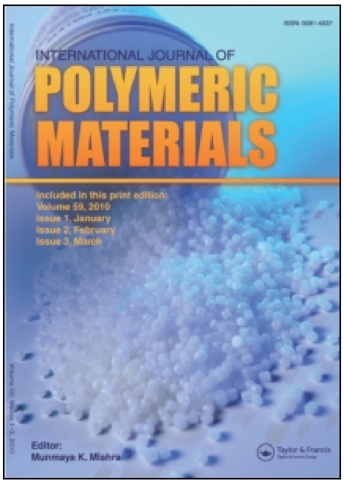

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ELECTRODEPOSITION COATING OF EPOXY RESIN ON PHOSPHATED STEEL: OPTIMIZATION OF KEY FACTORS

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ELECTRODEPOSITION COATING OF EPOXY RESIN ON PHOSPHATED STEEL: OPTIMIZATION OF KEY FACTORS

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Organic coating using electrodeposition method has attracted substantial attention in the last few years. This method of coating provides many advantages, including surface smoothness, less environmental pollution, and good performance of protection against corrosion. In the current investigation, an electrodeposition method was used to coat a uniform layer of epoxy resin on phosphated stainless steel plate. Epoxy resin was converted to cationic tertiary type amine resin. This cationic epoxy resin, which contains ammonium group in the end of the polymer chain, was synthesized by ring-opening reaction of an epoxy resin with secondary amine in the presence of a proton donor. The so prepared cationic resin was dispersed in water, giving an emulsion containing charged polymer particles. A layer of resin was successfully electrodeposited on the phosphated stainless steel plate and physical properties of the layer were studied. A detailed study aiming to obtain reliable information of coating properties was carried out. The effect of a number of factors, including electrodeposition voltage, electrodeposition time, pH value of the emulsion, solvent content, resin Epoxy Equivalent Weight (E.E.W.) resin concentration, and bath temperature on deposition yield and coating adhesion was studied with a view to optimize these factors. Variables affecting the rupture voltage were also investigated.

Keywords: electrodeposition, organic coating, epoxy resin, adhesion

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INTRODUCTION

Electrodeposition has become increasingly important in the coating industry because it offers lower environmental contamination [1], superior mechanical and corrosion performance properties [2], surface smoothness due to stronger throwing power [3], higher paint utilization [1], greater operating flexibility and definitely smoother film [4], and more susceptibility to the automatic process when compared with nonelectrophoretic coating [3,5].

The priming of car bodies by electrocoating was introduced into the automotive industry in the 1960s [1]. The systems employed were anodic with negatively charged paint particles deposited from an aqueous solution on the metal of the car body. In the middle of the 1970s, anodic electrodeposition primers were rapidly replaced by cathodic products due to their superior corrosion protection [3,6]. Today more than 90% of all automobiles are primed via cathodic electrocoat systems [3].

In early work on electrodeposition primers for automobiles, maleated linseed oil was used as a vehicle. However, due to their poor adhesion to steel the maleated oils were soon replaced with maleated epoxy esters and maleated polybutadiene, which had better hydrolytic stability and provided superior adhesion to steel [7]. All current cationic resins are based on epoxy, acrylic resins, and their copolymers [8]. Acrylic copolymers provide better environmental resistance and outstanding gloss, suitable for application as a topcoat [9]. However, epoxy resins and their copolymers offer a higher level of corrosion resistance and adhesion and, thus have been developed to provide the top or primer coating to a variety of products such as automotives bodies. The epoxy resin is still the best material for the cathodic electrodeposition because of advantages such as resistance to chemical agents and good adhesion and flexibility [8].

It is the aim of the current investigation to study electrodeposition-related factors in detail, as related to macroscopic properties of the coating. Such studies will enable engineers, fabricators, and designers to better understand the effects of optimization on macroscopic properties of epoxy coating. An optimized electrodeposition coating method using epoxyamine modified by ethyl hexanol was also derived.

EXPERIMENTAL

Reagents and Materials

Epichlorohydrin, bisphenol A, ethylene glycol mono n-butyl ether with the common name of butyl cellosive (BCS), toluene diisocyanate (TDI), and all other chemical reagents and solvents were obtained from

Merck Chemicals (Germany) and used as received. Commercial epoxy resin (200, 600) were obtained from Afsoon Chemical Company (Tehran, Iran).

Instrumentation

An IR spectrometer (Shimadzu IR-408), DC power supply (Sahand Pardazan, Iran, 0-380 Volt, 0-4 A), and adhesion tester (Erichsen, 525) were used throughout the investigation.

Procedures

]Polymer Synthesis

Epoxy resin (Epoxy equivalent weight 750) was synthesized according to a previously reported method [10]. A mixture of bisphenol A (303 parts by weight) and aqueous sodium hydroxide solution (155 parts by weight 10% solution) was introduce into a reactor equipped with a powerful agitator. The mixture was heated to 45°C and epichlorohydrin (123 parts by weight) was added rapidly with agitation, giving off heat. The temperature was allowed to rise to 95°C, where it was maintained for 80 min. Then, the agitation was stopped and the mixture separated into two layers. The heavier aqueous layer was drawn off and the molten product was washed with hot water until the wash water became neutral. The taffy-like product was dried at 130°C, giving a solid resin with a melting point of 78°C.

Synthesis of Epoxyamine Adduct

Epoxyamine adduct was synthesized according to a previously reported method [11]. 37.5 g TDI were charged into a three-necked glass flask equipped with a magnetic stirrer. 0.21 mol of 2-Ethyl hexanol (2EH) were added into the flask dropwise while the temperature was controlled below 10°C. The mixture was kept at 0°C over a period of 40 min. To complete the reaction, the mixture way stirred at 0°C for additional 40 min and then heated to 40°C and held for 1 h. Into a five-necked glass flask equipped with a Dean-Stark reflux trap and electric stirrer, 0.053 mol of epoxy resin and 50 ml toluene were added and the mixture was heated to reflux at 120°C with agitation to remove any water product by use of a Dean-Stark trap. Then the mixture was cooled down to 100°C. 5 drops of dibutyl tin dilaurate catalyst were added and the mixture was kept at this temperature for an additional 3 h. After cooling to 80°C, 0.1 mol of diethylamine was added into the flask. The mixture was heated to 90°C and kept at that temperature for 3 h for the completion of reaction. Finally, toluene was distilled off under reduced pressure.

Measurement of Rupture Voltage

Rupture voltage was measured according to a previously reported method [11]. The bath DC voltage was slowly increased as the current decreased. The potential in which the current value increases is called rupture voltage of electrodeposition coating.

Measurement of Adhesion

Adhesion was measured according to a previously reported method [12]. The pull-off test was performed by securing a loading fixture (dolly) to the surface of the coating with an adhesive. After the adhesive was cured, a testing apparatus was attached to the loading fixture and aligned to apply tension normal (perpendicular) to the test surface. The force applied to the loading fixture was then gradually increased and monitored until a plug of coating material was detached. The pull-off strength is computed based on the maximum indicated load, the instrument calibration data, and the original surface area stressed.

Preparation of Phosphate Conversion Coatings

A zinc phosphated coating was an excellent base for paint application. Phosphate conversion coating was carried out by immersion technique as previously reported [13]. Zinc phosphate bath consists of the composition indicated in Table 1.

2 ml of the bath solution diluted to 100 ml with deionized water. 0.02 g of sodium nitrite was added to the solution. The iron plates were immersed in zinc phosphating bath. The solution was then heated up to 75°C for 10 min. Then the samples were washed with distilled water and dried.

Determination of Epoxy Equivalent Weight (E.E.W.)

The epoxy resin was dissolved in a mixture of chlorobenzene and chloroform (1:1) and the solution was titrated directly with a standard solution of hydrogen bromide in glacial acetic acid. The hydrogen bromide reacted stoichiometically with epoxy groups to form bromohydrines, therefore, the amount of acid consumed in the titration corresponds to the epoxy content of the resin [14].

TABLE 1 Composition of Phosphating Bath

Component	Weight (%)
Zinc oxide	12.90
Phosphoric acid (75%)	54.96
Deionized water	32.14

Preparation of Electrodeposition Emulsion

8 g of cationic resins and 4 g of BCS were added into a three-necked flask equipped with an electric stirrer and heated up to 70–80°C. 88 g deionized water was added dropwise while the mixture was vigorously stirred. Three types of emulsions (A, B, and C), having epoxy resins with various E.E.W. were prepared. The E.E.W. of each emulsion (A, B, and C) was 200, 600, and 750, respectively.

Electrodeposition

Approximately 40 ml of emulsion was placed in the glass cell of electrodeposition. The pre-weighed electrodes (2.5 by 4 cm) were immersed in the emulsion and electrodeposition was carried out at various voltages. The cathode was removed from the emulsion and washed with water. To determine the deposition yield, the plate was heated to 140°C and then weighed again.

RESULTS AND DISCUSSION

Electrodeposition was carried out using the cationic epoxy resin emulsion at 25°C. The effect was investigated of a number of key factors influeincing the coating characteristics, such as deposition yield, coating adhesion, and rupture voltage.

The Effect of Electrodeposition Voltage

The electrodeposition was carried out at different voltages ranging from 50 to 175 V. The charge consumed during electrodeposistion, deposition yield, and adhesion of the deposited film were determined for a given deposition voltage (Table 2). It was found that the deposition yield increased as the voltage increased. As shown in Table 2, when the electrodeposition voltage increased, the charge consumed (in millicoulombs-mC) during electrodeposition also increased. This may increase colloidal weight per charged unit, which leads to higher efficiency when electrodeposited. However, the coating adhesion was not affected by electrodeposition voltage.

The Effect of Electrodeposition Time

The effect of electrodeposition time a deposition yield and the coating adhesion was investigated (Table 3). A constant voltage of 210 V was applied to the emulsion containing epoxy resin (E.E.W. = 600). Resin concentration and solvent (BCS) content were 8 wt% and 4 wt%, respectively.

TABLE 2 The Effect of Electrodeposition Voltage on Deposition Yield and Coating Adhesion

Electrodeposition voltage (V)	Charge consumed (mC)	Deposition yield ($mg \cdot cm^{-2}$)	Adhesion (Ib/in^2).100
50	2520	0.0020	0.33
75	3920	0.0024	0.33
100	6080	0.0030	0.33
125	18700	0.0043	0.33
150	34220	0.0090	0.33
175	48195	0.0160	0.33

Resin E.E.W. = 600. pH = 4.8. BCS content: 4 wt%. Resin concentration: 8 wt%. Deposition time: 10 min. Bath temperature: 27°C.

It appears that as deposition time increased, deposition yields of the emulsion was also increased but at a rather slow rate. The consumed changed and the adhesion, though, remained unaffected.

The Effect of Solution pH

The epoxy resin (E.E.W. = 600) with BCS content of 4 wt% and resin concentration of 8 wt% was electrodeposited at different pH values ranging from 3.5 to 4.8. A constant potential of 210 V was applied. In order to adjust the emulsion pH, a solution of acetic acid was used. It was found that as this pH increased the deposition yield also increased (Figure 1). This may be attributed to the fact that low pH value (high

TABLE 3 The Effect of Electrodeposition Time on Deposition Yield and Coating Adhesion

Electrodeposition time (min)	Charge consumed (mC)	Deposition yield ($mg \cdot cm^{-2}$)	Adhesion (Ib/in^2) .100
1	1080	0.0050	0.33
3	30700	0.0092	0.33
5	31200	0.0093	0.33
8	31270	0.0094	0.33
12	30740	0.0096	0.33
16	31320	0.0099	0.33
20	30500	0.0100	0.33

Resin E.E.W. = 600. pH = 4.8. BCS content: 4 wt%. Resin concentration: 8 wt%. Deposition voltage: 210V. Bath temperature: 27°C.

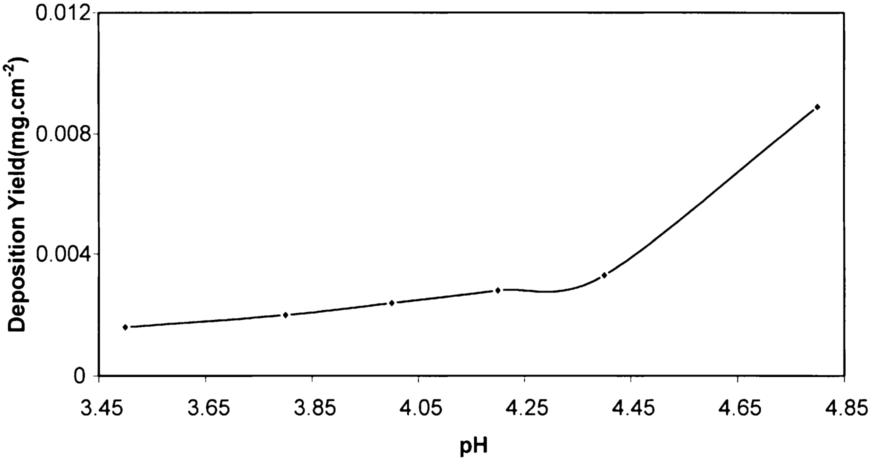

FIGURE 1 Effect of pH value of emulsions on deposition yield. Resin concentration 8 wt%. BCS content: 4 wt%. Applied voltage: 210 V. Deposition time: 10 min.

acidity) enhances the solubility of the deposited resin, lowering the yield.

Effect of Solvent Content

Table 4 shows the effect of solvent content on the deposition yield of resin. Lower organic solvent contents (BCS) give higher deposition yield. However, higher BCS contents produces films with a more pleasing appearance and smoothness. The lower organic solvent

TABLE 4 The Effect of Solvent Content on Deposition Yield and Coating Adhesion

BCS content (% wt)	Charge Consumed (mC)	Deposition yield (mg · cm^{-2})
4	33040	0.0089
6	33000	0.0060
8	24000	0.0051
10	21000	0.0036
12	16700	0.0020
14	Rupture voltage occurs	—

Resin E.E.W. = 600. Resin concentration: 8 wt%. pH = 4.8. Deposition voltage = 210 V. Deposition time: 10 min. Bath temperature: 27°C.

TABLE 5 The Effect of Epoxy Equivalent Weight (E.E.W.) on Coating Characteristics

Resin E.E.W.	Adhesion (Ib/in^2) .100	Deposition voltage
200	0.33	4.5
600	1	210
750	3.5	360

BCS content = 4 wt%. Resin concentration: 8 wt%. pH = 4.8. Deposition time: 10 min. Bath temperature: 27°C.

contents might cause chemical precipitation of the resin and then precipitated particles might migrate with the dispersed macrocations onto the cathode, leading to formation of films with rough surface as visually can be verified.

The Effect of Epoxy Equivalent Weight

So far, the study was carried out using epoxy resins E.E.W. = 600. In order to investigate the effect of E.E.W. on the coating characteristics, additional experiments were carried out. Three different types of resin having E.E.W. of 200, 600 and 750 were employed. It was found that the deposition potential was strongly affected by the E.E.W. of the resin (Table 5). The optimum potentials of 4.5, 150, and 220 V were obtained for the resins having E.E.W. of 200, 600, and 750, respectively. The deposited films were ruptured just over the determined potentials.

For each resin, the adhesion value was also obtained (Table 5). It was found that, unlike the other factors, adhesion of the coating was significantly affected by the E.E.W. of the resin. The coating adhesion increased as the E.E.W. increased. This is presumably due to the fact that as the E.E.W. increased the number of hydroxyl groups, which are responsible for adhesion was also increased.

Effect of Resin Concentration

Table 6 shows the relationships between resin concentration and deposition yield when the BCS content and pH value of the emulsion were kept constant. Deposition yield increased as the resin concentration increased. During the electrodeposition process, the ionized resin, dispersed and suspended in the deionized water, was deposited on the surface of the electrode to form a polymer film. Thus, the higher the concentration of the ionized resin in the emulsion, the higher the

TABLE 6 The Effect of Resin Concentration on Deposition Yield and Coating Adhesion

Resin concentration (% wt)	Charge consumed (mC)	Deposition yield (mg · cm^{-2})	Adhesion (Ib/in^2).100
4	2010	0.0020	0.33
6	2280	0.0040	0.33
8	5070	0.0061	0.33
10	7801	0.0079	0.33
12	9450	0.0160	0.33

Resin E.E.W. = 600. BCS content: 4 wt%. pH = 4.8. Deposition time: 10 min. Applied voltage: 150 V. Bath temperature: 27°C.

deposited yield under the same applied voltage. This has no effect on adhesion values.

Effect of Bath Temperature

Table 7 shows the relationship between bath temperature and deposition yield. Deposition yield increased as the bath temperature increased. Conductivity of emulsion increased when bath temperature increased. In general, the emulsion having higher conductivity may offer stronger electric power. Thus, the higher conductivity caused the greater deposition yield.

Determination of Rupture Voltage

The rupture voltage was determined by constant voltage method as described in the Experimental section. Table 8 shows the rupture

TABLE 7 The Effect of Bath Temperature on Deposition Yield and Coating Adhesion

Bath temperature (°C)	Charge consumed (mC)	Deposition yield (mg · cm^{-2})
17	15900	0.0082
27	31860	0.0089
40	162000	0.0090
48	167580	0.0140
60	Rupture voltage occurs	—

Resin E.E.W. = 600. BCS content: 4 wt%. Resin concentration: 8 wt%. pH = 4.8. Deposition time: 10 min. Applied voltage: 150 V.

TABLE 8 The Effect of E.E.W. of the Resin on Rupture Voltage

Resin E.E.W.	Rupture voltage (V)
200	4.8
600	230
750	270

pH = 4.8. Resin concentration = 8 wt%. BCS content = 4 wt%.

voltages measured for three types of resins. The rupture voltage increased with the increase of E.E.W. of resin. Films electrodeposited from emulsions having higher E.E.W. were more adheren (Table 5) to the substrate (phosphated steel plates). The increase in the rupture voltage may be due to fact that the more adherent coating as more stable against voltage deformation.

The effect of resin concentration (E.E.W. = 600) of the emulsion on the rupture voltage was also investigated (Figure 2). Rupture voltage increased as the resin concentration of the emulsion increased. The effect may be due to the emulsion concentration and the deposited film thickness. Thin deposited films will rupture easily at a lower applied voltage. On the contrary, the greater the film thickness, the higher

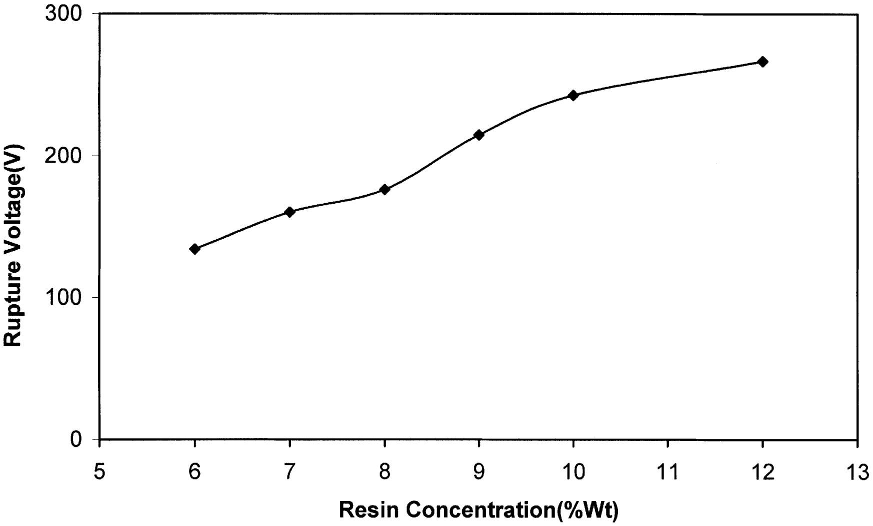

FIGURE 2 Influences of resin concentration of emulsion on the rupture voltage. BCS content: 4 wt%. Resin E.E.W. = 600. pH = 4.8.

TABLE 9 The Effect of Solvent (BCS) Content on the Rupture Voltage

BCS content (%wt)	Rupture voltage (V)
4	230
6	150
8	91
10	87
12	70
14	50

rupture voltage necessary because the deposited film can resist a higher voltage before being ruptured.

The effect of solvent (BCS) content on the rupture voltage was also investigated (Table 9). It was found that as the fraction of BCS in the emulsion increased the rupture voltage decreased. It has been shown [15] that usually, the better the electric insulation of the deposited film, or the thicker the deposited film, the higher the rupture voltage. In this case the reason for the decrease of the rupture voltage may be due to the thickness effect. As the BCS content increased the coating thickness decreased. This would decrease the rupture voltage (see Table 4).

The effect of emulsion pH on the rupture voltage of the deposited film was also studied. It was found (Table 10) that as the pH value of the emulsion decreased the rupture voltage also decreased. In the acidic media the resistance of the resin increases, film thickness and deposition yield decreases (Figure 1), and therefore, the rupture voltage decreases.

TABLE 10 The Effect of the Emulsion pH on the Rupture Voltage

Emulsion pH	Rupture voltage (V)
4.8	230
4.4	160
4.2	148
4	136
3.8	130
3.5	98

BCS content: 4 wt%. Resin E.E.W. = 600. Resin concentration: 8 wt%.

CONCLUSION

Epoxy resins with various E.E.W. (200, 600, 750) were synthesized and then converted to cationic tertiary-type amine resin. The cationic resin was dispersed in water, giving an emulsion containing charged polymer particles.

An electrodeposition method was used to coat a uniform layer of the epoxy resin on phosphated stainless steel plate. It was found that a number of factors affect the properties of the deposited layer.

The effects of electrodeposition voltage, electrodeposition time, pH value of the emulsion, solvent content, resin E.E.W., resin concentration, and bath temperature on deposition yield and coating adhesion were studied with a view to optimize were factors. The optimum value for each factor was determined.

Effect of pH value, solvent content, resin E.E.W., and resin concentration of the emulsion on the rupture voltage was also investigated.

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