

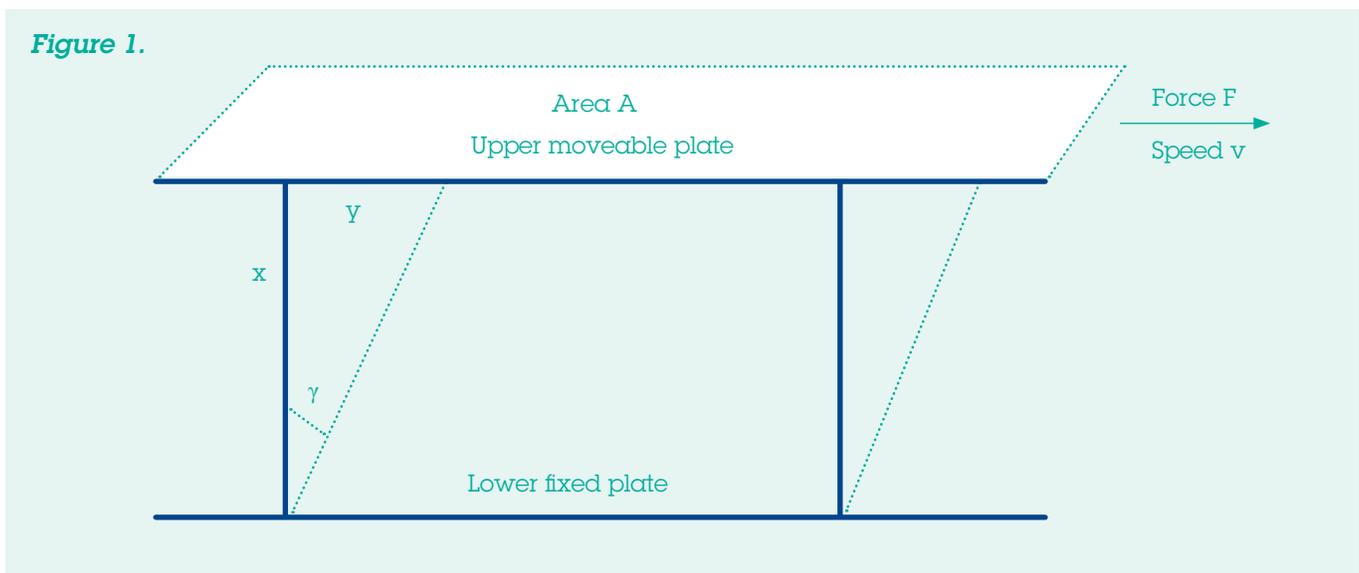


Thickeners + Rheology Guide



Rheology

Rheology is defined as the study of the deformation and flow of materials. When a force is applied to a liquid, the liquid will flow to relieve the strain from this force. Different systems will resist this flow more than others and the measurement of this resistance is a measure of the viscosity of the system. Newton first introduced a basic model for the flow measurement of a liquid between two parallel plates and this is represented in figure 1.



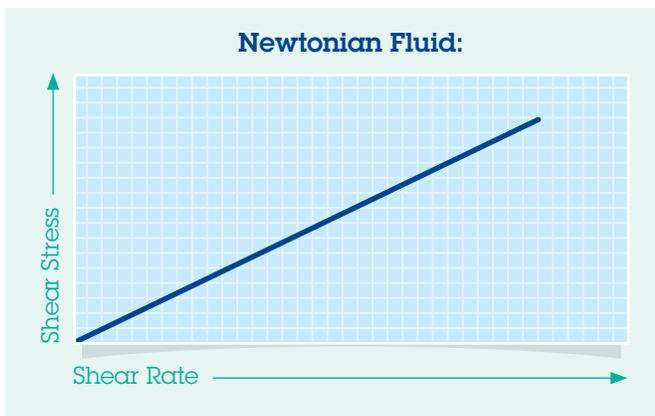
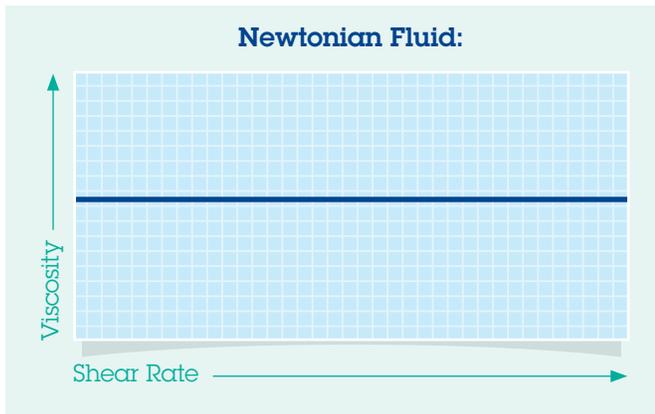
Using this model, a number of common rheology terms can be defined as follows:

Shear Stress – the force experienced by the liquid is proportional to the area of the upper plate and is defined as the shear stress, $\sigma = F/A = \text{Nm}^{-2} = \text{Pascal (Pa)}$.

Shear Rate – the velocity gradient or the rate of change of velocity at which one layer passes over an adjacent layer is the shear rate, $\dot{\gamma} = dv/dx = [\text{units} = \text{s}^{-1}]$.

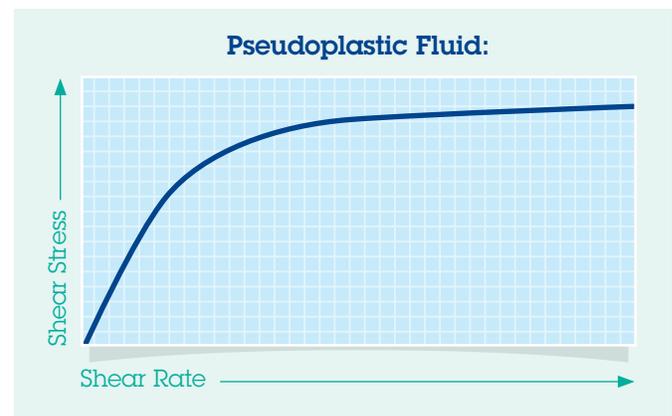
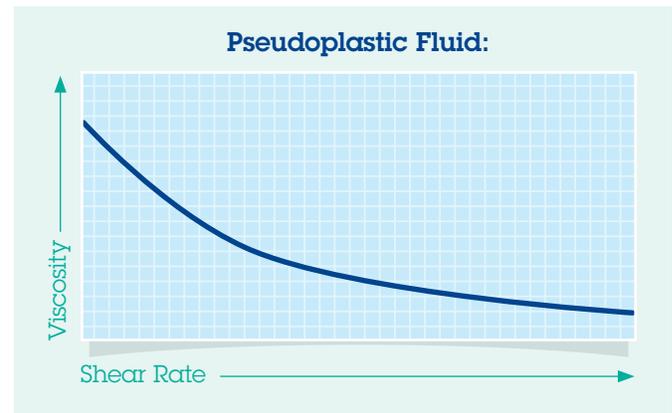
Viscosity – this is expressed mathematically as, $\eta = \text{shear stress}/\text{shear rate}$ and is the measurement of the resistance to flow of a fluid. Pascal.second (Pa.s) is the basic unit of viscosity, but Poise or centipoise (cp = one hundredth of a Poise) is often used and one cp is equivalent to a millipascal-second, mPa.s. When quoting viscosities, the shear rate (or measurement method/equipment used) should be stated together with the temperature at which the measurement was taken.

Newtonian Fluids – examples include, water, certain oils and dilute resin solutions. The viscosity of a Newtonian fluid, is independent of shear rate, or put another way, the rate of deformation is directly proportional to the applied force. This is shown in the two different plot types below:

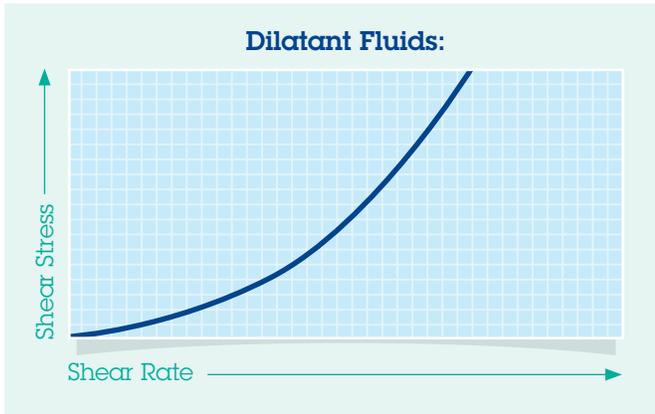


Non-Newtonian Systems – many systems show behavior that deviates from that of simple Newtonian flow and examples of this are defined opposite.

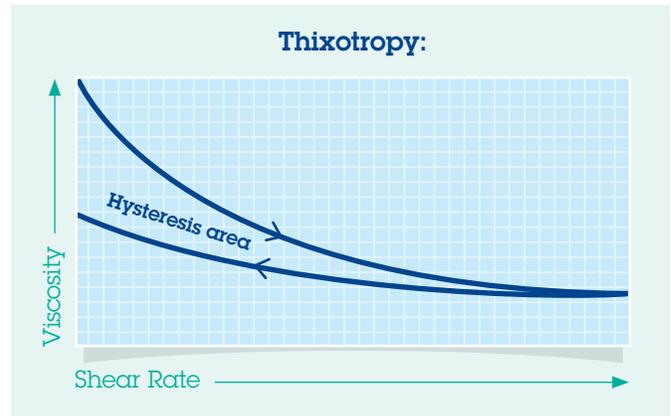
1) Pseudoplasticity (Shear thinning) – a large number of liquids show a large decrease in viscosity when the shear rate is increased and this type of flow is defined as pseudoplastic or shear thinning behavior. Emulsions, suspensions and dispersions are typically pseudoplastic as are many paint, ink and adhesive systems. At higher shear rates the flow behavior becomes more linear (Newtonian). A related type of flow behavior is that of plastic materials, which initially resist deformation until a certain yield stress is reached. Beyond this point the flow is that of a pseudoplastic fluid. Pseudoplastic behavior is portrayed below in two different plot types:



2) Dilatancy (Shear thickening) – dilatant fluids show the opposite type of behavior to pseudoplastic systems i.e. they show an increase in viscosity as the shear rate increases (shear thickening). It is seen in highly concentrated suspensions or slurries. This type of behavior is relatively uncommon, but is represented in the plot below:



3) Thixotropy – for thixotropic liquids the viscosity decreases over time for a given shear rate until a minimum is reached. Once the shearing force is stopped the viscosity recovers over time. The degree of thixotropy can be represented by what is termed a hysteresis area. This is typical of the behavior observed in gelled paints applied to a vertical surface, where the viscosity reduces under the shear of the brush, or roller, and then recovers to prevent sagging. This is represented in the plot below:



4) Rheopexy – rheopectic fluids show the opposite behavior to thixotropic fluids i.e. they increase in viscosity over time for a given shear force until a maximum is reached followed by a viscosity reduction over time when the shear is stopped. This type of behavior is extremely rare.



Practical Rheology for Formulated Systems

Formulators use a number of viscometer types and methods to measure and understand the behavior of their systems.

Some common viscometer types are listed below together with the shear ranges they typically represent:

Brookfield Viscometer	Low to medium shear
Stormer	Medium shear
ICI Cone and Plate	High shear
Rheometer	Low to high shear

The **Brookfield viscometer** is a very common type that is simple to operate and is often used as a QC tool to check a single viscosity measurement at a specified temperature, and they can also be used to get a basic rheology profile under lower shear conditions. For a more complete understanding of the rheology profile of your system it may be necessary to use a rheometer that can make multiple measurements over a wide shear range.

It is also worth mentioning that various different flow cup types exist and are used as QC tools and to check viscosities in production. They measure the time taken for a set volume of fluid to flow through a given size of orifice in the bottom of the cup and are not truly viscometers. However, the flow time is related to the viscosity of the liquid and higher viscosity liquids take longer to flow through the hole.

Many formulated systems show either pseudoplastic or thixotropic behavior and thus show a viscosity reduction when sheared. A knowledge of the rheology

of a system can be very useful in understanding its stability and flow behavior under different shear conditions.

Settling, sagging and leveling occurs under very low shear conditions, whereas application of the formulated product generally happens under relatively high shear conditions e.g. brushing, spraying or rolling. Pumping and general mixing of ingredients occur at low to medium shear rates. Paints, for example, often require a degree of leveling after application, so it may not be desirable to have fast recovery of viscosity. However, too slow recovery can lead to sagging and dripping. Other systems may require more instantaneous recovery of viscosity. In such cases a knowledge of the flow behavior imparted by different thickener systems will aid selection of the best product for the job.

Process	Shear Rate (S ⁻¹)
Settling	0.01 - 1.0
Sagging	0.01 - 0.10
Leveling	0.01 - 100
Mixing	20 - 100
Pumping	10 - 10,000
Dispersion	100 - 40,000
Brushing	5,000 - 20,000
Air Spray	1,000 - 40,000



Scott Bader – Inverse Emulsion Thickeners

Conventional emulsions, in technical terms, are oil-in-water emulsions i.e the continuous phase is water. Inverse emulsions are simply the opposite i.e water in oil emulsions with the continuous phase being an oil.

Texipol® inverse emulsions are manufactured directly from the pre-neutralized liquid monomers that are intimately dispersed in the oil phase followed by a controlled polymerization process to yield the liquid thickener. The diagram (right) shows the essential differences between conventional and inverse emulsions.

Mechanism and Benefits of Texipol Inverse Emulsion Thickeners

When Texipols are added to water or a waterborne system, the Texipol “inverts” with the help of the water soluble emulsifiers and water becomes the continuous phase. The hydrophilic polymer particles swell rapidly and the resulting highly swollen structure leads to a rapid increase in viscosity.

Texipol thickeners are supplied in a pre-neutralized form, which means there is no requirement for additional alkali or surfactant addition to achieve thickening. In most applications, Texipol thickeners can be added at any stage of formulating, including post-thickening of systems, thus allowing greater flexibility when formulating.

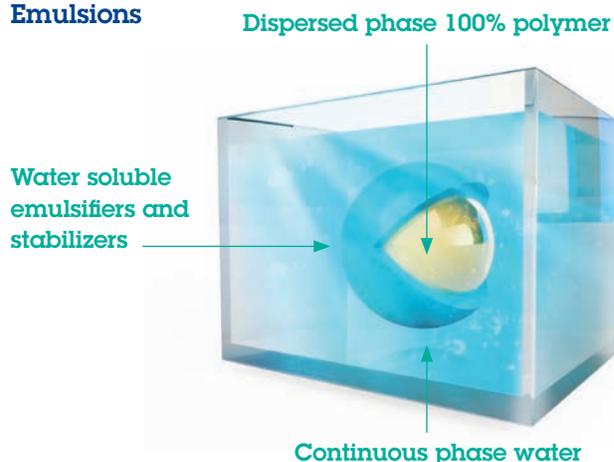
In general terms a thickener has three functions to fulfil in a typical formulation:

- To increase viscosity
- To stabilize the dispersion of insoluble components such as pigments
- To modify the flow.

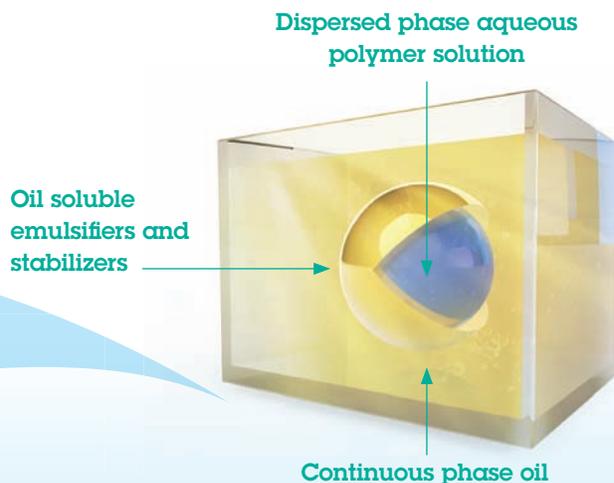
Formulation Guidelines for Texipols :

Product selection: The rheology, flow and viscosity efficiency is dependent on other ingredients in a formulation. Dissolved salts and surfactants are known to affect both the flow and efficiency of a Texipol thickened solution.

Emulsions



Inverse Emulsions



To determine the concentration level of Texipol

required in a formulation: The exact amount of thickener required can only be determined by experimentation and depends on the required viscosity and the nature of the other ingredients in the formulation. For typical applications of Texipols where paste-like viscosities are required, start with a 2% (on total) addition level of Texipol and increase the amount until the desired viscosity is achieved. For lower formulation viscosities, 1% or less of the Texipol may be needed. As the polymer is pre-neutralized the thickening effect is almost instantaneous under high shear stirring and can be added to thicken a formulation at any stage of the manufacturing process. Additional Texipol can be added at the end of a batch to conveniently adjust the viscosity up to the target level.

How to add: The batch to be thickened should be thoroughly and uniformly mixed to achieve a homogeneous product and to avoid local thickening. High shear mixing is recommended for the best results. Problems can arise if the stirrer is too slow or too small and does not move the total batch (i.e. a localized thickening effect is noticed around the blade, and the mix is not homogeneous). Texipol is shear stable, but thickened formulations do shear thin.

What to avoid: High concentrations of dissolved salts and some surfactants will dramatically reduce the viscosity efficiency of Texipol. The presence of polyvinylalcohol emulsions can cause sharp viscosity increases in some inverse emulsion thickened compounds.

Texipol selection chart

This chart is intended as a guideline to use when selecting a grade of Texipol for certain applications.

Texipol	Flow	Typical thickened viscosity mPa.s	Typical pH usage range
63-201	Long stringy	≥ 700 ⁽¹⁾	5.0 - 12.0
63-202	Short	≥ 35,000 ⁽²⁾	5.5 - 11.0
63-237	Extremely short	≥ 38,000 ⁽³⁾	6.0 - 12.0
63-253	Extremely short	≥ 45,000 ⁽⁴⁾	6.0 - 11.0
63-258	Extremely short	≥ 100,000 ⁽⁵⁾	6.5 - 10.0
63-510	Short	≥ 100,000 ⁽⁶⁾	2.0 - 12.0
63-511	Short	≥ 100,000 ⁽⁷⁾	5.0 - 13.0

1) 63-201: 1% in DI water – Brookfield RVT, Spindle 3, 50 rpm, @ 25C.

2) 63-202: 4% in DI water – Brookfield RVT, Spindle 6, 5 rpm, @ 25C.

3) 63-237: 2% in DI water – Brookfield RVT, Spindle 6, 5 rpm, @ 25C.

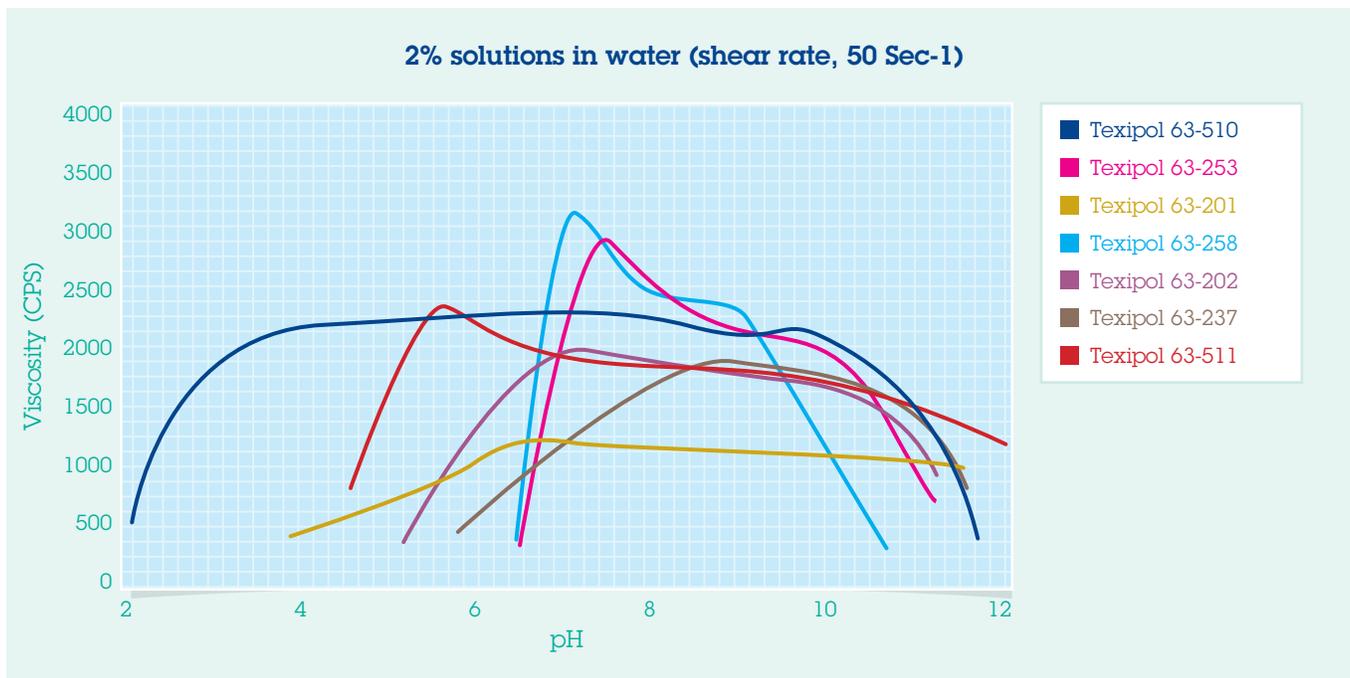
4) 63-253: 2% in DI water – Brookfield RVT, Spindle 6, 5 rpm, @ 25C.

5) 63-258: 2.5% in DI water – Brookfield RVT, Spindle 6, 5 rpm, @ 25C.

6) 63-510: 4% in DI water – Brookfield RVT, Spindle 6, 5 rpm, @ 25C.

7) 63-511: 4% in DI water – Brookfield RVT, Spindle 6, 5 rpm, @ 25C.

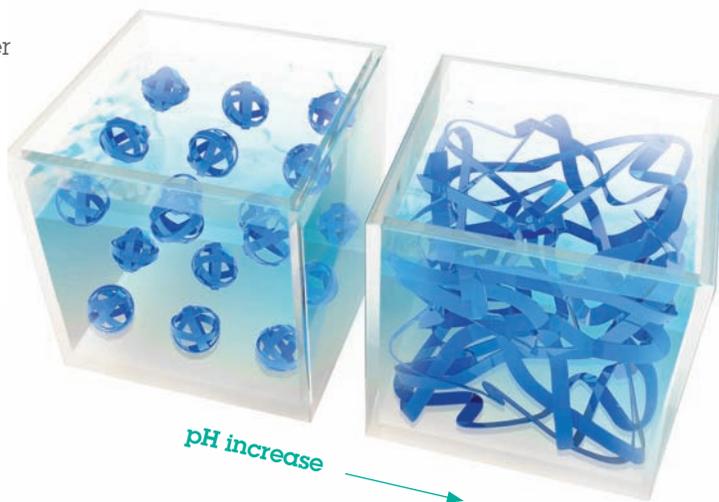




Scott Bader Texicryl® – Alkali Swellable Emulsions

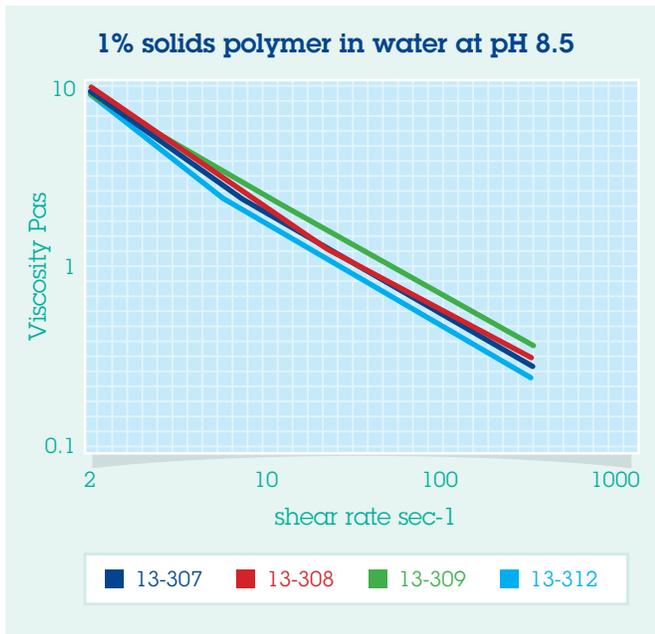
These are dispersions of acid functional acrylic polymers in water. They are supplied at low pH and the acid groups on the polymer chains need to be neutralized to allow the polymer to swell and thicken. Under acidic conditions the polymer has a tight, coil-like structure and after the addition of alkali to the system, the pH increases and the acid functional groups on the thickener begin to dissociate. As a result, the thickener becomes more water-soluble and starts to uncoil.

As the pH increases further, the polymer takes on a more open long-chain structure, leading to entanglement of thickener molecules with each other. This results in an increase in viscosity and is pictured schematically below:



Rheology and Efficiency

The graph below indicates the relative rheological behavior of the Scott Bader range of Texicryl alkali swellable emulsions for solutions of each in deionized water.



Texicryl 13-307 and 13-308 are both highly efficient thickeners giving high viscosities at relatively low usage levels. Both show significant shear thinning rheology with fast recovery. The main difference between these two products is that the Texicryl 13-307 shows slightly earlier thickening at lower pH than the Texicryl 13-308.

Texicryl 13-309 is also an efficient thickener, but gives slightly lower aqueous solution viscosities than the other two grades. It also provides a shear thinning rheology, but not so pronounced as for the other grades. This slightly more Newtonian rheology may allow a little more flow and leveling in certain systems.

Texicryl 13-312 also gives slightly lower aqueous solution viscosities than the Texicryl 13-307 and 13-308, but has been designed for systems where viscosity stability can sometimes be an issue. Texicryl 13-312 is shear thinning like all the grades shown.

Formulation Guidelines for Texicryl ASE's

The thickeners are supplied at low viscosity and at 25-35% solids depending on grade. They are easily mixed into aqueous based systems, and in many cases can be added directly to the system to be thickened followed by pH adjustment where necessary. The final pH of the thickened formulation should generally be in the range 8.0-9.5 to ensure optimum thickening efficiency and maintenance of a stable viscosity. If a volatile alkali such as ammonia is used, care should be taken to avoid loss of the alkali and lowering of the pH as viscosity reduction may occur. In some cases it may be necessary to dilute the thickener (up to 2:1 with water) before addition to certain latex systems to avoid any localized thickening and instability. Another option is to prepare a pre-gel where localized gelation and instability could be a problem. In this case at least two parts water to one part of thickener is recommended followed by neutralization in order that a handleable gel is obtained. Care should also be taken to avoid air entrainment when such a gel is prepared.

Scott Bader Texicryl – Hydrophobically Modified Alkali Swellable Emulsions (HASE)

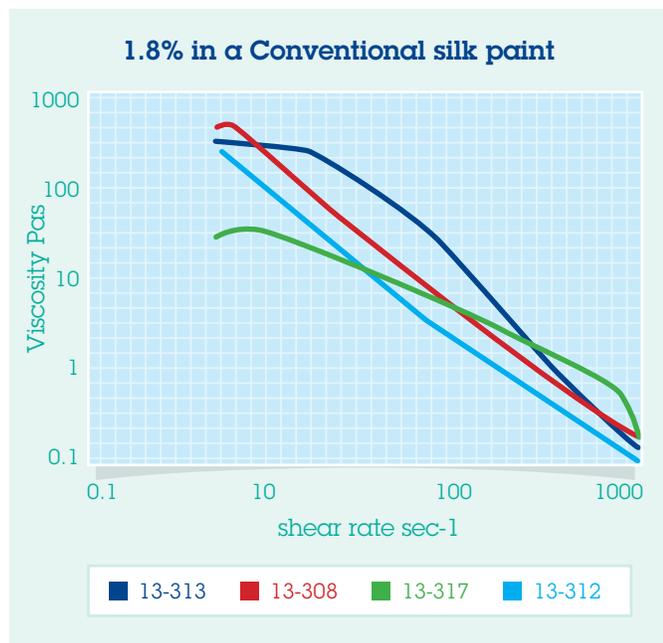
These are dispersions of acid functional acrylic polymers in water like standard ASE types. They are supplied at low pH and the acid groups on the polymer chains need to be neutralized to allow the polymer to solubilize. HASE systems have, in addition to the acid groups, long chain hydrophobes attached to the polymer backbone.

These hydrophobic groups can associate with each other (forming micelles analogous to surfactants) and with other hydrophobic ingredients in a formulated system. HASE thickeners are often referred to as associative thickeners because of this behavior.

The multiple associations between the HASE thickener and various formulation ingredients significantly impacts on the rheological properties of a given system. HASE thickeners generally allow a more Newtonian rheology to be achieved compared to standard ASE thickeners. HASE thickeners can be designed to give formulated system rheologies ranging from pseudoplastic to fairly Newtonian depending on the nature of the hydrophobe and the polymer design.

Rheology and Efficiency

The graph below indicates the relative rheological behavior of the Scott Bader range of Texicryl HASE thickeners in a simple matte paint formulation.



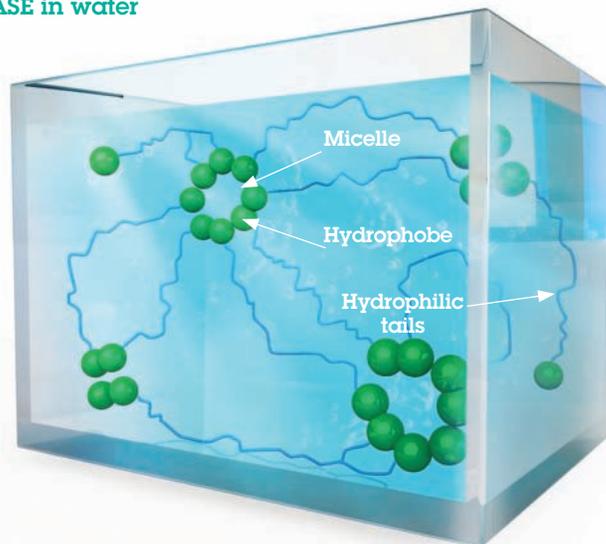
Texicryl 13-313 is a very efficient thickener with a high, low-shear viscosity and has excellent pigment suspension characteristics. It is quite strongly shear thinning, but shows somewhat different flow characteristics compared to a standard ASE thickener.

Texicryl 13-317 shows much less shear thinning behavior and therefore more Newtonian character leading to higher viscosities in the mid and high shear rate ranges. Improved flow and leveling as well as brush drag and film build is generally achieved when using this thickener.

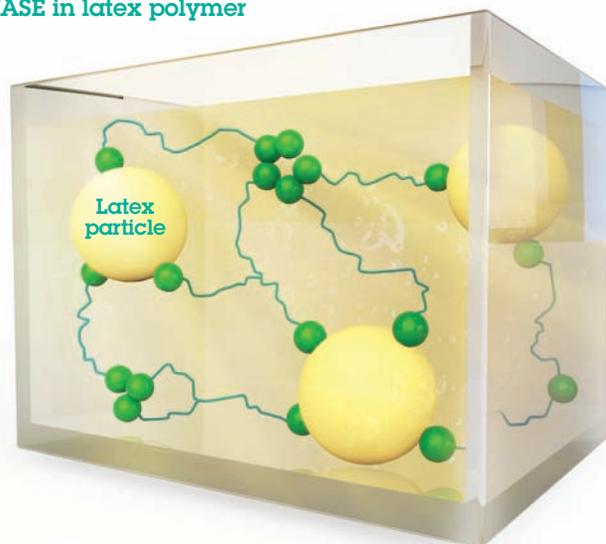
Thickening Mechanism of HASE Thickeners

The diagrams (below) illustrate how the HASE thickeners look in water and in a system containing latex particles.

HASE in water



HASE in latex polymer



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