Electrodeposition of Polymers from Nonaqueous Systems. I. Polyimides: Some Deposition Parameters

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Synopsis

The yield and quality of an electrophoretically deposited polyimide are strongly dependent upon a number of parameters that are closely related to the formulation and characteristics of a basic nonaqueous electrophoretic emulsion. Such parameters, which have been optimized for one specific polyimide, are solvent/precipitant ratio, type and concentration of surfactant, emulsion preparation sequence, apparent pH, and solids content.

INTRODUCTION

The electrophoretic deposition of organic polymers from aqueous media onto electrically conductive substrates has been the subject of intensive investigation.[1-3] This deposition process is based on the presence in the polymer of ionizable groups which render it water dispersable and provide the proper electrical charges for molecular or particle transport under the influence of an applied voltage. Polymers can also be electrophoretically deposited from non-aqueous systems,[4,5] but in this case the transport and deposition mechanisms that occur are different from those present in aqueous media. Since nonaqueous electrophoretic deposition of polymers onto metallic substrates offers interesting scientific and applied possibilities, we set out to investigate some of the parameters governing nonaqueous deposition of a number of polymers. The present paper deals with the electrophoretic deposition of a polyimide, and particularly with those parameters that must be controlled to obtain maximum liquid medium stability, polymer yield at the electrode, and quality of the deposited polymeric film. Even though the polyimide chosen had been already investigated,[5] its structural simplicity suggested its use as a model for a detailed parametric study which might lead to the establishment of general nonaqueous deposition on mechanisms.

EXPERIMENTAL

Materials

A commercially available polyimide supplied from E. I. duPont de Nemours Co. as the polyamic-acid precursor dissolved in N-methyl-2-pyrrolidone. This material is designated Pyre ML RC-5057. The solvents, nonsolvents, and amines (all reagent grade) were obtained from Fisher Scientific Co. and used without further purification.

Apparatus

All anodic electrodeposition experiments were carried out at constant applied dc voltages which were preset prior to immersion of the electrodes into the emulsion. The emulsion was contained in an 800-cc pyrex glass beaker. The electrodes were aluminum Q-panels (Mill finish) 6 in. × 1.5 in. × 0.025 in. obtained from the Q-Panel Co., Cleveland, Ohio, and were fastened to a Teflon block with a separation between the electrodes of 1 in. and an immersion depth in the emulsion of 1.5 in.; thus a total area of the immersed electrode surface of 4.5 in.^{2} was obtained. The dc power supply was an HP Model 711A capable of supplying 0–500 V (dc) and 0–100 mA. Current and voltage were measured using a Triplett Multimeter, Model 630NA and a Keithley Electrometer, Model 178. Conductance measurements were made using a General Radio Co. Impedance Bridge Type 1650-A.

Preparation of Electrophoretic Deposition Systems

Electrophoretic deposition of polymers is generally carried out from emulsions, i.e., dispersions of two mutually insoluble liquids. The polymer particles are usually of colloidal size (0.01–1 μ). To prepare this emulsion, the polymer is dissolved in a solvent to form a solution where the averge size of the dissolved species is <0.01 μ. A liquid that may be called a precipitant or nonsolvent is mixed with the polymer solution. This precipitant and the solvent are miscible with each other, but the former does not dissolve the polymer. As the precipitant mixes with the solvent, it also interacts with the polymer, causing the polymer partially to come out of (precipitate) solution. The result is the formation of droplets containing polymer, solvent, and precipitant in various proportions depending on the nature and amounts of the ingredients. These droplets are dispersed in the liquid medium forming an emulsion. The particle size and stability of this emulsion are governed by the properties of the components that make up the system. In addition to the polymer, solvent, and precipitant, a fourth component called a surfactant is added to the mixture to improve the properties of the emulsion. These dispersed droplets carry surface charges due to adsorbed ions and dissociation of surface groups. A schematic representation of the emulsion is shown in Figure 1.

The general preparation of the emulsions involved the dilution of the RC-5057 solution with solvent (NMP) to a solids content of 2.75 wt %. To this solution is added a surfactant (an amine), and the solution is heated for 20 min at 40°C. This solution is then added, via a dropping funnel, to the stirred precipitant; this action results in the formation of a milky colored emulsion. A typical emulsion is prepared as follows:

Emulsions were prepared as described above using 5 g RC-5057, 25 g N-methyl pyrrolidone (NMP), 100 mL acetone, and triethylamine (TEA) in concentrations both above and below the stoichiometric amount needed for complete neutralization of the carboxyl groups present in the polyamic acid. The amount of triethylamine added ranged from 0.25× to 5× the stoichiometric amount.
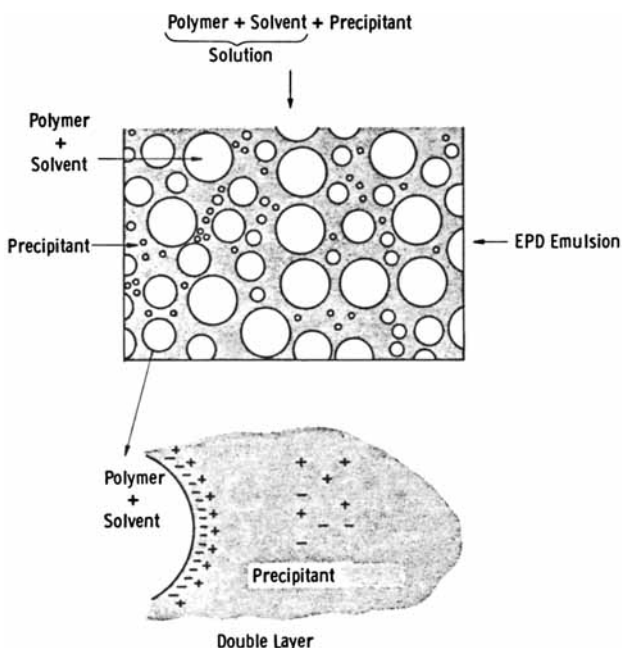
Fig. 1. Schematic of emulsion formation.

RESULTS AND DISCUSSION

Effect of Amine Concentration

Aluminum electrodes were immersed in the emulsions, and electrodeposition was carried out at 100 vdc for 60 s. The electrodes were immediately removed from the emulsion, dried 20 min at 100°C, and weighed. Apparent pH and conductivity measurements of the polymer solutions and corresponding emulsions were also made. These experiments are summarized in Table I. If we plot the yield of deposit at the anode vs. the mole ratio of amine/COOH (Fig. 2), we find that the yield goes through a maximum at a mole ratio of 0.5. It was observed that, as the amine concentration increased, the size of the droplets in the emulsion increased and the settling rate of these droplets also rose. Although the emulsion did not break (separate into two distinct phases), it is clear that the stability of the emulsion decreases with an increase in amine concentration

TABLE I
Effect of Amine Concentration on EP Yield

| Expt no.	pH soln	K solution (mhos × 10⁴)	pH emulsion	K emulsion (mhos × 10⁴)	Amount TEA added	Weight of deposited coating (mg)
1	8.6	1.05	8.1	0.181	stoichiometric	95.7
2	7.1	0.833	6.1	0.166	0.25× stoichiometric	72.3
3	8.0	1.03	7.3	0.175	0.5× stoichiometric	100.9
4	9.0	1.06	8.3	0.166	1.5× stoichiometric	84.1
5	9.2	1.11	8.4	1.66	2× stoichiometric	64.9
6	9.3	1.02	9.0	0.178	3× stoichiometric	24.9
7	9.6	1.0	9.5	0.181	4× stoichiometric	16.5
8	9.6	1.0	9.2	0.172	5× stoichiometric	10.8
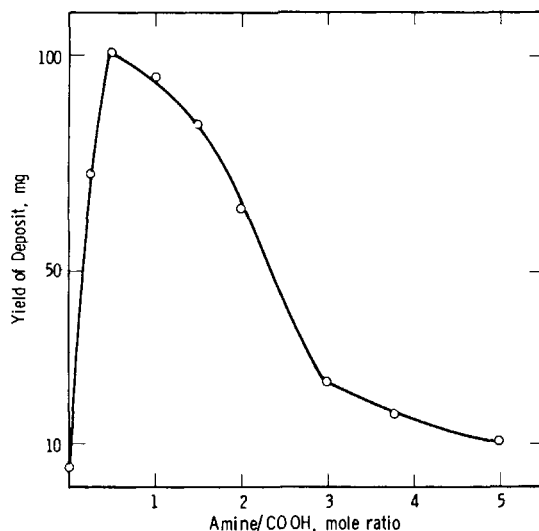
Fig. 2. Effect of amine concentration on deposition yield at anode.

beyond a certain value. Now, since the electric charges on the droplets are neutralized as emulsion stability is reduced, the number of droplets available to migrate to the electrode also diminishes, and thus the yield of deposit is affected.

Effect of Composition

Does one need an emulsion to get deposition? A series of experiments designed to answer this question was run. Various Pyre ML RC-5057 compositions were prepared and electrolyzed at 100 V (dc) for 60 s, using aluminum electrodes. The composition of these solutions and emulsions, and the amount of material deposited on the anode after electrolyzing, are shown in Table II.

Maximum deposition is obtained only when using the proper combination of ingredients, i.e., polymer + solvent + amine + precipitant, which provide a stable emulsion. However, deposition is obtained from other compositions as well, indicating that some migration to the electrode occurs even from solutions. The

TABLE II
Composition Effects on Deposited Yield

Item	Composition	Deposit at anode (mg)
A	polymer + solvent[a]	1.7
B	polymer + solvent + Precipitant[b]	4.2
C	polymer + solvent + amine[c]	10.6
D	polymer + solvent + amine + precipitant	77.9
E	polymer + solvent[d]	3.5
F	polymer + solvent + amine + precipitant[d]	0

[a] N-methylpyrrolidone.
[b] Acetone.
[c] Triethylamine (TEA).
[d] Electrode dip coated, no current passed.

species migrating in the polymer + solvent and/or amine system probably contains the carboxylate ion ($R—COO^-$), whereas the species in the emulsion is probably a charged droplet composed of polymer, solvent, amine, and precipitant. It appears that one of the roles of the precipitant is to counteract the action of the solvent by preventing dissolution of the deposited polymer at the anode and causing it to remain on the electrode. The amine enhances the conductivity of the solution and acts as an emulsifying and charge-giving agent. When the right combination of ingredients is not present, deposition, and dissolution at the electrode occur concomitantly (items A, B, C, E in Table II).

In the case of EP deposition from solutions, a passivating layer of deposited molecular species is formed early enough to prevent further deposition; thus low yields are obtained.

The conductance and apparent pH of the above compositions were also measured, and are shown in Table III. The conductances of items A and B in Table III are about two orders of magnitude lower than those of C and D, which could also account for the low yield of deposit at the anode. The fact that the current decayed indicates that a coating is being formed at the anode from all compositions listed in Table III.

Effect of Manner of Amine Addition

How the amine is incorporated into the deposition system affects the yield of deposit at the anode. Two Pyre ML RC-5057 emulsions were prepared containing exactly the same amount of polymer, solvent, amine (TEA), and precipitant. In one case the amine was heated with the polymer solution for 20 min at 40°C; in the other case the amine was mixed in at room temperature. The emulsions were electrolyzed at 100 V (dc) for 60 s using aluminum electrodes described previously. 80 mg of polymer was deposited on the anode from the emulsion prepared by heating the amine with the polymer solution, whereas 60 mg was obtained from the room temperature amine reaction. The original pH and conductance of both emulsions were the same. The only explanation that seems reasonable to account for this weight difference from the two emulsions is that reaction of the amine with the carboxyl groups of the polymer is more complete at an elevated temperature to form the amine salt of the polyamic acid.

TABLE III
Electrodeposition Parameters

Item	Composition	pH	K (mhos $\times 10^4$)	Current decay (mA)
A	polymer + solvent	7.1	0.033	6 → 5
B	polymer + solvent + precipitant	6.7	0.062	8 → 7
C	polymer + solvent + amine	8.7	1.1	90 → 38
D	polymer + solvent + amine + precipitant	8.9	1.1	18 → 12

Effect of Emulsion Preparation Methods

In another experiment, Pyre ML RC-5057 was mixed with solvent (NMP), and amine (TEA) to form a polymer solution. From the latter, two emulsions were then prepared by adding (1) the polymer solution to the precipitant and (2) the precipitant to the polymer solution. Both emulsions were electrolyzed, as described in the previous section. The amount of polymer deposited on the anode from the emulsion prepared by adding the polymer solution to the precipitant was significantly greater than from the emulsion made by adding precipitant to polymer solution (144 mg vs. 90 mg). It was observed that a greater amount of precipitate was formed on addition of precipitant to the polymer solution. The better dispersion of polymer particles, obtained when polymer solution is added to precipitant, leads to a more stable emulsion, and is probably due to concentration effects.

Effect of Type of Precipitant on Emulsion Properties

Pyre ML RC-5057 polymer solutions containing TEA were added to equal volumes of three different precipitants (acetone, methyl ethyl ketone, and cyclohexanone). A milky emulsion with a faint blue color was obtained in acetone, containing very fine particles in suspension with only a small amount of precipitate settling out of the emulsion (about 5% based on weight of polymer). In MEK an emulsion containing large particles in suspension and a large amount of precipitate was obtained (about 40% based on weight of the polymer). In cyclohexanone no emulsion was obtained, but copious amounts of a fibrous precipitate were obtained (about 70% based on the weight of the polymer). These experiments show that, under the above conditions, acetone is the best precipitant to obtain a good emulsion.

Effect of Precipitant/Solvent (P/S) Ratio

A series of experiments was made to determine how the quantity of precipitant affected the yield of deposit at the anode. Polymer solutions in NMP containing one-half the stoichiometric amount of TEA were prepared and added to various volumes of acetone (precipitant). These emulsions were then electrolyzed at 100 V (dc) for 60 s. The results of these experiments are shown in Table IV. There is a critical precipitant/solvent ratio at which maximum deposition occurs (see Fig. 3). The amount of material deposited on the anode is small below the cloud point of the polymer solution. This is probably due to the fact that there is not enough precipitant in the vicinity of the anode to prevent coagulation and that an equilibrium between deposition and dissolution of the deposited coating is maintained below the cloud point. Above the cloud point there is an abrupt increase in the amount of material deposited which subsequently goes through a maximum at a precipitant/solvent ratio of 2.6. It is not clear at this time why the deposition process follows this path.

The current decay curves for some of the emulsion compositions at various P/S ratios are shown in Figure 4. The initial current is controlled by the bath (emulsion) resistance. During deposition, and as a coherent layer of material is formed on the electrode, the film resistance leads to a decrease in current. It is readily apparent from Table IV and Figure 4 that an increase in precipitant

TABLE IV
Effect of Precipitant/Solvent Ratio on Deposition Yield

Expt no.	Precipitant/ solvent ratio[a]	Precipitant amount times the cloud point amount	pH emulsion	K emulsion (mhos $\times 10^4$)	Current decay (mA)	Yield at anode (mg)
1	0.09	0.20	7.8	1.25	110 → 34	14
2	0.43	cloud point	7.8	1.04	64 → 28	14
3	0.55	1.29	7.8	0.701	48 → 26	31
4	0.89	2.09	7.1	0.450	44 → 28	73
5	1.29	3.0	6.9	0.220	22 → 17	104
6	2.15	5.0	7.4	0.25	26 → 19	122
7	2.46	5.7	7.5	0.16	26 → 19	127
8	3.01	7.0	7.3	0.250	24 → 18	123
9	4.30	10.0	7.5	0.160	20 → 16	105
10	5.16	12.0	7.6	0.160	19 → 16	94
11	6.16	14.3	7.1	0.160	16 → 13	87

[a] By volume.

leads to a decrease in the initial current as well as to a lowered rate of current decay, due to the fact that the precipitant is relatively nonconductive.

Effect of Solids Content

In order to further characterize the polyimide system, emulsions of Pyre ML RC-5057 having different solids content were prepared. These emulsions had a P/S ratio of 2.6 and were neutralized with one-half of the stoichiometric amount of amine (TEA). These emulsions were electrolyzed at 100 V (dc) for 60 s. The
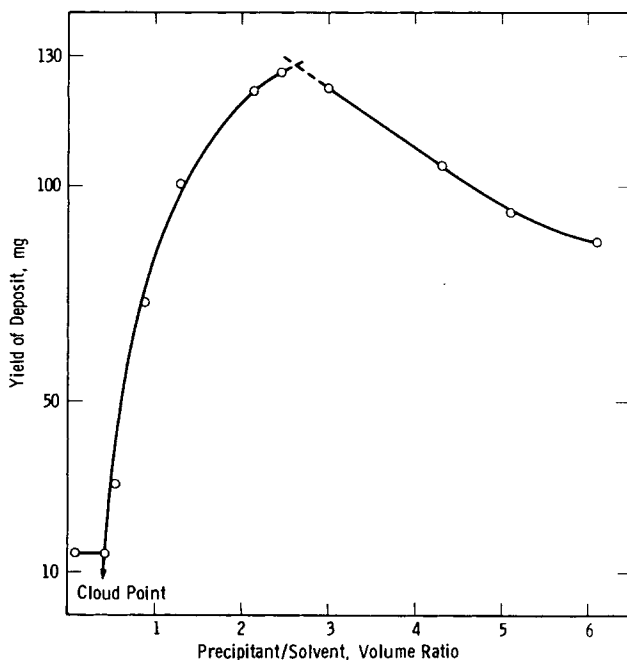

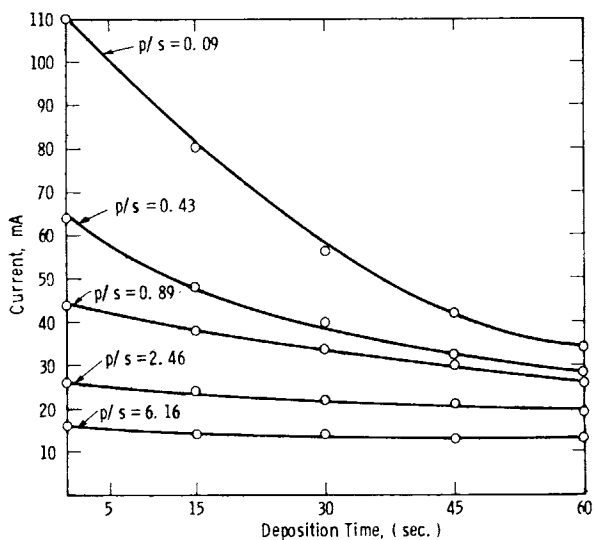Fig. 3. Effect of precipitant/solvent ratio on deposition yield at anode.

Fig. 4. Current decay for various precipitant/solvent ratios.

TABLE V
Effect of Solids Concentration on Deposition Yield

Expt no.	Total solids (%)	Yield at anode (mg)	Emulsion appearance
1	0.16	31	clear, transparent
2	0.36	60	hazy, transparent
3	0.50	98	cloudy, transparent
4	0.64	121	cloudy, transparent
5	0.77	131	cloudy, opaque
6	0.93	128	opaque, milky
7	1.05	122	opaque, milky
8	1.16	38	opaque, milky
9	2.15	0	polymer precipitated

results of these experiments are shown in Table V. As the solids content increases, the stability of the emulsion decreases and, at about 2% solids, no emulsion is formed and the polymer just precipitates during addition of the polymer solution to the precipitant. As with amine content and P/S ratio, the yield of deposit at the anode as a function of solids content also goes through a maximum. Maximum deposition at the anode occurs when the solids content of the emulsion is 0.77% (Fig. 5). We believe that this dependence on solids is related to emulsion stability. The higher the solids, the less stable the emulsion becomes, and hence the fewer number of charged droplets available for migration.

Germant[6] suggested that the mobility of electrically charged particles in an electric field is inversely proportional to the concentration, which would lead to a decrease in film thickness with an increase in solids concentration.
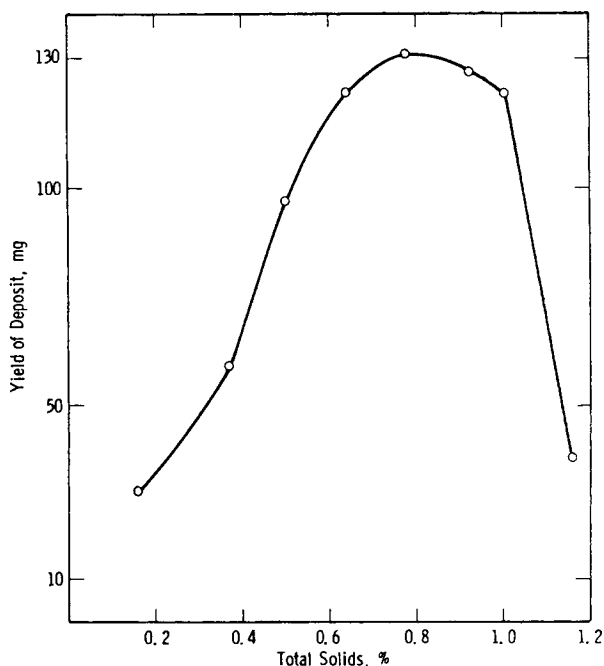
Fig. 5. Effect of solids content on deposition yield at anode.

Deposition from Aqueous Solution

A Pyre ML RC-5057 emulsion was prepared by adding the polymer solution to water which was substituted for acetone as the precipitant. The emulsion was tan colored and contained large particles suspended in the medium. Settling of these particles was rapid, a sign of an unstable emulsion. This emulsion had a pH of 5 and a conductivity of 2.63×10^{-4} mhos. Electrolysis was carried out at 25 V (dc) for 60 s using aluminum electrodes described previously. The initial current was 100 mA which decayed to 38 mA after 60 s. Considerable gassing at the electrodes was observed, and a poor, discontinuous coating was obtained on the anode (yield = 16 mg).

Effect of Amine Type

Using the conditions established for optimum deposition with triethylamine, i.e., 0.5× stoichiometric amount of amine and a P/S ratio of 2.6, two other amine types were examined, 1-methylimidazole (1-MI) and urea. Emulsions of Pyre ML RC-5057 prepared using these amines were electrolyzed at 100 V (dc) for

TABLE VI
Comparison of Effects of Amine Types on EP Yield[a]

Amine[b]	Yield at anode (mg)	Comments
TEA	80	blue-white emulsion
1-MI	25	blue-white emulsion
Urea	0	clear amber solution, no turbidity

[a] P/S = 2.6.
[b] Amine concentration = 0.5× stoichiometric amount.

30 s.   The quantity of material deposited at the anode differed considerably from that obtained from the TEA system (see Table VI).   Further studies with 1-MI and urea revealed that optimum deposition of material at the anode could be obtained at different amine concentrations and P/S ratios compared to those used with TEA (see Tables VII and VIII).

When using urea, no deposition at the anode occurred at a P/S ratio of 2.6.   In fact, the emulsion that initially formed reverted back to a clear solution as the P/S approached 2.6.   In order to get deposition, a P/S of 4.6 had to be used.   Even at this ratio, yields were poor and emulsion stability low.   Separation of the emulsion phases occurred in several hours.   Better yields were obtained with the 1-MI system, but they still fell short compared to the TEA system.   Table IX compares the optimum yield obtained from the three amine systems.   Conductance values for all three systems are considerably different from each other. For TEA and 1-MI we have 1.88×10^{-5} mhos, and for urea we have 6.66×10^{-6} mhos.   The apparent pH of the emulsions is also different.   At optimum conditions for deposition, the pH values are 7.8, 6.7, and 4.6, respectively, for TEA, 1-MI, and urea systems.   These values reflect the basicity of the three amines, the base strength increasing from urea to 1-MI to TEA.   The basic dissociation constants are 1.5×10^{-14}, 3.9×10^{-8}, and 5.6×10^{-4}, respectively.   These values

TABLE VII
Effect of Amine Concentration (1-MI) on Yield of Deposit[a]

Amine concentration	Yield at anode (mg)
Stoichiometric	42
0.25×	30
0.5×	25
1.5×	52
2×	57
3×	62
4×	59

[a] P/S = 2.6.

TABLE VIII
Effect of Amine Concentration (Urea) on Yield of Deposit[a]

Amine concentration	Yield at anode (mg)
Stoichiometric	20
0.25×	15
0.50×	11
1.5×	25
2.0×	18

[a] P/S = 4.6.

TABLE IX
Effect of Amine Type on Optimum Yield

Amine type	Concentration	Yield of deposit (mg)
TEA	0.5× stoichiometric	80
1-MI	3× stoichiometric	62
Urea	1.5× stoichiometric	25

could account for the observed differences in yields obtained for the three amines, for they would certainly influence salt formation with the carboxyl groups. On plotting the yield data in Table IX vs. K_b, an exponential relationship would be obtained, indicating the dramatic influence of the base strength of the amine on yield in the polyimide system.

CONCLUSIONS

The electrophoretic deposition of polymers has been found to be strongly dependent on a number of parameters that are critical to emulsion stability, deposition yield, and quality of deposit. These are: emulsion composition, precipitant/solvent ratio, emulsifier type and concentration, solids content, and how the emulsion is prepared. We have optimized these parameters for the deposition of polyamic acid, and found the following:

1. Precipitant/solvent ratio is critical and controls the amount of material deposited at electrode. It also varies with each polymer system.

2. The amine type and concentration also affect the quantity of material deposited at electrode and the stability of the emulsion.

3. Deposition occurs whether electrolyzing from a solution or an emulsion of the polymer. The latter offers maximum deposition.

4. A greater amount of deposition is obtained when the polymer solution is added to the precipitant rather than vice versa in preparing the emulsion for electrolysis.

5. Solids content is critical in obtaining maximum deposition.

6. To get maximum deposition at the electrode from a polyimide emulsion prepared using triethylamine, the following ratios are required: amine/COOH = 0.5, total solids of emulsion = 0.77%, precipitant/solvent = 2.6.

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