuts were completely smooth; none of the squares of the lattice was detached. Also, the inorganic additives were helped on the increasing of adhesion forces between the surface of carbon steel specimens and the formation dry films and with its self. One should be concluded that the validity of the formula F_{10}-F_{100} through the stability of the dry film formation on the surface of carbon steel specimen.

Holiday (pinhole) detection of the formed dry films on the surface of carbon steel specimens.

The data of holiday (pinhole) detection for the formation dry films were given in TABLE 5. Its were operated at the environmental condition, ambient temperature, relative humidity (R.H) at ≈ 50%, time duration for dry film 7 days and dry film thickness 80 ±5 µm. The measuring voltages were depended on the dry film thickness of the formation films according to the following equation.

Measuring voltages = 5 × DFT

The measuring voltages for the formation dry film were 400±25 volts. These data were matched with the net results obtained from the electrical conductivity method. Also, the protection value were depended on

TABLE 4 : The physical measurements for each formed films from F10-F100 wet and dry films at ambient condition and curing agent TDI.

Symbol	Weight of specimen (g)	One Surface area (cm^2)	Weight of wet films (g)	Normalized weight of wet films (mg/cm^2)	Weight of dry films (g)	Normalized weight of dry films (mg/cm^2)	Measuring dry film	Temp.	R. H	T.D (hr)	C.D (hr)
F10	90.0817	120	4.6437	38.6975	3.0918	25.765					
F20	92.1999	120	4.6573	38.8108	3.1099	25.9158					
F30	90.3065	120	4.6885	39.0708	3.1257	26.0475					
F40	92.4532	120	4.7135	39.2791	3.1421	26.1841					
F50	90.4321	120	4.7452	39.5433	3.1635	26.3625	80 ±5	Ambient temp.	?50%	3-5	72-96
F60	90.1837	120	4.7671	39.7258	3.1781	26.4841					
F70	90.0807	120	4.7958	39.965	3.1976	26.6466					
F80	90.3152	120	4.8013	40.0108	3.2009	26.6741					
F90	90.1321	120	4.8283	40.2358	3.2189	26.8241					
F100	90.5431	120	4.8760	40.6333	3.2507	27.0891					

TABLE 5 : The physical and mechanical properties of the formed films from formula F_{10} - F_{100} at ambient condition.

Symbol	Average WFT µm	Average DFT µm	Bending	Pinhole at 400±25	Adhesion		Hardness	Impact	E.C.(υ)	Resistance Ω
					X	Cr				
F10			Pass	pass	5A	5B	9H	pass		20000
F20			Pass	pass	5A	5B	9H	pass		20000
F30			Pass	pass	5A	5B	9H	Pass		22000
F40			Pass	pass	5A	5B	9H	Pass		22000
F50	130-140	80 ±5	Pass	pass	5A	5B	9H	Pass	Very good insulator resistance	24000
F60			Pass	pass	5A	5B	9H	Pass		24000
F70			Pass	pass	5A	5B	9H	Pass		24000
F80			Pass	pass	5A	5B	9H	Pass		24000
F90			Pass	pass	5A	5B	9H	Pass		24000
F100			Pass	pass	5A	5B	9H	Pass		24000

the resins additives ratios and the inorganic filler which were indicated on the good compatibility of the fillers with the organic resin to formation the poly urethane amide epoxy resin. These films were having good insulating properties. Therefore the formation dry films were promising the validity of the formation dry films as insulating (protected) the surface of carbon steel. One should be that the formation dry films were free from discontinuity (void, crack, foreign inclusion, thin spot or contamination) in the coating film.

Hardness data

TABLE 5 shows the hardness data from the pencil test for the formation dry films on the surface of carbon steel specimens from the formula F10-F100 were give the high value (9H). From these data were showed that the hardness values stable with increasing the furan ratio. One should be concluded that the validity of the formula F_{10}-F_{100} through the stability of the dry film formation on the surface of carbon steel specimen.

Impact data for formula F10-F100

The impact data for the drying films were recorded and given in TABLE 5. From these data were showed that the dry films free from any cracking which were made more visible by the use of magnifier and by the use of a pinhole detector. Also, these dry films were impact resistance and passed.

Bending data

The bending data for the drying films were recorded and given in TABLE 5. From these data were showed that the dry films free from any cracking which were made more visible by the use of magnifier and by the use of a pinhole detector. Also, these dry films flexibility and also they were bending resistance and passed. One should be concluded that the validity of the formula F_{10}-F_{100} through the stability of the dry film formation on the surface of carbon steel specimen at bending test.

Thermal cycling test for the formation dry films from formula F10-F100, FS10-FS100 and FA10-FA100 at ambient condition

The data of the thermal cycling test for the formation dry films from the formula F10-F100, were showed in TABLE 6. The degrees of temperature were ranged from 50 to 500 ?C by increasing 50?C intervals. The formation films from guide formula F10-F100 were affected, the loss weight were increased with increased the ratio of furan and temperature. The formation dry films from F_{10}-F_{100} were failed at 450?C and 500?C respectively.

Volatile of organic compounds VOC

The Volatile of organic compounds from the paints after curing were either estimated from the formulations and / or the using of organic solvent. In this situation the volatile organic compound were defined as blended organic solvent, and resins compounds. The emissions of volatile organic compounds were illustrated from the chemical formula. The chemical formula of F_{10}-F_{100} were contained on the blended solvent, which were evaporated after application of the paints on the surface of carbon steel specimens at ambient condition and more volatile during the thermal effect on the formation films. So that the weight of the formation films after every step of thermal effected were decreased until the weight were established. These phenomena were rule resulted for the hydrolyzed and emission of the organic compounds from some resin groups during the both curing process and the thermal cycling test. These data were showed in TABLE 6.

TABLE 6 : Thermal cycling test (stability) of the dry formed films at ambient condition from formula F10-F100 at temperature ranged from 50 to 500 °C and at optimum concentration of TDI

T °C	P.T.	Weight losses for each formed films $x10^{-4}$									
		F10	F20	F30	F40	F50	F60	F70	F80	F90	F100
50		0.0254	0.0367	0.0435	0.0562	0.0675	0.0812	0.0876	0.0954	0.1245	0.1534
100		0.0365	0.0485	0.0574	0.0673	0.0776	0.0893	0.0964	0.1321	0.1546	0.1754
150		0.0473	0.0612	0.0662	0.0754	0.0954	0.1134	0.1251	0.1453	0.1634	0.1778
200		0.057	0.0673	0.0754	0.0863	0.1045	0.1256	0.1342	0.1482	0.1685	0.1795
250	3hr' s	0.0657	0.0919	0.1023	0.1043	0.1065	0.1832	0.1107	0.1564	0.1741	0.1821
300		0.0843	0.0982	01026	0.1052	0.1076	0.1123	0.1325	0.1673	0.1823	0.1954
350		0.0976	0.1652	0.1734	0.1782	0.1875	0.1953	0.2143	0.2346	0.2465	0.2587
400		0.1564	0.1746	0.1935	0.1989	0.2314	0.2537	0.2764	0.2917	0.2946	0.2987
450		Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail
500		Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail

The effect of furan structure on the properties of the formation dry films

The furan structure was low molecular weight of heterocyclic compound and it's contained on the hydroxyl and carbonyl groups. These groups in furan structure were employed the very important rule for the curing and the stability of the formation dry films. The polyurethane network films were formed by curing of TDI with epoxy (oxirane), cintred glasses hydroxyl groups and novolac function groups, and formation imide and melamine bond, respectively. These were a principle idea for the mechanism of the formation dry polyurethane melamine films of furan on the surface of carbon steel specimens.

Mechanism

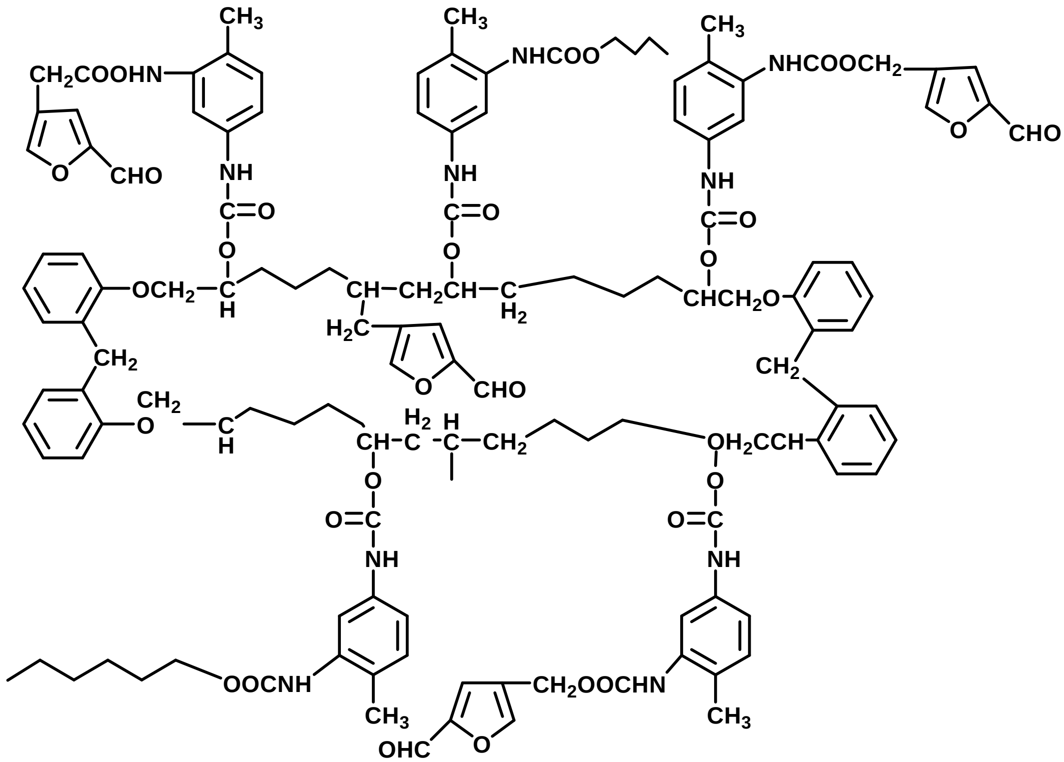
Furan structure having two important function groups hydroxyl and carbonyl groups, which were employed the very important rule in the formation of the coating films and curing of which on the surface of carbon steel specimens. The furan behavior two ways in the formation of coating films was cured reaction with cyano groups of TDI to form a polyurethane bonds and the other was cured with another groups to form the polyfurfural bonds. These bonds were forming a poly urethane furfural films, these were very strong adhesion resistance to mechanical and chemical environment.

The both terminal hydroxyl groups for macromolecules of the resin were capable of reacted with the curing agent TDI to form polyurethane as the following

Final schema of formation lattice films from formula F10-F100

Novolac has heat mechanical and chemical resistance and the functional groups of novolac were reacted with another group of TDI to form a polyurethane melamine bonds at high temperature. The formation film from the novolac was hard, compact, and having adhesion forces, chemical and mechanical properties.

Although the resins (furan, novolac, and epoxy] were give a very good properties to the surface of a cured coating. It was not sufficiently compatible with formulation to provide adequate storage stability. This was compared to resins, UV formulation were relatively polar. Even after high shear incorporation of the silicon into the coating, the clarity can be adversely affected and separation may occur on storage. Therefore, it was necessary to use some means of making the resins compatible with the coating and with each other. These resins can be reduced compatible with polar media. A well known method of doing this was by grafting polar groups with the resins groups. The resins chains can be attached any points along the length of the active site backbone, giving



a comblike structure. They can be also attached to the ends of the furan polymer and other resins, giving a linear structure. The structure of the copolymer had a profound effect on the behaviors of the copolymer as an additive. Optimized structures have been identified by designed experimentation to give suitable combination of compatibility desired effects. Compatibility was particular important in clear coatings.

Chemical evaluation

TABLE 7 & 8 illustrates the effect data of the Xylene, Toluene and Benzene mixture, MEK and chloroform on the formation dry films on the surface of carbon steel specimens. The forming dry epoxy polyurethane films from formula F10-F100 were not affected by the rubbing the formation films by MEK from 40–50 times. The net results were indicated on the stability of Zn, compatibility and adhesion forces with the surface of carbon steel specimens and with itself.

TABLE 9 illustrates the data of the effective of the 10% sulfuric acid on the formation films from different formula F10-F100. From these data we were observed that the effect of 10 % sulfuric acid on the formation films on carbon steel specimens at period time 50 days, DFT 80 ± 5μm and these data were valid to corrosion protection materials.

TABLE 7 : Visual inspection for the effect of organic solvents (Xylene, toluene and benzene) on the formed dry films for F10-F100 formula at room temperature.

Period immersion time (days)	Effect of the texture of the formed dry film									
	F_{10}	F_{20}	F_{30}	F_{40}	F_{50}	F_{60}	$F7_0$	F_{80}	F_{90}	F_{100}
6										
12										
24	No change the film surface									
48										
72										

TABLE 8 : Effect of (MEK) and chloroform on the formed dry films from formula F10-F100.

Solvent	F_{10}	F_{20}	F_{30}	F_{40}	F_{50}	F_{60}	F_{70}	F_{80}	F_{90}	F_{100}
MEK	No effective the film surface									
Chloroform	No effective the film surface									

TABLE 9 : Data of corrosion tests of the dry films formed from F10-F100 on the surface of carbon steel specimen in 10% H_2SO_4 for 50 days.

Period immersion time (days)	Visual inspection for the dry films formed in 10% H_2SO_4									
	F_{10}	F_{20}	F_{30}	F_{40}	F_{50}	F_{60}	$F7_0$	F_{80}	F_{90}	F_{100}
10										
20										
30	No Spots Appeared									
40										
50										Spots appeared

Salt spray tests

Salt spray test measures the ability of various types of coating to withstand in a corrosive cum-humid environment. Figure 1 illustrates the paint coated carbon steel samples after exposure to salt spray fog for 21 days at 40 C°. It can be seen that the formed films from formula F_{10}-F_{100} were free from any blistering, also can not removed in any direction from the areas surrounding the scribe edge with a pull by plastic tape. The formation film from formula F_{10}-F_{40} were founded a few rust at a long the scribe areas, these rust was not spreading up and under the coating films.

TABLE 10 : Visual inspection for the effect of salt spray test on the formed dry films from F10-F100 formula at 40C°.

Sample P.T	F_{10}	F_{20}	F_{30}	F_{40}	F_{50}	F_{60}	F_{70}	F_{80}	F_{90}	F_{100}
4 day 8 day	No spot blistering and no rusting appeared									
12 day	No spot blistering and few rusting appeared					No spot blistering and few rusting appeared at scribe edge				
16 day	No spot blistering and little rusting appeared					No spot blistering and rusting appeared at scribe edge and spread on surface				
21 day	No spot blistering and rusting was noticeable on the panel surface.					No spot blistering and rusting appeared at scribe edge and spread on surface				

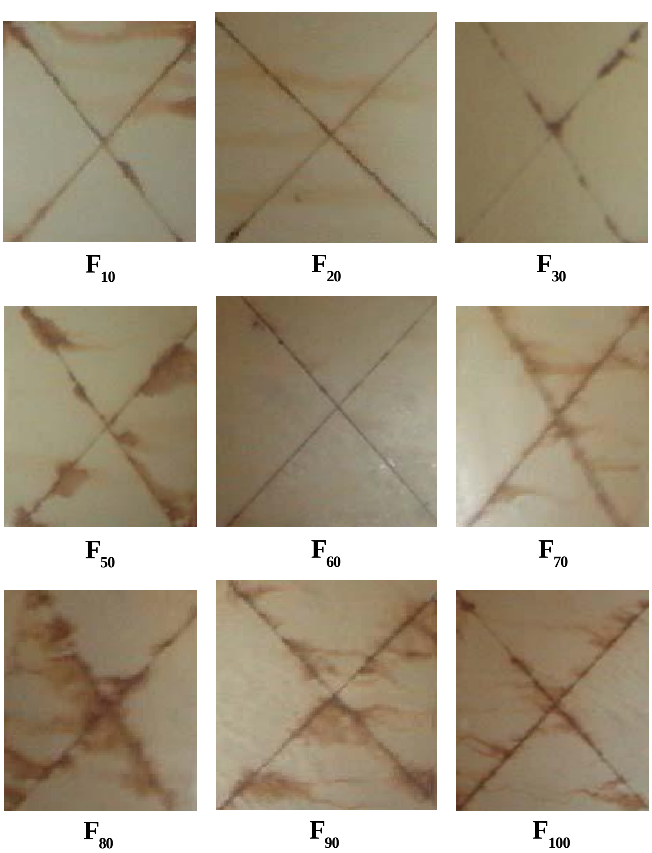


Figure 1 : The surface texture of the films formed from F10-F100 after subjected to salt spray test

Evaluation of electrochemical technique

The electrochemical studies were important for determination the validity of the dry film coating. In this study one could be used four types of electrochemical techniques open circuit potential, potentiodynamic polarization, Cyclicvoltametery polarization and electrochemical impedance spectroscopy. These studies were carried out for formula F10-F100.

Open circuit potential measurements

The open circuit potential values of the carbon steel (blank) and the formula F10, F20, F40, F50, F60, F70 and F90 were -0.399, 0.659, 0.595, 0.584, 0.512, 0.550, 0.658 and 0.599 V respectively. The variation of open circuit potential (OCP) with time for the formed films from formula F10, F20, F40, F50, F60, F70 and F90 in 3.5% NaCl was shown in figure 2 and TABLE 11. These curves were observed that, the blank specimens was pitted and cavity the surface that due to formation the of ferrous hydroxide and chloride, which were damaged and consumed the specimen, these phenomena was observed after 30 minutes and the formation of ferrous ion were failed and the curve was jumped

TABLE 11 : Data from open circuit potential measurements of uncoating and coating carbon steel electrode in 3.5 % NaCl containing different formulas of resins compounds without organosilicon compounds.

Sample	Blank	F_{10}	F_{20}	F_{30}	F_{40}	F_{50}	F_{60}	F_{70}	F_{80}	F_{90}	F_{100}
Potential	-399	-659	-595	-597	-584	-512	-550	-658	-510	-599	-588

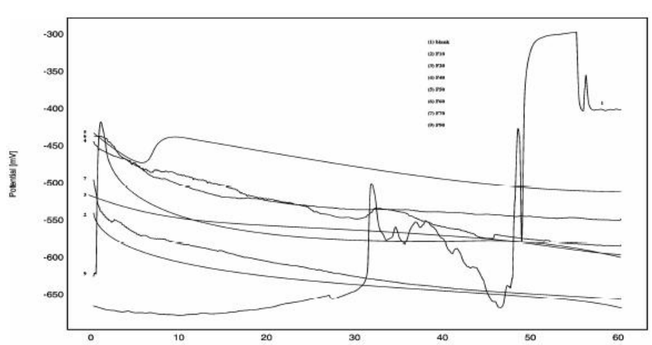


Figure 2 : The variation of open circuit potential for blank and formula F10, F20, F40, F50, F60, F70 and F90

again at 50 minutes, i.e these method was accelerated the corrosion phenomena.

On the other hand, the formula F10, F20, F40, F50, F60, F70 and F90 were homogeneous and not formation of any type of ferrous ions. These phenomena were observed for the coating specimens by formula F10, F20, F40, F50, F60, F70 and F90 which the OCP values of coated carbon steel specimen by formula F10, F20, F40, F50, F60, F70 and F90 were decreased initially and stable after 10 minutes passage and shifted to negative direction, From these data, this shows that the formula F10, F20, F40, F50, F60, F70 and F90 were able to protection of the carbon steel surface in 3.5% NaCl solution.

Electrochemical polarization for formula F10, F20, F40, F50, F60, F70 and F90

Figure 12 illustrates the polarization curves for formation films from formula F10, F20, F40, F50, F60, F70 and F90 in NaCl 3.5% as electrolyte at volt range from -1.0 – 0.5 V. From the curves could be showed that, the coating materials were played as cathadic / anodic protection. On the other hand, the formula F10 andF20 were high efficiency and protected as cathodic and anodic protection. It was depend on the pigments inorganic material. These data were matched with open circuit and salt spray test.

The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) calculated using Tafel extrapolation method were given in TABLE 12 and it was evident from the figure 3. the E_{corr} shifts toward higher cathodic at values -666.8 mV versus SCE than uncoated carbon steel specimen. The shifts in corrosion potential towards more cathodic values compared to uncoated carbon steel specimen was due to the presence of metallic zinc in the coating. On the other hand, the icorr for formula F20 and F50 were shifted towards cathodic/ anodic protection(in the range of -200 to -1000 mV) but also the formula F10, F40, F60, F70 and F90 were shifted towards cathodic protection compared to uncoated carbon steel specimens. The corrosion efficiency I% and the surface coverage θ were calculated from the following equations:

$$I\% = (1 - i_{corr} / i_o) \times 100$$

$$\theta = (1 - i_{corr} / i_o)$$

Where i_{corr} and i_o were the coated and uncoated current densities respectively. From the results obtained in figure 3 and TABLE 12, we note that I% and the surface coverage θ were decreased with furan concentration increased 96.25, 95.37, 94.35, 94.00, 93.87, 92.98 and 90.621 for formula F10, F20, F40, F50,

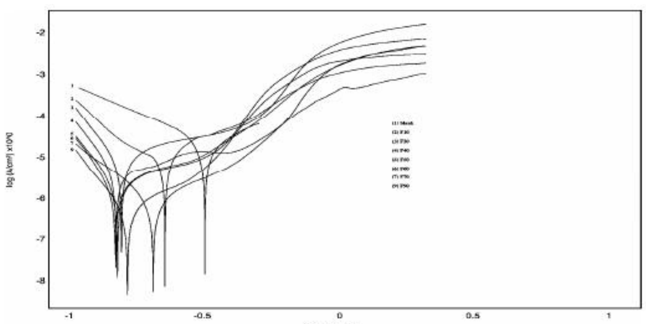


Figure 3 : Tafel potentiodynamic polarization curve for 1-blank and formula 2-F10 3-F20 4-F40 5-F50 6-F60 7-F70 and 9-F90 in 3.5% of NaCl as electrolyte and potential range from -1.0 to +0.5 volt.

TABLE 12 : Parameters of potentiodynamic polarization of carbon steel electrode coated specimen in 3.5% Na Cl concentrations containing different formulas of resins compounds without organosilicon compounds.

Samples	$-E_{corr}$	I_{corr} mA/Cm^2	Rp ohm.cm^2	b_a mv/dec	b_c mv/dec	θ	I%
Blank	518.8	0.02268	3562	436.9	-329.7	-	-
F10	666.8	0.00085	71558	217.4	-393.8	0.96252	96.252
F20	808.4	0.00105	50336	304.9	-203.9	0.953703	95.3703
F30	796.7	0.00119	44416	239.6	-243.5	0.950661	95.0661
F40	844.1	0.00128	34930	442.8	-133.0	0.943562	94.3562
F50	710.9	0.00136	31942	658.2	-117.6	0.940035	94.0035
F60	849	0.00139	31304	216.4	-189.2	0.938712	93.8712
F70	828.7	0.00159	22755	254.9	-124.6	0.929894	92.9894
F80	689.1	0.00205	15886	200.6	-120.9	0.909612	90.9612
F90	842.8	0.002127	18085	400.5	-114.9	0.906216	90.6216
F100	760.3	0.002248	8850	118.1	-75.7	0.900881	90.0881

F60, F70 and F90 respectively.

Electrochemical impedance (EIS)

EIS would generate quantitative data that relates to the quality of a coating on a metal substrate. EIS was useful for painting because using EIS to characterize a paint metal substrate simultaneously measures two phenomena:
The deterioration of the organic coating caused by exposure to an electrolyte and the increase in corrosion rate of the underlying substrate due to the deterioration of the coating and subsequent attack by the electrolyte.

The electrochemical impedance spectroscopy for carbon steel specimen (blank)

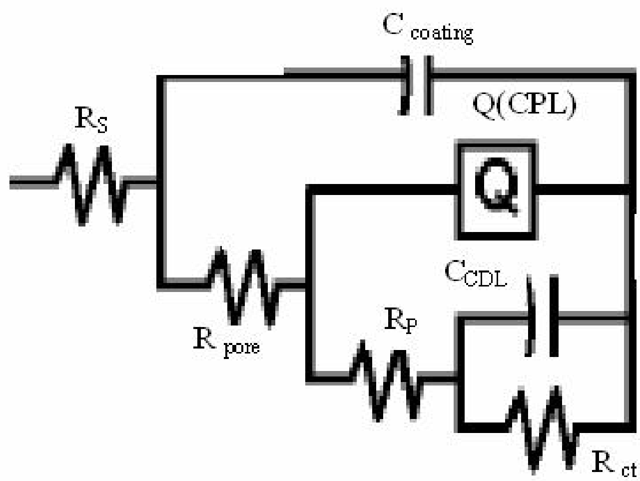


Figure 4 : Equivalent circuit used for represented the impedance response for blank, FS10, FS20, FS40, FS50, FS60, FS70 and FS90 formula

Figure 4 illustrates the component elements for equivalent circuit models for the carbon steel specimen, who these components were R_S was the electrolyte resistance; R_{pore} was the electric resistance, $C_{coating}$ was the capacitance of the protective coating; Q (CPE) was the constant phase element, R_p was the polarization resistance. While the parameters R_{ct} and C_{dl} yield information on the corrosion process. The values for these parameters R_S, $C_{coating}$, R_{pore}, Q(CPE), R_p, R_{ct} and C_{dl}, were tabulated in the TABLE 13. From these data, the value of R_s was very low and can be ignored; the value of $C_{coating}$ was indicated the beginning of constitution of the corrosion products on the substrate surface. The value of R_{pore} was much decreased which illustrated the increase quantity for porosity on the carbon steel surface and the increase was commonly attributed to corrosion products from the metal substrate blocking the pores. The value of R_p was the standard value for a carbon steel metal which the corrosion rate of the metal substrate was described by polarization resistance. The value of the Cdl was less than the standard value (10^4 to 10^6 n F) for carbon steel metal and also the Cdl value related to the corrosion rate. Finally, the values of the Q (CPE) and the n were indicated to the heterogeneity of the oxide layer formation on the carbon steel specimen. On the other hand, the electro-circuit from the Nyquist plot obtained for uncoated carbon steel electrode in 3.5% NaCl solution was given in Figure 5, the feature of the curve was a slightly depressed semicircle. Since there was not any coating on the electrode surface and a passivation could be expected under these conditions, the diameter of the curve must be equal to charge transfer resistance (R_{ct}) value and the semicircle at lower frequency was due to the double layer capacitance, which the values of Cdl was effected in the corrosion rate.

The electrochemical impedance spectroscopy for the specimens coating by dry film of formula F10, F20, F40, F50, F60, F70 and F90 in 3.5% NaCl electrolyte solution

In the case of a metal/paint system one of the most widely used equivalent circuit models was that shown in Figure 6, for the formula F10, F20, F40, F50, F60, F70 and F90. Where: R_S was the electrolyte resistance; R_{pore} was the electric resistance (pores, low cross linking) of the protective coating; $C_{coating}$ was the capacitance of the protective coating. R_p was the coating polarization resistance of the corrosive process. Q was the constant phase element (CPE). When water penetrates the coating and reaches the metal. It was also agreed that the general impedance may include the W the mass transfer (Warburg) impedance (W was the Warburg finite diffusion impedance). Their dielectric contribution was characterized by the R_{ct} and Cdl double layer capacitance parameters, while the parameters R_{ct} and C_{dl} yield information on the corrosion process at the bottom of the pores in the coating.

From these data in the TABLE 13, these data was different parameters in the equivalent circuit models. The R_s values were very low and can be negligible. The Coating capacitance (C_c) and pore resistance of the organic coating were very important parameters to measure during coating failure. The values of $C_{coating}$ were increased after immersion in an electrolyte and the values of R_{pore} were decreased with increasing furan ratio in the previous formula. An increase in Ccoating and decrease Rpore were indicated the beginning of detachment of the organic coating from the substrate because of adhesion loss and number of porous were increased due to the penetration of the electrolyte into the micropores of the coating.

The capacitive component of the paint film impedance was drawn as a CPE (Q). Also here its stability values with the immersion time were noteworthy. Likewise, typical values of n obtained for the corresponding CPE were shown in TABLE 14 for formula F10, F20, F40, F50, F60, F70 and F90, it can be seen that low n values, associated with the capacitance of the part of the coating film, gives 0.5 = n = 0.6. The agreement among the whole experimental data obtained for previous formula confirms the very good anticorrosive protection provided to steel structures through the combined barrier + cathodic passivation mechanisms of this painting system. N values were between 0.51-0.57 this effect due to surface roughness or caused by heterogeneity of the surface. On the other hand, the Warburg impedance was appeared at the low frequency and high resistance, the Warburg impedance values were tabulated in TABLE 14. From these data the diffusion was increased with increased the furan ratio in the previous formula at low frequency, the diffusion was influenced in the charge transfer to and from electrode.

These three parameters R_p, Cdl, and R_{ct} were related to the corrosion rate which both the R_p and R_{ct} were inversely proportional to the corrosion rate as following equation:

$$I_{CORR} = \frac{\beta_a \beta_c}{2.303(b_a + b_c)} . (\frac{1}{R_P})$$

$$R_{CT} = \frac{RT}{nFI_0}$$

Which I_{corr} and I_0 were the coated and uncoated corrosion current, R_p was the polarization resistance and R_{ct} was the charge transfer resistance, these parameters in the previous equation were indicated to corrosion rate. The b_a and b_c were anodic and cathodic Beta coefficient, T was temperature, R was gas constant, n was number of electron and F was Faradays constant. From these data for R_p, Cdl and R_{ct} were decreased with increasing the furan ratio for formula F10, F20, F40, F50, F60, F70 and F90. These results were represented the extent of ionic conduction through the coating film in electrolytic environments, The continuous decrease of Rp, R_{ct} and the continuous increase of Cdl values indicated widening of the corroding area beneath the coating as a consequence of the progressive degradation of the coating. On the other hand, the parameters values R_{pore}, $C_{coating}$, R_p, CPE, n, Cdl and R_{ct} were greater than the same parameters values for carbon steel specimen (blank), these data were indicated to the formula F10, F20, F40, F50, F60, F70 and F90 were corrosion protective and this behavior was giving evidence to barrier effect of the coating. The corrosion products modified by furan coating could provide a certain protection by covering the surface and also these

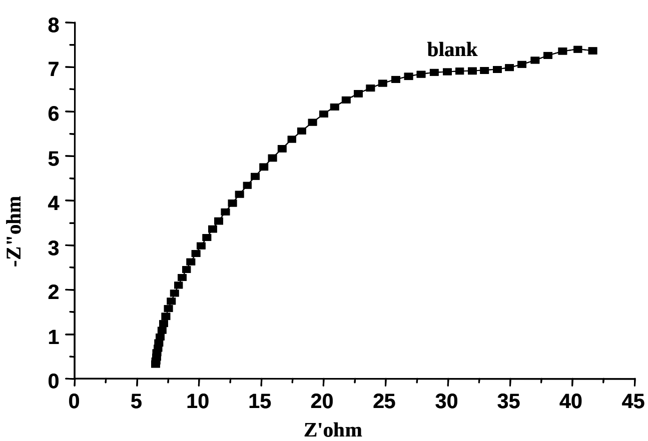


Figure 5 : The nyquist plot obtained for carbon steel specimen surface in 3.5% NaCl as electrolyte

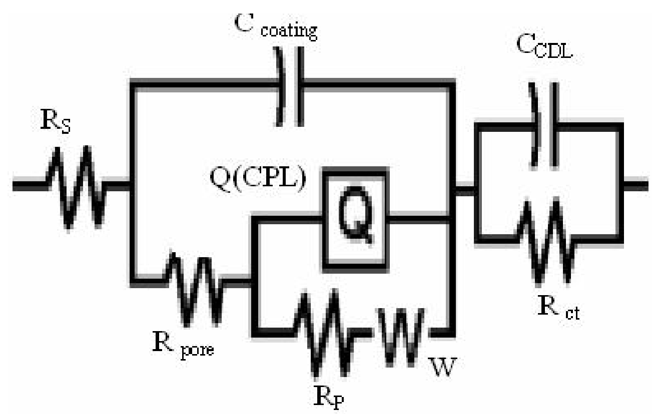


Figure 6 : Equivalent circuit used for represented the impedance response in the presence of diffusion control for F10, F20, F40, F50, F60, F70 and F90 formula

TABLE 13 : The variation parameters resistors and capacitors for the formula F10, F20, F40, F50, F60, F70 and F90

Parameters→ Formula↓	R_s	$C_{coating}$	R_{pore}	Q(CPE)	n	R_p	W	C(Cdl)	R_{ct}
Blank	64.32	$1.8x10^{-5}$	100	$9551x10^{-6}$	0.3668	4521		0.2256	6.203
F10	11.71	$1.3x10^{-8}$	$1x10^{6}$	$1.7x10^{-7}$	0.5765	$7.3 x10^{5}$	$1.14x10^{-5}$	$2.619x10^{-6}$	9076
F20	12.08	$1.6x10^{-8}$	$1.1x10^{6}$	$2.8x10^{-7}$	0.5641	$6.2x10^{5}$	$2.21x10^{-5}$	$7.202x10^{-6}$	8739
F40	15.54	$1.7x10^{-8}$	$2.2x10^{6}$	$3.4x10^{-7}$	0.5591	$5.1x10^{5}$	$3.12x10^{-5}$	$9.152x10^{-6}$	6543
F50	17.58	$3.8x10^{-8}$	$3.8x10^{6}$	$3.7x10^{-7}$	0.5406	$4.3x10^{5}$	$4.28 x10^{-5}$	$12.09 x10^{-6}$	5934
F60	18.78	$5.7x10^{-8}$	$3.9x10^{6}$	$3.9x10^{-7}$	0.5382	$3.5 x10^{5}$	$5.65x10^{-5}$	$13.003x10^{-6}$	5346
F70	19.57	$5.8x10^{-8}$	$4.4x10^{6}$	$4.5x10^{-7}$	0.5275	$3.1x10^{5}$	$6.29x10^{-5}$	$14. 209x10^{-6}$	4656
F90	23.78	$5.9x10^{-8}$	$4.7x10^{6}$	$4.9x10^{-7}$	0.5137	$2.7x10^{5}$	$7.16x10^{-5}$	$15.123x10^{-6}$	3590

TABLE 14 : Parameters of electrochemical impadance of carbon steel electrode coated specimen in 3.5% Na Cl concentrations containing different formulas F10, F20, F40, F50, F60, F70 and F90.

Parameters→ Formula↓	R_s ohm	R (R_{ct}+R_s) ohm	C nF/cm²	R_{ct}(R-R_s) ohm	I%
Blank	77.42	5391	186500	5313.58	
F10	23	115200	0.005178	115177	95.38
F20	25	102900	50.01474	102875	94. 83
F40	30	100635	0.0154	100605	94.71
F50	32	99567	0.01589	99535	94.66
F60	35	95723	0.03667	95688	94.44
F70	37	93934	0.13500	93897	94.34
F90	40	92562	0.5524	92522	94.32

products could increase the film resistance by accumulating within the pores.

Figure 7-13 was showed the Nyquist plots obtained for formula F10, F20, F40, F50, F60, F70 and F90 electrode in corrosive test solution. The diagram representing the measurement after 1 h was found to consist of a linear portion at low frequencies and a depressed semicircle at higher frequency region for formula F10 and F40 (Figure 7, 9)which the semicircle at high frequency was due to the coating capacitance and the value of $C_{coating}$ was effected in the barrier and coating properties. The diagram representing the measurement after 1 h was found to consist of a linear portion at high frequencies and a depressed semicircle at lower frequency region for formula F20, F50, F60, F70 and F90 (Figure 8, 10, 11, 12 and 13) which the semicircle at low frequency was due to the capacitance double layer and the value of Cdl was effected in the corrosion product. The total of the charge transfer resistance against anodic dissolution (R_{ct}) and the film resistance R_{pore} was called as R_p and the semicircle was attributed to this value. The protection efficiency values were calculated for some exposure times by the following equation:

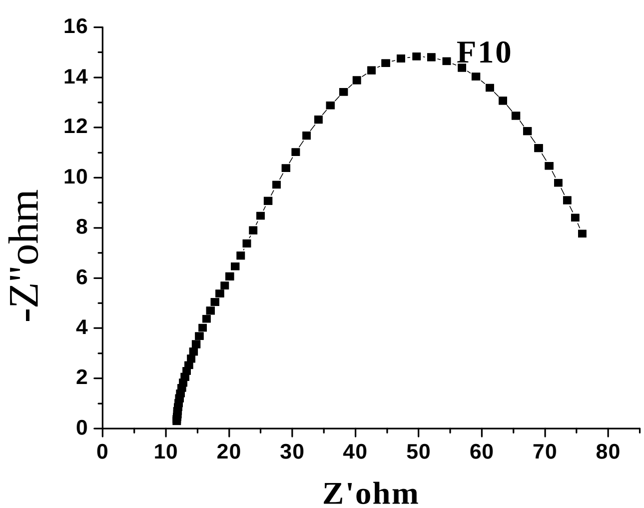


Figure 7 : Nyquist plot obtained for dry film formation from F10 formula on carbon steel surface in 3.5% NaCl as electrolyte

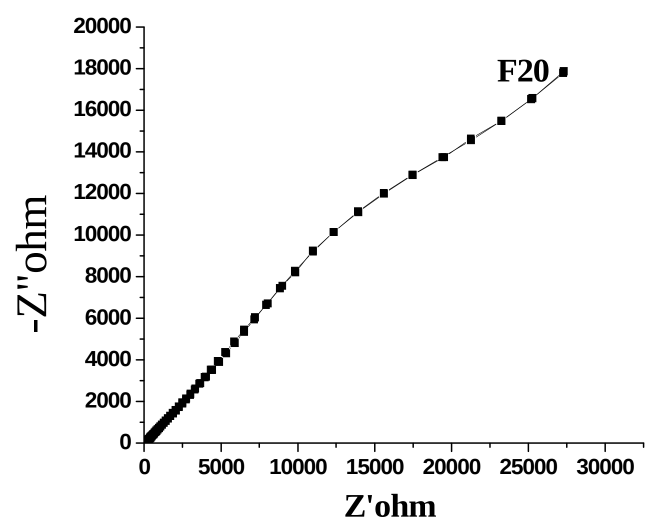


Figure 8 : Nyquist plot obtained for dry film formation from F20 formula on carbon steel surface in 3.5% NaCl as electrolyte

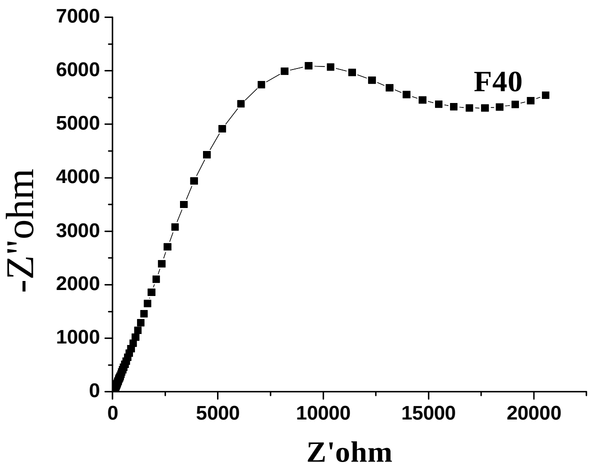


Figure 9 : Nyquist plot obtained for dry film formation from F40 formula on carbon steel surface in 3.5% NaCl as electrolyte.

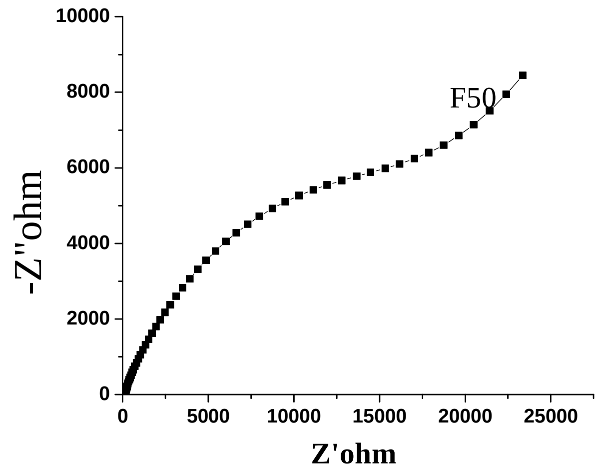


Figure 10 : Nyquist plot obtained for dry film formation from F50 formula on carbon steel surface in 3.5% NaCl as electrolyte.

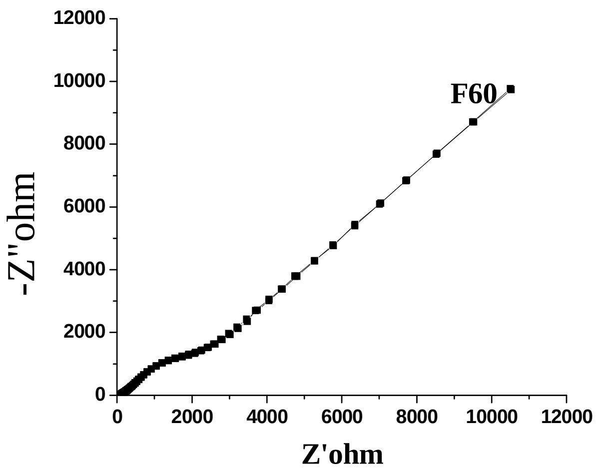


Figure 11 : Nyquist plot obtained for dry film formation from F60 formula on carbon steel surface in 3.5% NaCl as electrolyte

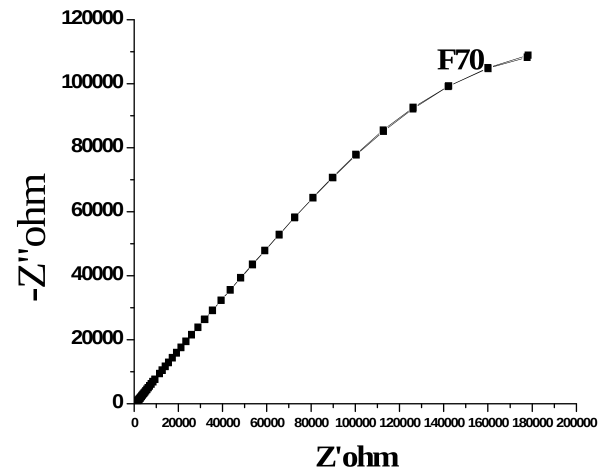


Figure 12 : Nyquist plot obtained for dry film formation from F70 formula on carbon steel surface in 3.5% NaCl as electrolyte

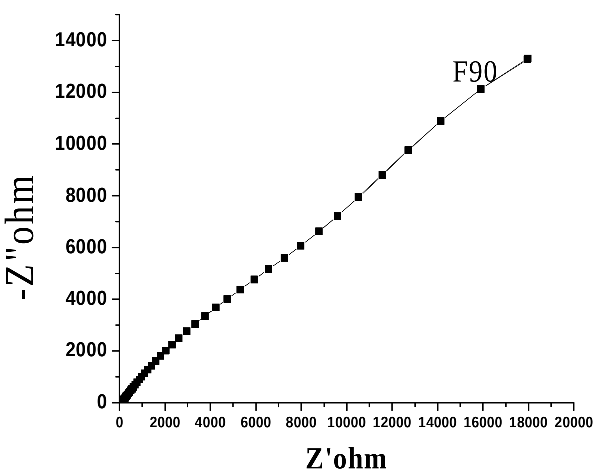


Figure 13 : Nyquist plot obtained for dry film formation from F90 formula on carbon steel surface in 3.5% NaCl as electrolyte

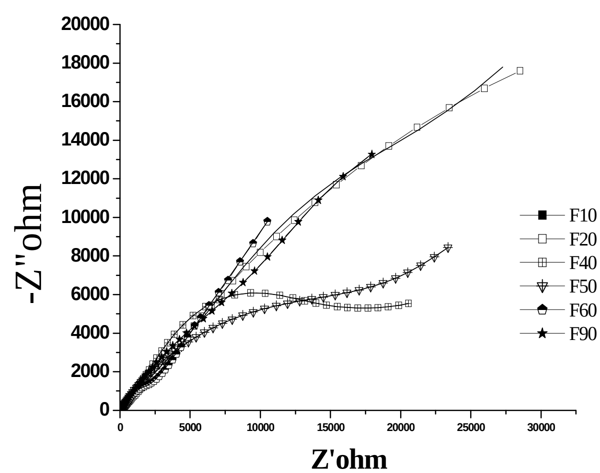


Figure 14 : Nyquist plot obtained for dry films formation from F10, F20, F40, F50, F60, F70 and F90 formula on carbon steel surface in 3.5% NaCl as electrolyt

$$I\% = \frac{R_{ct}(coated) - R^{o}_{ct}(uncoated)}{R_{ct}(coated)} \times 100$$

The diagrams representing 1 h measurements were found to have almost the same profile and suggested that the coating behaved like almost a perfect coating. This case was giving evidence for excellent barrier property of this coating which was previously showed by polarization and E_{ocp}–time curves.

The calculated protection efficiency values for formula F10, F20, F40, F50, F60, F70 and F90 were calculated from previous equation in TABLE 14. Which these values were 95.83, 94.83, 94.71, 94.66, 94.44, 94.34 and 94.32respectively. After the removal of electrode from the test solution, it was observed that there was no blistering or defects on the surface. Therefore, it was concluded that the film coating has lowered the porosity and water mobility through the pores. This event resulted in better protection with respect to single furan coating under the same conditions.

CONCLUSION

- Using of some organic resins, novolac, furan and epoxy compounds
- These resins blended with inorganic additive ZnO_2, TiO2, Talc and centered glasses to form formula F10 – $_{F100.}$
- Using TDI as curing agent
- The polyurethane films and other amid furfural linkage formed
- The preparation surface of carbon steel alloy specimens painted by formula F10 – F100
- The physical, mechanical and chemical properties for the forming films from formula F10 – F100 recorded and discussed.
- Electrochemical polarization OCP, electrochemical potentiodynamic, cyclicvoltametry and EIS studied and disscused.
- Surface morphology of dry films before and after polarization studies examinated.
- The net results from all examinations matched and indicating the validity of the formed dry films for protection of carbon steel alloy.

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