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Protection of petroleum equipments by blending of friendly environmental resins and pigments

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ABSTRACT

Protection of petroleum equipments from corrosion is carried out by painting using a polycarbohydrate naturally occurring compound, chitosan. The paint materials are prepared by blending of environmental resin with inorganic pigments. The chitosan and polyethyleneglycol-polydimethyl siloxane are prepared, purified and confirmed by FT-IR. The commercial novolac and epoxy resins are used. These resins are blended with each other at definite ratios. The inorganic pigments TiO_2 , Zn dust, Al_2O_3 and silica are also used at definite ratios. These materials are blended with each other to form different formulae A_1 - A_{12} . Toluene diisocyanate is used as a curing agent. These formulae are applied on the carbon steel alloy specimens and are approved at Suez Oil Company. The physical mechanical and chemical properties are investigated and recorded. The obtained data are performed for the formula A_4 - A_{10} to protect the petroleum equipments.

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KEYWORDS

Inorganic pigments;
Carbon steel alloy;
Corrosion.

INTRODUCTION

The carbohydrate polymers are not wholly synthetic, since they are based upon cellulose. They form about half of all the cell wall material of wood and plants. They behave friendly towards the environment^[1-9]. Advances in materials performance often require the development of composite system. The corrosion resistance of components can be greatly increased by protective painting and this is a growing industry of considerable economic importance. Paintings are used in wide range as onshore, offshore of petroleum, gases, petrochemical and other industries at low and high temperature applications. Petroleum and petrochemical equipments are subjected to high temperature and environmental corrosion. The alternative systems emphasise the necessity for the painting (protective) of the surface of

substrate^[10-15].

Polymethyl-methacrylate, like nitrocellulose, is a fairly brittle polymer and both must be plasticized for paint uses. It is sometimes convenient to increase flexibility and improve adhesion by blending with more flexible resin. It is known that less viscous solvents give less viscous solutions. For this reason, less viscous plasticizers give less viscous (or more flexible) plasticized polymer films^[7-14]. Paintings are one of the most suitable, less expensive and more efficient technique for corrosion protection that increase the life time of equipments^[3-15]. The aim of this work depends on the preparation of chitosan and polyethyleneglycol-polydimethyl siloxane. These are mixed with commercial novolac and epoxy resins and blended with inorganic TiO_2 , Al_2O_3 , Zn dust, CaCO_3 and silica gel at definite ratios for each. Substrate compatibility, adhesion, porosity, the effect

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TABLE 1 : Different ratios of chemical painting formulae

Formula/ Composition	A ₀	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇	A ₈	A ₉	A ₁₀	A ₁₁	A ₁₂
Chitosan	0	5	10	15	20	25	30	35	40	45	50	55	60
P(EG _{tri} -DESO)	10	10	10	10	10	10	10	10	10	10	10	10	10
Epoxy resin	15	15	15	15	15	15	15	15	15	15	15	15	15
Novolac	25	25	25	25	25	25	25	25	25	25	25	25	25
Zn	30	30	30	30	30	30	30	30	30	30	30	30	30
TiO ₂	9	9	9	9	9	9	9	9	9	9	9	9	9
Al ₂ O ₃	2	2	2	2	2	2	2	2	2	2	2	2	2
Silica gel	7	7	7	7	7	7	7	7	7	7	7	7	7
CaCO ₃	2	2	2	2	2	2	2	2	2	2	2	2	2
MEK	15	15	15	15	15	15	15	15	15	15	15	15	15

of thermal cycling, hardness, bending, impact, and resistance to petroleum, petrochemical products, and corrosion protections as well as cost are investigated. The mechanism of the formation protective films is also discussed.

EXPERIMENTAL

Preparation of chitosan

Polycarbohydrate derivative, chitosan was produced by alkaline deacetylation of chitin^[16]. Chitosan (poly[B-(1-4)-2-amino-2-deoxy-D-glucopyranose]) is also occurs naturally. After of preparation, purification, it was confirmed by FT.IR.

Preparation of polyethyleneglycol-polydimethyl siloxane P(ED_{tri}-DMSO)

In three necked flask equipped with mechanical stirrer, pressure dropping funnel, one mole of dimethyl dichlorosilane was reacted with one mole of triethyleneglycol in presence of the mixture of xylene and pyridine, the latter was used as acid acceptor. The reaction was carried out under inert atmosphere and gently heated at 30°C for 1 hr. The temperature was raised gradually until 80°C for 4 hrs and 100°C for 3 hrs to produce P(EG_{tri}-DMSO). Finally the product was purified and fractionally distilled under vacuum and confirmed by infrared analysis (FT.IR) and gel permeation chromatography (GPC).

Characterization techniques

Infrared analysis (FT.IR)

The IR spectra of the synthesized chitosan and P(ED_{tri}-DMSO) were recorded by Infinity series- using (FT.IR) Spectrometer Model Type Mattson Bench top

961. The wave number and intensities of the IR of the different types of the function groups were determined in range of 500-4000 cm⁻¹.

Molecular weight (M.Wt)

The average M.Wt of the synthesized polyethylene glycol polydimethyl siloxane P(ED_{tri}-DMSO) was measured by using gel permeation chromatograph (GPC) water model 600E. Detector: UV -visible spectrophotometer. Mobile phase: toluene HPLC grade. Column: styragel, Injection volume: 3µm.

Preparation of the chemical formula

Different parts (0,5,10,15,20,25,30,35,40,45,50,55,60) of polycarbohydrate compound (chitosan) were mixed with 25 parts of Novolac, 10 parts of P(EG_{tri}-DESO), 15 parts of epoxy resin, 30 parts of zinc dust, 9 parts of TiO₂, 2 parts of Al₂O₃, 7 parts of silica gel, 2 parts of CaCO₃ and 15 parts of methyl ethyl ketone (MEK) as solvent (TABLE 1).

Different parts of toluene diisocyanate (TDI) were used (5, 10, 15, and 20) as curing agent, which were mixed with each formula to form various painting formulation. Each formulation was applied on the surface of carbon steel alloy specimens (brushing method) and cured at room temperature and 90°C, respectively, to determine the optimum condition.

Resistivity measurements according to ASTM (D1125)

The resistivity meter model 515 digital apparatus was used for determination of the resistance degree of different formula A₀-A₁₂. The measurements were carried out at ambient temperature and K.ohm.

Preparation the surface of metal specimens

Unused tubes of carbon steel alloy type AG15 were provided from petroleum pipelines of Suez Oil Petroleum Company at Red Sea to be used as specimen's supplier. The specimens were cut as regular edged cuboids with dimension ≈8, 15, and 0.1. Each specimen was cleaned, polished with 150-600 grade of emery paper rinsed with distilled water, degreased with acetone, weighed and finally stored under vacuum after wrapping with adhesive thin paper. The specimens were divided to sets.

Optimization steps of the prepared coating

TABLE 2: The visual inspection after application of the painting wet films from formula A₀-A₁₂ at optimum concentration of TDI (15%)

Formula	Sealing	Sagging	Fish eyes	Shrinking	Coagulation	Smoothes	Homogeneity	Settling phenomena
A ₀	No sealing	No sagging	Fish eyes appeared	No Shrinking	No Coagulation	High Smooth	Homogeneity	Settling
A ₁	No sealing	No ssagging	Fish eyes appeared	No Shrinking	No Coagulation		Homogeneity	Settling
A ₂	No sealing	No sagging	No Fish eyes	No Shrinking	No Coagulation		Homogeneity	No Settling
A ₃	No sealing	No sagging	No Fish eyes	No Shrinking	No Coagulation		Homogeneity	No Settling
A ₄	No sealing	No sagging	No Fish eyes	No Shrinking	No Coagulation		Homogeneity	No Settling
A ₅	No sealing	No sagging	No Fish eyes	No Shrinking	No Coagulation		Homogeneity	No Settling
A ₆	No sealing	No sagging	No Fish eyes	No Shrinking	No Coagulation		Homogeneity	No Settling
A ₇	No sealing	No sagging	No Fish eyes	No Shrinking	No Coagulation		Homogeneity	No Settling
A ₈	No sealing	No sagging	No Fish eyes	No Shrinking	No Coagulation		Homogeneity	No Settling
A ₉	No sealing	No sagging	No Fish eyes	No Shrinking	No Coagulation		Homogeneity	No Settling
A ₁₀	No sealing	No sagging	No Fish eyes	No Shrinking	No Coagulation		Homogeneity	No Settling
A ₁₁	Sealed	No sagging	Fish eyes appeared	Shrinking	Coagulation		Un homogeneity	No Settling
A ₁₂	Sealed	No sagging	Fish eyes appeared	Shrinking	Coagulation	Un homogeneity	No Settling	

TABLE 3: The physical measurements for wet and dry films at room temperature and 15% TDI

Symbol	Weight of cleaning specimens (g)	Specimen area of one surface (cm)	Weight of wet coating (g)	Normalized weight of wet coating per unit area (mg/cm ²)	Weight of dry coating (g)	Normalized weight of the dry coating per unit area (mg/cm ²)	Curing Temp. °C	Relative humidity (R. H)	Touch dry (hr)	Complete dry (hr)
A ₀	70.6359	123.2819	4.4969	36.4765	2.6686	21.6463	Ambient Temp.	≈ 50 %	3 - 5	72 - 96
A ₁	71.3100	123.5913	4.4971	36.3868	2.6688	21.5937				
A ₂	70.0598	123.1248	4.4975	36.5279	2.6691	21.6780				
A ₃	70.7662	123.3725	4.4981	36.4595	2.6695	21.6377				
A ₄	71.8915	123.7254	4.4983	36.3571	2.6698	21.5784				
A ₅	70.7321	123.4987	4.5001	36.4384	2.6700	21.6196				
A ₆	70.9537	123.5767	4.5003	36.4500	2.6703	21.6084				
A ₇	70.4812	123.3940	4.5007	36.4742	2.6706	21.6428				
A ₈	71.5030	123.8910	4.5011	36.3311	2.6710	21.5592				
A ₉	70.8224	123.6126	4.5014	36.4153	2.6712	21.6094				
A ₁₀	70.5960	123.3215	4.5016	36.5029	2.6715	21.6628				
A ₁₁	70.3125	123.4142	4.5019	36.4779	2.6719	21.6489				
A ₁₂	71.9819	123.8193	4.5021	36.3602	2.6721	21.5806				

The optimization steps were generally carried out under statistic air at ambient pressure and at room temperature. A set of specimens was coated with every formula (A₀-A₁₂), which was cured with curing agent TDI at ambient conditions until completely cured. The painting specimens were gradually inspected to record the optimization conditions for each formula. The coating films over the surface of specimens were examined. Having determined the optimum conditions with the selected formula, at which the formulation of the best coating was achieved in steps, the selected optimum formula for chitosan compound was kept constant through the optimization procedure.

Evaluation of the physical and mechanical proper-

ties

The evaluations of the physical, mechanical and chemical properties of the prepared coating were carried out through the following characterization techniques:-

Physical properties

1. Visual inspection

The painting films on the surface of specimens were visually inspected after application to determine sealing, sagging, fish eyes, shrinking, coagulation, smoothes and homogeneity (TABLE 2).

1.1. Calculating the wet and dry film thickness

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TABLE 4: Physical and mechanical properties of the formed films from formula A₀-A₁₂ at room temperature and at optimum concentration of TDI (15%)

Symbol	Average WFT μm	Average DFT μm	Bending	Pinhole	Adhesion	Hardness	Impact	Electrical Conductive.	Resistance
A ₀			Fail	Fail	Fail	H	Fail	Fail	10000 K Ω
A ₁			Fail	Fail	Pass	H	Fail		
A ₂			Pass	Pass	Pass	H	Fail		
A ₃			Pass	Pass	Pass	H	Pass		
A ₄			Pass	Pass	Pass	H	Pass		
A ₅			Pass	Pass	Pass	1H	Pass	Passed at	
A ₆	130	95 \pm 5	Pass	Pass	Pass	1H	Pass	475 V	20000 K Ω
A ₇			Pass	Pass	Pass	1H	Pass		
A ₈			Pass	Pass	Pass	1H	Pass		
A ₉			Pass	Pass	Pass	1H	Pass		
A ₁₀			Pass	Pass	Pass	F	Pass		
A ₁₁			Fail	Pass	Fail	F	Fail	Fail	9000 K Ω
A ₁₂			Fail	Pass	Fail	F	Fail	Fail	9000 K Ω

TABLE 5: Visual inspection of the effect of organic solvents (Xylene, toluene and benzene) on the formed dry films

Period immersion time(Days)	Effect of the texture of the formed dry films												
	A ₀	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇	A ₈	A ₉	A ₁₀	A ₁₁	A ₁₂
6	No												
12	change	No	No	No	No	No	No	No	No	No	No	No	No
24	Change	Change	change	change	change	change	change	change	No	No	No	No	No
48	Change	Change	change	Change	change	change	Change	change	change	change	change	change	change
72	Change												
96	change	Change	change	Change									
120	change	Change	change	change	change	change	Change						

Wet film thickness was carried out by weighing the specimens before and after the coating immediately. The wet weight of coating was recorded and calculated with respect to the surface unit area. The calculation of the dry film thickness was also carried out by weighing the specimens after full curing and drying of coat. The dry weight of coating was recorded and calculated with respect to the surface unit area (TABLE 3).

1.2. Measuring the wet film thickness (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 formulation A₀ to A₁₂ at ambient temperature. The obtained results were recorded after coating immediately.

1.3. Measuring the dry film thickness (DFT) of coating according to ASTM (D-1186 and 1005)

The DFT of the formed films from all painting formulations A₀ to A₁₂ after curing at ambient temperature and 90°C were measured by using Posit-Ector, model 6000-FT₂, coating thickness with probe gauge 6000-FT₂. The average film thickness is computed from five

readings, one at the middle and the others at the four corners of regular cubed specimen's surface. The obtained results were recorded after complete curing (TABLE 3).

1.4. Adhesion technique according to ASTM (D 3359)

Pull cut these test methods cover procedures for assessing the adhesion of coating films to metallic substrates by two methods.

X-cut is made in the film to the substrate, pressure-sensitive tape is applied over the cut and then removed, and the adhesion is assessed qualitatively on the 0 to 5 scales. A lattice pattern with either six or eleven cut in each direction is made in the film to the substrate, pressure-sensitive tape is applied over the lattice and then removed, and the adhesion is evaluated by comparison with descriptions and illustration.

1.5. Thermal cycling test according to BS-6670

The sample was gradually heated from 50°C to 325°C (25°C per 3hrs), and quenched by immersing in water at ambient temperature. The coating was exam-

ined for signs of blistering or detachment under a magnifying viewer.

1.6. Electrical conductivity technique according to ASTM (D-4399)

The electrical conductivity of prepared poly carbohydrate coatings on the surface of carbon steel alloy specimens were measured and evaluated.

1.7. Pinhole test according to ASTM (D-5162)

The pinhole of the formed films of poly carbohydrate on the surface of carbon steel alloy specimens were measured by Holiday detector model Poro test DC KV 7= 34.3 ELECTRO PHYSIC. The results are tabulated (TABLE 4).

2. Mechanical properties

2.1. Bending test according to ASTM (D-522)

This test covers the determination of the resistance to cracking of attached organic coating of the formed films on the surface of specimens. This was measured by using bending tester 5mm-35mm Richmand Road

TABLE 6: Effect of MEK and chloroform on the formed dry films

Solvent	A ₀	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇	A ₈	A ₉	A ₁₀	A ₁₁	A ₁₂
MEK	No change of the surface of the formed films												
Chloroform	No change of the surface of the formed films												

TABLE 7: Corrosion tests for the formed dry films on the surface of specimens in synthetic seawater for 90 days at room temperature

Period immersion time(Days)	Visual inspection of the dry film formed in synthesis sea water												
	A ₀	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇	A ₈	A ₉	A ₁₀	A ₁₁	A ₁₂
10-30	No spots appeared												
40	10-20 spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared
50	Spots covered surface	Spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared
60	Spots covered surface	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared
70	Spots covered surface	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared
80	Spots covered surface	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared
90	Spots covered surface	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared

King stone type KT₂5BQ consisting of a metal cone, a rotating panel-bending arm, and panel clamps all mounted on a metal base. This cone, smooth steel, 8 in.(200mm)in length with a diameter of 1/8 in.(3mm) at one end and a diameter of 1/2 in. (38mm) at the other end. The obtained results were recorded and tabulated as shown in (TABLE 4).

2.2. Hardness of the forming films according to ASTM (D-3363)

The hardness of the formed coating on the specimen's surface was measured by using hardness pin test rod model 318. The hardness of the formed coating was measured at fine points, one at the middle of specimen and the others at the four corners. The results were recorded and tabulated (TABLE 4).

2.3. Impact techniques according to ASTM (D-2794) and (G14-88)

The deformations of the formed films on the surface of specimens were determined by using Richmond Road, Kingston type KT₂5BQ. The test specimen was placed in the apparatus with the coated side up. The specimen is flat against the base support and that the indenter is in contact with the top surface of the specimen. The weight is placed at the zero mark and dropped

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TABLE 8: Corrosion tests of the formed dry films on the surface of specimens in 10 % H₂SO₄ for 50 days

Period immersion time(Days)	Visual inspection of the dry film formed in 10 % H ₂ SO ₄												
	A ₀	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇	A ₈	A ₉	A ₁₀	A ₁₁	A ₁₂
10-30	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared
40	Chalking the film surface	Chalking the film surface	Chalking the film surface	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared
50	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared

TABLE 9: Corrosion tests of the formed dry films on the surface of specimens in 10 % HCl for 50 days

Period immersion time(Days)	Visual inspection of the dry film formed in 10 % HCl												
	A ₀	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇	A ₈	A ₉	A ₁₀	A ₁₁	A ₁₂
10-30	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared
40	Chalking the film surface	Chalking the film surface	Chalking the film surface	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared
50	Change the color of paints spots appeared	Change the color of paints spots appeared	Change the color of paints spots appeared	Change the color of paints spots appeared	Change the color of paints spots appeared	Change the color of paints spots appeared	Change the color of paints spots appeared	Change the color of paints spots appeared	Change the color of paints spots appeared	Change the color of paints spots appeared	Change the color of paints spots appeared	Change the color of paints spots appeared	Change the color of paints spots appeared

TABLE 10: Corrosion tests of the formed dry films on the surface of specimens in 10 % CH₃COOH for 50 days

Period immersion time(Days)	Visual inspection of the dry film formed in 10 % CH ₃ COOH												
	A ₀	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇	A ₈	A ₉	A ₁₀	A ₁₁	A ₁₂
10	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared
20	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared
30	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared
40	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared
50	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared

suddenly on the coated surface of the specimens. The test specimen was removed from the apparatus and the impact area for cracking the coating was estimated. The test was repeated five times at each of three heights and the impacted areas are examined by use magnification power. The results were recorded and tabulated as shown in (TABLE 4).

3. Evaluation of chemical properties

3.1. Evaluation of the effect of the organic solvents according to ASTM (G.44)

The test was carried out by immersion of coating specimens in a mixture of benzene, toluene and xylene for period time 6, 12, 24, 48, 72, 96, and 120 days, respectively at ambient temperature and at 90°C. The stability of the formed films from the polycarbohydrate compound formulation were examined and tabulated (TABLE 5).

3.2. Effect of methyl ethyl ketone (MEK) according to ASTM (D-4752)

The effect of MEK on the stability and compatibility of the formed dry films on the surface of carbon steel alloy specimen was carried out by the scratching of the films to 15 types by wetting cotton. (TABLE 6).

4. Evaluation of the formed films as corrosion protection by immersed method according to ASTM (D-468, 610, G31 and Bs6670)

The coating specimens were immersed in the different aggressive media according to the following procedure:-

4.1. Effect of Synthetic seawater (S.W) 3.5% NaCl on the formed films

The test was carried out on the films formed on the surface of carbon steel specimens at dry film thickness

TABLE 11: Corrosion tests of the dry films on the surface of specimens in 10 % NaOH for 50 days

Period immersion time(Days)	Visual inspection of the dry film formed in 10 % NaOH												
	A ₀	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇	A ₈	A ₉	A ₁₀	A ₁₁	A ₁₂
10	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared
20	Few spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared	No spots appeared
30	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared
40	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared
50	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared	Spots appeared

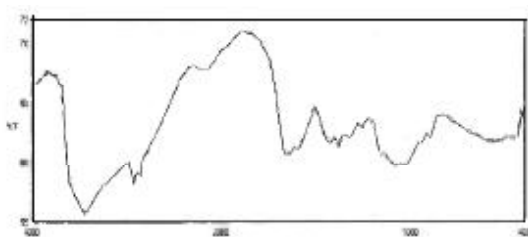
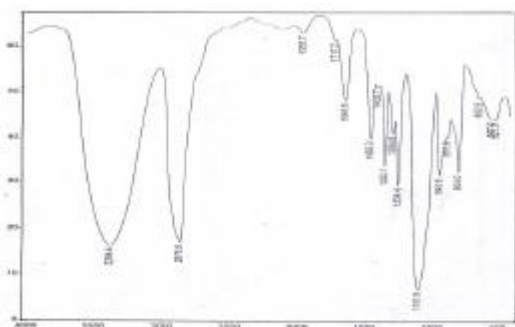
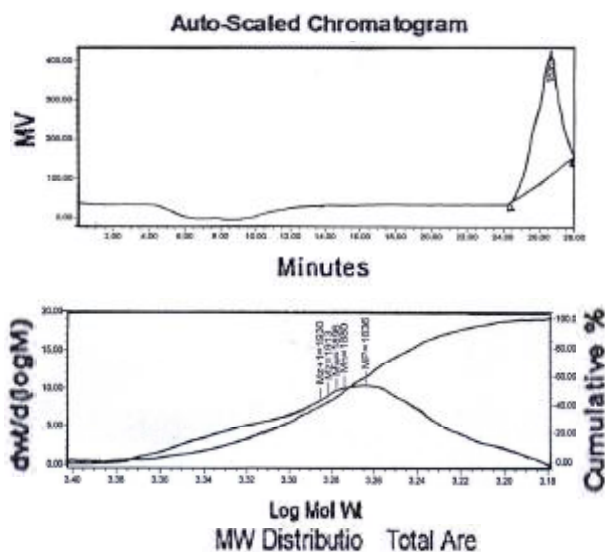


Figure 1: I.R spectra for chitosan

Figure 2: I.R spectra for P(EG_(tri)-DMSO)Figure 3: GPC spectra for P(EG_(tri)-DMSO)TABLE 12: Showing the GPC data for the compound of P(EG_(tri)-DMSO)

Type of polymer	Mn	Mw	Mz	z+1	Mp	Poly-dispersity
P(EG _(tri) -DMSO)	2891	3181	3544	3967	2616	1.10

95±5µm formed at room temperature and 90°C for 10,20,30,40,50,60,70,80 and 90 days. The visual inspections of the coating surface were investigated. The degree of rusting are computed and evaluated (TABLE 7).

3.5. Effect of H₂SO₄, HCl, CH₃COOH and NaOH (10% concentration)

The formed films from formula A₀-A₁₂ were examined by immersion in 10% H₂SO₄, HCl, CH₃COOH and NaOH. These results were carried out on the dry film thickness 95±5µm for 10, 20, 30, 40 and 50 days at ambient temperature. The visual inspections of the coating surface were investigated. The degree of rusting was computed and evaluated (TABLES 8-11 respectively).

RESULTS AND DISCUSSION

Infra -red technique (FT. IR)

Figure (1) shows the FT.IR spectrum for the characterization bands of the chitosan groups. The broad band at 3450 cm⁻¹ indicates the stretching vibration of -NH₂ and -OH groups, the sharp band at 2890cm⁻¹ indicates the stretching vibration of -CH₂ groups. Also the band at 1565cm⁻¹ indicates the -O-CH₂ groups and the bands between the ranges 1050-1350 cm⁻¹ indicate the stretching vibrations for the O-C & N-C bonds. Figure (2) illustrates the FT.IR spectrum for the prepared P(EG_(tri)-DMSO) compound. The character-

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TABLE 13: Curing agent TDI against curing time for chitosan formula at room temperature

The ratio of curing agent (TDI)(%)	Touch dry time for each formed films from the formula (hr's)												
	A ₀	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇	A ₈	A ₉	A ₁₀	A ₁₁	A ₁₂
5	7-9	9-13	9-13	9-13	9-12	9-11	9-11	9-11	9-11	9-10	9-10	8-9	8-9
10	3-5	3-6	3-6	3-6	3-5	3-5	3-5	3-4	3-4	3-4	3-4	3-4	3-4
15	2-4	2-3	2-3	2-3	2-3	1-2	1-2	1-2	1-2	1-1½	1-1½	1-1½	1-1½
20	½-¾	1-2	1-2	1-2	1-1¾	½-1½	½-1½	½-1	¼-1	¼-¾	¼-¾	¼-¾	¼-¾

TABLE 14: Thermal cycling test of the formed dry films at temperature ranged from 50 to 325°C and at optimum concentration of TDI (15%)

Temp.°C	Period time	Weight losses for each formed films x10 ⁻⁴												
		A ₀	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆	A ₇	A ₈	A ₉	A ₁₀	A ₁₁	A ₁₂
50	3hr's	5.11	5.15	5.15	5.17	5.17	5.18	5.19	5.19	5.21	5.20	5.19	5.19	
75		3.15	3.45	3.45	3.45	3.45	3.47	3.47	3.47	3.47	3.47	3.47	3.45	3.45
100		2.25	2.73	2.73	2.75	2.75	2.71	2.73	2.75	2.70	2.71	2.73	2.71	2.71
125		2.01	2.33	2.29	2.32	2.31	2.27	2.28	2.29	2.33	2.31	2.31	2.31	2.30
150		1.95	2.17	2.19	2.15	2.21	2.19	2.17	2.15	2.17	2.19	2.15	2.19	2.13
175		1.71	2.11	2.09	2.13	2.12	2.16	2.13	2.15	2.11	2.09	2.09	2.09	2.07
200		Fail	1.91	1.93	1.90	1.94	1.95	1.92	1.93	1.91	1.95	1.93	1.91	1.90
225		Fail	1.33	1.31	1.32	1.34	1.31	1.35	1.36	1.31	1.29	1.27	1.29	1.25
250		Fail	Fail	Fail	1.00	1.02	1.05	1.01	1.03	1.02	1.01	1.02	1.02	1.00
275		Fail	Fail	Fail	Fail	0.0	0.0	0.34	0.30	0.31	0.29	0.29	0.29	0.27
300		Fail	Fail	Fail	Fail	Fail	Fail	0.0	0.0	0.0	0.0	0.0	0.0	0.0
325		Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail

istic bands at 945.6 and 1101.5 cm⁻¹ for stretching vibration of -O-Si-O- and CH₂-O-Si groups, the band at 2875.6 cm⁻¹ for stretching vibration of Si-O and -CH₂ groups, the band at 1245.4 cm⁻¹ for stretching vibration of Si-C group and the band at 3360.7cm⁻¹ for stretching vibration of -OH and -Si-O-Si- groups.

Gel permeation chromatography (GPC)

Figure (3) illustrates the typical spectrum of P (EG_{tn}-DMSO) compound. The number average molecular weight Mn for the compound is 2891 and is given in TABLE 12. The number average molecular weight Mn depends on the number of polyethyleneglycol-polydimethylsiloxane molecules. The weight average molecular weight Mw of P (EG_{tn}-DMSO) compound is 3181. The polydispersity index (Mw / Mn) is found to be 1.10 (TABLE 12) indicating of a polymer of uniform molecular weight.

Chemical composition of the paintings formula A₀-A₁₂

TABLE 1 illustrates the chemical compounds ratios for the composition formula from A₁ to A₁₂. TABLE 13 illustrates the different percentages 5, 10, 15, and 20% of toluene diisocyanate (TDI) as a curing agent. The physical, mechanical and chemical properties for

each formation films from formula A₀-A₁₂ were investigated as the following:

Resistivity

The resistivity of formula 0-12 were clearly showed in figure 4. The resistivity was increased by increasing the addition of chitosan until 10 %, the resistivity become constant.

Optimization of curing agent

TABLES 13 illustrates the optimum ratio of the curing agent of toluene diisocyanate (TDI) for each formula from A₀-A₁₂. The touch curing time is the main factor to determine the (TDI) concentration for touch drying of the formation films on the surface of specimens. Also, the chemical composition for each formula from A₀-A₁₂ was affected by the chitosan ratio and/or inorganic additives. From the optimization studies of the curing agent (TDI) percentage, it was observed that the time of touch drying for each formula was decreased by increasing the chitosan ratio. The duration times were recorded at room temperature is 4-6 hr's for A₁-A₁₂. These results were computed for 15 % of (TDI) (TABLE 13). It was observed that chitosan lowers the touch drying time.

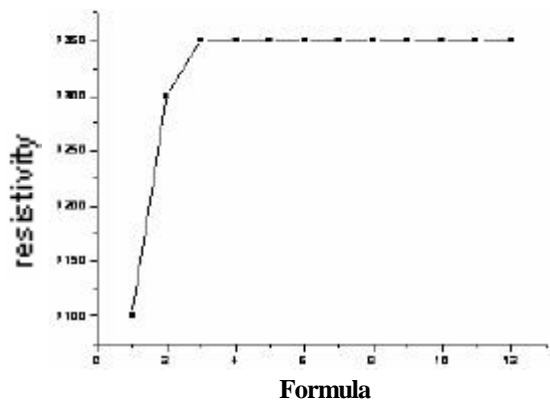


Figure 4: The resistivity of formula A₀-A₁₂

Visual inspection

TABLE 2 shows the visual inspection data during painting application and after drying (dry film). The films cover the surface of carbon steel alloy specimen by brushing method, and the data of the formed films were visually inspected directly. It was observed that, they were not sealing, and no shrinkable behaviour, unhomogeneity, and/or coagulation appear in the formed films of formula A₃ to A₁₀. The settling phenomena appeared in formula A₁ and A₂, while the fish eye appeared in the wet and dry films for formula A₁, A₂, A₁₁ and A₁₂. The formation of films during and after curing on the surface of carbon steel alloy specimens looks as one layer compatible with each other.

Calculation the wet and dry film thickness

The measurement and calculating data of the wetting and drying films on the surface of specimens at room temperature were recorded in TABLE 3. From these data, the films of wetting from formula A₀ depend on the molecular weight of filler and resins without chitosan. From these results the weight of formed films were increased by increasing the chitosan ratio. Also, the normalized weights of wetting films by unit area of these films increased. From these data it was observed that the normalized weights of films were increased by increasing the chitosan ratio. The wetting films were found in matching with the drying films.

Adhesive forces of dry films^[17]

The adhesion forces data of the formation of dry films from formula A₀-A₁₂ on the surface of specimens were given in TABLE 4. From these data, the adhesion

forces of the formation of dry films from formula A₀, A₁₁ and A₁₂ failed. These data indicate the effect of chitosan on the formula. Also, the inorganic additives Zn, TiO₂, Al₂O₃ and silica increase the adhesion forces between the surface of specimens and the formation dry films and with itself.

Electrical conductivity

The data of the electrical conductivity for the dry films from formula A₀-A₁₂ on the surface of specimens were given in TABLE 4. The electrical conductivity for the dry films from formula A₀ failed at 475 Voltage. While the formation films from formula A₁-A₁₂ passed. From these data it can be concluded that, the addition of chitosan and inorganic additives Zn, TiO₂, Al₂O₃ and silica increased the resistance of electrical conductivity of the dry films.

The resistor data of the electrical conductivity were observed due to the compatibility of the inorganic materials with resins (Chitosan, epoxy, novolac and P(EG_{tri}-DMSO).

Holiday (pinhole) detection

The data of holiday (pinhole) detection for the formation of dry films from formula A₀-A₁₂ on the surface of specimens were given in TABLE 4. The measuring voltages for the formation dry films depended on the dry thickness of the formation films according to the following equation.

$$\text{Measuring voltages} = 5 \times \text{DFT}^{[18]}$$

Since the dry film thickness for the formation dry films from formula A₀-A₁₂ were $95 \pm 5 \mu\text{m}$, so that, the measuring voltage for the formation dry film were 475 volts. The electrical conductivity for formation of dry films from the formula A₀ & A₁ were failed. These data matched with the net results obtained from the electrical conductivity method. These were indicated on the good compatibility of the fillers with the organic resin to formation the polyurethane melamine resin. These films had good insulating properties. Therefore the formations of dry films from formula A₂-A₁₂ were promising the validity films to protect the surface of carbon steel alloy.

Thermal cycling test for the formation of dry films^[19]

The data of the thermal cycling test for the forma-

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tion of dry films from the formula A_0 - A_{12} were recorded in TABLE 14. The temperature ranged from 50 to 325°C by increasing 25°C intervals. The formation films from guide formula A_0 were affected and failed at 200°C. While the formation dry film from A_1 - A_2 , A_3 , A_4 , A_5 - A_{12} failed at 250°C, 275°C, 300°C and 325°C, respectively. These phenomena were observed due to the formation of stable melamine bonds between Novolac and amino groups in chitosan, and formation of polyurethane melamine films.

Volatile organic compounds (VOC)^[18]

The volatile organic compounds from the paints after curing were either estimated from the formulations and/or using of organic solvent. In this situation the volatile organic compound was defined as blended organic solvent. The emissions of volatile organic compounds were illustrated from the chemical formula A_0 - A_{12} . However, the chemical formula A_0 - A_{12} had 15 parts solvent, which were evaporated after application of the paints on the surface of specimens at ambient condition. Also, some methyl groups of the P (EG_{tin}-DMSO) compounds were hydrolyzed and evaporated during the curing process, and during the thermal effect on the formation films. So that the weight of the formation films after every step of thermal effect were decreased until the weight were established.

Mechanical properties

1. Hardness

The hardness data for the formation dry films on the surface of specimens from the formula A_0 - A_{12} were given in TABLE 4. These data showed that the hardness values increased with increasing the added amount of chitosan. These data indicated the promising validity of the formation dry films from formula A_1 - A_{12} on the surface of carbon steel alloy.

2. Impact

It was another technique to evaluate the validity of the formation dry films from formula A_1 - A_{12} on the surface of carbon steel alloy specimens. The impact data for these films were recorded and given in TABLE 4. The formation dry films at room temperature from formula A_0 - A_3 and A_{11} - A_{12} failed, while the formation dry films from formula A_4 - A_{10} were passed. These data in-

dicated that, the formation dry films from formula A_0 - A_3 , A_{11} - A_{12} , were unvalied.

3. Bending

The bending technique was important mechanical test for evaluating the validity of the formation dry films on the surface of specimens. This mechanical test was given in TABLE. It depends on the chemical structure of the resins

4. Mechanism

Chitosan structure having two important function groups hydroxyl and amino groups. It behaves two ways in the formation of coating films firstly was cured by reaction of the hydroxyl groups with cyano groups of TDI to form a polyurethane bonds and the other was curing reaction by the amino groups with epoxy group to form the polyimide bonds. These bonds form polyurethane imide films. This coating has very strong adhesion and resistance properties to mechanical and chemical environment.

Novolac has heat, mechanical and chemical resistance and the functional groups of novolac were reacted with another group in chitosan and 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.

Polydimethyl siloxanes P (EG_{tin}-DMSO) compounds are highly surface active agents because the arrangement of methyl groups on the flexible, inorganic backbone of alternate silicon and oxygen atoms, and the rapid appearance of methyl groups at an interface, reduce the overall energy of the coating considerably. This is an important aspect of the leveling process and is also involved in substance wetting phenomena.

The presence of silicon on the surface of a cured film will improve the properties of the formation film on the surface of carbon steel alloy specimens. Mar resistance and anti-blocking were other features enhanced by the presence of silicon polymers at the film surface. For overcoat varnishes these features were essential in applications where high speed processing was used.

The overcoat varnish imparts glass and protects the surface of carbon steel alloy. To allow the coating item to pass through processing equipment at an acceptable

rate and to prevent blocking in stacks, the surface of the cured overcoat varnish must be modified.

Although the resins (chitosan, P(EG_{tri}-DMSO), novolac, and epoxy) give very good properties to the surface of a cured coating it was not sufficiently compatible with formulation to provide adequate storage stability. 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.

The resins chains can be attached any points along the length of the active site backbone, giving a comb-like structure. They can be also attached to the ends of the chitosan polymer and other resins, giving a linear structure. The structure of the copolymer had a profound effect on the behaviour of the copolymer as an additive. Optimized structure has been identified by designed experimentation to give suitable combination of compatibility desired effects. Compatibility was particular important in clear coatings.

The silicone-polyether chemistry P(EG_{tri}-DMSO) allows the additives to migrate to the coating/substance interface thus providing wetting. By incorporating into additive coatings hydrophobic solids particular such as, titanium oxide, Zn powder, Al₂O₃, CaCO₃ and silica, effective foam control, filler/pigment. The P(EG_{tri}-DMSO) will control the formation of the foams. Because of their excellent compatibility, these products have a low tendency to cause defects for the coating.

Chemical evaluation

1. The effect of the mixture of benzene, toluene and xylene on the dry films

The texture morphology of the formation dry films from formula A₀-A₁₂ were given in TABLE 5. The texture of the formation films from formula A₀-A₁₂ after immersed in solvents were not affected, that was due to the formation of polyurethane imide films as network, which were confirmed also by the interaction of some hydroxyl groups of the silica with some cyano groups of TDI and also, were indicated on the compatibility of the resins with the inorganic filler/pigments and complete reaction with curing TDI. The formation of dry polyurethane imide films resist to the organic solvent. Therefore, these results indicated that the formation of

dry films could be applied in organic media (petroleum media).

2. The effect of methyl ethyl ketone (MEK) and chloroform according to ASTM (D 4752-95)

The effect data of the MEK and chloroform on the formation of dry films on the surface of specimens were recorded in TABLE 6. The formation of dry polyurethane imide films from formula A₁-A₁₂ were not effected by rubbing with MEK from 15-20 times. The net results indicated on the stability of Zn, compatibility and adhesion forces with the surface of carbon steel alloy specimens and with itself.

3. The effect of 10 % H₂SO₄

The data of the effect of 10% sulfuric acid on the formation films from different formula A₀-A₁₂ were given in TABLE 8. From these data it was observed the effect of 10 % sulfuric acid on the formation films on carbon steel alloy specimens at period time 50 days, DFT 95 ± 5 μm and these data were evaluated according to (ASTM D772, 714 and 662).

The formation of dry films from formula A₀ was affected by 10% H₂SO₄ after 20 days, so that, these films did not protect the surface of carbon steel alloy specimens. While the formation films from formula A₁-A₁₂ were not affected by 10% H₂SO₄ up to 50 days. This phenomenon was shown for films formation at room temperature. Except formation film from formula A₁ is chalking after 40 days. On the other hand, the formation films from formula A₁-A₁₂ were not affected by 10% H₂SO₄ until 50 days. These ratios of corrosion spots appeared very low and should be neglected, so that the formation films from formula A₁-A₁₂ at DFT 95 ± 5 μm were valid to protect the surface of carbon steel alloy specimens against aggressive acids

4. The effect of 10% NaOH

The data of the effect 10% NaOH on the formation of dry polyurethane imide films on the surface of alloy specimens at 95±5 μm and 50 days and ambient condition were given in TABLE 9. These data illustrated the protectivity of the formation dry films to the surface of carbon steel alloy. The corrosion spots were appeared on the film surface for formula A₀ after 20 days, while little spots appeared on the surface of formation films from formula A₂ after 40 days, these spots

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must be neglected. While the corrosion spots were not appeared on the formation films from formula A_3 - A_{12} . These results indicated the validity of the formation films for protecting the surface of carbon steel alloy against aggressive media 10% in NaOH for long time.

5. The effect of 10% HCl

The data for the effect of 10% HCl on the formation of dry polyurethane imide films on the surface of specimens at $95 \pm 5 \mu\text{m}$ and 50 days at ambient condition were given in TABLE 10. These data illustrated that, the corrosion spots were not appeared on the formation dry films on the carbon steel alloy specimens from formula A_2 - A_{12} . This is due to the capability of the formation films to protect the surface of carbon steel alloy against aggressive media. i.e. the formation of dry polyurethane imide films help to protect the surface of carbon steel alloy against aggressive media.

6. The effect of 10% CH_3COOH

The data for the effect of 10% CH_3COOH on the formation of dry polyurethane imide films on the surface of carbon steel alloy specimens at $95 \pm 5 \mu\text{m}$ and 50 days at ambient condition for both curing temperature were given in TABLE 11. These data were illustrated that, the corrosion spots were not appeared on the formation dry films on carbon steel alloy specimens from formula A_0 - A_{12} . This is due to the capability of the formation films to protect the surface of carbon steel alloy against aggressive media. i.e. the formation dry polyurethane imide films help to protect the surface of carbon steel alloy against aggressive media.

7. The effect of synthetic (3.5% NaCl) sea water

The data of the effect 3.5% NaCl on the formation dry polyurethane imide films on the surface of carbon steel alloy specimens at $95 \pm 5 \mu\text{m}$ and 48 days at ambient condition were given in TABLE 7. It was observed that the corrosion spot does not appear on the formation films from formula A_0 up to 30 days, while the corrosion spots were appeared from 15-20 spots from 30 to 50 days and the corrosion spots covered the surface after 50 days. If calculating the ratios of spots respected to the total surface area of specimens it will be less than 0.1 %, that was rust grades 8^B (ASTM D-610), i.e. these ratios (spots) of corrosion should be neglected. This observation corresponds to SSPC initial surface

conditions and British Iron and Steel Research assn (BISR) 0.1 %, while the formation films from formula A_1 - the corrosion spots were not appeared until 60 days, but corrosion spots appeared on the surface of protection films for formula A_1 after 60 days, if calculating the ratios of spots respected to the total surface area of specimens it will be less than 0.01 %, this value was done under rust grade 10, i.e. no rusting, which must be neglected. This was in agreement with Swedish pictorial standards for rusting. On the other hand, few corrosion spots appeared on testing the effect of salt media on the formation dry films from formula A_2 - A_3 after 70 days. Also the corrosion spots 1-3 appeared on the surface of the formation dry films, these ratios were neglected as previously mentioned. On the other hand, the corrosion spots were not observed on the surface of the formation dry films for formula A_7 - A_{12} . These results were indicated that the formation dry films from formula A_4 - A_{12} protected the surface of carbon steel alloy specimen i.e., these films were valid for protection the surface of carbon steel alloy at $95 \pm 5 \mu\text{m}$.

CONCLUSION

- Chitosan and $(\text{PEG})_{\text{int}}$ -(PDMSO) compounds were prepared as friendly environmental resins.
- These compounds were confirmed by FT.IR and GPC.
- These compounds were blended with commercial novolac and epoxy resins at definite ratios.
- These resins were blended with definite ratio of inorganic pigments TiO_2 , Al_2O_3 , CaCO_3 , Zn dust and Silica gel to form a formula A_1 - A_{12} which was cured by TDI.
- Each formula was applied on the preparation of carbon steel alloy specimens.
- Physical, mechanical and chemical properties was measured for each formation dry films from formula A_0 - A_{12} .
- The net results indicated that the validity of formation films formulae A_4 - A_{10} for application and protection of petroleum equipments.

REFERENCES

- [1] O.M.Abo-Elenien, H.M.Abu-Elainin; Egypt.J. Petrol., **9**, 13-18 (2000).
- [2] O.M.Abo-Elenien; Ph.D.Thesis, Collage Seince, Ain Shams Univ., (1996).
- [3] G.James, L.Thomas; Eur.Coat.J., **9**, 626-629 (1988).
- [4] Nivedita S.Sangaj, V.C.Malshe; Prog.in Org.Coat, **50**, 28-39 (2004).
- [5] D.Fuente, E.Otero, B.Chico, M.Morcillo; Prog.In Org.Coat., **54**, 240-247 (2005).
- [6] M.S.Rickerby, R.J.Burnett; Surf.Coat.Technol., **33**, 191 (1987).
- [7] J.M.Dubois, S.S.Kang, J.J.Von Stlbbut; Mater.Sci., **10**, 537 (1991).
- [8] Guozhe Meng, Ying Li, Fuhui Wang, Electrochimica Acta, **51**, 4277-4284 (2006).
- [9] Velu Saraswathy, Ha-Won Song; Electrochimica Acta, **51**, 4601-4611(2006) .
- [10] O.M.Abo-Elenien; Egypt.J.Appl.Sci., **19(11)**, 144-160 (2004).
- [11] O.M.Abo-Elenien; Egypt.J.Appl.Sci., **19(11)**, 161 (2004).
- [12] Guofeng Cui, Ning Li, Deyu Li, Z.Jian; Surf.& Coatings Techn., **200**, 6808-6814 (2006)
- [13] Sakairi, M.Y.Uchida, K.Itabashi, H.Takahashi; Corr.Sci., **47**, 2461-2469 (2005)
- [14] Lei Shi, Chufeng Sun, Ping Gao, Feng Zhou, Weimin Liu; Applied Surface Science, **252**, 3591-3599 (2006)
- [15] B.K.Kima, B.U.Ahna, M.H.Lee, S.K.Lee; Prog.in Org.Coat., **55**, 174-200 (2006).
- [16] A.S.Aly, B.D.Jeon, Y.H.Park; J.Appl.Polym.Sci., **65**, 1939-19 (1997).
- [17] J.Graystone, R.Kennedy; Surface Coatings International, **8**, 389-398 (2000).
- [18] J.Huybrechts, K.Dusek; Surface Coatings International, **5**, 234-239 (1998).
- [19] P.Merino, C.Perez, A.Collazo, X.R.Novoa; Surf. Coat.Intern., **1**, 30-35 (1995).