

# Anodic Electrodeposition of Asphalt–Polystyrene Emulsions on Galvanized Steel

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**ABSTRACT:** Anodic electrodeposition of a commercial asphaltic emulsion modified with polystyrene emulsion and oleate of potassium was studied. The process was carried out at a constant voltage in a continuously agitated bath, employing galvanized steel electrodes maintained at a fixed distance of separation. Composition and operating conditions were determined to obtain uniform texture and compact films with a thickness usable by industry. It was found that the system obeyed Ohm's and Faraday's laws and presented film-dissolution behavior. In addition, a kinetic study was performed in which a mathematical model was proposed to predict film growth with time. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1078–1092, 1999

**Key words:** electrodeposition; asphalt; emulsions

## INTRODUCTION

Many substances have been the focus of investigations in the search for coatings with excellent chemical and mechanical properties. Asphalt, characterized for its waterproofing abilities, has been used on metal surfaces, imparting protection against moisture as well as electrical isolation, properties both of which are necessary in many metal applications.

The electrodeposition of asphalt films dates back to 1919, when Davey patented a technique to coat electroconductive materials with a polymer based on asphalt oil. Subsequently, McCoy<sup>1</sup> patented in 1964 an electrodeposition process for bituminous substances. However, asphaltic films have, in general, suffered from softening and tacky surface problems at relatively low temperatures.

In this investigation, polymers such as polystyrene (melting point of 100°C) have been used to overcome the difficulties presented by asphalt-

electrodeposited films. The polystyrene emulsion was added to a commercial anionic asphalt solution in a range of 1 to 4 wt %, maintaining a greater proportion of asphalt in the mixture.

The electrodeposition process is based on the migration of ions induced by the action of an electric field on a solution containing charged particles. These particles move toward the oppositely charged electrode, which is, in general, the material that is to be coated. If this material is positively charged, the process is referred to as anodic, whereas if the material is negatively charged, the process is referred to as cathodic. For organic coatings, this technique offers several advantages over conventional methods, such as:

- The production of thin, uniform, and electrically resistant films.
- High penetration capacity that allows confined areas of metal to be covered.
- Ease of control and automatization.

The use of water as the continuous phase in the emulsions has also contributed to rapid adoption of the electrodeposition process by industry, since

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the levels of contamination and risk of fire are considerably reduced.

In an emulsion, small particles of asphalt or polymer (the disperse phase) are surrounded by positively or negatively charged surfactant molecules. Together this entity is denominated as the micelle and represents the colloidal particles that migrate on applying an electric field. In this way, the surfactant defines the type of electrodeposition process. These micelles are suspended in a continuous phase, which is generally water, and homogeneously distributed due to thermodynamic stabilization (the balance of electrostatic forces).

Anodic electrodeposition has several disadvantages in comparison to cathodic electrodeposition, such as the electrochemical dissolution of the metal and the formation of spongy-looking films—caused by the occlusion of the gas produced by water electrolysis (when water is the continuous phase). However, these effects can be minimized during the electrodeposition of bituminous materials by regulating the operating conditions and adding relatively high concentrations of certain organic or inorganic salts. These salts are free of surface activity and act as metal-confiscating agents.<sup>1</sup> Taking into account these considerations, the effect of adding oleate of potassium to the asphalt-polystyrene system was studied in this investigation.

## KINETICS OF ELECTRODEPOSITION

Kinetic electrodeposition studies normally involve obtaining a model that describes the film growth of a system (thickness  $[\delta]$  versus time  $[t]$ ). A simple and generally accepted model has been formulated for processes that obey Faraday's and Ohm's laws:

$$\delta = kt^{1/2} \quad (1)$$

Faraday's law assumes that during the process of passing an electric current through an electrolyte the deposited mass is proportional to the amount of applied charge. Hence, the rate of film growth is proportional to the current density  $[j]$  at the electrode:

$$\frac{d\delta}{dt} = Cj \quad (2)$$

Equation (2) expresses the concept of Coulombic efficiency  $[C]$ , which is the relationship between the deposited mass and the applied current; this is related to the number of dissociated groups on the surface of the latex particle as well as to the amount of electrolytes (salts and surfactants) present in the system. This theoretically corresponds to  $[M/nF]$  (in the absence of the aforementioned groups and electrolytes), where  $M$  is the molecular weight of the deposited species;  $n$ , the number of equivalents/mol of these species; and  $F$ , Faraday's constant (96,487 C/equivalent). The Coulombic efficiency is generally considered to be independent of the disposition time and the applied voltage; however, in some cases, it has been found to increase with the voltage.<sup>2</sup> From eq. (2), it can be concluded that, by graphing experimental data of the film growth rate versus the current density, the slope represents the Coulombic efficiency.

Ohm's law states that the current density  $[j]$  is directly proportional the voltage  $[V]$  and inversely proportional to the resistance; this can be applied to an electrodeposition system as

$$j = \frac{\sigma_F V}{\delta} \quad (3)$$

where  $[\delta/\sigma_F]$  represents the resistance of the deposited film, expressed as a function of the film conductivity  $[\sigma_F]$  and the thickness  $[\delta]$ . Experimentally, it is possible to graph current density values versus  $[V/\delta]$ , giving a slope that represents the film conductivity  $[\sigma_F]$ .

By combining (2) and (3), the following kinetic electrodeposition model is obtained:

$$\frac{d\delta}{dt} = \frac{C\sigma_F V}{\delta} \quad (4)$$

By separating terms and integrating,

$$\delta = (2C\sigma_F V)^{1/2} t^{1/2} \quad (5)$$

Hence, from (1),  $k = [2 C \sigma_F V]^{0.5}$ . This indicates that, in order to define the electrodeposition kinetic model for a given system, it is important to experimentally determine the relationship between current density  $[j]$  and the factor  $[V/\delta]$  and between the film growth rate  $[d\delta/dt]$  and the current density  $[j]$ . Establishing the behavior of these relationships also determines if the emulsion to be electrodeposited follows Ohm's law.

### Kinetic Models with Film Dissolution

The majority of films deposited in a continuously stirred bath tend to redissolve; if the rate of electrodeposition is similar to the rate of dissolution, the film thickness reaches a limiting value. This phenomenon has been observed in the growth kinetics of oxide films and in corrosion.<sup>3</sup>

In the presence of film dissolution, it is necessary to modify Faraday's basic equation for electrolysis, including an additional term to account for dissolution. This term is known as the dissolution current [ $j_d$ ]. Theoretically, to prevent dissolution during constant current electrodeposition, the current density should be maintained above the dissolution current value, whereas during electrodeposition at a constant voltage, the current density is found to decay rapidly and tend toward the value of  $j_d$  asymptotically:

$$\frac{d\delta}{dt} = C(j - j_d) \quad (6)$$

Equation (6) shows that the film growth is constrained when  $j = j_d$ ; in other words, by graphing the film growth rate versus the current density, the intersection with the  $x$ -axis represents  $j_d$ .

### Nonohmic Kinetic Models

Some electrodeposited films, as well as some types of metal oxides, do not follow the model described in (1), mainly due to nonohmic characteristics. These systems present an exponential-type relationship between the current density [ $j$ ] and the factor [ $V/\delta$ ]:

$$j = A \exp(BV/\delta) \quad (7)$$

Depending on the parameters  $A$  and  $B$  (coating constants), nonohmic conduction can produce a very rapid initial film growth followed by a rapid current drop-off.

## EXPERIMENTAL

The first stage of the investigation consisted of a preliminary study to explore possible composition and operating conditions for the asphalt-polystyrene system. Based on these initial results, the second stage focused on evaluating the effects of adding oleate of potassium. The operating conditions and the composition of the emulsion were

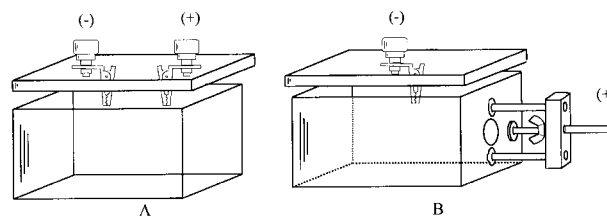


Figure 1 Electrodeposition cells.

established so that a uniform and compact film, with a thickness usable by industry, was obtained. The final stage of the investigation involved a study of the electrodeposition kinetics.

### Equipment

An automatically regulated power source was employed with a voltage range of 12–800 V and a current range of 0–10 amps. The electrochemical cell was designed in glass, with the following dimensions: 11 cm length, 7.5 cm width, and 8 cm height. For the preliminary study, the electrodes were placed in the upper cover and submerged in an agitated bath, using cell type A as shown in Figure 1.

For the second stage of the investigation and the kinetic study, cell type B (Fig. 1) was used. A hot-dipped galvanized steel plate acting as the anode was exposed to the emulsion through an orifice (area of 2.43 cm<sup>2</sup>) and fastened by a press with a polyurethane pad, which isolated the wheel used to supply current to the plate. Neoprene packing was installed between the plate and the cell wall to avoid leakage. The distance between electrodes was maintained constant at 4.7 cm in both cell set-ups.

Galvanized steel plates with dimensions of 2 × 3 cm and a thickness of 1 mm were used in the electrodeposition process. The plates were pretreated with a lime solution to remove solids and difficult stains and subsequently activated by immersion in a dilute sulfuric and hydrochloric acid solution.<sup>4</sup> Finally, the plates were washed with distilled water and surface-dried with hot air.

An Ultra Turrax T25 designed for discontinuous operation (velocity range: 8,000–24,000 rev/min) was employed to achieve satisfactory dispersion and emulsification in the system. This equipment is able to transmit 1000 times more energy to a confined liquid than can a conventional mixer. A 6000 FNS1 (DeFelsko) instrument was used to measure the deposited film thickness in the final stage of the investigation.<sup>5–8</sup>

**Table I** Composition of the Emulsions Used in the Preliminary Study

Notation		Composition		
% Asphalt/% Polystyrene		% Asphalt	% Polystyrene	pH (26°C)
2/0		2	0.0	10.28
2/1.5		2	1.5	10.25
5/0		5	0.0	10.33
5/1.5		5	1.5	10.12
12/0		12	0.0	10.59
12/1.5		12	1.5	10.77

## PRELIMINARY ELECTRODEPOSITION STUDY: ASPHALT-POLYSTYRENE SYSTEM

### Materials

The emulsions used in the electrodeposition process consisted of a mix of different weight proportions: commercial anionic asphaltic emulsion (50 wt % asphalt); polystyrene emulsion (13.19 wt % polystyrene) prepared by discontinuous polymerization of the monomer; and distilled water as the continuous phase to make up 100%. The asphalt was an ASF-CIB from a Colombian petrochemical plant (penetration at 5°C, 11 mm; viscosity at 40°C, 1370 poises).

Six asphalt-polystyrene emulsions were prepared with weight proportions as given in Table I. Each was mixed with the Ultra Turrax at 11,000 rev/min for 1 min.

### Methodology

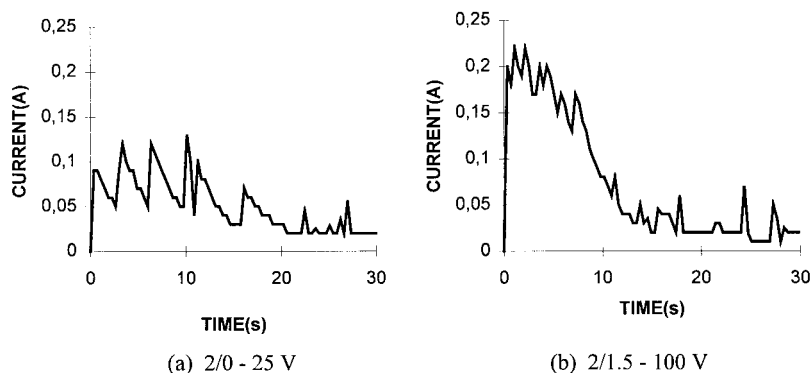
Each emulsion was employed to obtain three films, with voltage drops of 25, 100, and 200 V, respectively, and a fixed deposition time of 100 s for each experiment. The 18 resulting experi-

ments were carried out in no specific order, thus minimizing experimental error. The short electrodeposition time, as well as the random sequence of the experiments, guaranteed that the initial concentration did not change significantly between experiments using the same emulsion. Once the electrodeposition process was completed, the films were washed by immersion in distilled water, thus removing any leftover emulsion that did not form part of the deposited film.

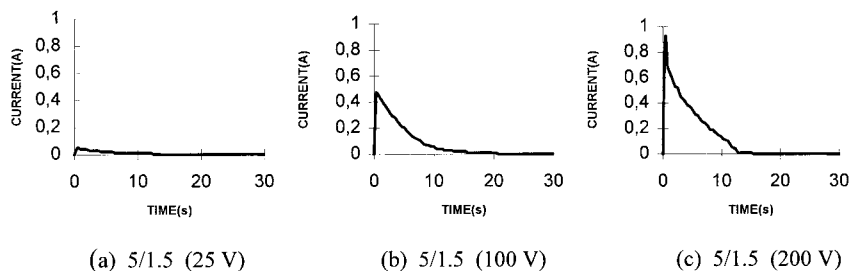
### Results and Analysis

Coatings were obtained in all of the preliminary tests with the asphalt-polystyrene emulsion. Figure 2 shows some of the current-time curves obtained with the 2 wt % asphalt emulsions. These films were characterized by their low adherence and the existence of bare patches on the metal. The curves demonstrate how the current oscillates throughout the experiment, indicating constant film ruptures. One possible explanation could be the low disperse solid concentration in the emulsion.

The remainder of the emulsions presented current-time curves where the current dropped to



**Figure 2** Current-time curves obtained with the 2 wt % asphalt emulsions.



**Figure 3** Current–time curves for the three working voltages.

zero (below the detection limit) within 30 s. Henceforth, this was selected as the electrodeposition time for the next stage of the investigation.

Figure 3 gives the current–time curves for the 5/1.5 wt % emulsion at the three working voltages. It is apparent that, by increasing the voltage, the curve oscillation tends to decrease, the maximum current value increases, and the drop in current after reaching this maximum is more rapid. This behavior was equally demonstrated in the current–time curves of the other emulsions.

By increasing the voltage, the maximum current value is expected to increase, since this occurs in the first moments of the electrodeposition process when the amount of the deposited material is at a minimum. The emulsion constitutes the principal resistance in the cell; this resistance is fairly constant at the start of each test since the amount of deposited material between tests is relatively small. The fact that, after reaching the maximum current value, the slope of the curve is more prominent with higher voltage values complies with a considerably higher film growth rate. However, this only occurs during the first moments of the process; thereafter the curve is smoothed in its decent. This behavior is corroborated by the results obtained in the kinetic study.

An increase in the asphalt concentration produces an increase in the maximum current value and a decrease in the curve oscillation. The first of these effects is related to increase in the number of charged particles, which enhances the conductivity and, hence, results in a reduction in the initial resistance.

Carrying out a similar analysis for polystyrene, it was found that it does not produce a constant effect on the current–time relationships. The maximum current value is not significantly affected by variations in the polystyrene concentration; it is also apparent that it does not affect the shape of the curve even with variations in electrodeposition time. However, the final texture of

the film was significantly improved. Emulsions without the presence of polystyrene produced films with a tacky surface, indicating a low melting point deposited material, whereas with the addition of polystyrene this aspect was greatly improved, indicating a change in the melting point of the coating.

Overall, the coatings obtained from the emulsions prepared with 5 wt % asphalt gave the most homogeneous and thin-surface films, characteristics that were enhanced by increase in the percentage of polystyrene. Based on these conclusions, and the fact that the films produced with 2 wt % asphalt presented surface ruptures, the second stage of the investigation was carried out with a fixed asphalt concentration of 5 wt %.

## EVALUATION OF THE EFFECT OF ADDING OLEATE OF POTASSIUM

### Materials

Electrodeposition trials were completed using three asphaltic emulsions (5 wt % asphalt), each with a different concentration of oleate of potassium ( $\text{KC}_{18}\text{H}_{33}\text{O}_2$ ) (see Table II).

### Methodology

Each emulsion was employed to obtain a new film using voltage drops of 12, 25, 50, 100, 150, 200, and 400 V and a deposition time for each experiment of 30 s.

### Results and Analysis

The resultant values of thickness, deposited weight, charge, and Coulombic efficiency for the experiments are given in Table II. Film thickness versus deposited weight for different concentrations of potassium oleate is plotted in Figure 4. In addition, the inverse of this relationship repre-

**Table II** Experimental Electrodeposition Data on the Effect of Organic Salt Addition

% Asphalt	% Oleate	pH	Variable	Voltage (V)								
				12	25	50	75	100	150	200	250	400
5	0	10.01	$\delta$ ( $\mu\text{m}$ )	99.4	198.6	397.8	287	275.4	182.2	166.6	165	95.8
			$W$ ( $\text{mg}/\text{cm}^2$ )	10.19	21.66	42.83	33.79	34.12	23.06	22.28	20.35	14.51
			$Q$ ( $\text{coul}/\text{cm}^2$ )	0	0.06	0.08	0.11	0.39	0.43	0.45	0.59	1.07
			$C$ ( $\text{mg}/\text{coul}$ )	—	351.1	513.3	298.4	86.95	56.94	49.32	34.76	13.54
5	1	10.38	$\delta$ ( $\mu\text{m}$ )	46.6	59	92.2	85	88.6	63	40.6	55.8	58.2
			$W$ ( $\text{mg}/\text{cm}^2$ )	6.41	8.55	7.89	7.69	6.7	6.29	5.55	5.59	5.01
			$Q$ ( $\text{coul}/\text{cm}^2$ )	0.07	0.14	0.22	0.29	0.55	0.73	1.10	1.32	1.32
			$C$ ( $\text{mg}/\text{coul}$ )	92.86	61.96	35.89	26.56	12.24	8.66	5.04	4.22	3.79
5	2	10.61	$\delta$ ( $\mu\text{m}$ )	21.8	36.6	28.2	36.2	23	33.8	27.8	34.2	90.2
			$W$ ( $\text{mg}/\text{cm}^2$ )	2.01	2.84	3.08	3.08	2.96	3.33	2.75	3.00	9.82
			$Q$ ( $\text{coul}/\text{cm}^2$ )	0.06	0.08	0.25	0.23	0.69	1.08	1.28	1.25	1.52
			$C$ ( $\text{mg}/\text{coul}$ )	31.41	34.28	12.42	13.59	4.25	3.09	2.15	2.39	6.46

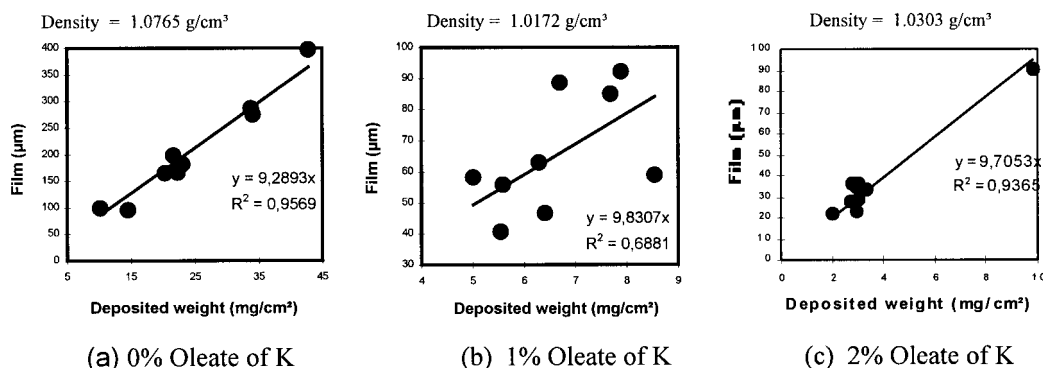
sents the film density; these values are also shown in the same graph. It was apparent that by adding potassium oleate to the emulsion it was possible to produce thin films, only slightly decreasing the density of the coating with respect to the asphaltic emulsion alone.

Based on these conclusions, potassium oleate addition was proposed since the coating thickness was diminished to values usable by industry (25–100  $\mu\text{m}$ ), without significantly affecting the film density. This inferred that the degree of film compacting was similar for the three emulsions, indicating that the use of a 1 wt % organic salt concentration is recommended from the point of view of its minimum concentration and desired film thickness. This range of concentration is also in agreement with literature reports.<sup>1</sup>

## EVALUATION OF THE EFFECT OF VOLTAGE AND POLYSTYRENE CONCENTRATION

### Materials

In accordance with the preliminary study, the emulsions used in the electrodeposition process consisted of a mix of different weight proportions: commercial anionic asphaltic emulsion, previously prepared polystyrene emulsion, potassium oleate (1 wt % with respect to the total emulsion), and distilled water to make up 100%. Four asphalt-polystyrene (ASPS) emulsions were prepared with weight proportions as shown in Table III; each was mixed with the Ultra Turrax at 11,000 rev/min for 1 min.



**Figure 4** Film thickness  $V$ 's deposited weight for different concentrations of oleate of potassium.

**Table III Composition and pH of the Emulsions Used to Evaluate the Effect of Voltage and Polystyrene Concentration**

Notation		Composition			
% Asphalt/% Polystyrene	pH	% Asphalt	% Polystyrene	% Oleate of K	
5/1	10.10	5	1	1	
5/2	10.09	5	2	1	
5/3	10.17	5	3	1	
5/4	10.08	5	4	1	

### Methodology

Each emulsion was employed to obtain a new film using voltage drops of 12, 25, 50, 100, 150, 200, and 400 V and a deposition time for each experiment of 30 s.

### Results and Analysis

The current–time curves for the four emulsions used in this evaluation showed similar voltage characteristics to the preliminary study, that is, an increase in the maximum current value and a rapid current drop off to zero (below the detection limit) within 30 s.

The film thickness, deposited weight, supplied charge, and Coulombic efficiency data for these experiments are given in Table IV. Film thickness versus deposited weight is plotted in Figure 5 for

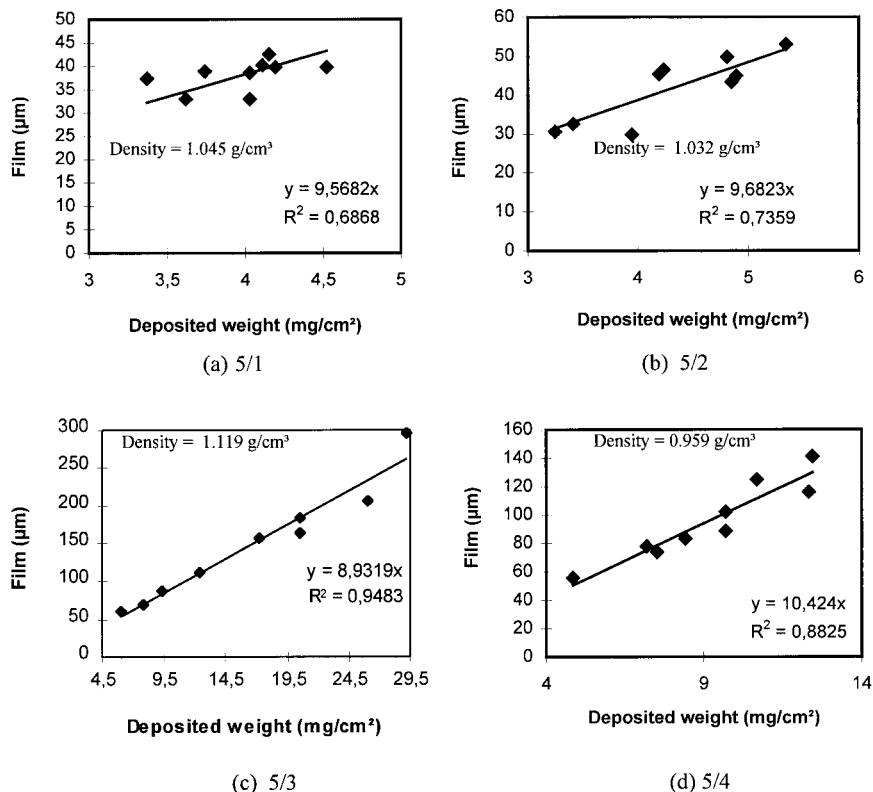
each of the four emulsions, together with the respective trend line, its equation, and its correlation factor. The inverse slope of this line represents the film density, which is also reported in the figure. The film density is an indirect means of expressing rugosity, which is equivalent to the porosity of the deposited film; densities greater than 1 usually give smooth and uniform films.<sup>3</sup>

Figures 6 and 7 show the effect of voltage on the deposited weight, supplied charge, and Coulombic efficiency. It is possible to observe that the charge increases with applied voltage, with this tendency diminishing above 200 V.

As can be appreciated from these figures, the concentration of polystyrene affects the deposited weight–voltage relationship; the 5/1 and 5/2 emulsions present smooth curves, where the weight does not vary significantly with voltage.

**Table IV Experimental Data on the Effect of Voltage and Polystyrene Concentration**

Emulsion	Variable	Voltage (V)								
		12	25	50	75	100	150	200	250	400
5/1	$\delta$ ( $\mu\text{m}$ )	37.40	39.00	33.00	33.00	42.60	39.80	39.80	38.60	40.20
	$W$ ( $\text{mg}/\text{cm}^2$ )	3.37	3.74	3.62	4.03	4.15	4.52	4.19	4.03	4.11
	$Q$ ( $\text{coul}/\text{cm}^2$ )	0.09	0.03	0.21	0.25	0.43	0.87	1.33	1.17	1.15
	$C$ ( $\text{mg}/\text{coul}$ )	32.17	74.53	20.96	8.90	9.37	7.32	4.29	4.02	3.47
5/2	$\delta$ ( $\mu\text{m}$ )	32.60	30.60	29.80	45.40	45.00	53.00	49.80	43.40	46.60
	$W$ ( $\text{mg}/\text{cm}^2$ )	3.41	3.25	3.95	4.19	4.89	5.34	4.81	4.85	4.23
	$Q$ ( $\text{coul}/\text{cm}^2$ )	0.11	0.04	0.19	0.47	0.52	0.73	1.12	1.21	1.22
	$C$ ( $\text{mg}/\text{coul}$ )	32.17	74.53	20.96	8.90	9.37	7.32	4.29	4.02	3.47
5/3	$\delta$ ( $\mu\text{m}$ )	111.40	156.20	114.60	94.20	91.40	83.00	86.20	70.20	61.40
	$W$ ( $\text{mg}/\text{cm}^2$ )	12.41	17.18	12.58	10.07	10.28	8.55	9.33	7.81	6.08
	$Q$ ( $\text{coul}/\text{cm}^2$ )	0.03	0.09	0.19	0.31	0.52	0.80	1.12	1.30	1.27
	$C$ ( $\text{mg}/\text{coul}$ )	466.05	184.95	65.15	32.41	19.81	10.66	8.31	5.99	4.77
5/4	$\delta$ ( $\mu\text{m}$ )	125.00	116.20	141.40	102.20	88.60	83.40	73.80	77.80	55.80
	$W$ ( $\text{mg}/\text{cm}^2$ )	10.69	12.33	12.45	9.70	9.70	8.43	7.52	7.19	4.85
	$Q$ ( $\text{coul}/\text{cm}^2$ )	0.14	0.10	0.28	0.31	0.54	0.91	1.18	1.27	1.20
	$C$ ( $\text{mg}/\text{coul}$ )	74.35	117.55	45.10	31.63	17.84	9.21	6.36	5.67	4.03



**Figure 5** Film thickness versus deposited weight.

However, there is an implied tendency toward a maximum, a characteristic that is more evident for the 5/3 and 5/4 emulsions. In addition, as the polystyrene concentration increases, the maximum amount of deposited weight is obtained at a lower voltage, around 150 V for emulsions 5/1 and 5/2 and 30 V for emulsions 5/3 and 5/4.

As expected from the previous results, the Coulombic efficiency decreases with voltage (this tendency significantly reduces around 75 V). This analysis indicates that, although the polystyrene concentration does not affect the current–time relation, it does, however, influence the deposited weight (or thickness) with respect to voltage, producing a noticeable change in the range 2–3 wt %. The reason why an increase in polystyrene concentration has this effect is not clear, but it is possibly related to electrophoretic migration.<sup>9–11</sup>

Overall, it is possible to conclude that the films obtained with the 5/1 and 5/4 emulsions were characterized as having tacky surfaces and relatively low compaction. The measured thicknesses for the 5/2 emulsion films were in the acceptable range for all the experimental voltages; these coatings were compact, but with only a barely acceptable texture.

The most compact and best texture films were obtained with the 5/3 emulsion, but only above a voltage of 75 V was it possible to achieve film thickness acceptable by industry.

## KINETIC ELECTRODEPOSITION STUDY

### Materials

To determine the film growth rate, tests were carried out with an emulsion of 5 wt % asphalt, 3 wt % polystyrene, and 1 wt % potassium oleate.

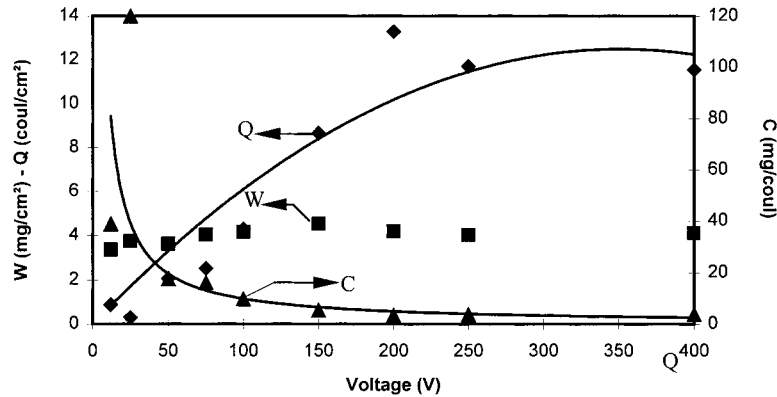
### Methodology

Runs were performed at four working voltages (25, 50, 100, and 200 V), and for each run, films were obtained at different deposition times (2, 5, 10, 15, 20, and 60 s).

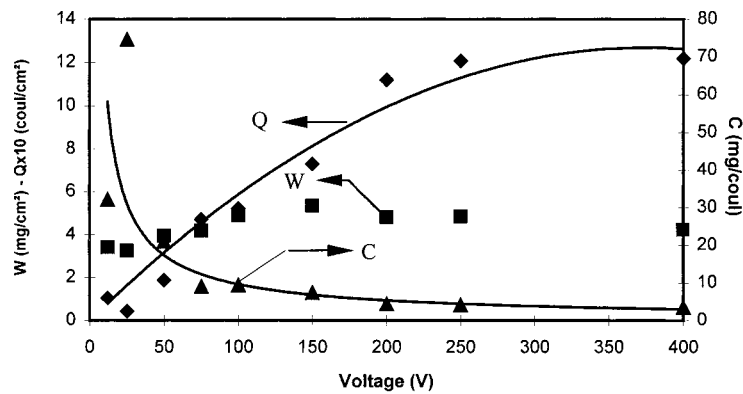
### Results and Analysis

Table V presents the experimental results obtained in the kinetic electrodeposition study. To determine the kinetic model of a given system, it is necessary





(a) 5/1



(b) 5/2

**Figure 6** Effect of voltage on the deposited weight, supplied charge, and Coulombic efficiency.

to evaluate properties such as film conductivity [ $\sigma_F$ ], Coulombic efficiency [ $C$ ], and dissolution current density [ $j_d$ ]. By graphing experimental data of current density [ $j$ ] against the factor [ $V/\delta$ ], it is possible to determine if the system follows Ohm's law, in which case the slope represents the film conductivity. Figure 8 presents this relationship for 25, 50, 100, and 200 V with the respective tendency lines and clearly shows that the asphalt-polystyrene system presents Ohmic behavior. At 200 V, the results show slight variation, presumably due to the film thickness not varying.

The equations derived from the experimental data and shown in Figure 8 can be represented by

$$j = \sigma_F \left[ \frac{V}{\delta} + \frac{V}{\delta_{I=0}} \right] \quad (8)$$

from which the following equations were obtained at the different voltages:

$$(25 \text{ V}) j = 35.57(V/\delta - 0.0319) \quad (9)$$

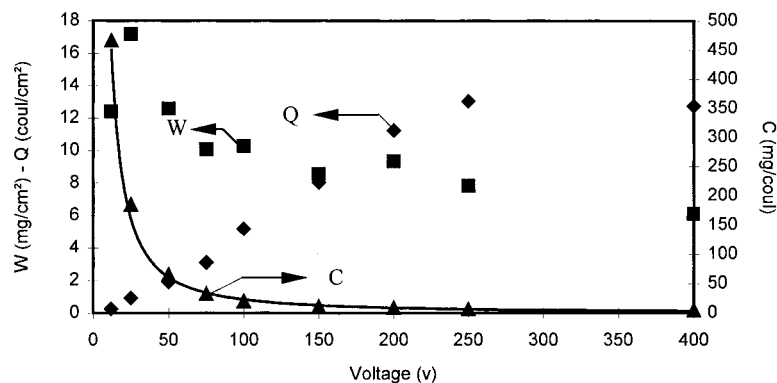
$$(50 \text{ V}) j = 50.51(V/\delta - 0.0853) \quad (10)$$

$$(100 \text{ V}) j = 163.81(V/\delta - 0.2173) \quad (11)$$

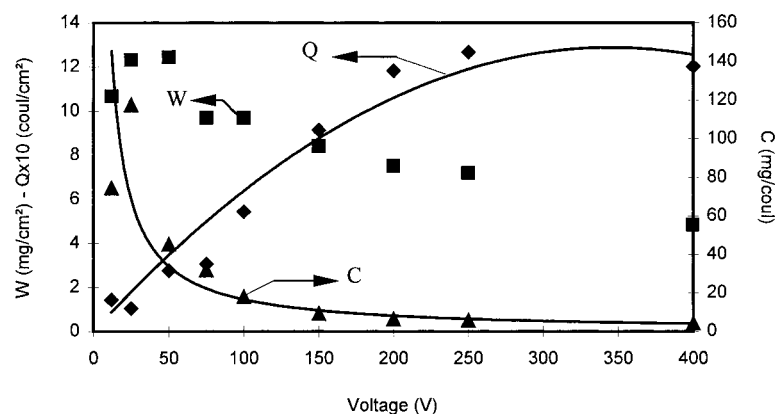
By analyzing eq. (8) at  $V = 0$ , the relation [ $V/\delta_{I=0}$ ] should be equal to zero, since without a potential difference, there should be no current ( $I$ ) circulating through the laminar. Figure 9 presents the relation [ $V/\delta_{I=0}$ ] versus  $V$  as a straight line passing through the origin with  $R^2 = 0.9772$  and, thus, represented by the equation

$$\left( \frac{V}{\delta_{I=0}} \right) = 0.02V = \frac{V}{500} \quad (12)$$

Theoretically, this relationship signifies that, in order for the current density to reach a value of



(a) 5/3



(b) 5/4

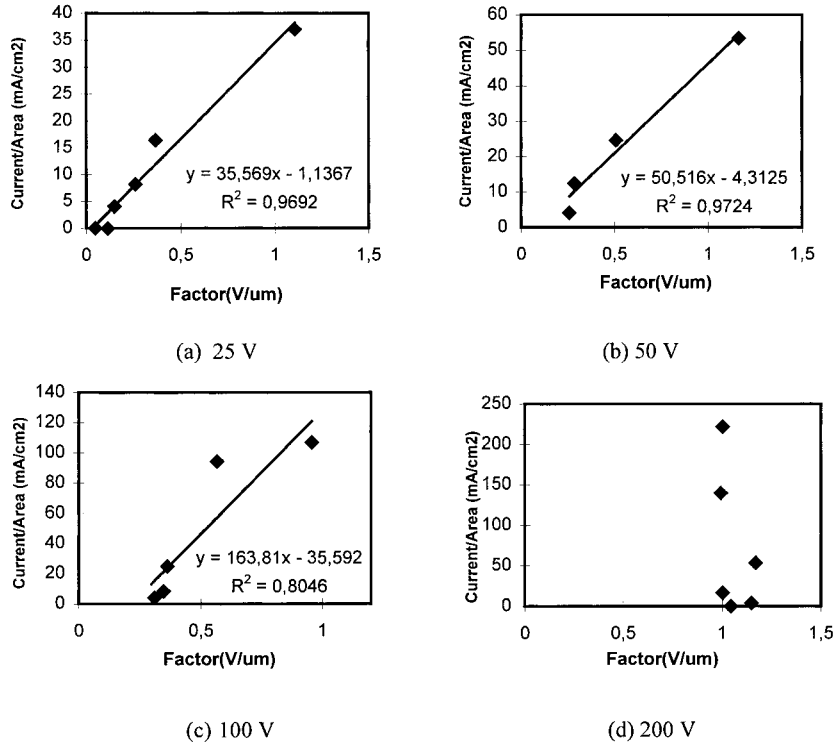
**Figure 7** Effect of voltage on the deposited weight, supplied charge, and Coulombic efficiency.

zero, the film thickness should be approximately  $500 \mu\text{m}$ ; if the system demonstrates film dissolution, this thickness is not experimentally achievable since a limiting thickness is reached in relation to the dissolution current.<sup>12-13</sup>

Equations (9)–(11) also suggest that the film conductivity  $[\sigma_F]$  varies with the applied voltage. In the absence of an applied potential difference, there would no migration of charged particles; hence, by graphing the conductivity  $[\sigma_F]$  versus

**Table V** Experimental Results Obtained in the Kinetic Study Using the 5/3 Emulsion W

<i>t</i> seg.	25 V			50 V			100 V			200 V		
	$\delta \mu\text{m}$	<i>W</i> $\text{mg}/\text{cm}^2$	<i>Q</i> $\text{coul}/\text{cm}^2$	$\delta \mu\text{m}$	<i>W</i> $\text{mg}/\text{cm}^2$	<i>Q</i> $\text{coul}/\text{cm}^2$	$\delta \mu\text{m}$	<i>W</i> $\text{mg}/\text{cm}^2$	<i>Q</i> $\text{coul}/\text{cm}^2$	$\delta \mu\text{m}$	<i>W</i> $\text{mg}/\text{cm}^2$	<i>Q</i> $\text{coul}/\text{cm}^2$
2	22.60	1.85	0.09	43.00	3.82	0.09	104.60	10.85	0.21	199.40	17.63	0.44
5	68.20	4.93	0.17	98.60	10.36	0.21	176.60	19.40	0.49	201.40	18.74	0.97
10	96.60	8.71	0.23	175.40	20.63	0.34	276.20	28.28	0.76	171.00	20.68	1.43
15	169.00	13.85	0.25	193.80	22.48	0.38	287.80	29.80	0.83	199.40	21.83	1.58
20	220.20	17.35	0.25	185.40	19.52	0.40	322.60	31.94	0.86	174.20	19.69	1.62
60	—	52.65	0.25	178.20	20.96	0.40	336.20	32.39	0.86	191.40	20.63	1.62



**Figure 8** Current density versus factor  $[V/\delta]$  for the emulsion 5/3.

the voltage  $[V]$ , the data should pass through the origin. This is presented in Figure 10, obtaining a straight line of  $R^2 = 0.9194$  that passes through the origin and is thus represented by the equation

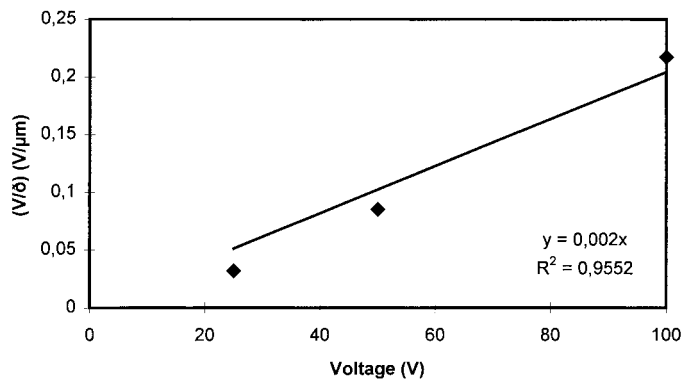
$$\sigma_F = 1.5083 V \quad (13)$$

Replacing the terms  $[V/\delta_{I=0}]$  and  $[\sigma_F]$  with the voltage, (12) and (13), respectively, in (8), the current density can be expressed as a function of the voltage and film thickness as

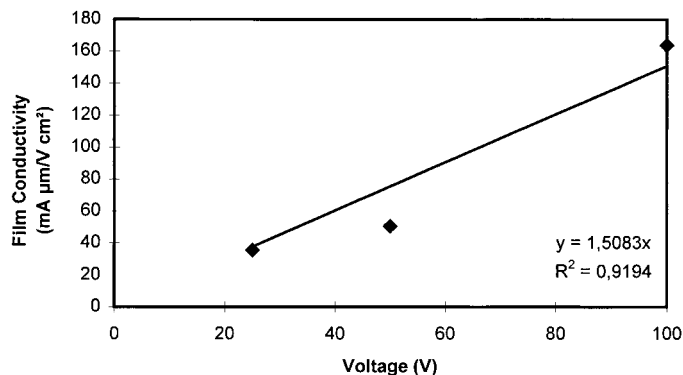
$$j = 1.5083V \left( \frac{V}{\delta} - \frac{V}{500} \right) \quad (14)$$

Figure 11 shows current density versus the term  $[V/\delta]$  at 25, 50, and 100 V, compared to the predicted values derived from eq. (14).

The Coulombic efficiency and the current density can be calculated by graphing  $[\delta/t]$  versus  $[Q/t]$ . Figure 12 was constructed from the experimental data given in Table V; the trend line and  $R^2$  are also given. The independent term indi-



**Figure 9** Experimental relation between  $V/\delta_{I=0}$  and supplied voltage.



**Figure 10** Experimental relation between the film conductivity and supplied voltage.

cates that the ASPS system presented film dissolution behavior.

Calculating the Coulombic efficiency gave a value of  $0.044229 \text{ cm}^3/\text{C}$ , which was consistent with similar calculations at each of the different voltages. However, the dissolution current density  $[j_d]$  did show variations with voltage. Taking into account that, theoretically, the film discontinues growth once the current density reaches the value of  $[j_d]$ , and that from the previous experiments it was found that the limiting thickness was dependent on the applied voltage, it was concluded that  $[j_d]$  will also vary with the applied voltage. In addition, Figure 12 indicates that the ASPS system follows Faraday's law given in (1), since  $[Q/t]$  is equivalent to the current density.

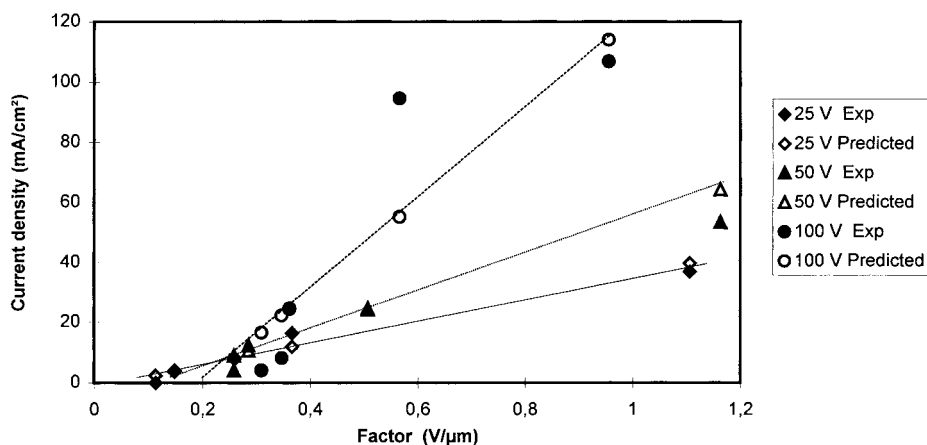
Film thickness versus deposited weight per unit area is given in Figure 13. Taking an inverse of the slope gives a film density of  $1008.7 \text{ mg}/\text{cm}^3$  and, hence, a Coulombic efficiency value (in mass terms) of  $44.614 \text{ mg}/\text{C}$ .

Based on the above analysis—which demonstrated that the asphalt (5 wt %)-polystyrene (3 wt %) system obeys Ohm's and Faraday's laws and also presents film dissolution behavior—the rate of film growth can be described by substituting (14) in (6), giving

$$\frac{d\delta}{dt} = C \left[ \sigma_F V \left( \frac{1}{\delta} - \frac{1}{\delta_{I=0}} \right) - j_d \right] \quad (15)$$

The values of  $[j_d]$  that correspond to each voltage can be determined from eq. (3).

Using the dissolution current values  $[j_d]$  given in Table VI and a Coulombic efficiency of  $0.44229 \text{ μm cm}^2 \text{ mA}^{-1} \text{ s}^{-1}$  (ensuring consistent dimensionality), eq. (15) was solved numerically at each of the applied voltages. This solution is presented in Figure 14, giving the predicted film growth for the electrodeposition system being investigated at different voltages.



**Figure 11** Current density versus the term  $V/\delta$  compared to the predicted values derived from eq. (14).

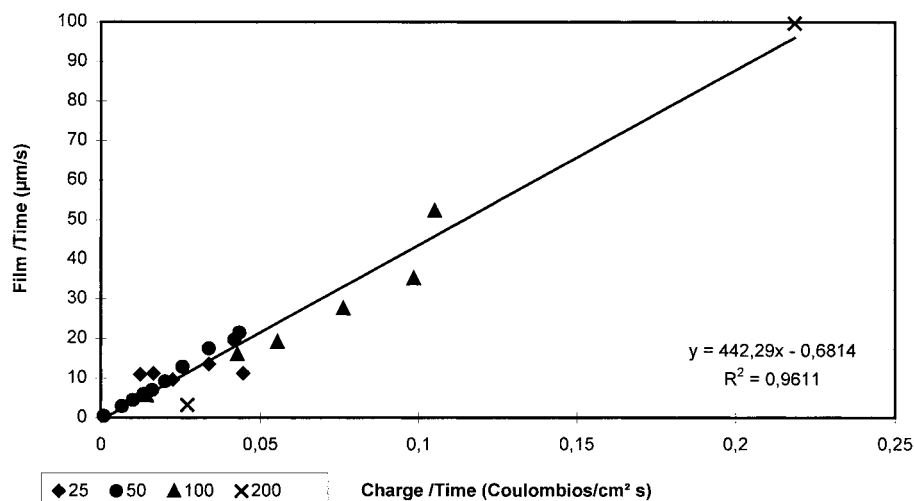


Figure 12 Experimental behavior of  $\delta/t$  versus  $Q/t$ .

The curves predict an initial growth rate that increases with voltage; this can also be appreciated from the current–time curves, where the initial current increases with voltage and has a greater slope in descent. Consequently, the film achieves limiting thickness in a shorter time since the dissolution current also increases with voltage. For example, if film growth data were needed at 200 V (before stabilization was reached), it would be necessary to realize tests within the first 2 s. This explains why the data plotted in Figure 8 do not show the same tendency as that of the other voltages. However, in Figure 14, it can be appreciated that the solution of (15) at 200 V does fit the experimental data.

## CONCLUSIONS

Coatings obtained with the 5 wt % asphalt emulsion gave homogeneous and thin surfaces in comparison with the other asphalt concentrations tested (2 and 12 wt %). The experiments carried out with the 2 wt % asphalt were characterized by surface ruptures and deficient films, where the current remained at a residual value.

By adding 1 wt % potassium oleate to the asphaltic emulsion, it was possible to achieve film thickness values of less than 100  $\mu\text{m}$  (a specification usable by the coating industry), without affecting film densities that remained above 1  $\text{mg}/\text{cm}^3$ . Densities greater than 1 are generally ac-

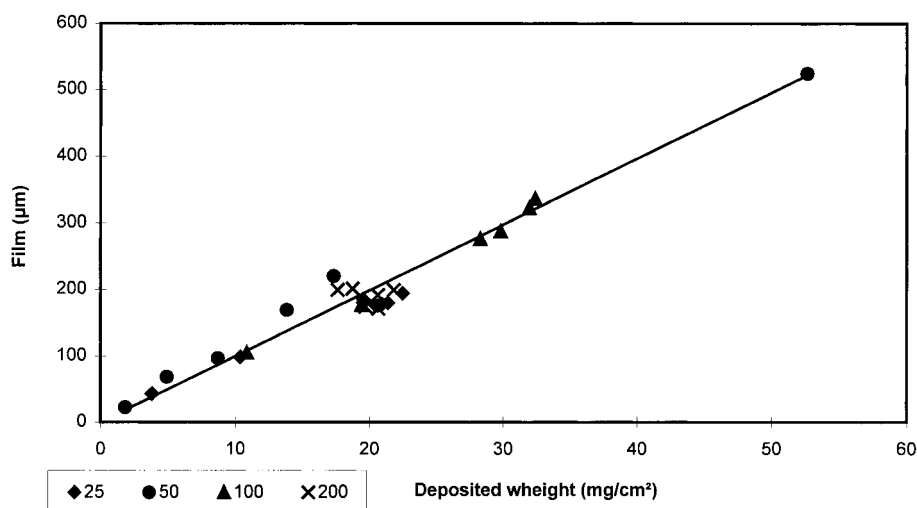


Figure 13 Experimental behavior of film thickness versus deposited weight per unit area.

**Table VI Dissolution Currents at Each Voltage**

Voltage (V)	Limiting Thickness ( $\mu\text{m}$ )	$j_d$ ( $\text{mA}/\text{cm}^2$ )
25	220.2	2.4
50	193.8	12
100	336.2	14.7
200	201.4	178.9

cepted as giving smooth and uniform films, since this is an indirect measure of the rugosity and porosity of the coating.

Polystyrene used at a 3 wt % concentration was shown to produce compact films with satisfactory textures. Statistical analysis demonstrated that by adding polystyrene to the emulsion the film thickness and deposited weight values increased, while the applied voltage decreased these respective parameters. Hence, the coatings produced with 3 wt % polystyrene emulsions with applied

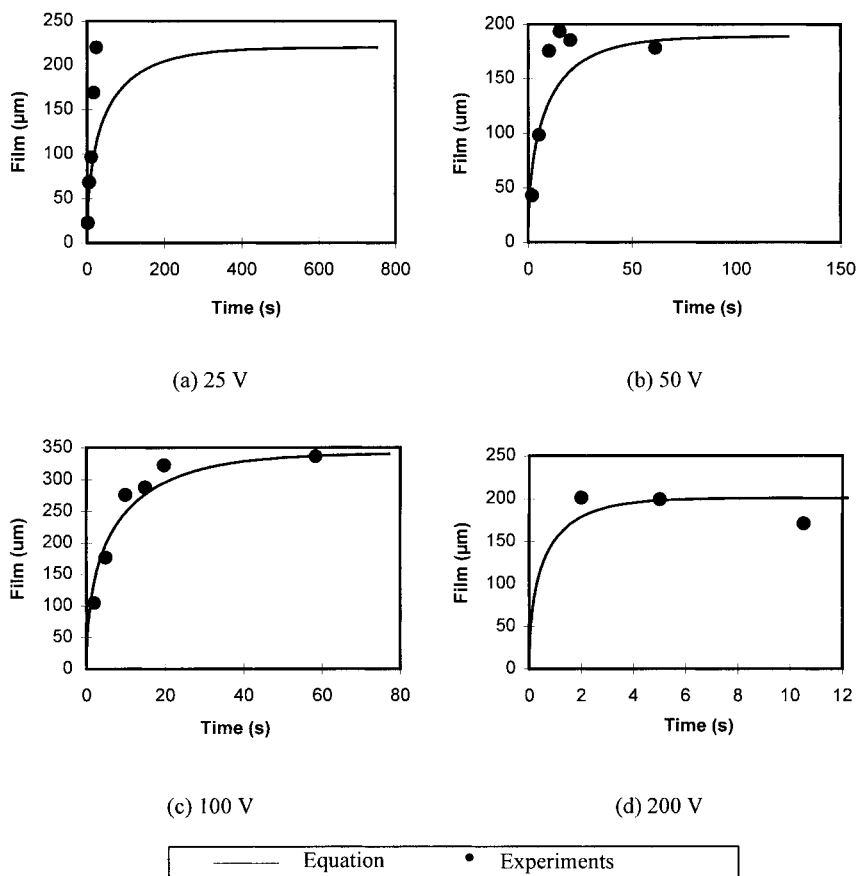
voltages above 75 V gave an industrially acceptable thickness.

The asphalt-polystyrene system was shown to obey Faraday's law; in other words, the rate of film growth is proportional to the current density at the electrode. For the asphalt-polystyrene system, the ohmic model contains an additional term that represents the maximum electrical resistance when the current drops to zero:

$$j = \sigma_F V \left( \frac{1}{\delta} \right) - \sigma_F V \left( \frac{1}{\delta_{I=0}} \right)$$

where  $[\delta_{I=0}]$  is the theoretical thickness at zero current density;  $[\delta]$ , the film thickness;  $[V]$ , the applied voltage; and  $[\sigma_F]$ , the film conductivity. The current density given by this equation is proportional to the applied voltage and inversely proportional to the film resistance (characteristic of an ohmic system).

The following mathematical model was proposed to approximate the kinetics of film growth



**Figure 14** Predicted film growth for electrodeposition system at different voltages.

with time. It is important to point out that this expression includes a dissolution current factor to account for film dissolution behavior:

$$\frac{d\delta}{dt} = C \left[ \sigma_F V \left( \frac{1}{\delta} - \frac{1}{\delta_{I=0}} \right) - j_d \right]$$

where  $[C]$  is the Coulombic efficiency ( $\mu\text{m cm}^2 \text{mA}^{-1} \text{s}^{-1}$ ),  $[\sigma_F]$ , the film conductivity ( $\text{mA } \mu\text{m V}^{-1} \text{cm}^{-2}$ );  $[V]$ , the applied voltage (volts);  $[j_d]$ , the dissolution current density ( $\text{mA}/\text{cm}^2$ );  $[d]$  the film thickness ( $\mu\text{m}$ ); and  $[t]$ , the time (s). This model only requires experimental evaluation of the limiting thickness at a determined voltage, which then allows the derivation of the respective dissolution current at this voltage.

The experiments carried out at low voltages gave results with a greater degree of uncertainty, due to difficulties with the supply source in maintaining the voltage within limits. This effect is apparent in the statistical analysis as an increased error between the mathematical model and the experimental data as the voltage is reduced.

## REFERENCES

1. McCoy, P. E. U.S. Patent 3159558, Dec. 1, 1964.
2. Pierce, P. E. *J Coat Technol* 1981, 53, 118–125.
3. Sudol, E. D.; El-Aasser, M. *Ind Eng Chem Prod Res Dev* 1985, 24, 550–560.
4. Normas ASTM B 322 (85), B 254, 1979.
5. Campbell, G. A. *Electrodeposition of Coatings; Advances in Chemistry Series 119*; American Chemical Society: Washington, DC, 1980.
6. Collins, E. *Experiments in Polymer Science*; Wiley: New York, 1973; pp 335–337.
7. Heitz, E.; Kreysa, G. *Principles of Electrochemical Engineering*; VCH: Stuttgart, Germany, 1986.
8. Ho, C. C.; Humayun, A.; El-Aasser, M. S.; Vanderhoff, J. W. *Ind Eng Chem Prod Res* 1989, 9, 236–241.
9. Klaus, A. *Cathodic Deposition of Paint*; Pergamon: London, 1994; Vol. 39, No. 8.9.
10. Pierce, P. E.; Kovac, Z.; Higginbotham, C. *Ind Eng Chem Prod Res Dev* 1978, 17, 520–526.
11. Santos, S.; Gomez, V. C. *Rev Iberoam Polím, Bucaramanga* 1993, 3, 39–46.
12. Schoff, C. K. *J Coat Technol* 1990, 62, 432–436.
13. Vega, C. *Cathodic Electrodeposition of Latexes*; Lehigh University: Bethlehem, PA, 1986.