

Rheology of Melts and Solutions Part 2: Viscoelasticity, Temperature, and Surface Flow

by Clifford K. Schoff, Schoff Associates*

This article continues the discussion of rheological behavior of polymer melts and solutions that was begun in Part 1 (JCT CoatingsTech, August 2007). It begins with a discussion of viscoelasticity of concentrated solutions, mainly in terms of qualitative ways to discern elastic behavior, but references for quantitative methods are also given. The coverage of viscosity-temperature effects includes both the Arrhenius relationship (Andrade's equation) and the Williams-Landel-Ferry treatment. The latter does a better job of relating viscosity and temperature for many coatings. The influence of solvents on rheology is mentioned. Surface flows and surface defects are discussed in terms of crater formation, crater edge velocity, surface tension gradients, and the rate of formation of craters. References are given for other defects and flows.

INTRODUCTION

This article deals with the rheological behavior of polymer melts and polymer solutions as related to organic coatings. Part 1 discussed melt and solution viscosity and described methods of measurement. Part 2 covers viscoelasticity of concentrated solutions, viscosity-temperature effects, influence of solvents on rheology, surface flows, and surface defects. The discussion is brief, but a number of references are given for additional study.

VISCOELASTICITY OF CONCENTRATED SOLUTIONS

Another aspect of rheology is viscoelasticity. Polymers and many of their solutions are elastic as well as viscous. Paint technologists try to avoid fluid elasticity, but do not always know that is what they are doing. They are concerned whether their paints apply properly at the

solids necessary to meet regulatory restrictions on VOC levels. In order to do this, it is well known that it is wise to avoid resins with high molecular weight "tails" in their molecular weight distributions, that the fastest (highest evaporation rate) solvents had better not be the only good solvents for the resins in the formula, and that too much structure in the paint is bad. Breaking these rules is likely to result in paints that produce spits or strings and cobwebs on spraying, are ropey or give misting/splattering on roll-coating, suffer severe orange peel, or exhibit other problems. What is not so well known is that the cause of these problems usually is fluid elasticity. Whereas viscosity is a measure of the resistance of a material to permanent deformation under stress, i.e., flow, elasticity is reversible deformation such that the deformed body returns to its original shape as in the snap-back of a rubber band.

Measurement of paint elasticity is not an easy matter (and there is no good method for measuring elasticity at high shear). Conventional viscometers measure only the viscous component even if the fluid is quite viscoelastic. This is because motion is only in one direction and the torque necessary to produce the motion is not affected by elasticity unless that component is very large (in which case the problem will be obvious). Oscillatory motion, creep measurement, or stress relaxation is necessary to measure elasticity. A number of research viscometers are capable of making such measurements, but they are expensive and rarely found outside large paint companies and a few universities. What can smaller laboratories and companies do? It turns out that careful qualitative methods can be very useful in this area. Examples include noting the forcing apart of a cone and plate during viscosity measurements, or the climbing of a resin or paint up the stirrer shaft during polymerization or mixing (both examples of the Weissenberg effect).

Another technique is to observe with a microscope the amount of swell in diameter of a stream of paint or other material extruded from a syringe. The greater the swell, the more viscoelastic is the fluid. Useful semi-quantitative

*4736 Magnus Dr., Allison Park, PA 15101.

measurements have been made with this method. With high-solids resins, paints (particularly after partial loss of volatiles on spraying or during the bake), or polymer melts, elasticity can cause chattering or bucking of the cone on a cone/plate viscometer. Good batches or components will give normal measurements, whereas elastic ones will give no measurable values, erratic ones, or very high values. Yet another way to look for elasticity is to observe behavior during bubble tube viscosity measurements of polymer solutions. A pointed tail in the rising bubble indicates elasticity. None of the rolling ball techniques discussed in Part 1 measure elasticity as such, but elasticity does affect the ball velocity. In addition, the path of the ball may show snap-back along the sides of the groove if the coating is elastic.

The use of oscillatory measurements, creep experiments, and stress relaxation in characterizing viscoelastic fluids is described in detail in the literature¹⁻⁵ and will not be discussed here.

VISCOSITY-TEMPERATURE EFFECTS

The dependence of viscosity on temperature is critical to the handling of molten polymers in molding, extrusion, and other manufacturing processes. In fact, the drop in viscosity with increasing temperature makes these operations possible. A similar decrease in viscosity occurs with most resin solutions and paints and is the reason that viscous products can be hot sprayed (and also is the reason that hot sag occurs). Therefore, viscosity-temperature relationships are important. Data for many polymers can be found in the literature,⁶⁻⁸ but paint viscosity dependence usually must be established via viscosity measurements over a range of temperatures.

The temperature dependence of viscosity for many paints, polymer solutions, and polymer melts at temperatures considerably above T_g approximates an exponential function of the Arrhenius type such that $\eta = A \cdot e^{B/T}$ or $\eta = A \cdot 10^{B/T}$ where A and B are constants and T is the absolute temperature in Kelvin. This relationship is called Andrade's equation and has been found to work well for a number of low molecular weight resin solutions, particularly alkyds.⁹⁻¹³ Estimation of the viscosity of a paint at a given temperature requires the knowledge of the viscosity at two different temperatures that bracket the temperature of interest. This allows the calculation of the constants A and B and subsequent determination of viscosities at other, intermediate temperatures.

Andrade's equation may be expressed in logarithmic form, $\log \eta = \log A + B/T$, which for two temperatures becomes

$$\log (\eta_1/\eta_2) = B(1/T_1 - 1/T_2)$$

Plots of $\log \eta$ versus $1/T$ tend to result in straight lines over a considerable range of temperatures. This allows the construction of a nomogram such as the one in Figure 1.⁹⁻¹⁰ The viscosity at an intermediate temperature (say, 35°C) is determined from the known viscosities at two other temperatures (15 and 45°C) by drawing straight lines connecting the viscosities and corresponding temperatures (the solid lines in Figure 1). The intersection of the lines gives the pivot point. The viscosity at 35°C was determined on the nomogram by drawing a dashed line through that temperature and the pivot point.

Andrade's equation holds for many paints and polymer solutions and for polymer melts well above their glass transition temperatures (T_g). For polymers closer to the T_g and for high-solids paints and concentrated polymer/oligomer solu-

tions, the Williams-Landel-Ferry (WLF) treatment does a better job of relating viscosity and temperature.¹¹⁻¹³ With the proper choice of reference temperature T_s (in Kelvin), the ratio of viscosity, η , to the viscosity at the reference temperature, η_s , can be expressed by a single universal equation:

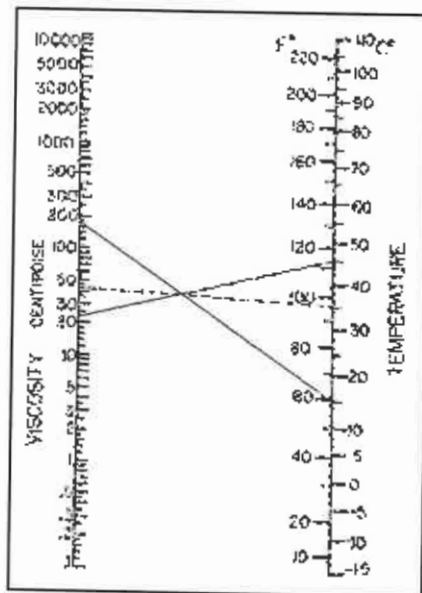
$$\log (\eta/\eta_s) = \frac{-8.86 (T - T_s)}{101.6 + (T - T_s)}$$

where T_s often is defined as the T_g or $T_g + 50^\circ\text{C}$. The WLF equation is considered to hold from the T_g to a temperature 100°C above that point. A form of the equation that has been shown to work for coatings is¹²⁻¹³

$$\ln \eta = 27.6 - \frac{A(T - T_g)}{B + (T - T_g)}$$

where the reference temperature is the T_g and the viscosity at the T_g is assumed to be 10^{15} mPa.s (= cP.s). As paints and resins move to higher and higher solids, it is important to know that the higher the concentration, the greater the reduction in viscosity with increasing tempera-

Figure 1—Viscosity-temperature nomogram for Andrade's equation.⁹



ture. The increased sensitivity to temperature is caused by the reduction in solvent, not by the reduction in the molecular weight of the polymer.¹⁴

Some waterborne paints do not show viscosity decreases with increasing temperature, and, in fact, exhibit viscosity increases. This presumably is due to the absorption of solvent by micelles or latex particles with increasing temperature leading to increases in particle size, which increases particle-particle interactions and, therefore, the viscosity.

INFLUENCE OF SOLVENTS ON RHEOLOGY

Solvents can have a considerable effect on rheology. The continuous phase in solventborne paints is a resin-solvent solution that is affected by the viscosity of the solvent blend and by resin-solvent interactions. In a waterborne coating, inclusion of different solvents can influence the extension or retraction of polymer chains to form a clear "solution" or a white latex-like dispersion with very different viscosity behavior. Some solvents will body or even gel a waterborne paint and can turn a free flowing waterborne clear into an elastic, glutinous mess more suited to forming cobwebs than spraying properly. Solvent borne paints are not immune from such problems. Formulations with badly designed solvent blends containing good solvents that flash off during application and/or poor tail-end solvents will give an unacceptable appearance due to insufficient flow or elasticity, or both.

In low-solids resins and paints, solvent viscosity and polymer-solvent interactions usually can be ignored. If the viscosity is too high, the formulator just adds more solvent. In high-solids products, viscosity must be minimized without using additional solvent. Solvent viscosity and interactions with other components become very important. Changing to a solvent blend with

Table 1—Solution Viscosities of a High Solids Acrylic Resin in Solvents with Different Viscosities (Solvent Concentration = 3.3 lb/gal of Solution.)

Solvent	Viscosity, cps	Viscosity, cps
MPK	0.50	80
MIBK	0.59	110
Ethyl acetate	0.44	121
MAK	0.80	147
Isopropanol	2.41	198
n-Butyl acetate	0.74	202
Toluene	0.59	290
Xylene	0.67	387
IBIB	0.83	387
Cellosolve acetate	1.3	440

Source: DuPont Eastman Chemical.

twice the viscosity of the original blend will not necessarily double the viscosity of the resin or paint, but it will raise it considerably. This increase is most noticeable as a raising of the high shear viscosity "floor," the relatively low viscosity that occurs at high shear rates, which is an indication of the ease of pumping, metering, and application. Therefore, using a low-viscosity solvent blend can improve handling and application properties.

Unfortunately, because of resin-solvent interactions, it is difficult to predict resin or paint viscosities from the viscosity of the solvent blend. This is illustrated in Table 1, which contains data from viscosity measurements on a high-solids acrylic resin.¹ The lowest solution viscosities were found with low viscosity solvents, but other solvents with low viscosities gave fairly high solution viscosities. However, it is well worth trying lower viscosity solvents if a lower application viscosity is needed.

SURFACE FLOWS AND SURFACE DEFECTS

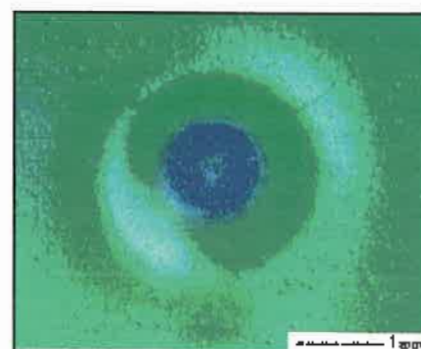
After paint has been applied and a coating has formed, a number of flows are possible. Leveling of brush

marks, roller patterns, or spray droplets begins immediately. Sagging may occur on vertical surfaces, but will not be noticeable right away. Surface-tension driven defects such as craters, sinks and bumps, Bénard cells (convection flow), dewetting, and fat edges may appear, usually very rapidly. The main driving force for leveling is surface tension as it acts to reduce the surface to a minimum. Sagging is gravity-driven flow. Both of these flows are covered in detail in the literature^{1,3,15-19} along with many other aspects of the rheology of coatings.

All wet paint films experience surface flows, but high-solids clearcoats probably suffer more defects because there is so little resistance to flow even after all the solvent is gone. Their Newtonian nature allows them to flow and level very well, thereby producing smooth, high-gloss coatings. However, they have less resistance to sagging and surface tension-related defects such as cratering, dewetting, telegraphing, and picture framing.

Surface flows other than leveling have not received much coverage in the coatings literature. Let us use a crater such as that shown in Figure 2 as an example of surface flow and apply one of the equations of Fink-Jensen.¹⁹ Craters form when a low surface tension contaminant is on

Figure 2—Crater with a distinct rim. This defect was formed by flow driven by surface tension gradients.



the substrate, is in the paint (and comes to the surface), or falls on the paint. There is flow from the area of low surface tension to the areas of higher surface tension. The velocity of the wave front, i.e., the crater edge, is

$$v = (\partial\gamma/\partial x) (h/\eta)$$

where $\partial\gamma/\partial x$ is the surface tension gradient (the driving force for flow), which is the difference in surface tension ($\partial\gamma$) over a distance (∂x), h is the wet film thickness, and η is the viscosity.

Let us see if we can calculate the velocity. We can measure or estimate the initial wet film thickness, h , and the initial viscosity after application, η . Let us assume that we have a clearcoat of initial wet film thickness of 100 μm (4 mils) and a viscosity after application of 0.5 Pa.s (500 cPs). Unfortunately, we do not know or even have a good estimate of $\partial\gamma/\partial x$, the surface tension gradient. The difference in surface tension probably is between 1 and 10 dynes/cm. The distance over which this distance occurs may be as little as 0.1 mm or as large as a few mm. These numbers give a range of possible values for the gradient of roughly 1 to 1000 dynes/ cm^2 , which is not much help. Fortunately, there are some data in the literature on the velocity of spreading of one liquid over another and the velocity of crater edges:

- Isobutanol on water spread very rapidly with a maximum velocity of 48 cm/s (480,000 $\mu\text{m/s}$). The velocity dropped as water was added to the butanol or butanol was added to the water (thereby increasing the solubility of one liquid for the other), but the maximum still was greater than 20 cm/s.²⁰

- Spreading velocities of surfactants on water ranged from 1 to 30 cm/s. The spreading speed was inversely proportional to the MW of insoluble surfactants.²¹

- The rate of increase in radius of a crater formed by placing a 0.5 mm diameter drop of silicone oil on a 75% glycerol/25% water film was²²:

$$\begin{aligned} &\sim 8 \text{ mm/s at } 0.25 \text{ s (8000 } \mu\text{m/s)} \\ &\sim 5.5 \text{ mm/s at } 0.5 \text{ s (5500 } \mu\text{m/s)} \end{aligned}$$

- The rate of increase in radius of a crater formed by placing a 110 μm diameter drop of silicone oil on an alkyd-amino varnish was²²:

$$\begin{aligned} &\sim 1.6 \text{ mm/s at } 0.5 \text{ s (1600 } \mu\text{m/s)} \\ &\sim 1.0 \text{ mm/s at } 1 \text{ s (1000 } \mu\text{m/s)} \end{aligned}$$

- In other research, the formation of craters in clearcoat was recorded via a video camera with a computer as the recorder.²³ Craters were made by placing a drop of a spray lubricant on a wet film that had been made by drawing down and flashing (5 min) an automotive acrylic clear that had been sprayed on a panel and allowed to run off into a jar. The crater crest or rim velocities were:

$$\text{Elapsed Time} = 0.1 \text{ s, velocity} \cong 12 \text{ mm/s} = 12000 \mu\text{m/s}$$

$$0.25 \text{ s, } v \cong 2 \text{ mm/s} = 2000 \mu\text{m/s}$$

$$0.5 \text{ s, } v \cong 1 \text{ mm/s} = 1000 \mu\text{m/s}$$

$$1.0 \text{ s, } v \cong 0.6 \text{ mm/s} = 600 \mu\text{m/s}$$

$$2.0 \text{ s, } v \cong 0.3 \text{ mm/s} = 300 \mu\text{m/s}$$

Although the velocities are lower than those of surfactants and other materials on water listed above, they still are high and are very comparable to those for silicone oil on a varnish. The higher viscosity of paints and varnishes compared to water undoubtedly is responsible for the difference.

Substituting the initial velocity of the acrylic crater into Fink-lensen's equation gives a very large gradient of 60 Pa (600 dyn/ cm^2). This high value presumably is due to the operation of a moderately large surface tension difference over a very short distance, say 6 mN/m (6 dyn/cm) over 0.1 mm. Such values

definitely are possible and initial gradients of 100 Pa (1000 dyn/ cm^2) undoubtedly are common.

Although initial crater front velocities are high, what does this mean in terms of how long it takes to form a crater? In the experiments mentioned above, the crater diameter reached 2 mm in 4 s for the varnish, and in 1 s for the acrylic. A crater may grow for several seconds, but will be noticeable in a very short time. This has implications for adding rheology modifiers to paints to prevent or reduce cratering. Unless the additive raises viscosity very rapidly after application, it will have little or no effect except perhaps to cause enough orange peel to mask the craters.

References 24–30 provide additional insights into surface defects and surface flows.

CONCLUSIONS

Melts and solutions are only part of the total picture of coatings, but knowledge of their behavior is useful in formulation, manufacturing, and problem solving. Certainly, control of their rheology and the ability to characterize their behavior is important. The body of literature concerning these materials is very large and may appear daunting, but references 1–7, 15, and 31–32 offer good places to start.

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