

**TA** *Instruments*

Thermal Analysis & Rheology



## **PAINT EVALUATION USING RHEOLOGY**

**Peter Whittingstall**

## INTRODUCTION

Paints and related coatings are complex systems usually comprised of three main components - a liquid phase (water or organic solvent), a film-forming polymer (latex or solution polymer), and pigments - as well as a variety of property-enhancing additives. Correct formulation of these ingredients allows the paint to be easily transferred from its container to an application surface and to form a uniform film of satisfactory appearance. Incorrect formulation, on the other hand, results in problems such as excessive sagging, poor leveling, creaming and/or sedimentation of pigments, and improper application. (Table 1).

**Table 1**

SAG	Flow down a vertical surface due to gravity
LEVELING	Flow out on a horizontal surface to yield a uniform coating and to remove brush marks
HIDING	Ability to cover and hide surface underneath
CREAMING	Separation into layers
STABILITY	Long-term sedimentation of pigments

Furthermore, optimizing paint formulations is not an easy task, particularly today as VOC (volatile organic content), for example, is increasingly regulated. To assure compliance, chemists are forced to find alternatives even for historically proven formulations. Fortunately, analytical techniques are available that make this optimization process easier. One of the most important of these techniques is fluid rheology.

Rheology is defined as the study of the deformation and flow of materials. When most chemists hear the word “rheology”, they immediately think of viscosity and, in fact, quantitative viscosity is one of the material properties that can be obtained from rheological measurements. However, a material’s viscosity is not a discrete value, as is temperature. Rather, viscosity is a property that depends on the conditions of measurement, for example, the rate of deformation (shear rate). This is significant for materials such as paints since they are exposed to a variety of different deformation processes during their useful lifetime (See Figure 1). Each of these processes represents a different deformation (shear) rate, and hence may result in a different “apparent viscosity”. Rheometers provide a means for evaluating this entire range of viscosity changes as well as material viscoelastic properties. Viscometers (e.g., Brookfield), on the other hand, cover only a small shear rate range and provide no viscoelastic information and are, therefore, useful only for quick qualitative comparisons of formulations.

### PAINT PROCESSES

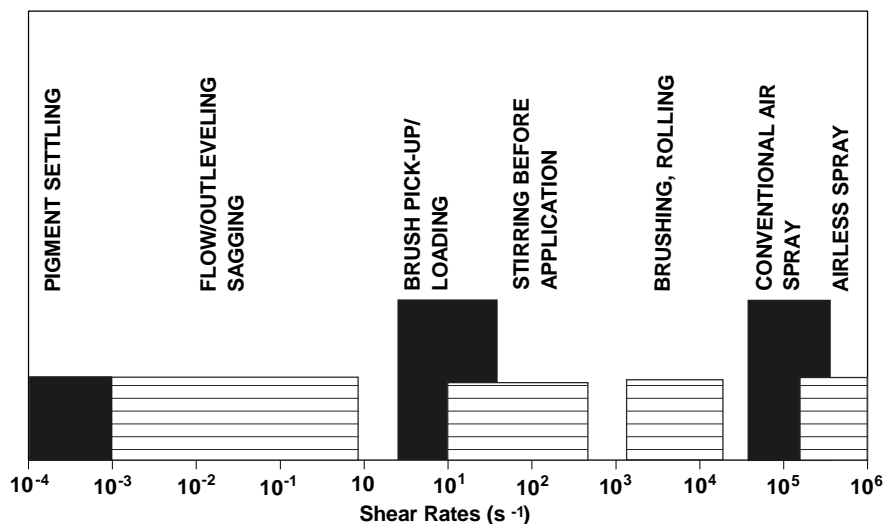


Figure 1

There are two common approaches for rheological measurements (Figure 2). These are controlled rate and controlled stress. In controlled rate, the material is placed between two surfaces. One surface is rotated at a fixed speed (strain rate) and the torsional force produced on the other surface is measured. In controlled stress, the material is again placed between two surfaces but a torque (stress) is applied to one surface and the resulting displacement or rotational speed of the same surface is measured. Although both approaches have inherent advantages, the controlled stress approach is preferred for paints because the results correlate directly with stress-driven processes such as sedimentation, creaming, sagging and leveling. Furthermore, since many paints have an apparent yield stress that has to be overcome before flow commences, as well as time-dependent flow properties (i.e., they are thixotropic), controlled stress is preferred because it allows measurements to be made with minimal destruction of the internal structure responsible for those properties.

## RHEOLOGY MEASUREMENT APPROACHES



Figure 2

## EXPERIMENTAL

In this study, a controlled stress rheometer (the TA Instruments CSL<sup>2</sup> Rheometer) was used to evaluate four commercial paints to illustrate some typical measurements. The rheometer was equipped with cone & plate and parallel plate geometries, autogap set, as well as a temperature control system (Peltier plate). Three evaluation modes (continuous flow, creep, and oscillation) were used. The specifics of this instrument's capabilities are described elsewhere (1,2). Measurements were made on samples pipetted from well-stirred quart containers and positioned on the Peltier plate. Sufficient time was allowed before evaluation for the paints to achieve an equilibrium short-term buildup of structure.

The paints evaluated represent typical water-base and oil-base house paints from the US and England. The results clearly show that the paints have considerably different properties that are obviously tailored for their respective consumer markets.

## RESULTS

### *Oscillation*

Oscillation measurements involve subjecting the material to a sinusoidal stress wave and measuring the resultant strain of this wave form in the material. If the material is purely elastic (more solid-like), then the stress and strain waves will be in-phase and follow Hooke's Law. If, however, the material is purely viscous (more fluid), then the stress and strain will be 90° out-of-phase. Most real-world materials exhibit a behavior between these extremes and are called viscoelastic. In fact, many complex materials such as paints are specifically formulated to achieve a balanced viscoelastic behavior. Figures 3 & 4 for example, show the  $\tan \delta$  results for the four paints as the oscillation stress and frequency respectively are varied.  $\tan \delta$  is the ratio of viscous (energy dissipation) to elastic (storage) behavior and values in the range 0.5-1.5 are desirable for paint. These curves indicate that the two UK paints (developed by the same company) exhibit similar balanced viscoelastic behavior that is fairly constant with stress and time. The two US paints are different. The water-base paint is similar to the UK paints, while the oil-base paint has a higher  $\tan \delta$  that implies less structured, more fluid behavior. Furthermore, its behavior changes most dramatically with increasing stress and frequency (shorter time scales). Thus, it would be anticipated that this paint would have poorer long-term storage (i.e., be more susceptible to pigment sedimentation) and would exhibit poorer "non-drip" behavior.

## US/UK PAINTS - OSCILLATION (TORQUE SWEEP)

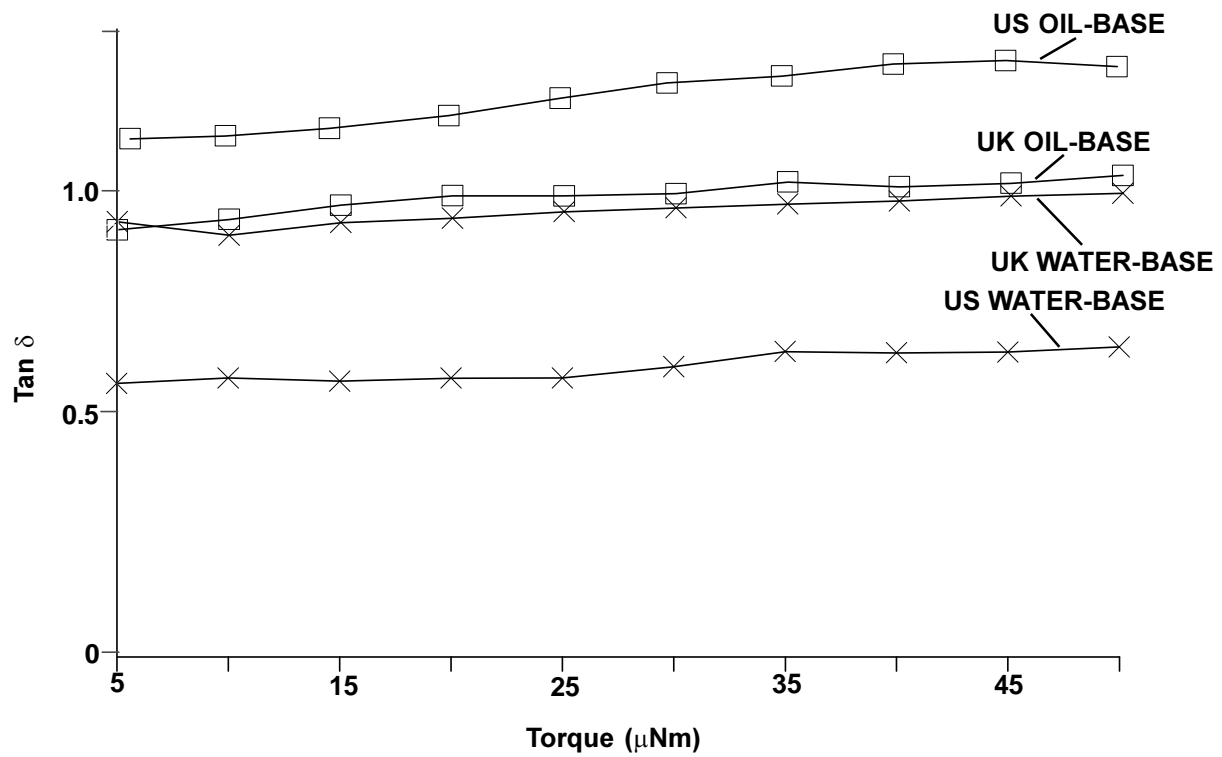


Figure 3

## US/UK PAINTS - OSCILLATION (FREQUENCY SWEEP)

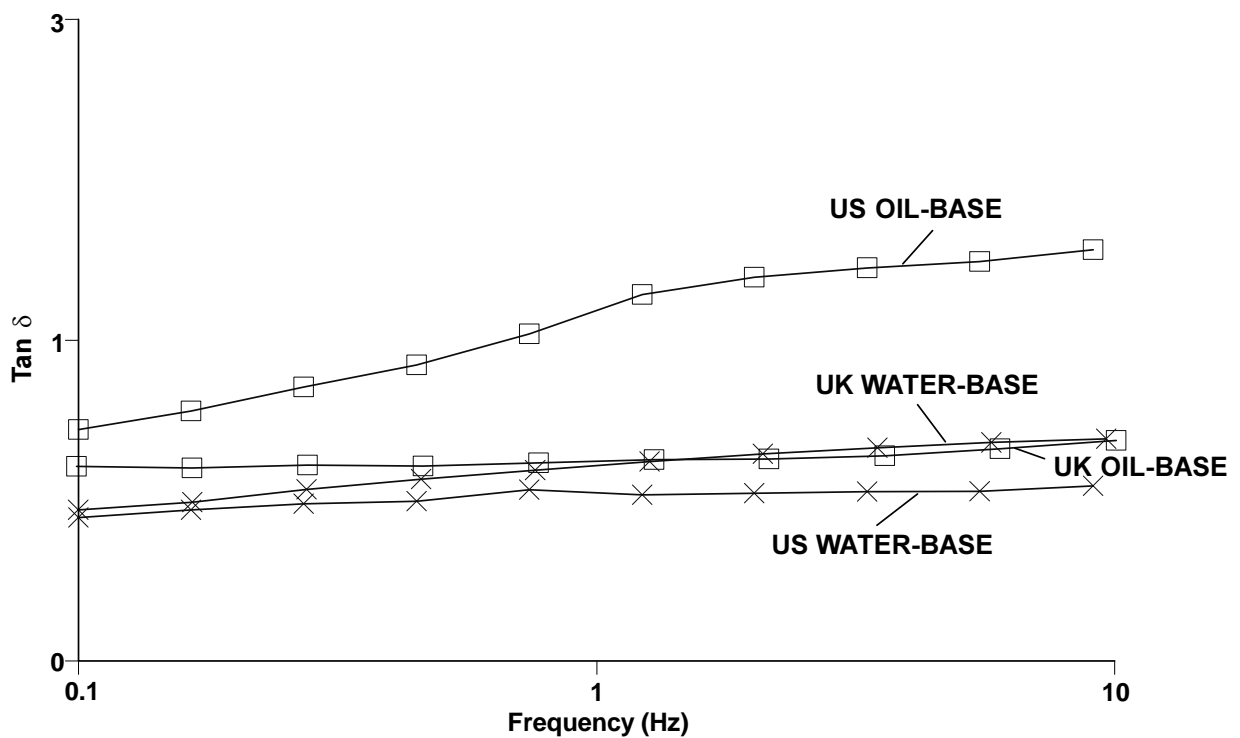
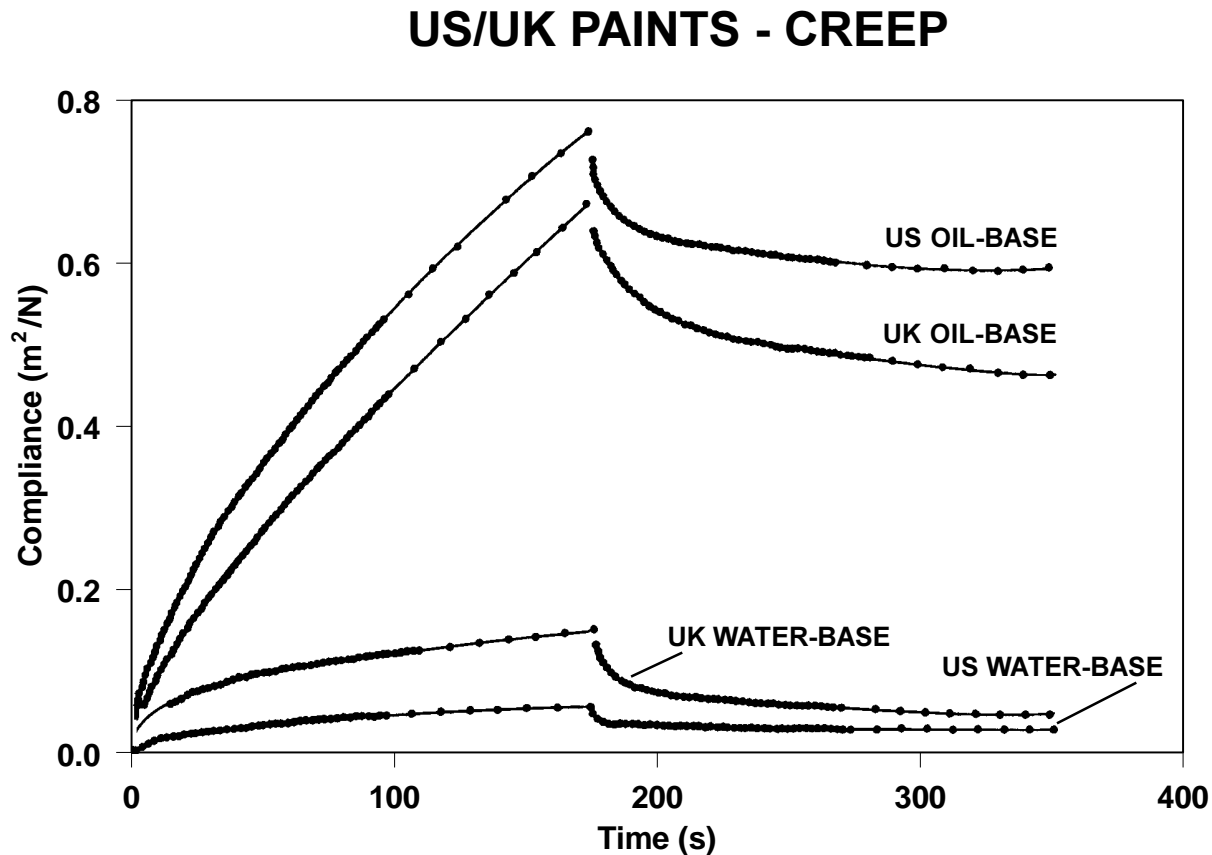


Figure 4

## Creep

Creep is a very sensitive technique where a small constant stress (force) is applied to the material and the resultant deformation with time is recorded. By running creep measurements for very long time periods it is possible to obtain information about a material's behavior at very low shear rates. Examination of the material's ability to recover from the deformation, which occurred during creep by removing the applied stress, provides additional useful information about the material's level of structure (elasticity). Figure 5 shows the creep curves for the four paints.

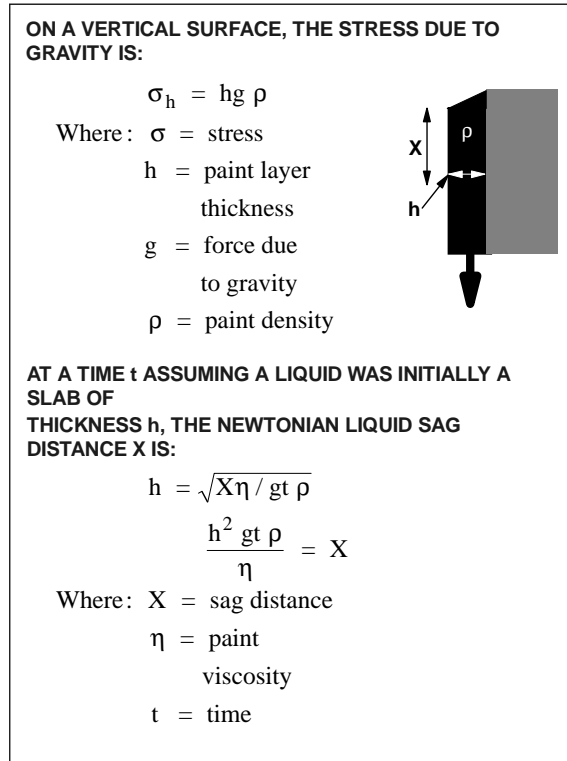


These results indicate that the oil-base paints (UK and US) are more compliant than the water-base paints. In fact, the compliance difference between these two different types of paint is pronounced enough to provide a rapid determination of the liquid phase used in the formulation. More importantly, these creep curves can be used to calculate the paints' Newtonian viscosities (viscosities at rest/zero shear). Those values are:

Water Base (US)	7200 Pa·s
Water Base (UK)	3050 Pa·s
Oil Base (US)	330 Pa·s
Oil Base (UK)	330 Pa·s

Sagging in paints once they are applied to a surface is a low stress (gravity), low shear rate ( $10^{-5} \text{ s}^{-1}$ ) deformation process. As Figure 6 indicates, this sag can be determined from creep tests if the stress applied approximates gravity. Although the stress applied in Figure 5, is not "equivalent to gravity", the differences observed clearly indicate that the water-base paints will be less susceptible to sagging. Hence, a thicker layer can be applied, making the water-base paints more suitable for roller application. Note, however, that the zero shear viscosity can not be too high because proper leveling, the surface tension effect which removes brush strokes and improves gloss, will not occur. Creep curves provide the quantitative information needed to balance these properties.

# ESTIMATION OF SAGGING



## Flow

Figure 6

In this mode, the material is subjected to a controlled increasing stress and the resultant strain and strain rates (shear rate) are measured. In paints, this mode is best for predicting ease of application. As shown earlier (Figure 1), the shear rates associated with the common modes of application such as brushing and rolling are  $10^3$  to  $10^6 \text{ s}^{-1}$ . These shear rates might seem high, but are primarily the consequences of the thin films involved. For example, brush speeds are typically 0.5 meter per second which, when applied to a wet paint film of thickness  $5 \times 10^{-5}$  meters, translates to a shear rate of  $10^4 \text{ s}^{-1}$ . For easy application, paints should shear thin (i.e., show a decrease in viscosity with increasing shear rate). A good viscosity for easy brush application is in the region 0.1 to 0.25 Pascal seconds. Figure 7 shows that all four paints shear thin to yield a viscosity less than 1 Pascal seconds and should be suitable for brush application.

## US/UK PAINTS - FLOW RESULTS

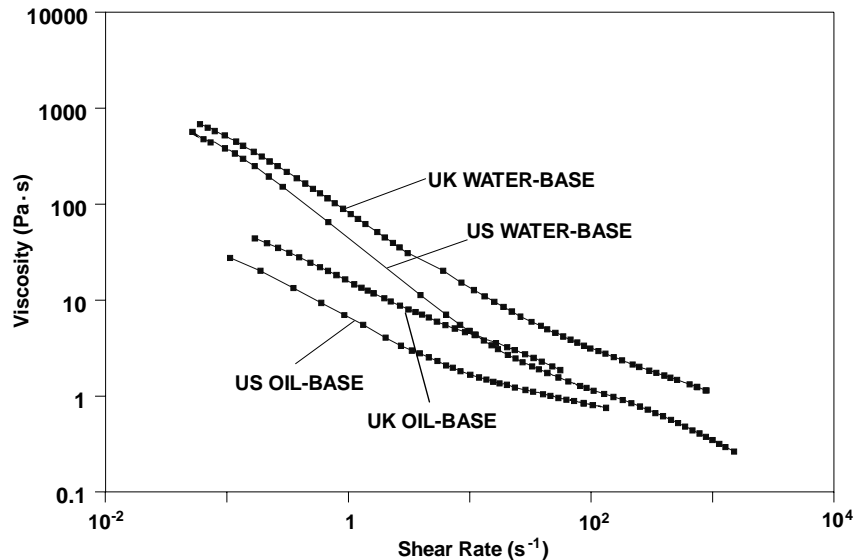


Figure 7

Figure 7 represents only the results when increasing stress. Figure 8 shows the same paints under first increasing and then decreasing stress. In an ideal Newtonian fluid, strain rate is directly related to applied stress and increases when stress increases. When the applied stress is subsequently decreased, moreover, the strain rate also decreases resulting in increasing/decreasing stress versus strain rate curves that overlay. This ideal behavior assumes that the rate of structure breaking (disruption) in the material when stress is increasing is instantaneous and is identical to the rate of structure rebuilding when stress is removed. However, just as most real-world materials don't follow ideal Newtonian behavior when stress is increasing, most also don't follow ideal behavior when stress is removed. Rather, materials exhibit a time dependence for structure rebuilding as well as structure breaking so that a "hysteresis loop" behavior is observed. Materials including paints that exhibit this behavior are called thixotropic. Paints are formulated to control thixotropy because it is an important factor in properties such as "non drip" behavior. Different additives and thickeners affect the size of the thixotropic loop observed. All four of the paints evaluated exhibit a similar, low level of thixotropy indicating that the thickeners used in each are probably similar.

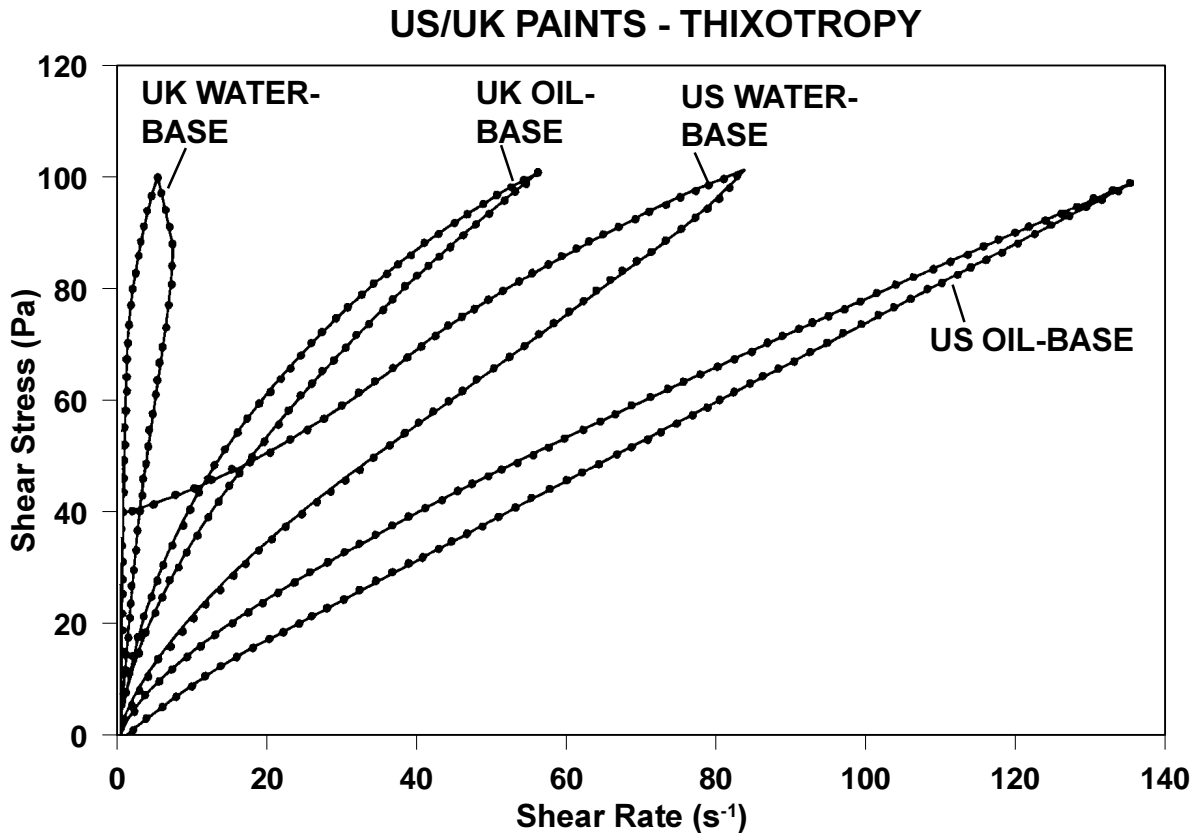


Figure 8

Flow information can also be rearranged to plot viscosity versus shear stress (Figure 9). The sharp drop in viscosity that occurs once a specific stress level is reached provides an "apparent yield stress". This stress is a qualitative measurement because it depends on the rate of measurement. Nevertheless, it provides further insight into the interactive forces present in the paint as well as the force required to initiate flow during application. In addition, the sharpness of the drop in stress seen is typical of that observed when clay thickeners have been added and suggests their presence in these paints.

## US/UK PAINTS - APPARENT YIELD STRESS

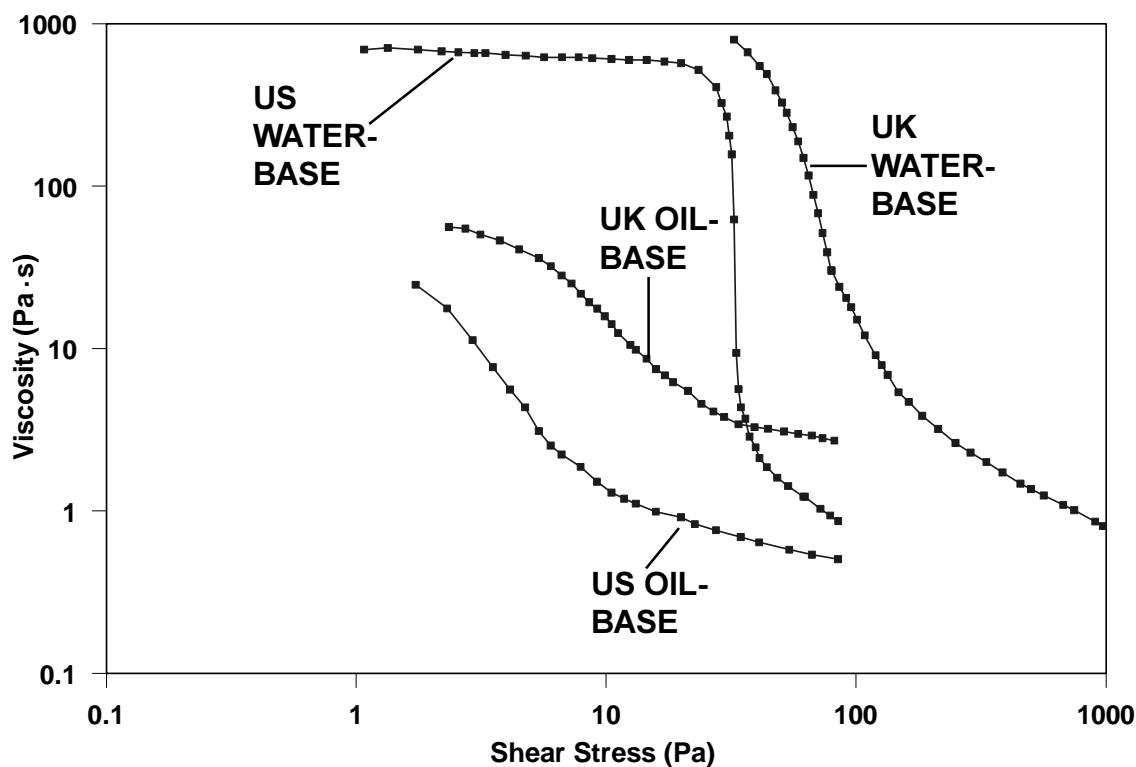


Figure 9

## SUMMARY

Paints are materials whose end-use characteristics and value are strongly influenced by their flow properties (rheology). This makes a versatile, easy-to-use controlled stress rheometer a necessary analytical tool for any laboratory involved in paint formulation or processing.

## REFERENCES

1. CSL<sup>2</sup> Rheometer Brochure, TA Instruments Publication RH001.
2. What is a Controlled Stress Rheometer, TA Instruments Publication RH007.

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For more information or to place an order, contact:

**TA Instruments, Inc.**, 109 Lukens Drive, New Castle, DE 19720, Telephone: (302) 427-4000, Fax: (302) 427-4001

**TA Instruments S.A.R.L.**, Paris, France, Telephone: 33-01-30489460, Fax: 33-01-30489451

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