A Mathematical Model for Three-dimensional Coating Flow with Thixotropy

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Presented at the 16th International Coating Science and Technology Symposium, September 9-12, 2012, Atlanta, Georgia*

A mathematical model is developed to predict the three-dimensional time-dependent flow of actual non-Newtonian liquid coatings on a non-planar substrate. In addition to shear-thinning rheology we also include the time-dependent viscosity effect known as thixotropy. The model employs the lubrication approximation and other simplifications. Theoretical results are compared with experimental observation of the evolving free surface of the coating as it drains out of an axisymmetric indentation in a vertical substrate. Two different architectural paints are used. As previously reported, the agreement between theory and experiment is good for one of the paints. For the other paint, while the previous procedure gives an accurate time sequence of surface profiles, the time intervals between profiles is not well predicted. Incorporating thixotropy into the model produces much better agreement.

”Thixotropy” signifies the influence of the previous stress history on the instantaneous value of viscosity of a moving fluid element. Overcoming thixotropic thickening, which is idealized as a reversible viscosity increase, is the purpose of the shaking machine that is usually found in a paint store. A review of thixotropy, including theoretical and experimental results, is given by Barnes [J. Non-Newt. Fluid Mech., v. 70 pp. 1 -33 (1997)]. The thixotropic effect is in addition to generalized Newtonian behavior where, for most architectural coatings, the viscosity is a strongly decreasing function of shear stress. Here, following the classical approach of Moore [Trans. Br. Ceram. Soc. v. 58, pp. 470 - 494 (1959)], the stress history influence is incorporated using a structure factor. Structure in our model is a calculated local property. It is convected and diffused in the moving liquid, as well as simultaneously growing over time and being reduced by the flow stresses, in the spirit of the Moore model.

A particular example of viscometry data showing thixotropy is in Fig. 1. The “ramp-up” data give the higher values of viscosity for each value of shear stress τ. The “ramp-down” data is lower, because the liquid has recently been been subjected to the higher stress levels leading to thixotropic

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lowering of viscosity. These data took several minutes for the full cycle to be traversed. Somewhat different results can be expected if the cycle were to be done more or less rapidly. Conversely, had the stress been maintained for a long time at a given constant value, one would expect a single unique viscosity for that stress value.

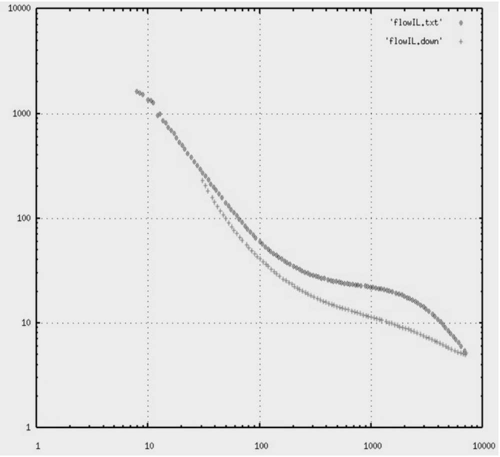

Figure 1: Measured viscosity in poise (vertical) versus shear stress in dyn/cm^2.

SInce liquid coatings are thin, the lubrication approximation is known to successfully model flow behavior in most cases. While it is possible to use a history-dependent thixotropy model to analyse the details of flow variation across the thin dimension for geometrically-simple two-dimensional problems, as in our recent work [see Livescu *et al* J. Non-Newt. Fluid Mech. v. 166, pp. 395 - 403 (2011)], here we will only use layer-averaged properties.

In this paper we incorporate layer-averaged thixotropy into our previously-reported quasi-three-dimensional, unsteady coating flow model [Schwartz & Eley, J. Engrg. Maths. v. 43, 153-171 (2002) and Eley & Schwartz, J. Coatings Tech. v.74, 43-53 (2002)]. For the particular example of drainage flow from a nail-head indentation on a vertical substrate, we show some of the additional effects due to stress history. The mathematical model can accommodate arbitrary generalized Newtonian rheology and has been compared to experiment.

We assume that λ is a layer-averaged quantity that satisfies a convection-diffusion equation of the form

$$(\lambda h)_t = -\nabla \cdot (\lambda \mathbf{Q}) + K_d \nabla \cdot (h \nabla \lambda) \tag{1}$$

where $\mathbf{Q}(x, y, t)$ is the area flux vector. The liquid surface corresponds to $z = h(x, y, t)$ where t is time. This equation is written in conservation form. Now λ is considered to be the layer-average value of structure, so that the “total structure” within a layer of thickness h is λh. The meaning of $\nabla \cdot (\lambda \mathbf{Q})$ is the outflow of structure, per unit of substrate area, due to convection. The last term is diffusion of structure where K_d is a diffusion constant. If the overall mass balance equation $h_t = -\nabla \cdot \mathbf{Q}$ is subtracted from (1), and two additional terms representing the Moore “set-up” and “break-down” of structure are appended, the λ equation can be written as

$$\frac{\partial \lambda}{\partial t} = \frac{K_d}{h} \nabla \cdot (h \nabla \lambda) - \frac{\mathbf{Q}}{h} \cdot \nabla \lambda + A(1-\lambda) - B\lambda|\tau| \tag{2}$$

where $|\tau|$ is the magnitude of the vector $\vec{\tau}(x, y)$, the shear stress on the substrate at a given location.

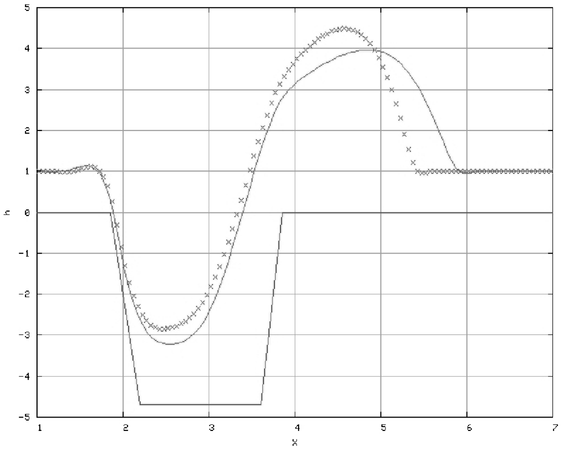

Figure 2: Centerline section of the coating free surface at 15 sec after the start of the motion. The substrate is also shown. The solid line is predicted free surface using viscometry data. The symbols have the data corrected for thixotropy and is close to the experimental observation. Thixotropy parameters are λ_0 = 0.8, λ^* = 0.3, a = 4, and A = B =2. The vertical scale is in units of coating thickness; the horizontal scale unit is the indentation radius.

Experiments were performed to reproduce the sagging of paint when applied to a vertical wall upon which there is a nailhead indentation. The lubrication form of the surface evolution equation is

$$h_t = -\nabla \cdot \mathbf{Q} = \frac{1}{3}\, \nabla \cdot \left(\frac{h^3}{\mu} \nabla p \right) \tag{3a}$$

where the pressure is the sum of capillary and hydrostatic components and σ is surface tension:

$$p = -\sigma \nabla^2 h + \rho g x \; . \tag{3b}$$

The local layer-averaged viscosity in (3a) depends on the local value of stress and the local structure

$$\mu(\lambda) = \mu_0(|\tau|) \exp a(\lambda - \lambda^*) \; . \tag{4}$$

λ_0 is the uniform structure value for the coating at the start of the sagging motion. It will depend, for example, on the elapsed "standing" time before stress application. The function $\mu_0(|\tau|)$ and the positive constants a and λ^* can be determined from viscometry data, such as Fig. 1. λ^* is seen to be the value of structure for which for which the history factor is equal to one; *i. e.* when the build-up and break-down rates are equal.

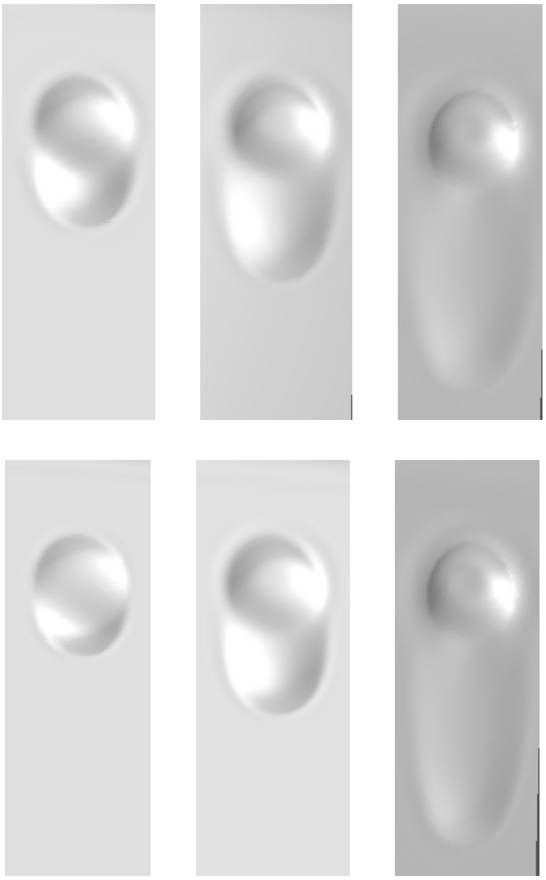

Figure 3: Rendered pictures of the emerging drop from simulation results. Times are 5, 15, and 55 sec. Top row are results using uncorrected viscometry data for viscosity. Lower row results have the addititional thixotropy effects.

The mathematical model is fitted to the viscometry data and solved numerically by an alternating-direction-implicit method. Results are shown in Figures 2 and 3. A drawdown blade was used to level the initial coating. The blade-applied stress is nonuniform however, and is smaller for the liquid in the indentation. Thus, the liquid initially within the indentation was not subjected to the same lowering of viscosity. When compared to observation, the model without viscosity has the liquid emerging from the indentation too rapidly. Figure 3 shows rendered pictures of the emerging drop with and without the thixotropy correction.