

Electrophoretic Deposition of Polymers. II.

Polyimides: A Coulombic Study

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Synopsis

Quantitative studies on the electrophoretic deposition of a polyimide polymer were carried out over the voltage range 25–100 V dc. Deposition yield was related to voltage, time, and coulombs and was found to obey Faraday's laws of electrolysis. Equations relating yield to voltage and coulombs were obtained from the plotted data. Results of coulombic studies indicate that the effective equivalent weight of the polymeric species being deposited is between 6800 and 7500 (i.e., amount deposited per faraday). The coulombic yield is 75 mg per coulomb. Information and speculation on the size and composition of the electroactive species are presented.

INTRODUCTION

In 1979, a number of parameters were identified that govern the electrophoretic deposition of polymers from nonaqueous media.¹ These were optimized with respect to the emulsion preparation and the yield of deposit. During the course of this work, it became clear that the properties of the emulsions influenced the deposition process far more strongly than those of the chemical entities enclosed in the emulsion. Our purpose here was to optimize the emulsion preparation and to characterize and quantify the deposited materials with respect to Faraday's laws of electrolysis.

The relationship between the quantity of electricity passing through an electrolyte and the amount of material deposited or dissolved is expressed by Faraday's laws. These laws state that (1) the amount of chemical change produced by electrolysis is proportional to the total amount of charge passed through the cell, and (2) the amount of chemical change produced is proportional to the equivalent weight of the substance undergoing chemical change. If the reaction is electrodeposition, then the amount of change is usually expressed as the weight of the deposit, and Faraday's laws may be expressed by the following equations:

$$M = Z \int_0^t i dt = Zq \quad (1)$$

$$Z = E/F \quad (2)$$

where M = mass of substance deposited at the electrode, i = current in amperes, t = time in seconds, q = quantity of electricity in coulombs, Z = electrochemical equivalent (coulombic yield), E = chemical equivalent weight, and F = faraday = 96,500 coulombs.

It should be noted that Faraday's laws only apply to the primary electrode reactions, i.e., to reactions at the electrode surface between species in solution and the electrical charges of the electrodes. In the Faraday equation, if $i \times t$ is equal to F , then the mass (M) of the material deposited is equal to E : this can be calculated by measuring M and q . These values are known for all the elements. The electrolytes containing these elements are characterized by single ionic species with definite molecular weights, dimensions, and charge. However, polymers are not so simply characterized: there exists a distribution of species of various molecular weights that could influence the dimensions and charge of the colloidal particle.

EXPERIMENTAL

Description of Apparatus

All electrodeposition experiments were carried out at constant applied voltages which were preset prior to immersion of the electrodes into the emulsion. The emulsion was contained in a Pyrex glass beaker. The anode was an aluminum rod (Type 6061T6) 0.250 in. in diameter and 8 in. long, which was fastened to a Teflon block equipped with a nickel screen cathode to give an electrode gap of 1 in. The nickel screen was obtained from the Exmet Corp., Bridgeport, CT. The designation is 10Ni 12-2/0. The electrodes were immersed 2 in. into the emulsion, thus obtaining a total immersed area of 1.57 in square. The dc power supply was a model 407D, 0-600 volts, from the John Fluke Mfg. Co., Seattle, WA. Current and voltage were measured using a Triplet multimeter model 630NA and a Keithley electrometer model 178, respectively. Current vs. time was recorded using a L&N Speedomax recorder model XL-680. The quantity of electricity was measured with a Koslow Scientific model 541 coulometer. A schematic of the apparatus is shown in Figure 1.

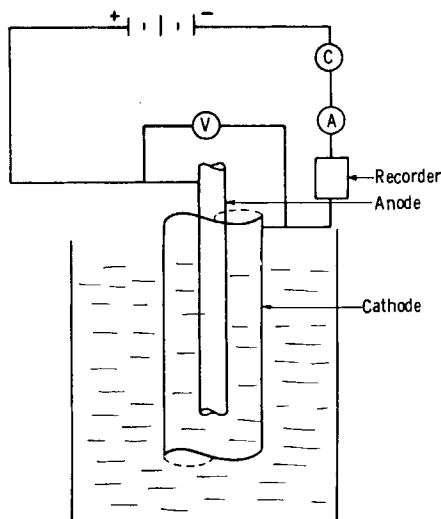
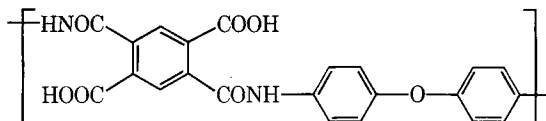


Fig. 1. Schematic of electrodeposition cell.

Material

RC-5057 Pyre ML 1 was used in all experiments. It is a polyamic acid solution in *N*-methylpyrrolidone at 16.5 wt % solids, supplied by the DuPont Co. The structural formula for the polyamic acid is shown below:



Preparation of Coating Solutions

Electrodeposition of polymers is generally carried out from emulsions. To prepare the emulsion, a dilute polymer solution is mixed with a nonsolvent to precipitate the polymer from solution in the form of fine droplets dispersed throughout the mixture. A more detailed description can be found in Ref. 1.

RESULTS AND DISCUSSION

Emulsion Preparation

The preparation of polymer emulsions in the past¹ has always been based on the reaction at 40°C of an organic amine with the polymer containing suitable functional groups to form the amine salt, which was subsequently dispersed in a nonsolvent. Electrodeposition was predicated upon migration of charged species, formed by the ionization of the amine salt. Heating of the amine with the polymer was considered necessary. While good emulsions were thus obtained, some large polymer particles precipitated out, and the size of the particles remaining in the emulsion was generally larger than is desirable for long-term stability and coating uniformity.

We have found that it is not necessary to react the amine with the polymer before adding the polymer solution to the nonsolvent. In fact, adding the polymer solution to a nonsolvent containing the amine yields an emulsion that is finer in particle size and has improved long-term stability and deposition yield.

Two emulsions were prepared using a polyamic acid material (Pyre ML-RC5057) as follows: In emulsion A, the amine and the Pyre ML were heated for 20 min at 40°C prior to adding it to acetone. In emulsion B, the polymer solution was added to the acetone containing the amine. The composition of both emulsions is as follows: 10 g Pyre ML, 62 g NMP, 0.4 g triethylamine (Et₃N), and 178 mL acetone.

The emulsion prepared by procedure A was opaque white in color and had some fibrous polymeric precipitate on the bottom of the beaker. The emulsion from procedure B was opalescent with no precipitated polymer. These emulsions were electrolyzed at 50 V dc for 60 s using aluminum electrodes 1½ in. wide and immersed 2 in. with 1 in. separation. The yield of deposit on the anode was 31 and 36 mg for A and B, respectively. The coulombic yield was 63 and 72 mg/C, respectively.

These emulsions were covered and left to stand at room temperature for two

months. More precipitate formed in emulsion A and none formed in B. The precipitate in A was about 10% of the total weight of the polymer. A probable explanation to account for the emulsion differences is that when the emulsion is formed by adding the polymer solution to the nonsolvent containing the amine, it is emulsified better due to the large concentration of amine present at any given time relative to the concentration of polymer during addition. This increased amine concentration has the effect of reducing the interfacial tension between polymer solution and nonsolvent, thus promoting a more intimate dispersion.

Composition of the Deposited Coating

Emulsions using Pyre ML-RC5057 were prepared as per procedure A above. Electrodeposition was carried out at 50 V dc for 30 s. The coated electrode was heated to 300°C and the weight of the deposited coating was found to be 0.0432 g. This is the actual weight of the imidized form of the migrating species.

Another electrode was coated under the same conditions and immediately weighed after removal from the deposition bath. The weight of the wet coating was 0.2992 g and represents the combined weight of polymer + solvent + non-solvent. From the above two weights, one can calculate the solids content of the wet deposit, which is approximately 14%. This compares with 0.77% solids of starting emulsion. If the coated electrode is left to air dry, a constant weight is reached after about 6 h (see Fig. 2). From this result, it is apparent that the wet deposit contains a concentrated amount of resin solids; however, there still is a large decrease in volume on curing the deposit since the wet coating contains 86% volatiles.

During electrodeposition, three major processes are thought to occur: electrophoresis, electrocoagulation, and electro-osmosis. The last process should result in a dense deposit at the anode as the solvent-nonsolvent liquid medium moves away from the electrode surface through the porous coating and back into the bulk of the emulsion. So the solids content of the deposit should be a function of the extent of electro-osmosis. Because the solids content of the wet deposit is relatively low (~14%), the mechanistic contribution from the elec-

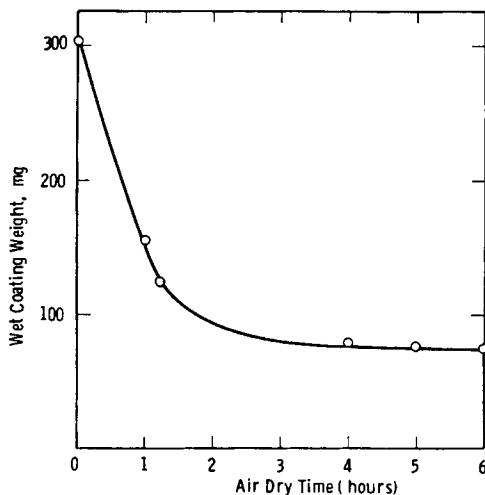


Fig. 2. Effect of air drying on coated electrode weight.

TABLE I
Effect of Voltage on Solids Content of Anodic Deposits

Sample	Voltage	Solids content (%) ^a vs. deposition time			
		15 s	30 s	45 s	60 s
1	25	10	9	10	10
2	50	13	12	14	14
3	75	15	14	15	16
4	100	16	15	17	18

^a Average of three values.

tro-osmosis is small. This means that the migrating species that is deposited on the electrode is a highly swollen state in which polymer, solvent, and non-solvent coexist. The composition of the film at the anode appears to be dependent on the applied voltage and relatively independent of the time of electrodeposition. Table I presents data on the effect of voltage on the solids content of the wet coating at voltages ranging from 25 to 100 V dc. The data indicate that the electro-osmotic effect becomes stronger as the voltage increases, as shown by the increased solids content of the wet coating at the higher voltages.

Effect of Successive Depositions from the Same Emulsion

Compositional changes in the emulsion were determined as functions of multiple depositions from the same emulsion. A polyimide emulsion (procedure B) was prepared from 10 g Pyre ML-RC5057, 62 g NMP, 0.4 g triethylamine, and 178 mL acetone. This composition had the following properties: solids content 2.29% (based on the weight of the polymer and NMP), precipitant/solvent ratio (P/S) 2.6, and amine/polymer mole ratio 0.5. Twenty successive depositions lasting 60 s each were made from this emulsion using aluminum electrodes at 50 V dc. The data from this experiment are shown in Table II.

The amount of polymer deposited decreases linearly with the number of depositions (see Fig. 3). In addition, the number of coulombs passed also decreases (Table II). Obviously, the number of charge-carrying species present in the

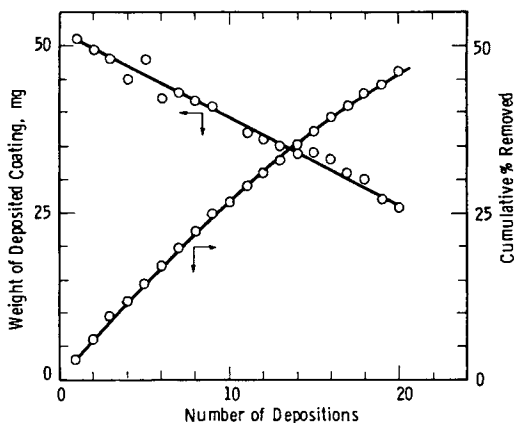


Fig. 3. Change in yield deposited on anode as function of successive depositions under identical electrocoating condition.

TABLE II
Compositional Changes as Functions of Multiple Depositions

Sample No.	Coulombs	Deposit weight, mg	% Removed per 60 s	Cumulative % removed	Weight of polymer left in emulsion, g	E^a	Z, mg/C ^a
1	0.74	51	3.08	3.08	1.59	6,067	63
2	0.75	49	2.97	6.05	1.55	5,974	60
3	0.76	48	2.92	8.97	1.50	5,595	58
4	0.69	45	2.73	11.70	1.45	5,736	59
5	0.76	48	2.92	14.62	1.40	5,595	58
6	0.73	42	2.65	17.27	1.36	5,297	55
7	0.71	43	2.61	19.88	1.32	5,309	55
8	0.71	42	2.55	22.43	1.27	5,216	54
9	0.70	41	2.47	24.90	1.23	5,123	53
10	0.68	32	1.92	26.82	1.20	5,042	52
11	0.66	37	2.23	29.05	1.17	4,898	51
12	0.66	36	2.18	31.23	1.13	4,817	50
13	0.66	35	2.13	33.36	1.09	4,671	48
14	0.64	34	2.06	35.42	1.06	4,670	48
15	0.63	34	2.04	37.46	1.03	4,671	48
16	0.66	33	1.99	39.45	0.99	4,391	46
17	0.63	31	1.87	41.32	0.96	4,319	45
18	0.60	30	1.84	43.16	0.93	4,385	46
19	0.58	27	1.66	44.82	0.91	4,145	43
20	0.58	26	1.57	46.39	0.88	3,921	41

^a Calculated from the Faraday equation.

TABLE III
Decrease in Polymer Concentration with Successive Depositions

Run No.	Weight of polymer remaining, g
0	1.65
1	1.59
5	1.40
10	1.20
15	1.03
20	0.88

emulsion is being depleted. Table III shows the decrease in concentration of polymer after successive depositions.

There is a direct relationship between yield deposited at the electrode and the concentration of polymer remaining in the emulsion (see Fig. 4). If one plots yield vs. reciprocal of the weight of polymer remaining in the emulsion (Fig. 5), the equation of the line gives an intercept value of about 77 mg for the yield of polymer. This is in excellent agreement with the 75-mg yield predicted by the yield-vs.-coulomb data shown in Figs. 5-7. This information indicates that the emulsion bath must be kept at the optimum solids in order to maximize the yield deposited at the electrode, at least with this system.

The decrease in solids content of the emulsion alone could account for the lowering of the yield, but Faraday's laws predict, at least for metals, that the coulombic yield (Z), in mg/C, should remain constant. That is the ratio of the coulombs to the yield, and the equivalent weight of the depositing species should be constant. This is not the case in this situation; the ratio of coulombs/yield initially is 0.014, and after the 20th deposition it is 0.022. This represents an increase of 57%, and the Z values in Table II reflect this change. In addition, the cumulative yield does not increase in a linear fashion with the number of depositions (Fig. 3), indicating a change in rate of deposition as the emulsion is

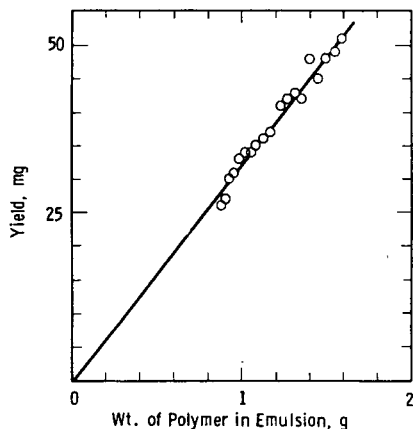


Fig. 4. Yield deposited on anode as function of weight of polymer in emulsion. $y = 32.89x - 1.30$; corr. coeff. = 0.966.

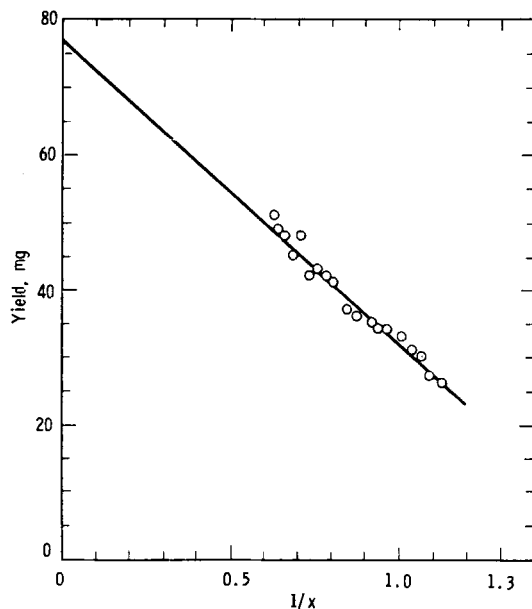


Fig. 5. Yield deposited at anode vs. reciprocal of residual polymer concentration in emulsion. x = Weight of polymer in emulsion, g; $y = -46.01x + 77.68$; corr. coeff. = 0.958.

being depleted of polymer. After about the fifth deposition, there is departure from linearity and the rate of deposition slows down. Furthermore, the initial current at the start of the deposition decreases as the number of depositions increases (see Fig. 6). The concentration dependence of the yield is predicted by Faraday's laws but the change in Z values is not. These data suggest that other reactions are occurring that affect both the coulombic and material yield. It is not known what these reactions are, but they could be related to electrolysis of the solvent and nonsolvent or to the nature of the electroactive species, i.e., a change in the mass-to-charge ratio of the emulsion droplet. If the amine concentration in the bulk of the emulsion increases with successive depositions,

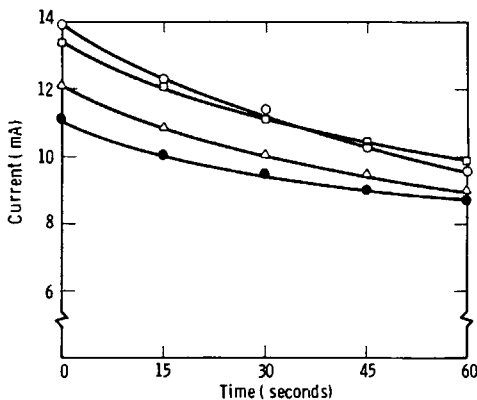


Fig. 6. Current vs. time after successive depositions at 50 V dc: (O) first five depositions, average; (●) second five depositions; (Δ) third five depositions; (■) fourth five depositions.

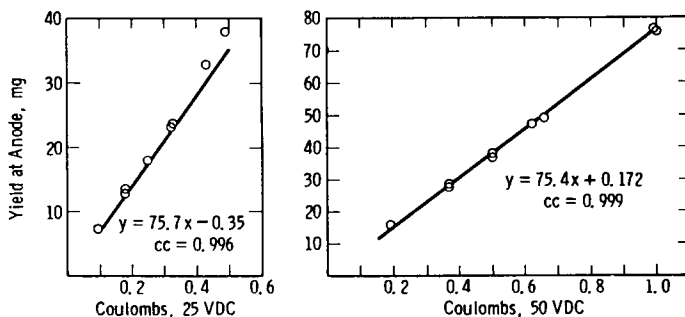


Fig. 7. Effect of coulombs on yield of polyamic acid deposited at anode (25 and 50 V dc).

one would expect an increase in the number of charges per molecule, because the amine can react with the COOH group on the remaining polymer. This has the effect of decreasing the coulombic yield.

Coulombic Studies

From a technologic standpoint, a major field of investigation in electrodeposition is the choice and control of the electrical conditions to give maximum process efficiency. In order to study these conditions, Faraday's laws were applied to the deposition process to relate the yield deposited with the quantity of electricity passed through the electrophoretic medium. Deposition at constant voltage is normally applied in industrial practice.

Polyimide emulsions consisting of Pyre ML-RC5057 + NMP solvent + TEA + acetone (nonsolvent) were prepared by procedure B having the following properties: amine/COOH ratio 0.5, nonsolvent/solvent ratio 2.6, and a solids content 0.77%. These emulsions were electrolyzed using standard conditions from 25–100 V dc. A compilation of all the experimental data is shown in Table IV.

The relationship between the quantity of electricity passed through the emulsion and the yield deposited on the electrode is given by Faraday's law. We plotted yield vs. coulombs at constant applied voltages of 25, 50, 75, and 100 V dc (see Figs. 7–9). The line drawn through the points was obtained by linear regression analysis. We found that the amount of polymer deposited is, like in the case of metals, directly proportional to the amount of coulombs, i.e., the process obeys Faraday's laws of electrolysis. The equations of the lines as shown in the figures show that the coulombic yield in milligrams per coulomb (slope) is independent of voltage. The coulombic yield Z is about 75 mg/C.

It is interesting to note that in the absence of amine in the emulsion, the same coulombic yield is obtained (75 mg/C). However, the material yield (25 mg) is considerably smaller, indicating greater migration velocity with the emulsion containing amine. The strong interdependence of the two variables is confirmed by the high correlation coefficient ($CC = 0.99$). There was a variable delay period before deposition began, so the plots did not pass through the origin. The exact nature or significance of this delay period is not known. However, it has been reported that it can vary widely with resin type and operating conditions.² When it does occur, it is not due simply to a fault in experimental technique. The view

TABLE IV
 Coulombic Data from Electrodeposition^a

	Deposition time, s				
	15	30	45	60	90
<i>25 V dc</i>					
Yield, g	0.0072	0.0134	0.0179	0.0234	0.0354
Coulombs	0.093	0.175	0.250	0.329	0.460
Approx. solids, %	10.5	9	10	10	8
<i>E</i>	7458	7384	6895	6852	7433
<i>Z</i>	77.2	76.5	71.4	70.9	76.9
<i>50 V dc</i>					
Yield, g	0.0153	0.0283	0.0375	0.0482	0.0765
Coulombs	0.195	0.373	0.504	0.639	1.00
Approx. solids, %	13	12	14	14	13
<i>E</i>	7570	7343	7182	7275	7333
<i>Z</i>	78.3	76	74.3	75.3	75.9
<i>75 V dc</i>					
Yield, g	0.0224	0.0422	0.0569	0.0704	0.1067
Coulombs	0.293	0.562	0.777	0.926	1.39
Approx. solids, %	15	14	15	16	14
<i>E</i>	7393	7248	7062	7336	7423
<i>Z</i>	76.6	75	73.1	75.9	76.9
<i>100 V dc</i>					
Yield, g	0.0293	0.0536	0.0748	0.0900	0.1458
Coulombs	0.407	0.747	1.04	1.19	1.95
Approx. solids, %	16.5	15.5	17	18	13
<i>E</i>	6934	6919	6946	7310	7217
<i>Z</i>	71.8	71.6	71.9	75.7	74.7

^a Average of two determinations.

is taken that during the delay period, resin is arriving at the anode but is not yet depositing on it.

Pierce and Kovac³ have shown that deposition in aqueous systems does not occur simultaneously with the application of voltage, but that a finite time is

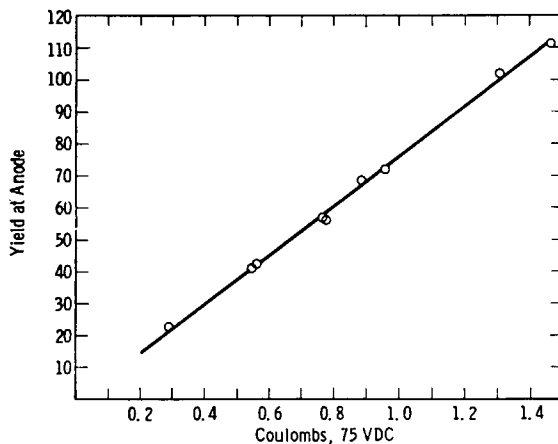


Fig. 8. Effect of coulombs on yield of polyamic acid deposited at anode (75 V dc): $y = 76.7x - 0.90$; corr. coeff. = 0.998.

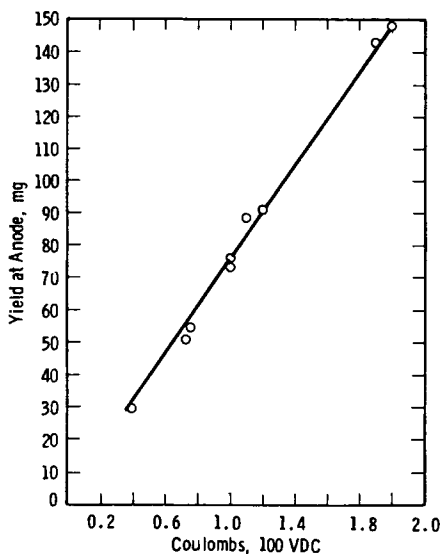


Fig. 9. Effect of coulombs on yield of polyamic acid deposited at anode (100 V dc): $y = 75.8x - 2.25$; corr. coeff. $cc = 0.998$.

required to establish a boundary layer around the electrode before deposition begins. Whether this is due to a finite time being required to establish a boundary layer near the vicinity of the electrode or to a slow onset of electro-osmosis relative to electrophoresis has yet to be resolved. We suspect that it is due to the formation of a boundary layer composed of the proper balance of solvent and nonsolvent, since we have found that the yield of deposit increases substantially as more nonsolvent is added to the emulsion.¹

Although under given conditions the amount of material deposited is directly related to the number of coulombs passed, variation primarily in current density and also in factors affecting the rate of diffusion of the ionic atmosphere around the anode will influence the actual process efficiency. In Figure 10 is plotted

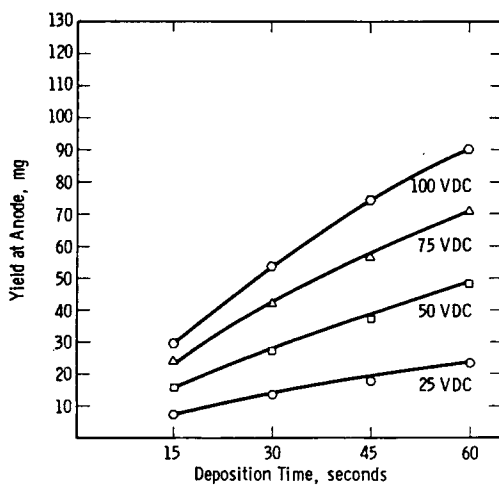


Fig. 10. Yield of polyamic acid deposited at anode vs. time at four voltages.

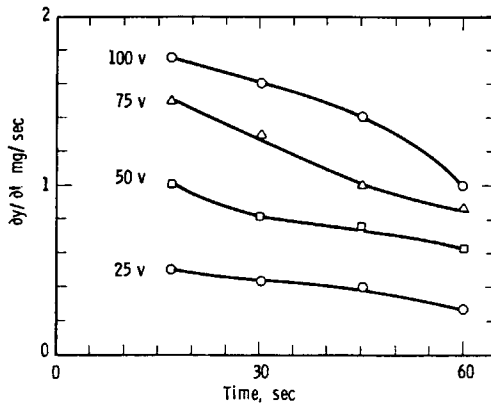


Fig. 11. Rate of change of film growth with deposition time.

yield deposited vs. time at constant voltage. There is a nonlinear relationship that becomes more pronounced at higher voltages. This is not unexpected since the deposited coating acts as a partial insulator as it coats the electrode. As the thickness of the deposit increases, the resistance to current flow increases, reducing the rate of deposition at a given voltage (Fig. 11 and Table V). Of course, the rate of deposition increases with increasing voltage. This rate should increase in a linear fashion, and it does (Fig. 12). Deviations from linearity begin to occur at higher voltages (100 V dc) where dy/dt is 1.75 instead of 2.0 (extend straight-line portion at 17 s) and at longer times >45 s (Fig. 12). During the deposition process, the current decays to a limiting value depending on the applied voltage. This is also a consequence of the insulating character of the deposited film. The above deviations from linearity with increasing voltage are probably due to the increased resistance of the film, not necessarily because of increased thickness of the deposit, but because at higher voltages the electro-

TABLE V
Effect of Voltage and Time on Rate of Film Growth

Voltage, V dc	Time, s	dy/dt , mg/s
25	17	0.500
	30	0.433
	45	0.400
	60	0.266
50	17	1.00
	30	0.813
	45	0.753
	60	0.633
75	17	1.50
	30	1.30
	45	1.03
	60	0.866
100	17	1.75
	30	1.60
	45	1.40
	60	1.06

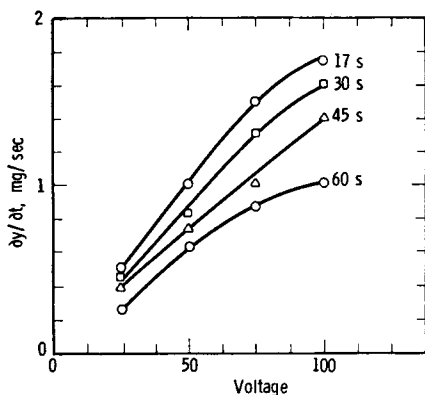


Fig. 12. Rate of film growth with voltage at constant time.

osmotic effect gives rise to a more densely packed deposit. This was shown to be the case by the increase in solids content of the deposited film with increasing voltage (see Table I).

Effect of Voltage

Yield of polymer deposited on the anode is plotted as a function of voltage in Figure 13 for various times. Mass deposited increases linearly with voltage over the time period studied. The higher the voltage, the faster is the rate of deposition. If one compares the slopes of the yield-voltage curves (Fig. 13) with the calculated values, a substantial deviation is observed. For example, using the slope of the line obtained at 15 s as a starting point, we can calculate what the slope should be after each deposition time. These data are shown in Table VI.

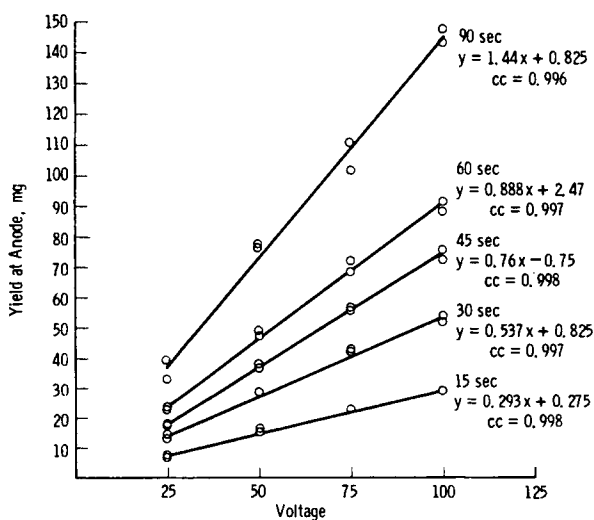


Fig. 13. Effect of voltage on yield of polyamic acid deposited at anode for various times.

TABLE VI
Rate of Film Growth as a Function of Voltage

	Deposition time, s				
	15	30	45	60	90
$(dy/dv)_{\text{observed}}$	0.293	0.537	0.76	0.888	1.44
$(dy/dv)_{\text{calculated}}$	—	0.586	0.879	1.172	1.70

At times greater than 30 s, the rate of deposition deviates from the expected values. This fact is confirmed by the yield-time data of Figure 10. As the film builds up on the anode, it acts as an insulator and a high resistance path forms which slows the rate of deposition. It was observed that the current decays very rapidly after a high initial value, and the rate of decay was faster with increasing voltage.

Nature of the Deposited Species

It is generally accepted that deposition from aqueous media is due to charge neutralization of the functional group migrating to the electrode (e.g., protonation of the COO^- anion by H^+ due to electrolysis of water). Coupled with this is the change in the environment in the vicinity of the electrode. We do not feel that the above explanation can account for deposition in nonaqueous media. In nonaqueous emulsions, we have particles or droplets composed of polymer molecules, solvent, and nonsolvent. These droplets carry a charge which is made up from individual polymer molecules through dissociation of surface groups, emulsifying agents, and miscellaneous ions in the emulsion. It is this charge that is responsible for emulsion stability. The stability is affected by electrostatic repulsion and van der Waals attraction forces. The charges on the particles must be compensated by an equal or opposite countercharge so that together they form an electrical double layer. The distribution of this countercharge is crucial to the stability of the emulsion. If it is diffuse, close contact of the particles cannot occur and stability is preserved. If not diffuse, then the particles can approach each other more closely and van der Waals attraction becomes strong, resulting in particle aggregation and destruction of stability. It is this kind of charge destabilization that we feel is responsible for the coagulation of the particles migrating to the electrode surface. In addition, the change in the environmental conditions in the vicinity of the anode (i.e., balance between nonsolvent and solvent) also promotes coagulation of the emulsion droplets. What causes this destabilization in nonaqueous systems is unknown, but we feel certain it is not due to protonation of carboxyl groups because polymers without these groups can be electrophoretically deposited.¹ What do these charged particles look like? Figure 14 is a schematic representation of the emulsion particle and the deposition process.

In the emulsion, we can have particles with few or many charges. The charge is affected by the properties of the emulsion medium, the polymer, and the emulsifying agent. If the particle has many charges, the equivalent weight will be low, and vice versa (assuming mass of particle is constant). In other words, if the mass-to-charge ratio is high, more polymer should be deposited per unit of charge.

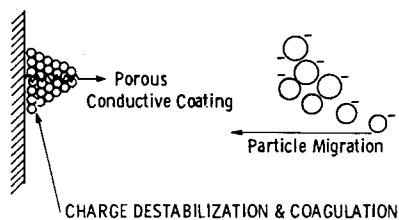
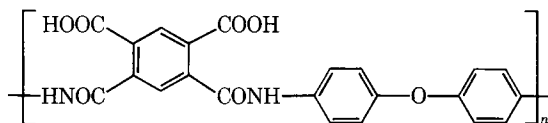


Fig. 14. Schematic of charged emulsion droplets.

Since the deposition process obeys Faraday's laws, we can calculate the effective equivalent weight (E) of the polymeric species being deposited. The values calculated for the polyimide polymer are between 6800 and 7500 (see Table IV). This is the amount of material deposited per faraday (96,500 coulombs). The molecular weight per polymer unit for the polyamic acid is 418 for $n = 1$, as shown below,



so that for the above E values, n would be between 16 and 18. This suggests that the emulsion particle contains many polymer molecules, but only one charge transfer per 16 to 18 repeat units is utilized in the deposition process. In an earlier study,¹ the value of n was found to be about 12. The difference could be due to synthesis conditions which would affect the size of the polymer molecules, or it may be that each batch of polymer has its own optimum emulsion parameters. More work needs to be done in this area. These E values do not change appreciably over the voltage range studied; this confirms the dependence of the process on Faraday's laws.

CONCLUSIONS

The electrophoretic deposition at constant voltage of a polyimide polymer has been found to obey Faraday's laws of electrolysis. Deposition yield is a linear function of coulombs and voltage. Yield as a function of time at constant voltage is not linear above 30 s, and this departure from linearity is due to the high resistance of the coating being deposited on the electrode.

The stability and nature of the emulsion is affected by the method of preparation. Increased stability and slightly better yields are obtained if the emulsion is prepared by adding the polymer solution to the nonsolvent containing an emulsifier, generally an amine.

The composition of the deposited coating is richer in resin than was the starting electrophoretic emulsion. The solids content of the deposited coating increases with increasing voltage and time and ranges from 9% to 25 V dc to about 18% at 100 V dc. The increase in solids content is attributed to an increase in electro-osmosis effects on the solvent and nonsolvent at higher voltages and longer deposition times.

Successive depositions from the same emulsion give rise to a linear decrease in deposition yield as polymer concentration decreases, in coulombic yield, and in effective equivalent weight. These observations suggest that additional electrolytic reactions were possibly occurring with the solvent and nonsolvent, or that a change in the electroactive species being deposited (mass-to-charge ratio changes) occurred.

Quantitative studies over the voltage range 25–100 V dc indicate that the effective equivalent weight of the polymeric species being deposited is between 6800 and 7500 (i.e., the amount of material deposited per faraday). Coulombic yields are about 75 mg per coulomb, and the electricity requirements are about 13 coulombs per gram of material deposited.

The electroactive species in the emulsion is most probably a droplet containing many polymer molecules, but only a portion of these is utilized in the deposition process. This portion, about 16–18 repeat units, is associated with a unit charge transfer. This particle has a certain mass-to-charge ratio, determined by the polymer solvent, nonsolvent, and amine, which influences the deposition yield.

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