A Semi-Empirical Model For Dip Coating: Thickness and Thickness Uniformity Control

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Abstract

Dip coating is the preferred method for manufacturing photoconductor drums. For high quality color applications, thickness and thickness profile uniformity control is essential. We have developed a semi-empirical model capable of predicting these two quantities at various coating conditions. We have found that the coating withdrawal speed, the viscosity of the coating fluid, its surface tension, and the boiling point (vapor pressure) of the coating solvent are sufficient parameters to characterize the coating space for a given formulation/coating machine system. The model was developed using the theory derived by P. Groenveld in "Thickness Distribution in Dip-Coating."[1]

Introduction

A very critical issue in dip coating is the control of both thickness and thickness profile uniformity. In "Thickness Distribution in Dip-Coating"[1], P. Groenveld derived a theory for the varying thickness of a film on a vertical, flat plate being withdrawn from a bath of paint. He argued that part of the dipped plate, was covered by a constant-thickness paint film. An uneven, parabolic thickness distribution covering the whole plate was obtained when the plate was allowed to drain after removal. Eventually, if no solidification takes place, the entire film will be uneven. In most situations however, the paint film solidifies during withdrawal, for example, through evaporation. In that case, a distribution is obtained depending on the rate of solidification.

The equation describing the Groenveld model is very complicated. This report describes a semi-empirical model developed based on Groenveld theory. The model predicts coating conditions for achieving flat thickness distribution, as well as conditions to control the length of the uneven portion of the coating.

Results and Discussion

Experimental Design

An analysis of Groenveld model suggests that the important parameters controlling the dip coating process are: solution viscosity, withdrawal speed, surface tension, and evaporation rate of the coating solvent. Three of these parameters can be reduced to the dimensionless capillary number:

$$Ca = (m*v)/S \quad (1)$$

where v is the withdrawal velocity in cm/sec., m the dynamic viscosity of the coating solution in poise, and S the surface tension of the solution in dyne/cm.

We designed an experiment around three parameters. Evaporation rate was varied, using toluene, tetrahydrofuran (THF), and dichloromethane (DCM). We modulated viscosity by adjusting percent solid. We used two different surfactants to modify surface tension (Table 1).

The capillary number was calculated using equation 1, and the conditions of Table 2 were realized, and the drums coated.

The thickness of the even part, T_{even} of each drum was measured and the data statistically analyzed using a linear regression model. We found that T_{even} of the drum was a function of the following parameters:

$$T_{even}(cm) = f(m*v);\ m\ (poise);\ v\ (cm/sec) \quad (2)$$

$$\mathbf{T_{even}} = 0.001169 + 0.001423_{*}(\mathbf{m_{*}v}) \quad (3)$$

(Statistics: F value = 847; R square = 0.98; T value for intercept = 20.2; T value for ***m*********v*** *= 40.9)*

The length of the uneven portion of the drum, L_{uneven} was measured for each drum. L_{uneven} was found a function of the following parameters:

$$L_{uneven} = f(v*bp, Ca*bp);\ bp = °C;\ v = cm/sec;$$
$$Ca = dimensionless \quad (5)$$

$$L_{uneven}(cm) = -2.0293 + 0.1262*(v*bp) + 0.7988*(Ca*bp) \quad (6)$$

*(Statistics: F value =693; R square = 0.980; T value for intercept = -6.84; T value for v*bp = 17.66; T value for Ca*bp = 7.71)*

When we set L_{uneven} to zero

$$A + B*(bp*v) = C*(bp*Ca) = 0 \quad (7)$$

$$bp*(B*v + C*Ca) = -A \quad (8)$$

$$bp*(B*v + C*m*v/S) = -A \quad (9)$$

$$v*bp*(B + C*m/S) = -A \quad (10)$$

$$v_{even} = -A/(bp*(B + C*m/s)) \quad (11)$$

From equation 11 it can be seen that for a solution of a certain surface tension S, and a given solution viscosity m, there is a unique coating speed v for the thickest coating possible with uniform profile.

More generally, there exists a unique coating speed for a given thickness profile (defined uneven length) at any given solution viscosity and surface tension. It is given by:

$$v = (L_{uneven}-A)/(bp*(B + C*m/S)) \quad (12)$$

Once the unique coating speed is calculated from equation 12, the coating speed and viscosity values can be plugged back into the thickness equation to calculate the thickness of the even portion of the drum.

The results are presented on Table 3 for a Toluene-DC-510 solvent system, Table 4 for a THF-DC-510 solvent system; Table 5, a DCM-DC-510 solvent system, where L_{uneven} = 0, i.e. 100% profile uniformity. Table 6 and Table 7 show the results for a THF-DC510 and DCM-DC510 systems respectively, for a condition where L_{uneven} = 0 .05, i.e. 95% profile uniformity.

These calculated profiles were confirmed successfully with experiments.

Conclusion

We have successfully developed and confirmed a semi-empirical model that only takes into account coating viscosity, surface tension, evaporation rate of the coating fluid, and the coating withdrawal speed. It is important to keep in mind two key assumptions of the model:

1. A portion of coated film is completely dried before the full withdrawal of the substrate from the coating solution.
2. The dew point in the coating environment is controlled to match the heat capacity of the coated substrate, while noting the evaporation rate of the coating solution.

In general a high evaporating coating solution is preferred to maximize the thickness of a coated layer with uniform profile.

Table 1. Solvent-Surfactant Coating Solution Systems

Solvent System	Solvent	Solvent bp (ºC)	Surfactant	Surface Tension (Dynes/cm^2)
1	Toluene	109	DC-510	26.8
2	Tetrahydrofuran (THF)	66	DC-510	26.1
3	Tetrahydrofuran (THF)	66	FC-431	22.8

Table 2. Experimental Coating Conditions: viscosity m, withdrawal speed v, capillary number Ca

η, m (Cps)	Coating Speed (Cm/sec)	Capillary Number Ca				
		Solvent Toluene-DC510	Solvent THF-DC510	Solvent THF-FC431	Solvent THF No surfactant	Solvent DCM-DC510
600	0.09	0.0201	0.0207	0.0237	0.0203	0.0208
600	0.18	0.0403	0.0414	0.0474	0.0406	0.0415
600	0.26	0.0582	0.0598	0.0684	0.0586	0.0600
600	0.79	0.1769	0.1816	0.2079	0.1782	0.1823
400	0.13	0.0194	0.0199	0.0228	0.0195	0.0200
400	0.26	0.0388	0.0398	0.0456	0.0391	0.0400
400	0.39	0.0582	0.0598	0.0684	0.0586	0.0600
400	0.52	0.0776	0.0797	0.0912	0.0782	0.0800
300	0.18	0.0201	0.0207	0.0237	0.0203	0.0208
300	0.35	0.0392	0.0402	0.0461	0.0395	0.0404
300	0.52	0.0582	0.0598	0.0684	0.0586	0.0600
300	0.69	0.0772	0.0793	0.0908	0.0778	0.0796
150	0.35	0.0196	0.0201	0.0230	0.0197	0.0202
150	0.69	0.0386	0.0397	0.0454	0.0389	0.0398
150	1.03	0.0576	0.0592	0.0678	0.0581	0.0594
150	1.38	0.0772	0.0793	0.0908	0.0778	0.0796
300	0.18	0.0201	0.0207	0.0237	0.0203	0.0208

Table 3. v_{even} coating speed and L_{even} (100%) calculation for charge transport layer using toluene-DC-510 Solvent System

Viscosity **m**	Coating Speed **v (even)**	Maximum Uniform Layer Thickness
(Cps)	(Cm/sec)	(μm)
100	0.196	14.5
200	0.163	16.3
300	0.14	17.7
400	0.123	18.7
500	0.109	19.5
600	0.098	20.1
700	0.09	20.6
800	0.082	21
900	0.076	21.4
1000	0.07	21.7

Table 4. v_{even} coating speed and L_{even} (95%) calculation for charge transport layer using tetrahydrofuran-DC-510 Solvent System

Viscosity **m**	Coating Speed **v (even)**	Maximum Uniform Layer Thickness
(Cps)	(Cm/sec)	(μm)
100	0.118	13.4
200	0.099	14.5
300	0.087	15.3
400	0.074	15.9
500	0.066	16.4
600	0.06	16.8
700	0.054	17.1
800	0.05	17.4
900	0.046	17.6
1000	0.043	17.8

Table 5. v_{even} coating speed and L_{even} (100%) calculation for charge transport layer using dichloromethane-DC-510 Solvent System

Viscosity **m**	Coating Speed **v (even)**	Maximum Uniform Layer Thickness
(Cps)	(Cm/sec)	(μm)
100	0.369	16.9
200	0.308	20.5
300	0.265	23
400	0.232	24.9
500	0.206	26.4
600	0.186	27.5
700	0.169	28.5
800	0.155	29.3
900	0.143	30
1000	0.133	30.6

Table 6. v_{even} coating speed and L_{even} (95%) calculation for charge transport layer using tetrahydrofuran-DC-510 solvent system

Viscosity **m**	Coating Speed	Layer Thickness
(Cps)	(Cm/sec)	(μm)
100	0.384	17.1
200	0.32	20.8
300	0.275	23.4
400	0.241	25.4
500	0.214	26.9
600	0.193	28.2
700	0.176	29.2
800	0.161	30
900	0.149	30.7
1000	0.138	31.4

Table 7. v_{even} coating speed and L_{even} (95%) calculation for charge transport layer dicholoromethane-DC-510 Solvent System

Viscosity **m**	Coating Speed	Layer Thickness
(Cps)	(Cm/sec)	(μm)
100	0.723	22
200	0.604	28.9
300	0.519	33.8
400	0.454	37.6
500	0.404	40.5
600	0.364	42.8
700	0.331	44.7
800	0.304	46.3
900	0.281	47.6

Reference

1. P. Groenveld, "Thickness Distribution in Dip-Coating," *J. Paint Technology*, Vol. 43, No. 561, October 1971.

Author Biography

Michel (Mike) Frantz Molaire is currently a senior associate chemist at Nexpress Solutions Inc., a Kodak Company. He received his B.S. in chemistry, M.S. in chemical engineering, and MBA from the University of Rochester. His research experience includes polymer synthesis, photo-polymerization, organic monomeric glasses, optical recording materials, photo-electrophotographic masters, organic photoconductor formulation, infrared sensitive pigments, and dip coating technology. Mr. Molaire is the recipient of 38 US patents, more than 70 foreign patents, and author of several scientific publications. In 1984, he received the Eastman Kodak Research Laboratories C.E.K. Mees Award for excellence in scientific research and reporting. In 1994, he was inducted into the Eastman Kodak Distinguished Inventor's Gallery (Inventor Hall of Fame) for reaching the milestone of 20 or more patents. He is a member of the American Chemical Society and the Image Science & Technology Society. He is presently program vice president for the Rochester, NY IS&T local chapter council.