Introduction

Rheology is the study of how materials deform and flow under the influence of external forces. Understanding the background to this science is essential when formulating modern paint systems. Rheological additives control the flow characteristics of a system. They not only “thicken” a liquid, they also modify the flow behavior and structure in a predictable way to control sag resistance, storage stability, application behavior, spatter resistance, leveling, film thickness, and film appearance.

Viscosity Profiles

A viscosity profile or rheogram shows the dependence of viscosity on the applied shear rate. There are three main time-independent viscosity profiles:

1. Newtonian flow describes a constant viscosity independent of the applied shear rate (e.g., mineral oil).
2. Dilatant flow behavior is an increase in viscosity with increasing shear rate, often seen in highly concentrated pigment pastes or with quicksand.
3. Pseudoplastic or shear thinning flow describes a decrease in viscosity with increasing shear rates. All three profiles are time-independent, and the viscosity is exactly defined at any given shear rate.

Plastic flow is another type of behavior. It is seen when a pseudoplastic material has a yield value. This is best shown when shear stress is plotted against the shear rate.

Thixotropic flow behavior is the time-dependent decrease of viscosity under constant shear or stress. A system will lose its internal structure under shear (mixing, rolling, spraying, etc.) but recover it over a period of time when the shear is removed. This will result in an upper (sheared) and lower (recovery) curve when running a viscosity against shear rate profile.

Relationship between Shear Rate and Coatings

The way a fluid flows over the entire shear-rate range influences the other properties. Every part of a rheogram is important. The success or failure of any coating depends on getting the whole rheogram optimized across its entire profile.

For good storage stability, a high viscosity at the very lowest shear rates generated by gravity and vibration is usually necessary. However, modern measurement methods, such as oscillation, also show that the structural strength (elasticity) rather than simple viscosity is a better indication of storage stability. For sag resistance and reduced penetration, high viscosity or quick recovery in thixotropic systems is again required at relatively low shear rates. On the other hand, good leveling needs either low viscosity or slow recovery at ultra-low shear rates.
To meet this contradiction, an additive should usually provide sufficiently high viscosity to prevent sag and penetration but also be sufficiently thixotropic to allow good leveling. The mid-shear rate range gives information about how the product appears to the user—that is, how it reacts to gentle stirring or shaking—and reflects the aesthetic appearance of the fluid material. Performance under high shear indicates how well a coating will apply. A relatively high viscosity suggests good brush drag or roller resistance whereas a low viscosity indicates good spray properties.

**Measurement**

Viscometers (such as the Krebs-Stormer or Brookfield) typically used in quality control measure viscosity in the medium shear rate range only (1-200 s⁻¹). Settling, sag, leveling, and application properties are usually assessed with paint drawdowns and brushouts. Precise measurement of low-, medium-, and high-shear rate viscosities can be made with more advanced rheometers. These rheometers can work in a controlled shear stress mode (apply known forces/measure resulting strain), controlled shear rate mode (apply known strain/measure resulting forces), or oscillatory mode. Through continuous or ramped measurement, these instruments follow the change in flow parameters and accurately measure shear rates, shear stresses, and viscosities over a wide range of conditions.

**Effect of Rheological Additives on Coatings Properties**

Rheological additives alone do not determine the overall flow properties of a coating. The solvents, binders, extenders, and pigments together with the rheological additive and all their physical/chemical interactions are important. The low-shear behavior of a coating system is typically modified by either associative (viscosifying) or onassociative (structured, gellant) rheological additives. When using a gellant additive, such as clays, the high-shear behavior is typically dominated by the major paint ingredients: binder, pigment, and solvent. However, associative thickeners, such as polyurethane thickeners or hydrophobically modified alkali-swellable emulsions, contribute to high-shear viscosity due to their large hydrodynamic volumes. Dispersions (both solventborne and waterborne) also differ in behavior from true emulsion systems.

**Storage stability**

Gelling additives, such as clays and organoclays, develop a strong elastic structure at rest that prevents or controls pigment settling. The structure creates a storage modulus high enough to counter gravitational forces when at rest as well as the vibrational forces associated with transportation. Too high a storage modulus should also be avoided because it might cause syneresis. Associative thickeners, however, typically develop a balanced ratio between storage and loss moduli, with a storage modulus often, but not always, just high enough to prevent settling.
Sag resistance and leveling

Additives that increase the elastic modulus typically impart a good sag resistance due to the recovery of the stable structure after application. The recovery of the storage modulus relative to loss modulus needs to be fast enough to prevent sagging but slow enough to allow for good leveling. Associative thickeners with balanced loss and storage moduli coupled with quick recovery can allow for good sag resistance and good leveling due to the relatively low elastic modulus.

Ease of application

The degree of shear thinning developed using a rheological additive influences the feel and flow of a paint system during application. The ease of application is predominantly influenced by the viscous behavior. Shear thinning behavior is typically required to improve ease-of-handling and paint pick-up.

Film thickness and roller spatter behavior

Pure or partially associative rheological additives can improve the film thickness of a coating system as well as its roller spatter behavior. Associative thickeners are volume filling polymers and increase the viscosity of a paint system at high shear. This leads to a higher film build when applied by roller or brush. Roller-spatter behavior of a coating is also influenced by flow at high shear. Additives that give long entangled networks and have a high so-called elongational viscosity tend to give poor spatter. However, those that develop shorter range structures, such as the nonionic synthetic associative thickeners, do not encourage droplet formation at the brush or roller and show good spatter resistance. Whether the viscoelasticity of the system contributes to this is still under investigation.

Structure and Composition of Acrylic Thickeners

Acrylic thickeners for aqueous systems are based on acrylic chemistry. They are available both in the traditional, alkali-swellable form as well as hydrophobically modified, which thicken partially by association. Both are offered as APE- and VOC-free flowable liquids at 25% to 30% active contents in water.

Mechanism

The alkali-swellable products are related to polyacrylic acid and are present in suspension as tight, coiled chains. The pH of these products as delivered lies between 3 and 5. When the pH is raised to around 7.0, the acid groups begin to dissociate and the polymer chains uncoil or swell. On complete dissociation (normally around pH 9), the chains reach their maximum extension and develop viscosity in the system by macromolecular entanglement. The hydrophobically modified products have both acid as well as other less polar side groups attached along their polymer backbone. When the pH is raised, the chains uncoil and swell through dissociation. However, the side groups also interact— or associate—with each other.
and with other formulation components. This dual thickening mechanism is very important for the performance of the additive in the final formulation.

**Incorporation of Acrylic Thickeners**

Acrylic thickeners are water-thin and can, in most cases, be post-added directly under moderate shear conditions. Under certain circumstances—such as small particle-sized binder, zero-VOC, or a large pH difference between the additive and the system—rapid, localized gelation might occur that results in the formation of isolated gel particles or seeds. In extreme cases, the whole system might shock and give an unworkable mass. Although Elementis Specialties acrylic thickeners have been developed to avoid this problem, its occurrence can be prevented simply by diluting the additive with water (and/or glycol if appropriate) before use: Acrylic additive 1 part and Water and/or glycol 1 part. Mix until uniform and then add slowly into vortex at end of letdown/dilution. This is generally recommended when only low-shear mixing is available or when the thickeners are used with very fine particle-size binders. The alkali-swellable products can be used to give a thixotropic mill-base, assuming the appropriate pH can be achieved. For this, only a part of the total additive (ca. one third) should be used. The remainder should be added in the letdown as normal. As the hydrophobically modified products thicken by a dual mechanism, they take time to equilibrate fully. It is important to allow for this during initial formulation. Approximately 80% of the full viscosity is developed 2 hours after manufacture; the rest builds overnight. This effect is totally reproducible and can easily be accommodated in quality control testing.

**Viscosity and system pH**

As the polymers swell in alkali, it is clear that the pH of the system needs to be controlled. For optimum performance, a pH range of 8 to 10 is desirable. The correct pH is required both for viscosity stability and batch-to-batch reproducibility.

**Coalescing agents**

Coalescing agent chemistry tends to have little influence on the performance of alkali-swellable products. However, it is very important for hydrophobically modified products. In general, the more polar or water-miscible the coalescent, the more it will reduce the viscosity developed under low- or mid-shear. The coalescent influences the associative interaction as described later. On the other hand, the less water-miscible coalescents tend to enhance the associative effect and cause a rise in low-shear viscosity. This behavior can be used to fine-tune sag and leveling performance.

**Surfactants and wetting agents**

The thickening efficiency of the acrylic thickeners and, particularly, the stability of the final formulation can be significantly influenced by interactions with surfactants and wetting
agents. The most stable formulations are prepared with standard anionic surfactants. With some nonionic products, post-thickening and even “livering” or flocculation might occur over time. An accepted explanation for this is that, because the acrylic polymer carries a slightly negative charge, it might displace the nonionic surfactant from whichever surface it is protecting. The long-chain thickener polymer can then bridge between particles and allow flocculation or at least a significant increase in viscosity. Experience has shown that the organic pH buffers can also help to reduce this problem if it occurs. In general, post-thickening is more common with the alkali-swellable products than the hydrophobically modified, but much depends on the full formulation and strength of associative interactions.

Nonionic Synthetic Associative Thickeners (NiSATs)

Nonionic synthetic associative thickeners (NiSATs) are nonionic copolymers. Their structure can be schematically represented as two hydrophobic heads and a hydrophilic backbone. The analogy with the traditional representation of a surfactant is obvious and indeed these materials behave in many respects like surfactants, which dictates their behavior in coatings formulations. Elementis Specialties offers two classes of NiSATs: polyether polyurethane products and polyether polyol products. Polyether polyurethane thickeners are more accurately described as hydrophobically modified ethoxylated polyurethanes. Polyether polyol products do not contain urea or urethane linkages and have a more branched structure. The properties of the NiSAT thickeners are controlled by changing the frequency and chemistry of the hydrophobic units. More hydrophobic caps give stronger association and shear-thinning flow. If the caps are less hydrophobic, association is weak and the additive gives flow behavior tending toward Newtonian. The products are all flowable liquids. Some are also available in powder form. All are APEO-free and are available in VOC-free forms.

Mechanism

When NiSATs are added to a coating formulation, they organize into micelles or polymeraggregates and interact with other components in the formulation. Most important are the interactions between the hydrophobic units and the binder surface. This is not a chemical reaction but a temporary adsorption and is responsible for the rheological activity. In water alone, they give little structure until their micelles start to link. In the presence of latex and other suitable surfaces, however, a continuous network forms throughout the system and the viscosity increases. The micelles are dynamic and not rigid units. The individual polymer molecules are in constant exchange with the aqueous phase, analogous to the behavior of normal surfactants. The network, therefore, has a relatively low elastic component. It can relax at rest and thus provide excellent leveling. Under high shear, the additive micelles are no longer associated with the other components in the system. However, they have a large hydration sphere that is volume filling. This is the likely reason for the high viscosity the additives provide under these conditions. Although both classes of NiSATs give viscosity in much the same way, the polyether polyol grades tend to interact differently with the other co-ingredients in comparison to the polyether polyurethane products. They are, therefore, very useful tools to overcome specific incompatibility problems.
Rheological performance

The flow given by NiSATs is governed by the nature and frequency of the hydrophobic units. Higher viscosities at low- and mid-shear rates are achieved with the more hydrophobic thickeners. These are efficient thickeners for this shear range and are useful for spray applications because they then do not develop significant viscosity under high shear. The viscosity at low-shear rates gives sag-control, but the nature of their recovery still allows excellent leveling and optical properties to be maintained. The more hydrophilic thickeners associate only weakly with the latex and so do not build much structure at low-shear rates. However, because they are very volume-filling, they do still contribute to viscosity in the high-shear rate range. They are, therefore, useful for optimizing film build and brush drag properties. Their large volume also means that they are effective at controlling syneresis. They prevent the system from shrinking in on itself and bleeding-out the aqueous phase. The type of flow achieved is frequently described as “approaching Newtonian” when compared to other traditional waterborne rheological additives. Low viscosities at low-shear rates give good leveling, whereas relatively high viscosities at high-shear rates give good film build and coating characteristics ideal for one-coat hiding in paints. The additives are totally compatible with each other and can simply be blended to achieve a specific flow for a particular application. NiSATs give three general classes of viscosity/shear response. This gives the formulator wide latitude when designing a specific rheological profile. In comparison to cellulose ethers, NiSATs generally give lower ultra-low shear viscosity and improved leveling behavior. The type of structure they develop under shear (non-elongational) gives excellent resistance to roller spatter and over-spraying.

Incorporation of NiSAT thickeners

Liquid NiSATs are all free-flowing and can usually be added directly to the formulation under moderate shear. However, these products are surface active polymers, so care should be taken in sensitive formulations to avoid possible shock or destabilization. Normally, it is sufficient to add the thickener either just before letdown or at the very end of the paint manufacture. In fine particle-sized or hydrophobic latex systems, when association can be strong, it is advisable to dilute the thickener first with an equal quantity of water. In nonsensitive systems, the additive can be incorporated at any convenient stage.

Latex particle size and surface chemistry

The hydrophobic additives are best with latex systems that have very hydrophilic surfaces to ensure some build of structure. If the latex has a rather hydrophobic surface, then the Newtonian additives give best flow. Note: This also has a bearing on the reproducibility of the coating viscosity. If the latex itself shows wide batch-to-batch variations either in particle-size distribution or in surface chemistry treatment, then the association and developed viscosity will vary correspondingly. In general, the polyether polyol products show less sensitivity to latex particle-size variations than do the polyether polyurethane products.


**Surfactants and wetting agents**

NiSATs are surface active co-polymers. It is, therefore, not surprising that the other nonionic surfactants in a formulation can have a significant influence on the flow they produce. This is normally dependent on the HLB (hydrophilic-lipophilic balance) values of surfactants used. The surfactant effect is less when using polyether polyl products but still needs to be borne in mind. Nonionic surfactants with an HLB value of 10 produce the highest mid-shear rate (Stormer and Brookfield) viscosity efficiency. More hydrophilic, nonionic surfactants with HLB values greater than 15 will depress the low- and mid-shear rate viscosity efficiency. Using a surfactant with an HLB below 10 may result in pigment flocculation and poor color acceptance and is not recommended. The loss of viscosity with higher HLB nonionic surfactants is attributed to surfactant drift in the formulation. The added surfactants can displace the NiSATs from their micelles, but because they do not have associating units, the network weakens and viscosity drops. Unfortunately, this effect might not occur immediately but can be observed after several months’ storage as the formulation gradually equilibrates. Storage stability studies are particularly important when evaluating NiSATs. For these, modern techniques to measure changes in viscoelastic behavior over time can be of tremendous value.