

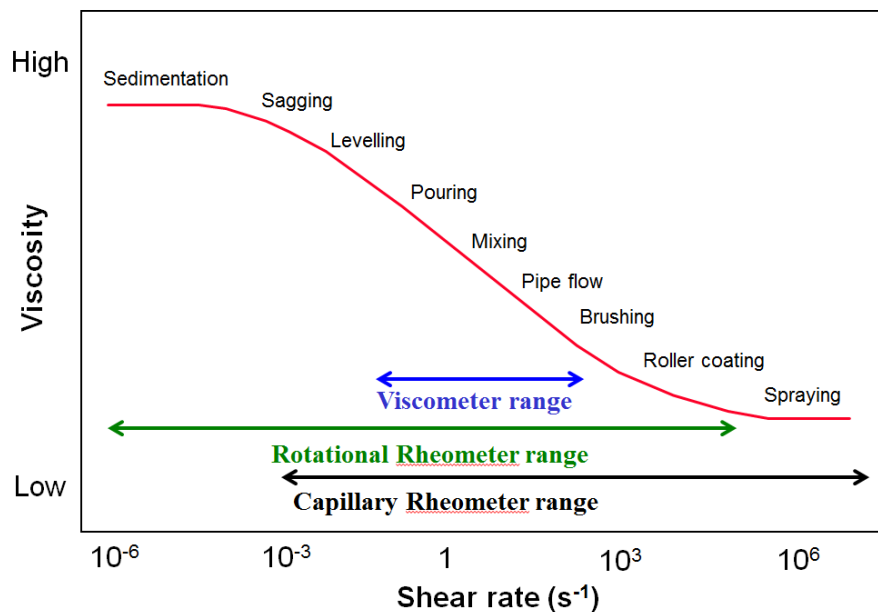
# Optimizing Rheology for Paint and Coating Applications



## RHEOLOGY AND VISCOSITY

## INTRODUCTION

Paints or coatings, like many commercial products, must be optimized for their end use performance, which for paints and coatings includes leveling behavior, pigment dispersability, sag resistance, applicator loading and film thickness, all of which depend on a coatings rheological behavior. Each of these processes will have an associated shear stress, shear rate and timescale, with temperature another potential variable. For Newtonian materials where viscosity is independent of applied shear stress then temperature is the main variable, however, to provide the requisite functionality most paints and coatings tend to be non-Newtonian, where viscosity is a function of the applied shear stress or shear rate.



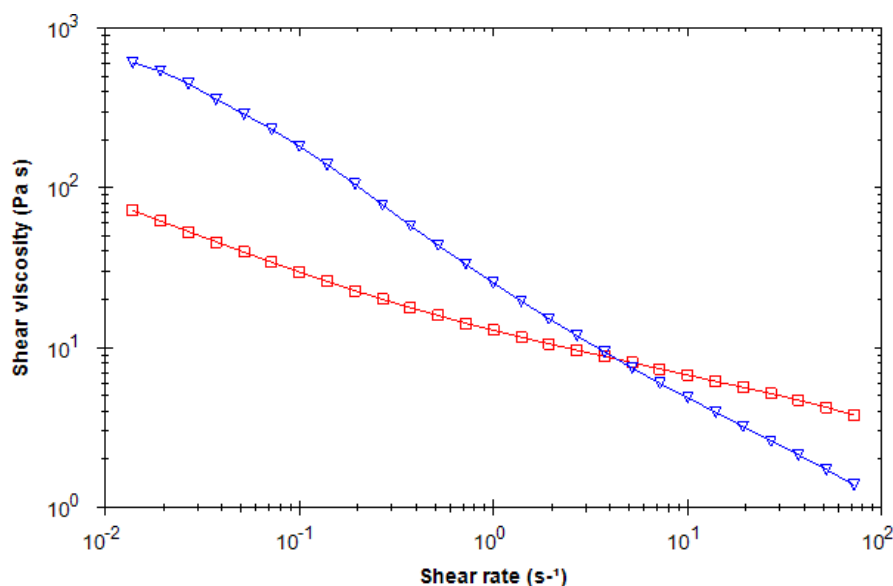
**Figure 1 – Typical shear rate ranges encountered during common coating processes**

For such systems a single value of viscosity measured at an arbitrary rotational speed or shear rate is insufficient to describe the rheological properties of a

coating, and unless the shear stress or shear rate has been carefully selected or calculated with a specific application or process in mind, it cannot be associated with such. While it can sometimes be difficult to link a rheological measurement with a real in-situ process or application, especially when there are various environmental factors to be considered, making measurements at an appropriate shear stress or shear rate allows for a more relevant comparison [1,2].

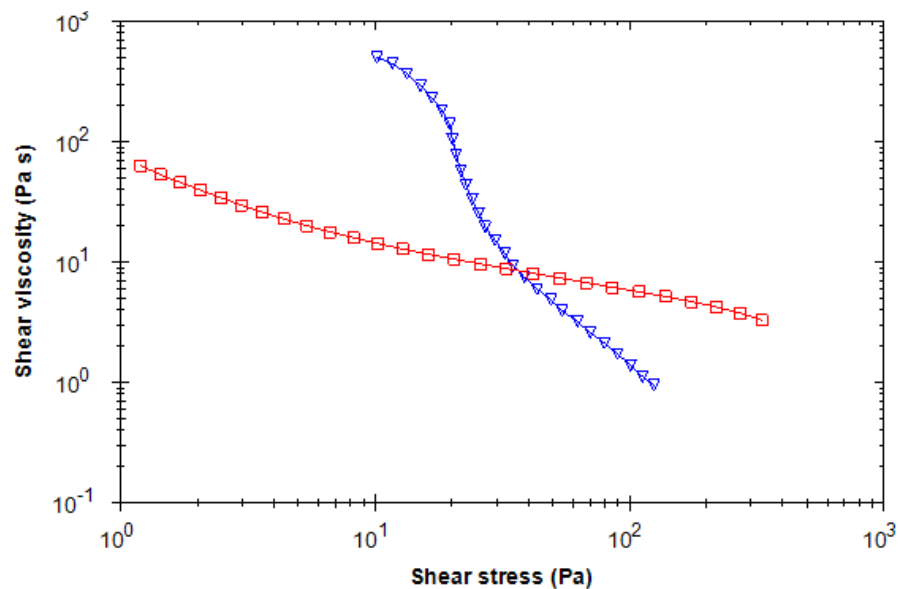
This point is illustrated in figure 1 which shows a flow curve and the corresponding shear rate ranges associated with various processes. All of the listed processes are important, albeit to different extents, and the ideal scenario would be to have the optimum viscosity at each shear rate to meet all performance requirements. Figure 2 shows flow curves for two commercial gloss paints. Based on the criteria illustrated in figure 1 this would indicate that Paint A would be more stable to sedimentation and less likely to sag due to its higher low-shear viscosity while Paint B would most likely result in a thicker paint layer on brushing due to its higher high-shear viscosity.

Clearly single point viscosity measurements could not provide the information required to describe the complex rheological behavior of such non-Newtonian paints. A rotational rheometer with the appropriate measurement system and test settings can however access a broad range of representative shear rates, typically up to  $10,000 \text{ s}^{-1}$  depending on the sample. For higher shear rates a capillary rheometer may be required.



**Figure 2 – Log Viscosity plotted against log shear rate for two gloss paints**

Although viscosity curves in figures 1 and 2 are plotted as a function of shear rate, it is sometimes better to plot data as a function of shear stress to make a proper comparative assessment; particularly as many processes are stress controlled or stress driven. Such a plot is shown in figure 3 for the two commercial paints and highlights key differences that would not be easily apparent when plotted against shear rate.



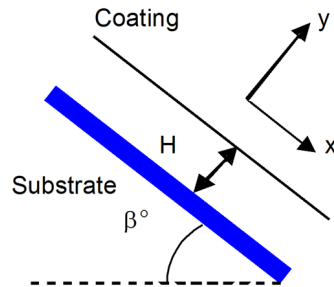
**Figure 3 – Log Viscosity plotted against log shear stress for two gloss paints**

Taking sedimentation, sagging and leveling as examples, the main driving force for these processes is gravity so clearly a stress driven process, with the resultant shear rate dependent on the viscosity at these stresses as well as other contributory factors such as surface tension in the case of leveling. Although all flow processes are the result of an applied stress, it is often necessary or sometimes habitual to control the rate of a flow process, with the stress input being that required to maintain flow at the desired shear rate. For example, when manually pouring or stirring paints the likelihood is that the applied stress will be adjusted for low or high viscosity paints to maintain an optimum pouring or mixing speed. Also in the case of spray paints, it is a necessary requirement that the paint be sprayable and that means being able to apply sufficient stress to give the desired flow rate or shear rate. A more detailed discussion of this subject is given in the excellent review article by Eley [2].

In the remainder of this document we will focus on specific performance criterion such as sagging, leveling and stability with intermittent discussions about the properties controlling such behavior and measurements required to assess them such as yield stress, thixotropy and viscoelasticity.

## SAGGING

Sagging is due to the action of gravitational forces on a coating applied to an inclined surface as shown in Figure 4. This results in a linear stress distribution across the coating that is maximum at the substrate interface and zero at the air interface.



$$\sigma_{max} = \rho g h (\sin \beta)$$

$$\dot{\gamma}_{max} = \rho g h (\sin \beta) / \eta$$

**Figure 4 – Illustration showing the origins of ‘sagging’ and associated expressions for shear stress and shear rate**

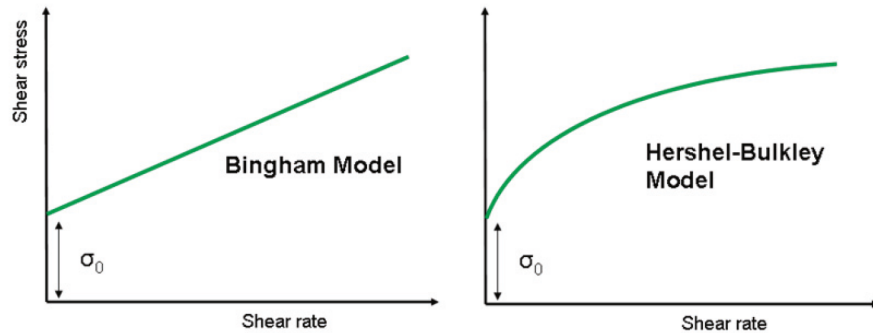
Gravitational stresses will increase with film thickness, density and incline, with the highest shear stress occurring on a vertical plane. The maximum shear rate will occur at the substrate interface and will be dependent on the viscosity at the corresponding shear stress.

To reduce sagging it is therefore necessary to increase the viscosity at the corresponding shear stress, which will slow the process, ideally until the film has dried sufficiently. To prevent sagging (no flow) then the viscosity would have to be infinite and hence solid-like under such stress conditions. This criterion can be met if the coating has an apparent yield stress that exceeds the maximum stress at the substrate. Below the yield stress the coating will display solid-like behavior due to micro-structural associations or interactions that result in an effective elastic network. This network is broken down above the yield stress meaning that the same material can also flow when it needs to for brushing as an example.

## YIELD STRESS

There are various methods for estimating yield stress as discussed in a Malvern whitepaper and recent article on the subject [3,4]. The most appropriate method is one that best represents the process you are trying to predict. Often yield stress measurements can be classed as either static or dynamic. Static yield stress relates to the stress required to initiate flow from a state of rest, while dynamic yield stress relates to the stress required to go from a flow to a rest state.

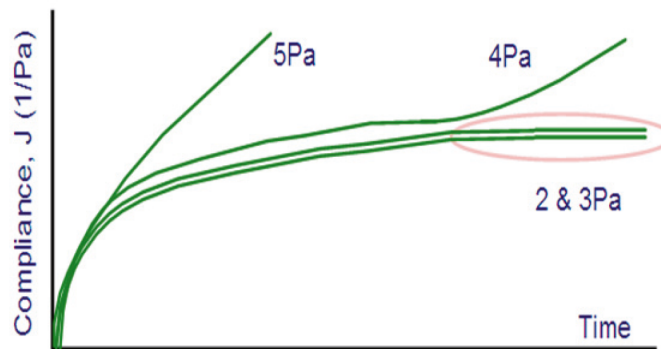
The best way to determine a value for the dynamic yield stress is fitting a flow curve with an appropriate yield stress model such as the Bingham, Casson or Herschel-Bulkley models as illustrated in figure 5. Using this approach you are effectively predicting the onset of solid state behavior from an initial flow state by means of extrapolation. Potential issues and variability with this approach are the range of data included in the model and also whether it gives a representative yield stress value, since under real conditions the structure may continue to evolve (and yield stress increase) once a solid state has been reached, which will depend on the samples thixotropic behaviour. Hence static yield stress measurements may be more representative.



**Figure 5 - Illustration of Bingham and Herschel-Bulkley model fits using linear scaling**

There are a number of methods for estimating the static yield stress including stress ramp, stress growth, creep testing and oscillatory methods. Again the most relevant method is likely to depend on the process you are trying to mimic. In terms of sagging a key variable is time and since non-Newtonian viscoelastic materials relax (dissipate elastic or stored energy) with time of applied stress their elasticity and hence yield stress values will likely reduce with longer tests.

An obvious choice of test then is a multiple creep test, where incremental stresses are applied to a sample for a period of time and the creep compliance (strain/stress) recorded as shown in figure 6. Below the yield stress plots of creep compliance versus time should overlay with a deviation observed above the yield stress. While being an accurate and relevant method it can be a long test which requires multiple iterations.



**Figure 6 - Illustration showing a multiple creep test with yielding at 4 Pa**

Another method which has generated yield values that correlate well with sagging is an oscillatory amplitude sweep test [2]. Here measurements are made in oscillatory mode on a rotational rheometer, where the oscillatory strain amplitude is increased incrementally and the elastic stress ( $\sigma'$ ) or component of the stress associated with  $G'$  (elastic modulus) recorded. By recording  $\sigma'$ , only that stress required to stretch and yield any connected structure is measured i.e. that associated with solid-like behavior.

A peak in the elastic stress indicates the yield point and its value the yield stress as illustrated in figure 7. In oscillatory testing the angular frequency ( $\omega$ ) corresponds with the inverse time of applied stress ( $1/t$ ) hence lower frequencies may be more representative of the sagging process, although as with creep testing this can result in longer tests. For more information on viscoelasticity, see the corresponding section at the end of this paper.

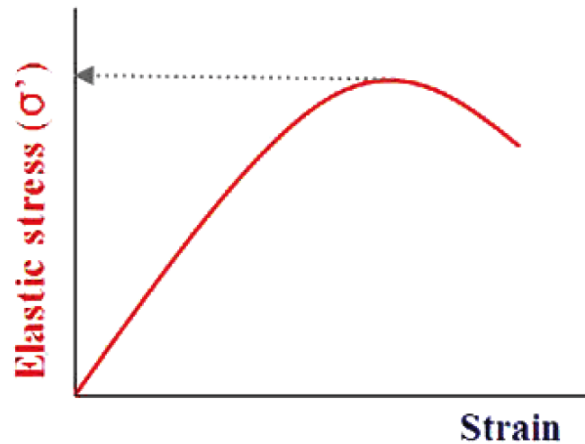


Figure 7 - Illustration showing a common approach for determining the yield stress and strain from an oscillation amplitude sweep

A quicker method which accounts for some time dependency is a stress growth test, which involves applying a constant shear rate and measuring the resultant stress as illustrated in figure 8. The yield point corresponds with the peak stress and its value the yield stress. A recommended shear rate value to use in this test is  $0.01 \text{ s}^{-1}$ , which allows for some relaxation in the material before it yields.

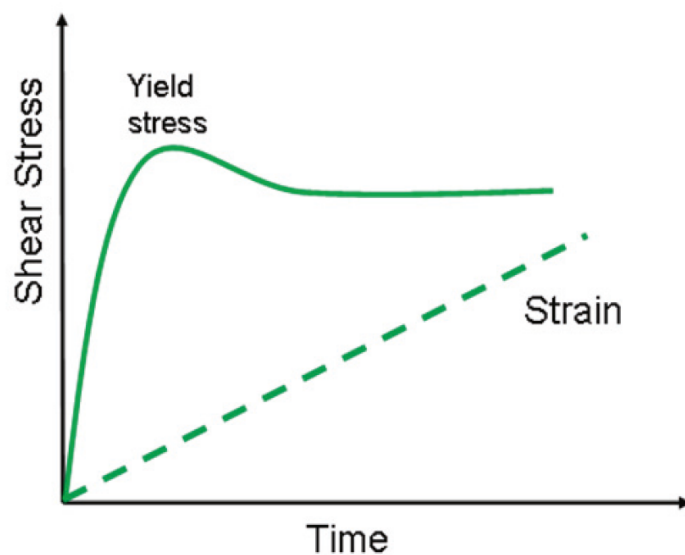


Figure 8 - Illustration showing the stress evolution of a yield stress material at constant shear rate

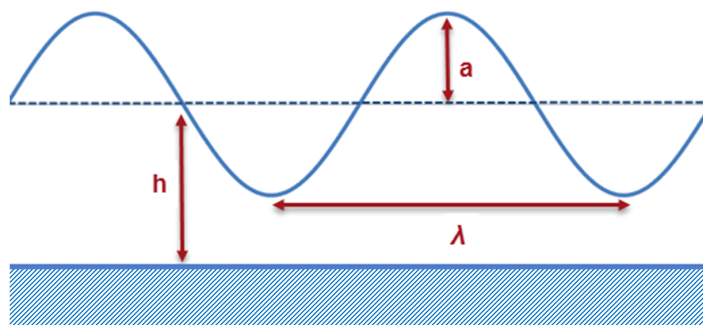
## LEVELLING

Once a coating is applied to a substrate, especially if it has striations resulting from brush marks or the pile profile of the roller, it tends to form an undulated or rippled surface. Subsequent leveling is then driven largely by surface tension forces which try to minimize the area of the free surface and hence produce a uniform film of constant thickness. The rate at which the amplitude of these sinusoidal undulations level out for a Newtonian fluid can be described by the so-called Orchard equation [5],

$$a = a_0 \exp \left\{ -\frac{16\pi^4 h^3 \gamma t}{3\lambda^4 \eta} \right\}$$

$$\frac{da}{dt} = \left\{ -\frac{16\pi^4 h^3 \gamma t}{3\lambda^4 \eta} \right\}$$

with  $a$  the amplitude,  $\lambda$  the wavelength of the sinusoid,  $h$  the coating thickness and  $\gamma$  the surface tension as shown in figure 9. A modified form of the Orchard equation can be written to account for non-Newtonian behavior [6]



**Figure 9 - An illustration showing an ideal sinusoidal profile of an unlevelled film and the equations describing such behavior for a Newtonian fluid**

According to the Orchard equation the amplitude decays exponentially with time as a function of the coating thickness raised to the power of three ( $h^3$ ) and the inverse wavelength raised to the power of four ( $\lambda^{-4}$ ), hence these are the two dominant variables [2]. Since higher application viscosities tend to correlate with thicker coatings then the application viscosity will affect leveling indirectly, since it will result in a higher value of  $h$ . There is also evidence to suggest that higher application viscosities give a smaller striation wavelength which will also drive faster leveling rates [2]. While viscosity as a direct variable is less critical than coating thickness and striation wavelength in the Orchard equation it can still be highly significant if the viscosity is high or if the yield stress exceeds the leveling stresses, in which case no leveling will occur. The maximum leveling stress can be estimated from the following equation and the viscosity corresponding with this stress should be used in the Orchard equation [6].

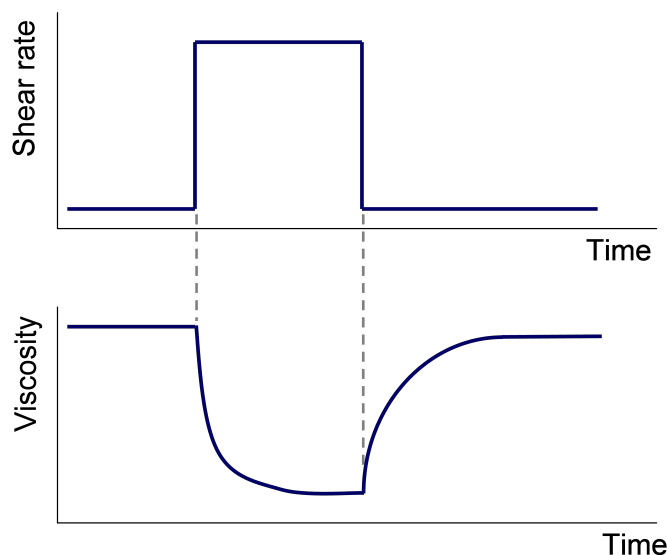
$$\sigma_{max} = 8\pi^3 \gamma a h / \lambda^3$$

## THIXOTROPY

When measuring the ‘flow’ attributes of a paint or coating and also its leveling behavior an important property to consider is thixotropy, which is the time dependent viscosity change under application of shear [7].

Applying shear to a structured material reduces its viscosity if sufficient stress is applied to overcome any associative or randomising forces in the material. In general the breakdown and subsequent recovery of any such structure does not occur instantaneously but can take some finite time - the longer the breakdown or recovery process takes, the more thixotropic the material is. Whether or not thixotropy is beneficial depends on the system and application in question. For example, thixotropy is usually important for paint leveling or coating finish since lower viscosity will facilitate flow out before high viscosity is regained.

This becomes even more critical if the coating has a yield stress, in which case the elastic structure should only reform after leveling is complete. Too much thixotropy, however, may be detrimental as an extended period of low viscosity will enhance sag and possible drip formation, so finding the right balance is important.



**Figure 10 - An illustration showing the response of a thixotropic material to step changes in shear rate**

The most suitable test for assessing thixotropy is a step shear test. Here a low shear rate is applied until a steady viscosity value is attained and then the shear rate is increased stepwise to a value ideally corresponding with the shear rate of interest, such as brushing or rolling. After a period of time under these high shear conditions, the shear rate is dropped back to the initial low value and subsequent recovery followed with time. Thixotropy can then be quantified in terms of the amount of time it takes to recover a percentage of the original viscosity or the amount of recovery attained after a given time. Thixotropic recovery can also be modeled using the stretched exponential model as below, with the time constant  $\tau$  a measure of recovery rate. Here  $\eta(t_0)$  represents the viscosity at the onset of recovery and  $\eta(t_\infty)$  the viscosity after infinite shearing time [7].

$$\eta(t) = \eta(t_\infty) - \left( [\eta(t_\infty) - (\eta(t_0))] \times \left[ 1 - e^{-t/\tau} \right] \right)$$

## STABILITY

Achieving product stability is a critical aspect of a paint or coatings formulation. Since many coatings are suspensions of multiple components in an organic or aqueous continuous phase, the functionality of the finished product relies on maintaining these suspended components in a dispersed state for the life time of the product, under all the conditions that will be encountered.

Controlling the size of pigment particles can be critical to achieve this stability, however, the control of particle size for stability may be limited since from a performance perspective particle size also influences the way in which light interacts with a particle and consequently affects the hue or tint of the finished coating. Particle size and size distribution may also impact other important features such as coating transparency, level of gloss, weather resistance and



stability. Clearly pigment particles can be added to a formulation as particles of a defined size. The more difficult issue is how to maintain that particle size once all the ingredients of the paint are combined. Stability studies are often not only one of the most important aspects of paint formulation but also one of the most time-consuming.

The factors that contribute to the stability of a suspension may be classified as either kinetic or thermodynamic in origin [8]:

- Kinetic stability is associated with particle motion. Increasing the viscosity of a suspending medium slows down particle movement thereby reducing the likelihood of aggregation and sedimentation. Increasing viscosity therefore increases kinetic stability.
- Thermodynamic stability, on the other hand, is related to steric and electrostatic effects. Generally speaking thermodynamic stability is induced by encouraging strong particle repulsion, either through size modification, or by altering electrostatic charge. However, in certain systems it is possible to increase thermodynamic stability by encouraging particle attraction and the formation of a strong stable network structure.

Many coatings contain suspended particles in the sub-micron region. For such small particles Brownian motion is usually significant in maintaining the dispersion. However, as particles become larger the effect of gravity becomes more significant. Gravitational forces will also dominate if there is a significant difference between the density of the dispersed and continuous phase. This is often the case with pigment particles which can be extremely dense, relative to the solvent.

The ratio of gravitational to Brownian forces directly correlates with the likelihood of sedimentation, a defining feature of instability, which can be predicted from the equation below,

$$a^4 \Delta \rho g / k_B T$$

[where  $a$  is the particle radius,  $\Delta \rho$  is the density difference between the dispersed and continuous phases,  $g$  is acceleration due to gravity,  $k_B$  is the Boltzmann constant and  $T$  is the temperature.]

This equation is very helpful for determining a strategy for improving the stability of a dispersion:

- If the value of the ratio represented by equation 1 is greater than unity then some degree of sedimentation can be expected. This suggests that kinetic stabilization is required.
- A ratio of less than one is indicative of a stable system. However, any potential for flocculation/aggregation risks an increase in  $a$ , the particle size, and a swing towards kinetic instability. A ratio of less than one therefore puts the focus on safeguarding thermodynamic stability.

A more detailed discussion of this subject is given in [8]

Rheology can also be used to assess the dispersion state of a pigment or suspended component using viscoelastic measurements as detailed in the next section.

## VISCOELASTICITY

The rheology toolkit for paints and coatings is not limited to viscosity measurements; viscoelastic measurements can also be important since this information can tell us about the underlying microstructure, including the dispersion state of the pigment. Making oscillatory measurements on a rotational rheometer is the most common approach for investigating linear viscoelastic characteristics (those relating to the intact microstructure under small stresses) but elastic effects during flow can also be assessed using normal force measurements (non-linear viscoelasticity).

A frequency sweep measurement is used to assess the time dependent properties of a material under low stresses since for complex structures their viscoelastic properties can change with time of applied stress. Here the time of applied stress corresponds with the inverse of the angular frequency, with long times relating to low frequencies and short times high frequencies. The timescale of the process that you are interested in is what becomes important in this respect, with stability being a long process and touching a wet paint film a relatively short one.

What we are primarily interested in is the magnitude and ratio of the elastic modulus ( $G'$ ) and viscous modulus ( $G''$ ) which describe the relative stiffness of the elastic and viscous components of the material respectively, or the stress required to deform the respective components by a given amount. The dispersion state of the pigment is sensitive to such measurements since any pigment association will increase the elastic modulus [9]. If a gel state is established due to the formation of a percolated particle network, then  $G'$  will eventually exceed  $G''$  even at low frequencies as illustrated in figure 11.

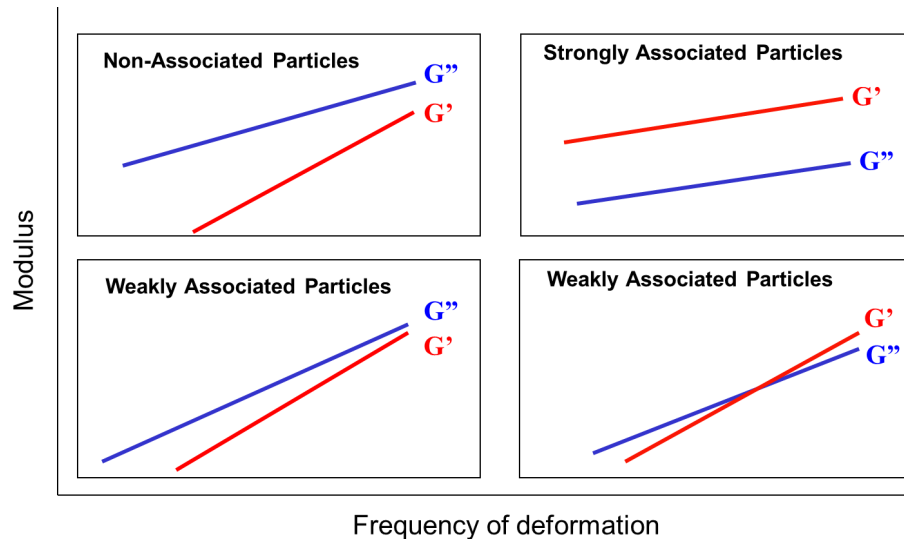


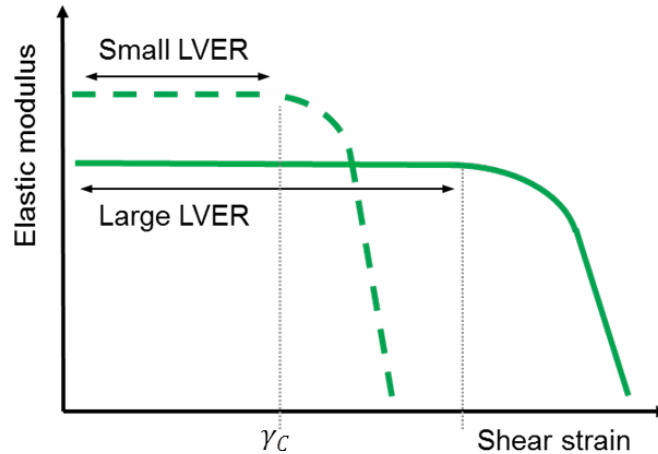
Figure 11 – Illustration showing  $G'$  and  $G''$  frequency profiles for different particle dispersion states

$$CE = G'\gamma_c/2$$

The strength of any such particle interactions can be assessed through a single frequency amplitude sweep by increasing the strain amplitude and seeing at which stress or strain  $G'$  begins to decrease; since this indicates the onset of yield in a percolated or aggregated structure. Such behavior can be quantified by the

cohesive energy (CE) which is effectively the work or energy required to separate aggregated particles, with  $\gamma_c$  the critical strain [10].

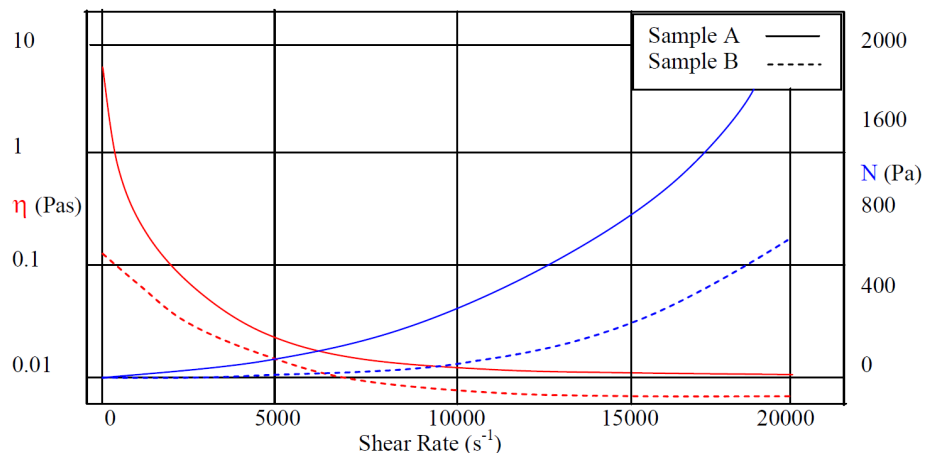
This is illustrated in figure 12 below where the well dispersed sample will have a larger linear viscoelastic region LVER (less brittle) and lower elastic modulus compared with a poorly dispersed sample, everything else being the same.



**Figure 12 – Illustration showing  $G'$  and  $G''$  shear strain profiles for different particle dispersion states**

Non-linear viscoelastic effects may be important also; by this we mean elastic effects resulting from anisotropy in the microstructure during flow. For example, if there are high molecular weight polymers present in the coating formulation these can be stretched in the flow field causing tension which may lead to flow instabilities.

This tension can be estimated from measurements of normal force or axial force while applying a steady shear stress or shear rate using a cone-plate measuring system. From the normal force the normal stress can then be calculated, which is the equivalent to the shear stress but in terms of elasticity rather than viscosity [11]. An example is given in figure 13 for two gloss paints. Sample A generates much higher normal stresses than Sample B at shear rates likely to be encountered during brushing even though the viscosities are similar. This may lead to differences in the thickness and evenness of an applied coating and may also increase the likelihood of filaments forming between the applicator and substrate during the coating process.



**Figure 13 – Normal stress and viscosity profiles for two commercial coatings as a function of shear rate**

## SUMMARY

Paint or coatings must be optimized for their leveling behavior, stability, sag resistance, applicator loading and film thickness, all of which depend on a coatings rheological behavior. Such processes can have a range of shear stresses, shear rates and timescale's associated with them and since many coatings are non-Newtonian and viscoelastic they can show different rheological behavior under these varying conditions. As a consequence it is important to measure the rheological properties under conditions relevant for the process or application, which in most cases can be correlated with end-use performance.

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**Malvern Instruments  
Limited**

Groveswood Road, Malvern,  
Worcestershire, UK. WR14  
1XZ

Tel: +44 1684 892456  
Fax: +44 1684 892789  
[www.malvern.com](http://www.malvern.com)

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