Rheology of High Solid Coatings. II. Analysis of Combined Sagging and Leveling*

SOUHENG WU, *E. I. duPont de Nemours & Company, Central Research and Development Department, Experimental Station, Wilmington, Delaware 19898*

Synopsis

The rheology of combined sagging and leveling of high solid coatings is analyzed in terms of non-Newtonian power-law model. The results indicate that, in order to have good leveling, good sag control, and good sprayability at the same time, high solid coatings should have pseudoplastic rheology with power constant of about 0.5 and viscosity at 1 sec^{-1} of about 50 poises. This theoretical prediction is confirmed experimentally.

INTRODUCTION

In the preceding paper,[1] we analyzed the rheology of sagging and slumping for high solid coatings, and established the rheological requirements for the control of sagging and slumping. It was found that the tendency to sagging increases in the order: pseudoplastic fluids, Bingham fluids, Newtonian fluids, and dilatant fluids. It was also found that good sag control and good sprayability can be achieved simultaneously only for pseudoplastic fluids. However, pseudoplastic fluids are known, from experience, to be difficult to level. Factors which retard sagging will also retard leveling. Good sag control and good leveling are very difficult to achieve simultaneously in practice. In fact, it is not known, either experimentally or theoretically, if adequate leveling is possible with good sag control and good sprayability for one-package high solid coatings (as against two-package high solid coatings in which the sagging is controlled by rapid gelation).

This paper will analyze the rheology of combined sagging and leveling in terms of non-Newtonian power-law model, and establish the rheological requirements for achieving good leveling, good sag control and good sprayability at the same time for high solid coatings.

RHEOLOGY OF LEVELING OF POWER-LAW FLUIDS

The leveling of Newtonian fluids has been analyzed by Patton,[2] Orchard,[3] and Rhodes.[4] An analysis for viscoelastic fluid was given by Bierman.[5] Murphy[6] extended Orchard's treatment for a pseudoplastic fluid. Here, we will analyze the leveling of non-Newtonian power-law fluids by extending Patton's approach.

Consider a coating of uniform thickness having a wavy surface consisting of alternating cylindrical crests and troughs (Fig. 1). Let h be the coating thickness,

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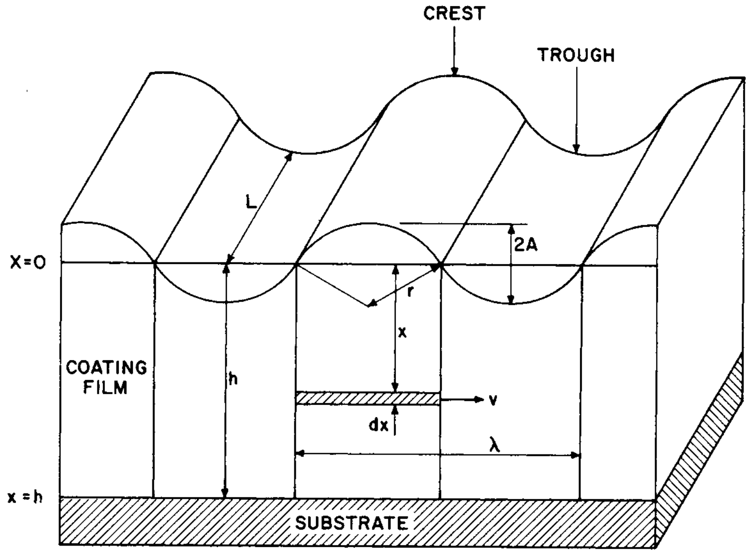

Fig. 1. Model for analyzing the leveling.

x the coordinate in the direction of thickness measured from the coating surface, σ the surface tension of the coating, λ the wavelength of the surface wave, A its amplitude, r its radius of curvature, η the viscosity of the coating, and v the horizontal flow velocity of the fluid. During leveling, the fluid in the crest regions flows to fill the trough regions.

During leveling, surface tension acts to push and slip sidewise the fluid in the crest regions to fill the trough regions. The velocity gradient of this flow is given by[2]

$$dv/dx = (2\sigma/r\eta\lambda)x \tag{1}$$

where, in general, η is dependent on shear rate and time.

Consider the power-law fluid whose shear stress and shear rate relation is given by

$$\tau = \eta_0\gamma^n \tag{2}$$

where τ is the shear stress, γ is the shear rate, η_0 is the viscosity constant (i.e., the viscosity at 1 $\sec^{-1}$), and n is the power constant. Applying eq. (2) in eq. (1) gives

$$dv/dx = \left(\frac{2\sigma}{r\eta_0\lambda}\right)^{1/n} x^{1/n} \tag{3}$$

The volumetric flow rate for the fluid flowing from the crest region to the trough region per unit width can be shown to be

$$\frac{-dV}{dt} = \left(\frac{2\sigma}{r\eta_0\lambda}\right)^{1/n} \left(\frac{n}{2n+1}\right) h^{(2n+1)/n} \tag{4}$$

The volume of the crest portion per unit width is $V \cong \lambda^3/96r$; the radius of curvature r is related to the amplitude A and the wavelength λ by $r \cong \lambda^2/32A$. Thus, we have

$$dV \cong (1/3)\lambda dA \tag{5}$$

Applying eq. (5) in eq. (4) gives

$$\frac{dA}{dt} = -3(2)^{6/n}\left(\frac{n}{2n+1}\right)\left(\frac{\sigma}{\eta_0}\right)^{1/n}\lambda^{-(n+3)/n}A^{1/n}h^{(2n+1)/n} \tag{6}$$

which is the general expression for the rate of leveling, i.e., the rate of decrease of the amplitude for power-law fluids.

For Newtonian fluids, $n = 1$, and integration of eq. (6) gives

$$t = [2.303/(2)^6](\eta_0/\sigma)(\lambda^4/h^3)\log_{10}(A_0/A) \tag{7}$$

where A_0 is the initial amplitude, and t is the time required for the coating to level from A_0 to A.

For non-Newtonian fluids, $n \neq 1$, integration of eq. (6) gives

$$t = [3(2)^{6/n}]^{-1}[(2n+1)/(1-n)](\eta_0/\sigma)^{1/n}\lambda^{(n+3)/n} \times h^{-(2n+1)/n}(A^{-(1-n)/n} - A_0^{-(1-n)/n}) \tag{8}$$

For the special case of $n = 0.5$, eq. (8) becomes

$$t = [1/3(2)^{10}](\eta_0/\sigma)^2\lambda^7 h^{-4}(A^{-1} - A_0^{-1}) \tag{9}$$

For fluids having yield stress, part of the driving force for leveling (the surface tension force) is used to counteract the yield stress. The effective surface tension then becomes $\sigma - \sigma'$, where σ' is the part of the surface tension counteracting the yield stress and is given by[2]

$$\sigma' = \tau_0\lambda/8\pi^3 Ah \tag{10}$$

where τ_0 is the yield stress. Thus, for fluids having yield stress, the surface tension σ should be replaced with $\sigma - \sigma'$ in the above equations. In particular, for Bingham fluids, eq. (7) becomes

$$t = [2.303/(2)^6][\eta_0/(\sigma - \sigma')](\lambda^4/h^3)\log_{10}(A_0/A) \tag{11}$$

COMBINED SAGGING, SLUMPING AND LEVELING

Newtonian Fluids

We previously defined the distance traveled by a surface element in time period t during sagging as the sag length s_0 given by (1)

$$s_0 = t(\rho g/2\eta_0)h^2 \tag{12}$$

where ρ is the coating density and g is the gravitational acceleration. Combining eqs. (7) and (12) gives

$$\log_{10}(A_0/A) = [(2)^7/2.303][(\sigma/\rho g)(h/\lambda^4)s_0 \tag{13}$$

which relates the sag length to the extent of leveling.

Bingham Fluids

We have previously established that for a coating to be nonsagging and nonslumping, the yield stress should be[1]

$$\tau_0 = \rho gh \tag{14}$$

Combining eqs. (10) and (14) gives

$$A_f = \rho g\lambda^3/8\pi^3(\sigma - \sigma') \tag{15}$$

where A_f is the final amplitude for the wavelength λ, i.e., when the amplitude decreases to A_f, the leveling will cease.

Power-Law Fluids Without Yield Stress

We previously established that the sag length for power-law fluids without yield stress is[1]

$$s_0 = t[n/(n+1)(\rho g/\eta_0)^{1/n} h^{(n+1)/n} \tag{16}$$

Combining eqs. (8) and (16) gives

$$A^{-(1-n)/n} - A_0^{-(1-n)/n} = 3(2)^{6/n}\left(\frac{1-n^2}{n(2n+1)}\right)\left(\frac{\sigma}{\rho g}\right)^{1/n} \lambda^{-(n+3)/n} h s_0 \tag{17}$$

For the special case, $n = 0.5$, eq. (17) becomes

$$1/A - 1/A_0 = 9(2)^{10}(\sigma/\rho g)^2 \lambda^{-7} h s_0 \tag{18}$$

APPLICATIONS

Newtonian Fluids

Consider a coating of 2 mils thickness, 1 g/cm^3 density, and 40 dyn/cm surface tension. Let the initial amplitude be 2.5×10^{-4} cm. We require that the final amplitude to be less than 0.25×10^{-4} cm to be adequately smooth and the sag length be less than 0.1 cm. These are typical of practical systems, not arbitrary numbers. Thus, from eq. (13), we find that those roughnesses with wavelengths smaller than 0.2 cm will level adequately, but those with wavelengths greater than 0.2 cm will not level adequately. We thus conclude that for Newtonian fluids, the initial roughness should have wavelengths smaller than about 0.2 cm to be able to level adequately when the sagging is adequately controlled.

On the other hand, high solid coatings with Newtonian rheology are not suitable for spray applications. To be properly sprayable, the viscosity should be about 1 poise at the spray shear rate (about 2500 sec^{-1}). For Newtonian fluids, at this viscosity, a 2 mil coating of density 1 g/cm^3 and surface tension 40 dyn/cm will sag 8 cm in 10 min (or 0.8 cm in 1 min). This is quite unsatisfactory. Only if the coating can gel (by crosslinking or other mechanisms) in less than one minute, can the sagging be adequately controlled.

Bingham Fluids

Consider again a typical coating of density 1 g/cm^3, and surface tension 40 dyn/cm. From eq. (15), we find that only those roughnesses with wavelengths smaller than 0.06 cm can level adequately, when the yield stress is sufficiently high to prevent sagging and slumping. We have experimentally determined that those wavelengths between 0.1–0.5 cm tend to cause the undesirable appearance known as orange peel. Thus, we conclude that when the yield stress is high enough to prevent sagging and slumping, the coating will have extensive orange peel appearance.

Pseudoplastic Fluids

Consider again a coating of 2 mils thickness, 1 g/cm^3 density, and 40 dyn/cm surface tension. Let the initial amplitude be 2.5×10^{-4} cm, and the final amplitude less than 0.25×10^{-4} cm to be adequately smooth. Equation (17) is thus plotted numerically for these conditions, as shown in Figure 2. $\lambda_{\max}$ is the maximum wavelength of the surface roughness which will level adequately. All wavelengths greater than $\lambda_{\max}$ will not be able to level adequately.

We previously established that the power constant n should be less than about 0.6 for a coating to have both good sag control and good sprayability.[1] Taking $n = 0.5$, from Figure 2, we see that those roughnesses with wavelength greater than about 0.1 cm will not level out adequately, when good sag control and good sprayability are obtained simultaneously. Thus, we conclude that it is very difficult to achieve good sag control, good sprayability and good leveling simultaneously in high solid coatings. The optimum is for the power constant to be about 0.5 and the viscosity at 1 sec^{-1} to be about 50 poises. Even at this optimum condition, some orange peel appearance will result. This slight orange peel may not be objectionable, and may be eliminated by improved spray atomization and certain solvent and gelation controls.

COMPARISON WITH EXPERIMENTS

We will show below that the above theoretical results are consistent with experimental results.

Materials

The three sprayable high solid coatings of the preceding paper[1] are used. Their rheological properties conform to the power-law equation, as given in Table I and also in the preceding paper.[1] No thixotropic (time-dependent behavior) is observed.

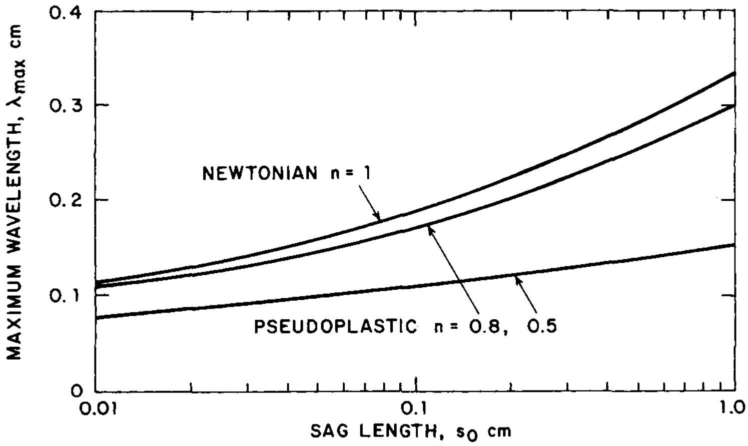

Fig. 2. Maximum wavelength $\lambda_{\max}$ for leveling as functions of sag length s_0 and power-law constant n for a 2 mil coating, 1.0 g/cm^3 density, 40 dyn/cm surface tension, initial amplitude 2.5×10^{-4} cm, final amplitude 0.25×10^{-4} cm. Those roughnesses having wavelengths greater than $\lambda_{\max}$ cannot level adequately.

TABLE I

Rheological Properties of Three Experimental High Solid Coatings and Their Sag-Leveling Data (10 min at 25°C)

Code	Characteristics	n	η_0 poise	ρ g/cm^3	σ dyn/cm	h mil	$\bar{\lambda}$ cm	s_0[a] cm	hs_0 cm^2
N-3	Newtonian	1.0	0.95	1.119	41.4	0.50	0.40	0.48	0.240
						0.82	0.58	1.40	1.148
						1.25	0.78	3.60	4.500
P-2	Pseudoplastic	0.75	7.2	1.117	41.8	0.85	0.26	0.20	0.170
						1.10	0.31	0.24	0.264
						1.60	0.38	0.52	0.832
						2.52	0.46	1.60	4.03
						3.00	0.64	2.20	6.60
P-3	Pseudoplastic	0.50	50	1.123	42.2	4.2	0.23	0.15	0.630
						5.8	0.26	0.30	1.740
						6.5	0.26	0.35	2.275
						8.7	0.31	0.82	7.134

[a] The sag lengths are interpolated from the experimental data given in Figure 13 of the preceding paper.[1]

Leveling Experiments

The high solid coatings are sprayed with compressed air onto smooth, 4 in. × 12 in. aluminum panels. The thickness of the coating is measured gravimetrically. The coatings are left in the horizontal position to level for 10 min at 25°C. Then, the coatings are cured by UV radiation. The UV radiation gels the coating in a few seconds. Final curing is done by baking at 250°F for 15 min. During the UV and the heat curing, the surface topography of the coating is not detectably changed.

The surface topography of the cured coatings is measured with a SURFANALYZER (Model 21, Gould Inc., 3631 Perkins Ave., Cleveland, Ohio 44114). The average wavelength of the surface undulations is thus obtained.

Results

The results of the leveling experiments are given in Table I. In order to compare the experimental results with theory, it is necessary to relate the average wavelength $\bar{\lambda}$ to the characteristic parameters of the system. This is done as following.

Actual surfaces are composed of undulations of various wavelengths. These undulations superimpose to form the real surfaces. Each undulation undergoes the leveling according to eq. (6). Those undulations with small wavelengths will level faster than those with long wavelengths, as evident from eq. (6). Consequently, as the leveling proceeds, the average wavelength of the surface undulations will appear to grow. From eqs. (13) and (17), the wavelength of a given undulation may be written

$$\lambda = (\beta/\alpha)^{n/(n+3)}(hs_0)^{n/(n+3)} \tag{19}$$

where $\alpha = \alpha(n,A,A_0)$ and $\beta = \beta(n)$. The average wavelength $\bar{\lambda}$ is thus given by

$$\bar{\lambda} = \frac{\sum \lambda_k}{\sum m_k} = \frac{\sum (\beta_k/\alpha_k)^{n/(n+3)}}{\sum m_k}(hs_0)^{n/(n+3)} \tag{20}$$

where m_k is the number of undulations with wavelength λ_k. If the leveling proceeds to the extent that β/α is roughly constant, then eq. (20) becomes

$$\bar{\lambda} = C(hs_0)^{n/(n+3)} \tag{21}$$

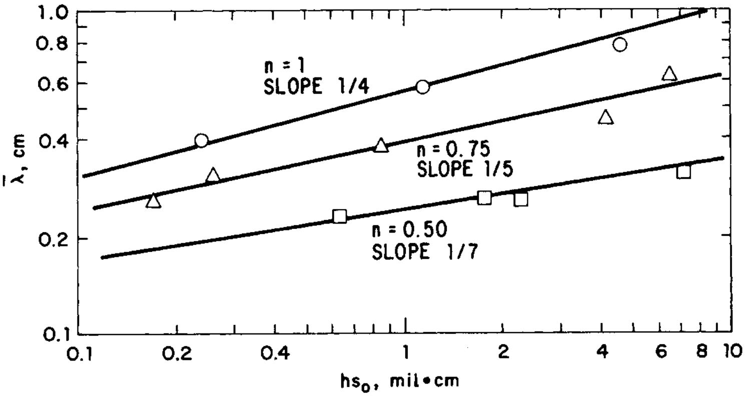

Fig. 3. Plots of log$\bar{\lambda}$ vs log(hs_0) for three high solid coatings of $n = 1.0, 0.75$, and 0.50, showing that the slopes conform to the theoretical values of $n/(n+3)$; data from Table I.

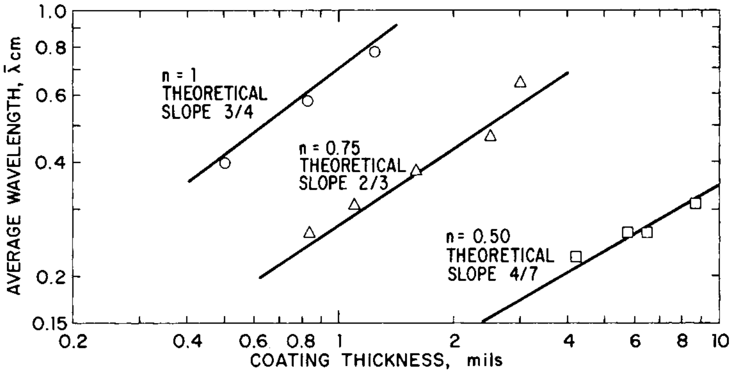

Fig. 4. Plots of $\log\bar{\lambda}$ vs $\log h$ for three high solid coatings of n = 1.0, 0.75, and 0.50, showing that the slopes conform to the theoretical values of $(2n + 1)/(n + 3)$; data from Table I.

where C is a constant. Thus, a plot of $\log\bar{\lambda}$ vs $\log(hs_0)$ will give a straight line with a slope of $n/(n + 3)$. This is indeed found to be true, as shown in Figure 3.

On the same token, from eqs. (7) and (8), it can be seen that the average wavelength is related to the coating thickness and time by

$$\bar{\lambda} = C't^{n/(n+3)}h^{(2n+1)/(n+3)} \tag{22}$$

where C' is a constant. Thus, a plot of $\log\bar{\lambda}$ vs $\log h$ will give a straight line with a slope of $(2n + 1)/(n + 3)$, when t is constant. This is indeed found, as shown in Figure 4.

CONCLUSION

The rheology of combined sagging and leveling of high solid coatings is analyzed in terms of non-Newtonian power-law model. The results indicate that good leveling with good sag control and good sprayability can be obtained only when the high solid coating has a pseudoplastic rheology with a power constant n of about 0.5 and a viscosity at 1 sec^{-1} of about 50 poises at the temperature of interest. Any deviations from this optimum conditions will tend to result in extensive sagging or extensive orange peel appearance. Any yield stress must be kept to a minimum, perhaps less than 1 dyn/cm^2; otherwise extensive orange peel appearance will result. The theoretical relations developed are confirmed experimentally.

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