

## **FORMULATING WITH ASSOCIATIVE RHEOLOGY MODIFIERS**

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The addition of a rheology modifier to provide necessary processing and performance characteristics is typical of many formulations. Commonly referred to as thickeners, or viscosifiers, these additives have more influence on a system than simply altering the thickness, or viscosity, of the compound. The product must display an acceptable response to the shear induced deformation encountered in the manufacture of the product, as well as in application. A thorough understanding of the rheological requirements of an application is essential to successful product development. The key to this understanding is building a solid knowledge base regarding the effect a change in rheology has on the established critical parameters of a system. Regardless of the method used to evaluate the rheology, a basic understanding of the thickening mechanism, combined with knowledge of the affect of the system components on the rheology modifier and one another, will enable formulators to more effectively utilize their resources in developing new products, and improving existing formulations.

### **CLASSIFICATION OF RHEOLOGY MODIFIERS**

Rheology modifiers may be classified as either naturally, or synthetically derived products. Examples of the former include starch, cellulose, alginate, and protein. These naturally occurring polymers incorporate building blocks of polysaccharide units, or amino acids, to provide efficient, water soluble rheology modifiers. Grafting of selected moieties onto the backbone of the more widely utilized natural products, such as starch and cellulose, provides for numerous modified versions of the products, developed to address specific application requirements.

Three general classes of acrylic-based synthetic polymers comprise a group of products that have been utilized as rheology modifiers in various applications for many years. The first class is based on homopolymers of (meth)acrylic acid and copolymers of (meth)acrylic acid, (meth)acrylate esters, and maleic acid, among many others. This group is typically referred to as the alkali swellable (or soluble) emulsions (ASE).

Modification of the structure of ASE polymers by addition of hydrophobic moieties defines the second class of synthetic rheology modifiers known as the hydrophobically modified, alkali swellable emulsions (HASE). This group of polymers, more commonly referred to as associative thickeners, provides the potential for greater control of the compound rheology, over a broader range of shear rates than the traditional ASE class of synthetic polymers.

The third class of synthetic rheology modifiers is the hydrophobically modified, ethoxylated urethane resins (HEUR). This group of polymers typically consists of

polyethylene glycol units of varying length, connected by urethane linkages, and terminated with hydrophobic end groups. Unlike the ASE and HASE classes, HEUR rheology modifiers are nonionic substances, and are not dependent on alkali for activation of the thickening mechanism.

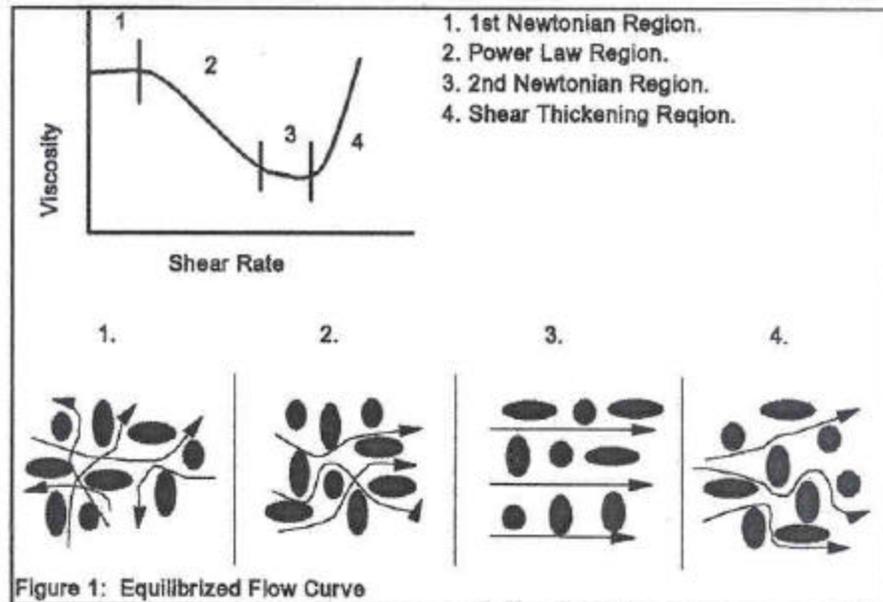
## RHEOLOGY TERMINOLOGY

Rheology may be described as a compound's response to a stress placed on the material during production, processing, and/or application. Rheology measures the change in viscosity of a substance under changing shear rates, or a change in viscosity over time, at a constant shear rate.

The rheology, or flow, of a compound may be classified as Newtonian, pseudoplastic, thixotropic, or dilatant, based on the measured response of the compound to a known shear rate, compared to classical models. Newtonian flow describes a compound that exhibits no change in viscosity with increasing shear rate. A classical example of a compound with Newtonian behavior is water. Paint may be considered as an example of an application requiring Newtonian behavior.

Pseudoplastic flow describes a system that exhibits a reduction in viscosity with increasing shear rate. The viscosity will recover as the shear is removed; though it may not follow the same viscosity profile as exhibited with increasing shear. This type of flow is also referred to as shear thinning. Most ASE and HASE type rheology modifiers will provide pseudoplastic rheology to a formulation (Figure: 1).

Thixotropic flow describes a compound that exhibits a reduction viscosity over time, at a constant shear rate. Like shear thinning behavior, thixotropic materials may recover their viscosity upon removing, or reducing shear from the system.

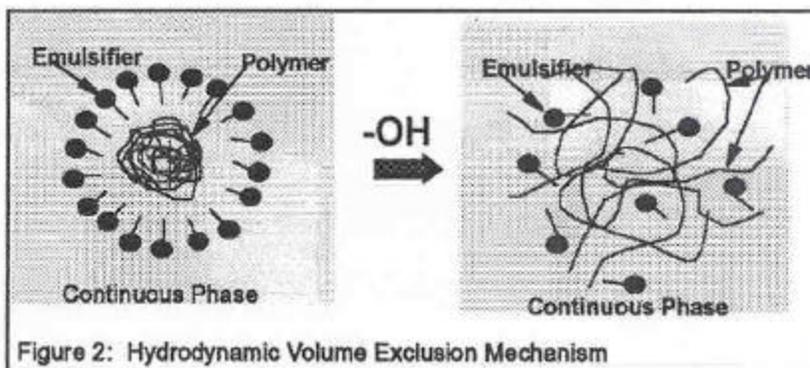


A final class of rheological behavior is defined as dilatant, or shear thickening flow. This type of flow exhibits an increase in viscosity with increasing shear rate, and is generally an indication of instability in a system. When the stress imparted on a system becomes excessive, the particles begin to grind against one another, resulting in an increase in viscosity. While this type of behavior may be desirable for a specific application, it is impractical from a processing standpoint, as the material would thicken when pumped causing lines, screens, etc, to plug.

Rheological properties that may have a significant impact on a compound's performance in addition to viscosity under shear include yield point and elasticity. The measurement of the rheology of a system includes both a viscous and an elastic component. The visco-elastic characterization of a formulation provides information that is essential in determining the potential for a compound to gel, or for predicting the leveling and sag characteristics of a compound in application. These measurements may be obtained on equipment designed to provide control of the stress placed on the sample, and are not predictable from measurements made by typical process control instruments such as a Brookfield viscometer.

## THICKENING MECHANISMS

Water soluble rheology modifiers of the type described above, impart their effect on a system through one, or more, of three distinct mechanisms. The most prevalent is the hydrodynamic, volume exclusion (HDV) mechanism. The mechanism derives its name from the simple fact that a substance in solution occupies some volume with the solution, thereby excluding the possibility of any other substance occupying that same volume.



As more solute is added, less volume is available within the solution, with the observable effect noted as an increase in solution viscosity. The particle size of a typical (H)ASE product averages approximately 0.2 microns (200 nanometers). Within this surfactant stabilized particle, exists the water insoluble, tightly coiled polymer, of a typical molecular weight in the 200,000 to 1.5 million range. Addition of alkali to the polymer emulsion results in neutralization of the carboxylic acid groups, generating an anionic charge at the acid sites along the polymer chain. The like charges repel one another resulting in swelling and uncoiling of the polymer. This extremely large increase in the hydrodynamic volume of the neutralized ASE polymer, versus the same polymer in its

emulsion state, is responsible for a significant build in compound viscosity, at relatively low polymer concentration (Figure: 2).

The presence of hydrophobic groups along the backbone of HASE polymers allows the associative thickening mechanism to be defined. Hydrophobic groups in an aqueous environment results in an inherently unstable, high free energy system. Association of the hydrophobic groups with “other” hydrophobic species in the formulation creates hydrophobic “domains”, ultimately providing a reduction in overall free energy of the system and a more structured compound. The formation of the hydrophobic domains is thermodynamically driven, and is most prevalent under static and low shear conditions. Increasing shear rate deforms the network of water soluble polymer chains interwoven with the hydrophobic domains, physically separating the hydrophobic domains and preventing the association from occurring. The domains will reform once the shear has been removed, at a recovery rate dependent on a number of factors, including polymer structure, addition level, and the various system components.

A third thickening mechanism is based on the particle-particle interaction of formula components. The attractive forces between charged species are exploited to provide optimized rheology in a number of applications. Thickening through particle-particle interaction is typically due to adsorption phenomenon between specific components of the rheology modifier and charged surfaces of system components, and the affect of charge-charge repulsion forces. An example of rheology control that involves particle-particle interaction, but does not involve increasing viscosity, is the effect of low molecular weight polyacrylate dispersant to reduce viscosity and allow for higher solids pigment slurries.

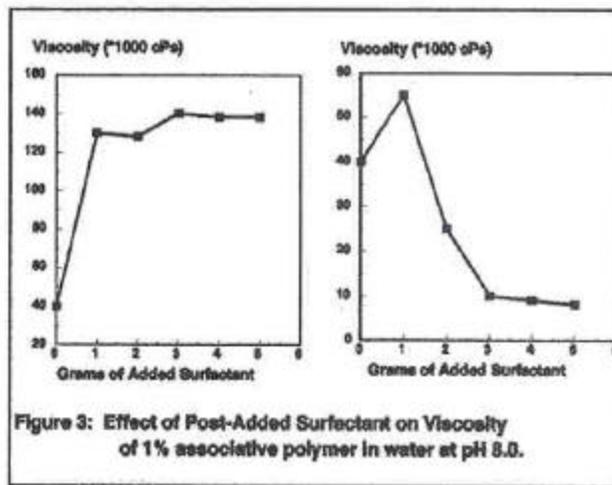
These mechanisms are easily observed in water, but very few applications are directed at thickening only water. Formulations containing rheology modifiers typically contain a pigment or filler, a latex binder, and any number of accompanying or post-added processing aids, surfactant and dispersant. These components offer the potential for all three mechanisms to occur within the same system. Therefore, the key to formulating with ASE and HASE rheology modifiers is an establishing a thorough understanding of potential system interactions to enable the formulator to optimize a product that meets the requirements of the application in an effective and cost efficient manner.

## SYSTEM INTERACTIONS

Associative thickeners may provide viscosity to a compound by all three of the thickening mechanisms discussed above. The HDV mechanism is activated at alkaline pH, domains are formed by the association of the pendent associative monomers with one another and with other hydrophobic substances in the compound, and the particle-particle interaction mechanism is occurring through adsorption of alkoxyated species resent in the thickener, onto charged edges and surfaces of pigments and surfactant stabilized latex particles. Factors that have an influence, either positive or negative, on the operation of the three mechanisms with therefore, have an influence on the final compound rheology.

## Influence of Surfactant

Surface active agents present in formulations containing an associative thickener have a direct impact on properties of the hydrophobic domains formed in solution. The performance of a surfactant is a function of the ratio of the hydrophobic portion of the molecule to the hydrophilic portion. A surfactant molecule in water, is in an energetically unfavorable state, analogous to the hydrophobic associative monomer discussed above.



In an attempt to reduce the overall free energy of the system, the surfactants will interact with one another, forming lipid bilayer and, as the concentration increases, eventually forming micelles. Such behavior allows the surfactant molecules to establish a hydrophobic environment within the bulk water phase, expelling water molecules, and providing a reduction in overall free energy to the system. Surfactant added to an associatively thickened formulation will tend to migrate toward the associative groups of the rheology modifier, aligning their hydrophobic component with those of the thickener. Added at concentrations below the critical micelle concentration (CMC), the surfactant may form “bridges” between hydrophobes of the thickener, providing a more structured matrix to the formulation, which is observed as an increase in compound viscosity (1). Continued addition of surfactant will ultimately allow each individual associative group to become surrounded by surfactant, effectively reducing the hydrophobic character of the associative monomer and prohibiting the associative mechanism from operating (Figure: 3). Careful selection of post-added surfactant allows the formulator to exert some degree of control over the phenomenon.

## Influence of pH and Salt

An alkaline pH is essential to achieving performance from ASE and HASE rheology modifiers. The products are activated at a pH greater than 7.0, with optimized thickener compositions capable of maintaining a stable compound viscosity through pH 12.0. A drop in viscosity at elevated pH is related to a change in the solution’s ionic strength, reducing the charge repulsion of the anionic groups along the polymer chain. The result is a less expanded polymer occupying less volume, and is observed as a reduced compound

viscosity. The ionic strength of the solution also has an impact on adsorption of the thickener onto charged surfaces of pigment containing formulations. Similar response is seen when salt is introduced to the system, again due to a change in ionic strength and the subsequent effect on the expansion of the polymer. The negative impact of salt on the viscosity of a compound may be offset by addition of surfactant to the system.

#### Other Variables

Additional factors that should be considered when formulating with associative rheology modifiers include the choice of neutralizing agent, the presence of co-solvents, and order of addition of the formulation components. Monovalent neutralizing agents are recommended. The use of a di- or tri- valent base creates the potential for one base molecule to neutralize more than one acid group, restricting the ability of the polymer to fully expand, and resulting in generation of a lower compound viscosity. Selected co-solvents, alcohols in particular, may interfere with the associative domains through improved solubility of the hydrophobes in the mixed solvent system. Organic alcohols are commonly used to suppress the associative mechanism to provide reduced as-is viscosity and easier handling of the product. The order of addition of formulation components will have an impact on processing, and may affect the performance of the compound. Optimum processing is achieved when all components are added before addition of the neutralizing agent. This procedure allows for satisfactory mixing of all the components prior to activation of the thickener and the accompanying increase in viscosity.

#### SUMMARY

ASE, HASE, and HEUR rheology modifiers are highly efficient additives for numerous applications. An understanding of the fundamental thickening mechanisms involved in application of the products, along with factors which influence the thickening mechanism, allows the formulator to achieve successful product development in a predictable and timely manner.

#### LITERATURE CITATIONS

1. Lochhead, R.Y., Water-Soluble/Water-Dispersible Copolymers Short Course, Sec. 7, p. 74, (May 23, 1994).

#### ACKNOWLEDGEMENTS

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