

Modeling Constant Voltage Electrophoretic Deposition from a Stirred Suspension

Mercedes González-Cuenca, P. Maarten Biesheuvel, and Henk Verweij

Laboratory for Inorganic Materials Science, Dept. of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

In electrophoretic deposition, a voltage difference is applied across a suspension, and a layer ("cast" or coating) is formed on one of the electrodes. Based on first principles, cast growth is described in this work for a well-stirred suspension, a constant voltage difference across the deposition cell, and a nonionic solution. The influence of cast formation on cast growth is implemented, which is a refinement of the model described in 1999 by Biesheuvel and Verweij. Simulation results are compared with experimental data. From the derivation it follows that a smooth cast layer is formed when the particle permittivity is lower than that of the liquid. Catastrophic cast growth occurs when the particle permittivity is higher than that of the liquid.

Introduction

In electrophoretic deposition (EPD) a layer of particles is formed on a conducting substrate under the action of an electric field. EPD has the advantages of a high homogeneity of the final cast, short deposition times, and low surface roughness (Biesheuvel and Verweij, 1999).

EPD is used industrially to apply ceramic, glass, or polymer materials as a coating or paint on a substrate of arbitrary shape. Especially important is the application of ceramic layers as paint on metal components in the automotive industry (Holland and Berger, 1993). EPD is used as well to dehydrate suspensions and emulsions (Heavens, 1990), and to remove colloidal contaminants from aqueous suspensions (such as removal of coal or clay in water clarification; Johnson and Davis, 1999).

Despite its importance, not many articles can be found in the open literature that consider the processing aspects of EPD. Therefore, many aspects of the process are still to be investigated. The aim of this work is to describe the growth velocity of the particle layer ("cast") based on the theory of an earlier article (Biesheuvel and Verweij, 1999), in which a model for EPD was developed for an unstirred suspension while neglecting the influence of the growing cast on the formation rate. An expression for the cast formation rate was obtained that describes the more-than-linear cast growth with

increasing suspension concentration, but that does not describe the change of cast growth with time.

In the present article, one-dimensional cast growth at constant voltage EPD from a stirred suspension is considered, including the influence of the growing cast. Both cast and suspension are regarded as dielectric media, which is a reasonable assumption for a suspension with a low enough concentration of ions (such as organic solvent). On the one hand, the potential drop over the electrostatic double layers that form at the electrodes decreases with decreasing ion concentration (being zero for a dielectricum), while, on the other hand, the formation time of these double layers will increase when the ion concentration in the suspension decreases, because the ionic flux toward the double layers decreases. When the formation time of the double layers becomes much longer than the time required for cast formation, particle deposition can be considered to take place in a dielectricum. Furthermore, when the ion concentration is decreased, stirring of the suspension will increasingly inhibit net ionic movement to the electrodes, and therefore double layer formation, by the same mechanism as just discussed. These phenomena can be quantified more thoroughly by solving the Nernst-Planck equations together with the Poisson equation and continuity equations for each ion species (Murphy et al., 1992) while considering macroscale mixing due to stirring using empirical expressions (such as Kaminoyama et al., 1994; Zlokarnik and Judat, 1988). However, this endeavor is not part of the present work.

Correspondence concerning this article should be addressed to H. Verweij.

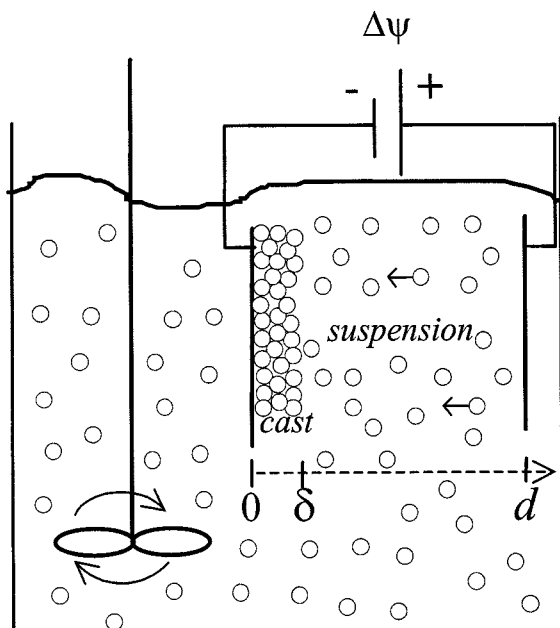


Figure 1. EPD from a stirred suspension.

Reactions at the electrodes (electrolysis) are not considered either, which is reasonable for a sufficiently low voltage difference; at higher voltage differences, electrode reactions can be implemented using the Butler-Volmer equation (Murphy et al., 1992).

Results are presented for a planar and cylindrical geometry of the deposition cell. From the integrated equation for the field strength, a new criterion arises that predicts under which conditions a smooth layer is formed or when catastrophic cast growth occurs.

Theoretical Background

Introduction

In the present article, EPD from a well-stirred suspension consisting of one particle type is described in a two-phase system with a planar geometry (see Figure 1). The two phases that are present in the deposition cell are cast and suspension. The field between the two electrodes is considered unidirectional (straight field lines, perpendicular to the electrode surfaces); curved flow lines at the edges of the electrodes are not considered. Although a well-stirred suspension is considered, resuspension of particles that have moved into the cast is neglected.

Cast-suspension boundary

The cast growth rate u_c is given by a mass balance over the moving cast (such as Biesheuvel and Verweij, 1999):

$$u_c = \frac{d\delta}{dt} = -v_s \frac{\phi_s}{\phi_c - \phi_s}, \quad (1)$$

with δ the cast thickness; t time; v_s the velocity of particles in the suspension at the suspension-cast boundary; ϕ_s the

volumetric particle concentration in the suspension; and ϕ_c the cast packing factor (unity minus porosity). Here, it is assumed that the cast does not grow denser over time, which is a reasonable assumption if a dispersed suspension is used (Bergström et al., 1992).

Particle mass balance

For a stirred suspension, concentration gradients $\nabla\phi_s$ will not form and ϕ_s is given by an overall mass balance for the particles in the suspension:

$$\frac{d(\phi_s V)}{dt} = \phi_s \frac{dV}{dt} + V \frac{d\phi_s}{dt} = -Su_c \phi_c. \quad (2)$$

Here, V is the volume of the suspension and S is the electrode surface area. We have assumed that the mass density of the liquid and the particles is constant. To solve Eq. 2, an overall mass balance for the entire suspension phase must be set up:

$$\frac{dV}{dt} = -Su_c. \quad (3)$$

Incorporation of Eq. 3 in Eq. 2 results in

$$\frac{d\phi_s}{dt} = -\frac{S}{V} u_c (\phi_c - \phi_s). \quad (4)$$

Particle velocity

The velocity v_s of a suspended particle in an electric field E is given by (Hunter, 1987)

$$v_s = \mu E. \quad (5)$$

Ordinary diffusion as a means of particle transport in the suspension phase has been left out of Eq. 5 because gradients $\nabla\phi_s$ will not form in the suspension. Note that the convective motion move due to the stirring of the suspension becomes parallel to the cast surface when it is approached. Therefore, stirring does not change the component of v_s that is perpendicular to the cast as considered in Eq. 5, which is the component that adds to the cast growth. By choice a positive mobility μ and a negative electric field E are chosen to comply with the system shown in Figure 1. This results in a negative particle velocity in the suspension v_s and a positive cast growth u_c .

Mobility

The mobility μ of a charged colloidal particle follows from the simultaneous solution of the Poisson equation with the Navier-Stokes equations and conservation of ions (Russel et al., 1989). For a single particle immersed in an infinitely extended pure liquid, the analytical solution is the Henry equation (Hunter, 1987; Probstein, 1989):

$$\mu = \frac{2\epsilon_r \epsilon_0 \zeta f_1(\kappa r_p)}{3\eta}. \quad (6)$$

Here, ϵ_r is the relative permittivity; ϵ_0 the permittivity of vacuum ($\epsilon_0 = 8.854 \times 10^{-12}$ F/m); ζ the zeta potential (V); κ is the inverse of the Debye screening length (m^{-1}); r_p the particle radius (m); and η the (Newtonian) viscosity ($\text{Pa}\cdot\text{s}$). The function f_1 varies between 1.0 at $\kappa r_p = 0$ (Debye-Hückel equation) and 1.50 at $\kappa r_p = \infty$ (Helmholtz-Smoluchowski equation). For a concentrated suspension, an analytical solution exists (Ohshima, 1997) in which the mobility does not depend on the permittivity of the particles. Since this expression is not verified experimentally yet, we will use a simpler approach based on qualitative arguments: if the Debye screening length is low compared to the average distance between particles x ($x \cdot \kappa \gg 1$), the potential drops to zero before a "new" particle is encountered, so the pure liquid permittivity ϵ_L can be used. However, for $x \cdot \kappa \ll 1$, many particles are present within the Debye length of the particle under study, so it is reasonable to use the effective permittivity of the suspension as a whole ϵ_s . The average interparticle distance x follows from the particle radius r_p and the volumetric suspension concentration ϕ_s , assuming there is a certain particle structure in the suspension. The close-packed structure (either cubic or hexagonal; Shriver et al., 1994) is most appropriate, as in this case x is the largest of the possible packing structures, and charged particles (of the same charge, as in EPD) naturally tend to maximize the interparticle distance. Now, the interparticle distance x (along the line connecting the centers of the particles) is given by

$$x = 2r_p \left[\left(\frac{\pi\sqrt{2}}{6\phi_s} \right)^{1/3} - 1 \right]. \quad (7)$$

The Debye screening length for a fully dissociated symmetrical salt is given by (Probstein, 1989):

$$\kappa^{-1} = \left(\frac{\epsilon_r \epsilon_0 RT}{2 F^2 z^2 c} \right)^{1/2}. \quad (8)$$

Here, R is the gas constant (8.3144 J/mol·K); F Faraday's constant (9.65×10^4 C/mol); z the charge number; and c the concentration of either the negative or the positive charged particles (mol/m^3).

Effective permittivity

The effective permittivity of a particle-liquid (two-phase) medium depends on the volume fraction of particles and is different for the cast and the suspension. Here, the Clausius-Mossotti approach (Sareni et al., 1996) is used:

$$\epsilon = \epsilon_h \frac{\epsilon_f + 2\epsilon_h + 2\phi_f(\epsilon_f - \epsilon_h)}{\epsilon_f + 2\epsilon_h - \phi_f(\epsilon_f - \epsilon_h)} \quad \phi_f < 0.45. \quad (9)$$

Host h and filler f must be chosen to comply with $\phi_f < 0.45$ (according to the figures in Sareni et al.). For the suspension (such as $\phi_s = 0.20$) this implies that the liquid is the host ($\epsilon_h = \epsilon_L$), the particles are the filler ($\epsilon_f = \epsilon_p$), and $\phi_f = \phi_s$. For the cast (such as $\phi_c = 0.6$), this changes to $\epsilon_h = \epsilon_p$, $\epsilon_f = \epsilon_L$, and $\phi_f = 1 - \phi_c$.

Field strength

Electrostatics starts with the Maxwell equations, and for the subject under study we confine ourselves to Coulomb's law (Fromhold, 1976):

$$\nabla \cdot \mathbf{D} = \rho. \quad (10)$$

Here, \mathbf{D} is the displacement vector, given by $\mathbf{D} = \epsilon \cdot \mathbf{E}$; and ρ the charge density [C/m^3]. Because SI units (rationalized or MKSA system) are used here, the factor 4π is left out of Eq. 10. Together with the definition equation

$$\nabla\psi = -\mathbf{E}, \quad (11)$$

the electrostatics of EPD are described. Here ψ is the electrical potential. From this point on, a one-dimensional planar system with parallel electrodes and particles moving along only one axis is considered (see Figure 1). Therefore, vectors \mathbf{D} and \mathbf{E} can be simplified to the scalars D and E . To solve the electric field throughout the deposition cell, Eq. 10 is used first to determine the change in field strength E over the cast-suspension boundary. It is assumed that no charge is present in the boundary, and therefore D becomes independent of location, which results in

$$\epsilon_c E_c = \epsilon_s E_s. \quad (12)$$

Second, both the permittivity of cast ϵ_c and of the suspension ϵ_s are considered to be independent of place, which reduces Eq. 10 to

$$\nabla E = \frac{\rho}{\epsilon}. \quad (13)$$

Together with Eq. 11, the well-known Poisson equation is obtained:

$$\nabla^2\psi = -\frac{\rho}{\epsilon}. \quad (14)$$

A simplification of the Poisson equation can be made if the (net) charge density ρ is zero in the entire system. This is true at the start of the process when suspended particles as well as all ions are homogeneously distributed over the entire suspension, and is valid as well for a pure nonelectrolyte (dielectric medium or nonionic solution). Possibly, as a first approximation, oxidic particles in an organic solvent can be modeled as a pure nonelectrolyte during the entire EPD process. The charges at the particle surface and in the surrounding cloud are then neglected in the calculation of the field E . In this case, both cast and suspension are regarded as dielectric media, and the Poisson equation simplifies to the Laplace equation:

$$\nabla^2\psi = 0. \quad (15)$$

Assuming that Eq. 15 is valid within each phase, and taking Eq. 12 into account at the cast-suspension boundary, the solution for the field strength E_s in the suspension at the

cast-suspension boundary results in

$$E_s = \frac{-\Delta\psi}{\left(\frac{\epsilon_s}{\epsilon_c} - 1\right)\delta + d} \quad (16)$$

Here, $\Delta\psi$ denotes the voltage difference $\psi_d - \psi_0$ over the electrode distance d , and ϵ_s and ϵ_c , which are calculated with the Clausius-Mossotti equation (Eq. 9), represent the effective permittivities of suspension and cast, respectively.

Cylindrical substrate

To describe cast formation on cylindrical substrates (such as on wires), the preceding set of equations is still valid, but Eq. 16 changes to

$$E_s = -\Delta\psi \left\{ (a + \delta) \left(\frac{\epsilon_s}{\epsilon_c} \ln \left(\frac{a + \delta}{a} \right) + \ln \left(\frac{b}{a + \delta} \right) \right) \right\}^{-1}$$

Here, a is the radius of the substrate and b the radial coordinate of the counterelectrode ($b > a$). Furthermore, the surface area at which deposition takes place depends on the cast thickness by $S = l2\pi(a + \delta)$, with l the length of the substrate.

Results and Discussion

Analytical expressions

The set of Eqs. 1, 3, 4, 5, 6, 9 and 16 describes EPD on a flat substrate. The initial conditions for the three differential equations are

$$V|_{t=0} = V_0 \quad \phi_s|_{t=0} = \phi_{s,0} \quad \delta|_{t=0} = 0.$$

For $\kappa \cdot r_p \ll 1$ and $x \cdot \kappa \ll 1$ (see below), the Debye-Hückel equation for particle mobility μ can be used as well as the effective suspension permittivity ϵ_s :

$$\mu = \frac{2\epsilon_s\zeta}{3\eta} \quad (17)$$

Only numerical solutions can be found for this coupled set of differential equations, but an explicit solution is obtained if the suspension volume V is large enough that the suspension concentration remains constant, that is, $\phi_s = \phi_{s,0}$.

In that case, combination of Eqs. 1, 5, 16, and 17 results in

$$\delta = \frac{\epsilon_c}{\epsilon_s - \epsilon_c} \left(\sqrt{d^2 + \frac{4(\epsilon_s - \epsilon_c)\epsilon_s\zeta\phi_s\Delta\psi t}{3\epsilon_c\eta(\phi_c - \phi_s)}} - d \right). \quad (18)$$

A further simplification of Eq. 18 can be made if the second group in the square root is small compared to d^2 , which results in

$$\delta = \frac{2\epsilon_s\zeta\phi_s\Delta\psi t}{3\eta(\phi_c - \phi_s)d}. \quad (19)$$

For a dilute suspension ($\phi_s \ll \phi_c$; $\epsilon_s = \epsilon_L$), Eq. 19 becomes

$$\delta = \frac{2\epsilon_L\zeta\phi_s\Delta\psi t}{3\eta\phi_c d}. \quad (20)$$

This equation is equivalent to Hamaker's law (Hamaker, 1940; Biesheuvel and Verweij, 1999).

An explicit expression incorporating dilution can be obtained for suspension concentrations ϕ_s that are low enough. In that case, cast growth neither influences the field strength in the suspension E_s nor the volume of suspension V , while the permittivity of the suspension ϵ_s equals ϵ_L . The field strength in the suspension E_s now simplifies to $E_s = -\Delta\psi/d$ and the mobility μ becomes independent of time: $\mu = 2\epsilon_L\zeta/(3\eta)$. Combining Eqs. 1 and 4 results in

$$\frac{d\phi_s}{dt} = \frac{S}{V_0} v_s \phi_s. \quad (21)$$

Equation 21 is integrated and the result implemented in Eq. 1. If the assumption $\phi_s \ll \phi_c$ is made, the following expression is obtained:

$$\delta = \frac{V_0}{S} \frac{\phi_{s,0}}{\phi_c} \left\{ 1 - \exp \left\{ -\frac{S}{V_0} \frac{\mu\Delta\psi t}{d} \right\} \right\}. \quad (22)$$

For $(S/V_0)(\mu\Delta\psi t/d) \ll 1$, Eq. 22 will result in Eq. 20.

Comparison with experiments

Several authors measured the decreasing cast growth in time for constant-voltage EPD (Avgustinik et al., 1962; Malov et al., 1974; Das et al., 1979; Nass et al., 1989; Heavens, 1990; Hirata et al., 1991; Zhang et al., 1994; Ishihara et al., 1996; Sarkar and Nicholson, 1996; Hector and Clasen, 1997), but only Zhang et al. give enough information to test our equations.

To evaluate the data in Zhang's figure 4 (Table 1, third row), we first evaluated the value of $x \cdot \kappa$ and $\kappa \cdot r_p$; see Eqs. 7 and 8. To this end, the autoprotolysis constants from Coetzee and Ritchie (1969) for methanol and 2-propanol are used ($pK = 16.7$ and 20.8 , respectively), which results in a volume-averaged concentration c of 3.44×10^{-6} mol/m³ ($c = 10^{3-pK/2}$) and a value of $\kappa^{-1} = 3081$ nm. With $x = 436$ nm, $x \cdot \kappa = 0.14$ and $\kappa \cdot r_p = 0.013$ follow, so Eq. 17 is used.

Table 1. Data Used by Zhang et al. (1994)

$\phi_{s,0}$	0.00276
ϕ_c	0.60
ρ_p	3,624 kg/m ³ *
S/V_0	300 m ⁻¹
ϵ_L	27.71 · ϵ_0 *
ϵ_p	10.14 · ϵ_0 *
ζ	4.45 mV
η	9.24 × 10 ⁻⁴ Pa · s
$\Delta\psi$	50 V
d	0.025 m

* Volume averages for the components ZrO₂ and SiC, based on data from Lide (1994).

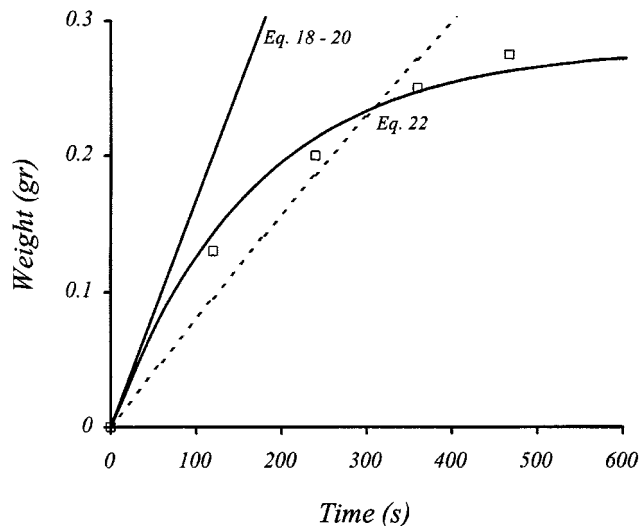


Figure 2. Weight increase of cast formed by EPD.

Squares are measurements by Zhang et al. (1994), the dashed line is the best fit based on $\zeta = 4.45$ mV and $S = 520$ cm² (Eq. 22), and solid lines are based on $\zeta = 55.9$ mV and $S = 84$ cm². Other data from Table 1.

Calculations based on the numerical model (or on Eq. 22, as ϕ_s very low) using the data from Table 1 and $\text{Weight} = S\phi_c\rho_p\delta$ are best fitted to the experimental data using $S = 520$ cm² (see Figure 2). However, the quality of the fit is moderate, and this value for the surface area seems large when considering the setup as drawn in Figure 1 of Zhang et al. (1994).

If we multiply the value for the ζ -potential by 4π (corresponding to the conversion of the esu/emu/Gaussian/cgs-system to the SI/MKSA/rationalized system; Jackson, 1975), measurements can be fitted much better and with a more reasonable electrode surface area of S of 84 cm². Note that the resulting ζ -potential (56 mV) is more in accordance with typical ζ -potentials measured by other authors (~ 30 – 200 mV; Sarkar and Nicholson, 1996; Sussman and Ward, 1981). That Zhang et al. (1994) work in a Gaussian unit system is further emphasized by the fact that they also use a factor 4π in their expression for the cast growth.

The numerical model and the explicit equation (Eq. 22) give the same results because the suspension concentration and final cast thickness are extremely low (Figure 2). The explicit expressions Eq. 18, 19, and 20 do not consider the dilution of the suspension, and therefore violate the overall mass balance for times over ~ 200 s.

To show the differences between the numerical model and the explicit expressions more clearly, simulations were made with an initial suspension concentration that was increased 100 times ($\phi_{s,0} = 0.276$), (see Figure 3). The explicit solutions now significantly deviate from the numerical model: the initial cast growth rate is significantly lower for Eqs. 20 and 22 than for the numerical model, as the equations do not properly implement the mass balance over the growing cast. For $t > 100$ s, Eqs. 18–20 overestimate the cast thickness because they neglect the dilution of the suspension.

Other authors also modeled the decrease in cast growth rate in time and attributed this to the “resistance” of the cast

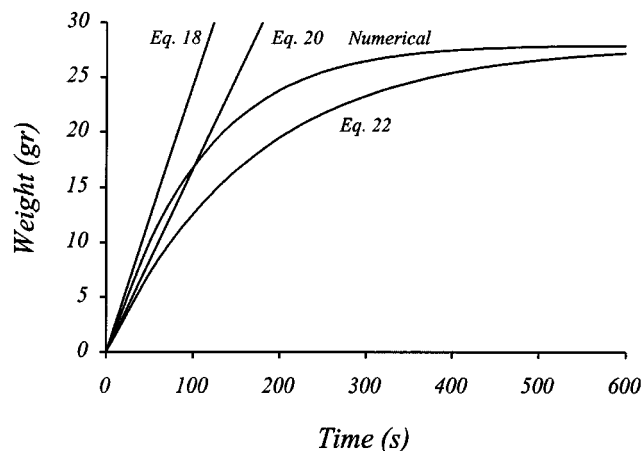


Figure 3. Simulation results using data from Table 1, $S = 84$ cm², but $\phi_{s,0} = 0.276$ and $\zeta = 55.9$ mV.

(Sussman and Ward, 1981), to depletion of the suspension (Laubersheimer et al., 1998; Zhang et al., 1994), or to both (Sarkar and Nicholson, 1996). These models err with respect to the Kynch theory (that is, implicitly assume that $\phi_s \ll \phi_c$ in Eq. 1) and assume that neither the particle mobility μ nor the suspension volume V change in time. Furthermore, it is unclear how the concept “resistance” relates to the more fundamental properties as particle and liquid permittivity and system geometry (such as planar vs. cylindrical).

Uniformity of cast thickness

EPD is often used because a cast with a uniform thickness can be obtained (that is, a smooth surface). Still, finding recipes that result in smooth cast surfaces is often more art than science, and a clear explanation based on first principles is lacking. However, this phenomenon is explained by Eq. 16. If we assume $\{\epsilon_c < \epsilon_s\}$, clearly a locally larger δ results in a decreasing magnitude of E , and therefore less deposition. This results in smoothing of the cast surface. The inequality $\{\epsilon_c < \epsilon_s\}$ holds for $\{\{\epsilon_p < \epsilon_L\}$ and $\{\phi_c > \phi_s\}\}$ (see Eq. 9), and is equivalent to $\{\epsilon_p < \epsilon_L\}$, because $\{\phi_c > \phi_s\}$ holds by definition. However, Eq. 16 also predicts that for $\{\epsilon_c > \epsilon_s\}$, any (naturally occurring) slight variation in cast thickness will be increased, which results in an extremely rough surface, with particles only depositing on the highest cast “peaks.” The resulting structure may easily collapse with particle clumps “dripping” (Krishna Rao and Subbarao, 1979) from the electrode due to gravity, without forming a cast layer. The criterion for uniform deposition is therefore $\{\epsilon_p < \epsilon_L\}$, which can be validated by the following measurements:

- Krishna Rao and Subbarao (1979) note that deposition of β -alumina occurs in media with permittivities ϵ_L in the range of only 12–25 (implying that 25 is not an upper limit). The permittivity of alumina is, according to Lide (1994), $9.34 < \epsilon_p < 11.54$, which is indeed just below the lower limit for the range of appropriate ϵ_L -values.

- In their table 1, Krishna Rao and Subbarao show that magnesia ($\epsilon_p = 9.65$; Lide, 1994) is not deposited in dichloromethane ($\epsilon_L = 9.08$), but is in benzyl alcohol ($\epsilon_L = 13$) and liquids with higher ϵ_L .

• Ishihara et al. (1996) report anomalous deposition of yttria-stabilized zirconia (YSZ) films from 3-pentanone ($\epsilon_L = 15.4$), but uniform deposition in cyclohexanone ($\epsilon_L = 18.3$) and other liquids with higher ϵ_L , which is in agreement with the criterion given earlier, if ϵ_{YSZ} is between 15.4 and 18.3. A single value for ϵ_{YSZ} does not exist, because it also depends on the crystallinity of the powder (Thompson et al., 1992), but for (calcium-stabilized) zirconia values between 13.5 and 26 are reported (Thompson et al., 1992). At least, this range of values does not contradict the criterion.

Conclusions

Based on the assumption that the charge is zero in the entire system (as for suspensions in nonionic liquids), equations are derived from first principles to describe cast formation during constant-voltage electrophoretic deposition on flat and cylindrical substrates. The equations describe experiments from the literature on the decrease of cast formation rate with time, and indicate that smooth layers are obtained only if the particle permittivity ϵ_p is lower than the liquid permittivity ϵ_L ($\epsilon_p < \epsilon_L$). For $\epsilon_p > \epsilon_L$, anomalous cast growth occurs without uniform deposition.

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