R & D NOTES

A Note on Instabilities in Rapid Coating of Cylinders

G. M. HOMSY

Department of Chemical Engineering
Stanford University
Stanford, California 94305

and

F. T. GEYLING

Bell Laboratories
Murray Hill, New Jersey 07974

The coating of wires and fibers is an important industrial process with regard to the coating and protection of optical fibers for communication systems. A coating of uniform thickness is required, and therefore the question of the stability of a coating flow is paramount.

In this short note, we wish to expand upon three aspects of both old and recent work on this problem. The first involves a reinterpretation and strengthening of a method due to Deryaguin (1945) for computing the maximum coating thickness in open-bath withdrawal. The second section treats the linear stability of coating flow using long-wave expansions, as recently reported by Lin and Liu (1975) and Krantz and Zollars (1976). The surprising prediction is that there exists an optimal coating speed in open-bath coating. We conclude with some tentative remarks regarding the onset of instabilities.

PREDICTION OF FILM THICKNESS

Coating of fibers is typically performed in one of two modes, either by drawing through a die or by open-bath withdrawal. In the latter case, the prediction of the final film thickness is a problem with a large and sometimes confusing literature. For convenient summaries, see Deryaguin and Levi (1964), Tallmadge and White (1968), and Gutfinger and Chiu (1971). Consider a cylinder of radius R, withdrawn from a bath with velocity V, resulting in a coating of thickness $h - R$. Dimensional analysis shows that the dimensionless film position $\xi = h/R$ is a function of at most three dimensionless groups. Convenient choices are $Ca = \mu V/\sigma$, capillary number; $T = \rho g R^2/\mu V$, inverse pulling speed; and $Re = \rho V R/\mu$, Reynolds number. Withdrawal theory then seeks to establish a relationship between ξ and the remaining groups. [It is well known that the choice of groups is not unique. Other authors have used different dimensionless groups. In particular the so-called Goucher number, $Go \equiv (CaT/2)^{1/2}$ is also in common usage.] We will focus here on inertialess, high speed coating, $Re \to 0$, $Ca \to \infty$, since the application involves rapid coating with liquids of high viscosity on thin optical fibers.

Deryaguin (1945) has considered the related problem of high capillary number withdrawal of plates. He observed that in this limit, the final film thickness is that which results in a maximum volume flux of liquid being entrained by the plate. We will show that this observation is a result of assumptions commonly made in withdrawal theory. These assumptions are that there is strictly one-dimensional flow in the film and that surface tension has no effect upon the meniscus, the shape, or the final film thickness as $Ca \to \infty$. It is easy to show that, given the first assumption above, the velocity profile is

$$u(r) = 1 - T\left(\frac{1-r^2}{4} + \xi^2 \frac{\ln r}{2}\right) \tag{1}$$

where u, r are made dimensionless with respect to V, R, respectively. The dimensionless volume flux is

$$Q = \int_1^\xi u(r)\,dr = \frac{\xi^2 - 1}{2} - T\left(\frac{\xi^2-1}{8} - \frac{\xi^4-1}{16} + \frac{\xi^4 \ln\xi}{4} - \frac{(\xi^2-1)}{8}\right) \tag{2}$$

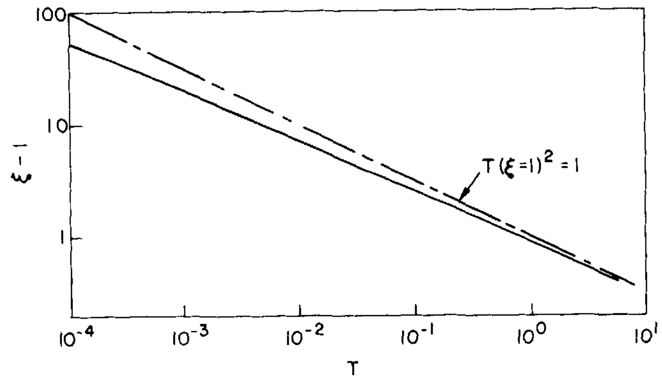

Fig. 1. Dimensionless film thickness as a function of *T*.

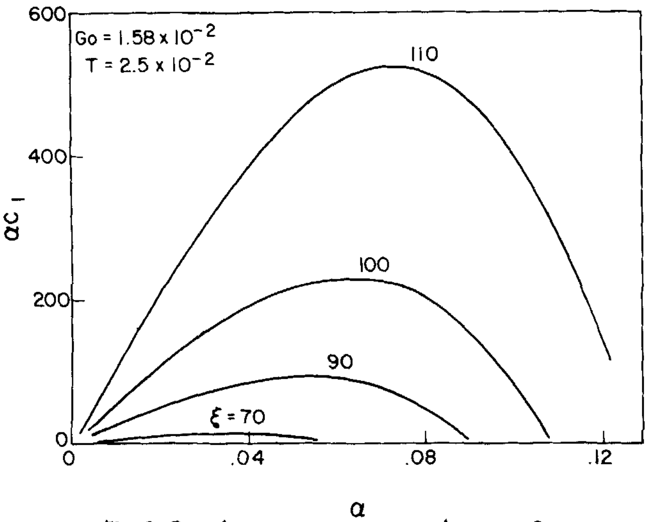

Fig. 3. Growth constant vs. wave number, case B.

Now, in the limit of zero surface tension, the film thickness is an abruptly changing function of distance measured in the direction of movement of the cylinder. (Of course, surface tension acts in the immediate vicinity of the meniscus to relieve the singularity.) If we adopt a reference frame that moves with the cylinder, the interface recedes as a shock or singular surface. The flux relative to this frame is simply

$$Q' = Q - \frac{(\xi^2 - 1)}{2} \tag{3}$$

The kinematic condition relating ξ to Q' reads

$$\frac{\partial \xi}{\partial t} + \frac{1}{\xi}\,\frac{\partial Q'}{\partial z} = 0 \tag{4}$$

It is well known that (4) admits steady shocklike solutions $\xi(z, t) = \xi(z - ct)$ if the shock speed

$$c = \frac{1}{\xi}\,\frac{\partial Q'}{\partial \xi} \tag{5}$$

However, $c = -1$ by our choice of reference frame, so combining this with (3) and (5), we find that ξ and T are related via the equation $dQ/d\xi = 0$; that is, the final thickness is indeed that resulting in the cylinder entraining a maximum flux of fluid. Thus, Deryaguin's result is recovered.

The final thickness at high capillary number is thus given as a solution of

$$T\left(\frac{1 - \xi^2}{2} + \xi^2 \ln \xi\right) = 1 \tag{6}$$

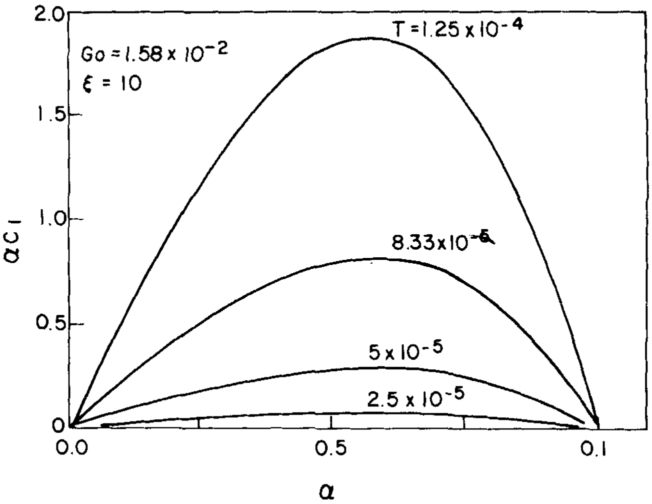

Fig. 2. Growth constant vs. wave number, case A.

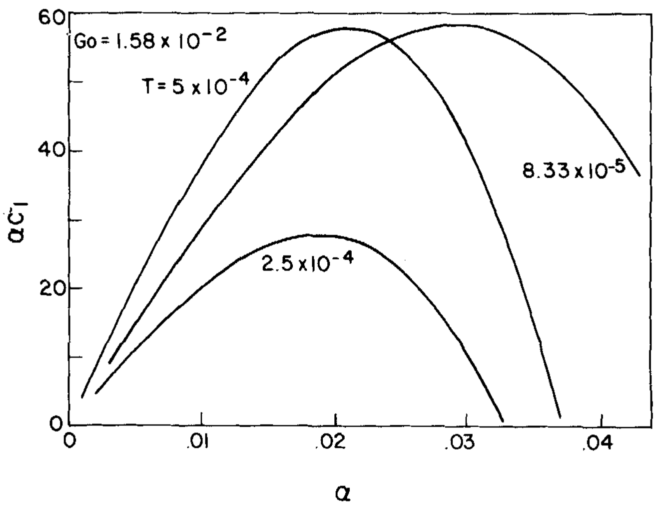

Fig. 4. Growth constant vs. wave number, case C.

obtained by the relation $\partial Q/\partial \xi = 0$. We will denote the solution of (6) as $\xi^*(T)$.

We have numerically determined the roots of Equation (6) over a wide range of values of T. The dimensionless film thickness $(\xi^* - 1)$ is shown in Figure 1 as a function of the independent parameter T. We see that the solution does not vary significantly from that for plates, which in these variables reads $T(\xi^* - 1)^2 = 1$. Figure 1 reproduces results of Gutfinger and Tallmadge (1964), which were derived by solving the initial value problem for Equation (4).

Comparison of high Ca theories with experiment shows that the predicted film thickness represents an upper limit to that observed experimentally. Finite surface tension, inertial effects, and two-dimensional flow in the meniscus all serve to reduce the final thickness (Gutfinger and Chiu, 1971).

LINEAR INSTABILITIES

We wish to examine the stability of the final rectilinear flow with respect to long surface waves which are well recognized to occur in film flows of this type. Because of the fact that there is a nonzero mean radius of curvature, the film will always be unstable to a capillary mode first discussed by Rayleigh and extended by Goren (1962). While the present work was near completion, Lin and Liu (1975) published an essentially equivalent treatment of the stability problem. Thus we will only briefly detail our own results.

Through the use of long-wave expansions, one may develop an instability theory which describes the fate of small surface disturbance waves of the form $\eta = \eta_0 \exp[i\alpha(z - ct)]$. Expansion of all dynamic variables in an asymptotic representation for small α yields an evolution equation for $\eta(z, t)$ (Lin and Liu, 1975; Atherton and Homsy, 1976). From this equation, the complex wave speed c may be calculated. As is common in long wave expansions of this type, the leading terms are $c = c_o + i\alpha c_1 + 0(\alpha^2)$. Thus, the wave is nondispersive, travels with wave speed c_o, and has growth constant (αc_1). The results are algebraically complex; we record for future reference the result for c_o, namely

$$c_o = 1 - T\left(\frac{1 - \xi^2}{2} + \xi^2 \ln\xi\right) \tag{7}$$

We have computed the growth constant (αc_1) as a function of wave number α for the following parameterizations: case A—fixed ξ, varying $\{T, Ca\}$ corresponding to die coating with a fixed die gap, fixed fluid, but varying pulling speed; case B—fixed Ca, fixed T, varying $\xi \leq \xi^*$, corresponding to die coating with fixed fluid and coating speed, varying gap; case C—varying Ca, T, but fixed Go, with $\xi = \xi^*$, corresponding to high Ca open-bath coating, with varying coating speed. Figures 2, 3, and 4 give the growth constants for each of these cases, respectively. The chosen values of Go were appropriate to the application alluded to in the introduction.

Figure 2 (case A) indicates that at a fixed thickness and varying speed, the growth constant decreases with increasing speed, and that the wave number of maximum growth remains approximately constant. The decrease of the growth constant with increasing speed for fixed ξ may be understood by noting that as $T \to 0$, fixed ξ, the velocity profile becomes more like a plug flow, thus eliminating the long surface wave which relies on the base flow shear for its energy.

Figure 3 for fixed velocity, varying thickness illustrates this same trend. As the thickness increases, the growth constant also does, indicating the increased importance of the shear wave; there is a slight shift to shorter waves in this particular example, but the opposite trend was observed for higher values of T (lower pulling speeds).

Figure 4 for fixed Go, with T and ξ determined from Figure 1 (open-bath coating), is perhaps the most interesting. It shows a decrease followed by an increase in the growth constant for increasing coating speed (decreasing T). We interpret this as follows. At low speeds, the Rayleigh-Goren capillary mode is the dominant instability mechanism. For moderate coating speeds, the film thickens, resulting in an increase in the mean radius of curvature of the interface and hence a decrease in the growth constant for capillary pinching. At still higher speeds, however, the film becomes quite thick, and the surface waves owing to the shear in the base state profile ultimately dominate.

Finally, we wish to note an interesting feature of the instability in open-bath coating. Combining the expression for the wave velocity with the relation between T and ξ^*, we find that the phase velocity in open-bath coating is zero. The onset is therefore predicted to be nearly stationary in space, oscillatory in time. On the other hand, for die coating at high speeds, the phase velocity will be close to the cylinder velocity, as it would be for a simple capillary mechanism.

THE WAVE ONSET PROBLEM

Even though the growth rate and wave have been computed from the above results, the problem remains of predicting the distance past a die or the surface of a bath at which waves first become visible. There is virtually no information on this problem in the literature for coating on cylinders. Gutfinger and Chiu (1971) apparently observed both capillary and long-wave instability modes but did not make a careful study. However, there are experimental studies available for both flow down a flat plate (see references in Atherton and Homsy, 1973) and the closely related problem of plate withdrawal from an open bath (Tallmadge and Soroka, 1969).

In the case of film flow, there exists an upper portion of the film which is virtually flat. At a reasonably well-defined distance, waves appear on the interface. Experiments show that this distance is a strongly decreasing function of Reynolds number. Using the theoretical growth rates and the experimental data, Atherton and Homsy attempted to back calculate the amplification experienced by a disturbance in its growth to visibility. The results obtained were inconclusive.

Tallmadge and Soroka (1969) have observed wave instabilities in the related problem of plate withdrawal from an open bath. They found empirically that the wave-point criterion (that is, the velocity at which waves were observable in their apparatus), was well correlated by use of a Reynolds number based upon film thickness and the difference between the plate velocity and the average film velocity. This differs from the definition introduced above, so we use Re' to denote this Reynolds number. Thus, $Re' \equiv \dfrac{\rho(V - \overline{u})(h - R)}{\mu}$. Using this definition and the results above, we find that Re' is, in fact, proportional to the growth rate of long waves. Tallmadge and Soroka's wave-point criterion $Re' \sim 0(1)$ apparently states that for their apparatus, the dimensionless growth rate had approached $0(1)$ when the waves experienced an amplification sufficient to become visible.

If we adopt the criterion $Re' \approx 1$ for wave onset, a routine calculation gives

$$Re' = -\left(\frac{VRT}{\nu}\right)\left\{\frac{1}{8} - \frac{3\xi^2}{8} + \frac{\xi^4 \ln\xi}{2(\xi^2 - 1)}\right\}(\xi - 1) = 1 \tag{8}$$

Equation (8) may be used to predict wave onset as a function of the important physical variables. We consider both die and open-bath coating.

In the case of die coating, the film thickness is expected to depend primarily on the die characteristics and is relatively insensitive to drawing speed. From Equation (8), we find that wave onset depends strongly on coating viscosity and is independent (to a first approximation) of drawing speed. This follows from introducing the definition of T and rearranging

$$\frac{gR^3}{\nu^2} \geq \frac{1}{|f(\xi)|} \tag{9}$$

where

$$f(\xi) = (\xi - 1)\frac{1}{8}(1 - 3\xi^2) + \frac{\xi^4 \ln\xi}{2(\xi^2 - 1)}.$$

For a given fiber, this yields the estimate $\nu \leq [gR^3 |f(\xi)|]^{1/2}$ for instability, or the reverse inequality as a lower bound on ν to insure stability.

In the case of open-bath withdrawal, the film thickness and the drawing rate are not independent quantities. From Figure 1

$$(1 - \xi)^2 T = (h - R)^2 \frac{\rho g}{V\mu} = g(\xi) \tag{10}$$

where $g(\xi)$ is a weak function of ξ, and $g(1) \to 1$. Combining (8) and (9), we find a relation between drawing rate and viscosity

$$\frac{V}{\nu} R \frac{f(\xi)}{(\xi - 1)} \geq 1 \qquad (11)$$

where ξ and T are related through (10).

We may state the following conclusions.

1. Deryaguin's method for computing the maximum film thickness has been confirmed.
2. In both open-bath and die coating, the growth rate of a disturbance decreases with increased pulling speed at a fixed thickness. For any given pulling speed, open-bath coating is relatively more unstable than die coating.
3. There is apparently an optimum coating speed in open-bath coating.
4. In die coating, the onset of waves is dependent mainly upon coating viscosity. In open-bath drawing, the criterion is the ratio of drawing speed to viscosity. Increases in V or decreases in ν lead to wave inception.

There is a great need for experiments to substantiate these predictions.

NOTATION

c = wave or shock speed, dimensionless
Ca = capillary number
g = acceleration of gravity, m/s^2
Go = Goucher number
h = radial location of film surface, m
Q = volumetric flux, dimensionless
R = cylinder radius, m
Re = Reynolds number
Re' = modified Reynolds number
T = inverse pulling speed, dimensionless
u = velocity, dimensionless
V = cylinder velocity, m/s
z = axial distance, dimensionless

Greek Letters

α = wave number, dimensionless
η = wave amplitude, dimensionless
μ = fluid viscosity, N/s m^2
ν = kinematic viscosity, m^2/s
ρ = fluid density, kg/m^3
σ = surface tension, N/m
ξ = radial location of film surface, dimensionless

LITERATURE CITED

Atherton, R. W., and G. M. Homsy, "A Note on Wave Inception in Film Flow," *Chem. Eng. J.*, **6**, 273 (1973).

———, "On the Derivation of Evolution Equations for Interfacial Waves," *Chem. Eng. Comm.*, **2**, 57 (1976).

Deryaguin, B. V., "On the Thickness of the Liquid Film Adhering to the Walls of a Vessel After Emptying," *Acta Physicochimica URSS*, **20**, 349 (1945).

———, and S. M. Levi, *Film Coating Theory*, Focal Point Press, New York (1964).

Goren, S. L., "The Instability of an Annular Thread of Fluid," *J. Fluid Mech.*, **12**, 309 (1962).

Gutfinger, C., and H. C. Chiu, "An Experimental Study of Continuous Free Withdrawal of Wires from Newtonian Fluids," in "Progr. Heat Mass Trans.," Hestroni et al., ed., **6**, 753 (1971).

Gutfinger, C., and J. A. Tallmadge, "Some Remarks on the Problem of Drainage of Fluids on Vertical Surfaces," *AIChE J.*, **10**, 774 (1964).

Krantz, W. B., and R. L. Zollars, "The Linear Hydrodynamic Stability of Film Flow Down a Vertical Cylinder," *AIChE J.*, **22**, 930 (1976).

Lin, S. P., and W. C. Liu, "Instability of Film Coating of Wires and Tubes," *ibid.*, **21**, 775 (1975).

Tallmadge, J. A., and A. J. Soroka, "The Additional Parameter in Withdrawal," *Chem. Eng. Sci.*, **24**, 377 (1969).

Tallmadge, J. A., and D. A. White, "Film Properties and Design Procedures in Cylinder Withdrawal," *Ind. Eng. Chem. Process Design Develop.*, **7**, 503 (1968).

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Predicting Diffusion Coefficents

T. SRIDHAR
and
O. E. POTTER

Department of Chemical Engineering
Monash University
Clayton, Victoria 3168, Australia

Lynch (1974) showed that most available correlations for predicting diffusion coefficients underestimate the magnitude. It is clear that there is a need for a simple expression which can predict gas-liquid diffusivities with confidence.

Hildebrand (1971), following the work of Batschinski (1913), has shown that liquid molal expansion is, in reality, very small, and therefore conventional theories for the liquid state are likely to be unrealistic. When applied to diffusivity, this means that there is little basis for using an Arrhenius type of relationship for the temperature dependence of diffusion coefficients, especially at lower temperatures.

In this note we use this concept of Hildebrand to arrive at an equation for gas liquid diffusivities. Following Hildebrand, we write

$$D_{AB} = D_{BB} \left(\frac{V_B^*}{V_A^*} \right)^{2/3} \qquad (1)$$

where D_{BB} is the solvent self-diffusion coefficient, and V_B^* and V_A^* are the critical molal volumes for solvent and solute, respectively.

Dullien (1972), using the effective molecular diameters in liquids, has developed an equation for predicting self-diffusion coefficients in liquids:

$$D_{BB} = 0.088 \left(\frac{V_B^*}{N} \right)^{2/3} \frac{RT}{\mu V_B} \qquad (2)$$