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Rheology Control Additives

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Rheology Control Additives

The exercise of rheological control over water is a significant challenge for formulators. Water is an invaluable solvent and vehicle, but it is not without certain deficiencies. It is, above all, watery. It is often too thin, it is generally runny, and it is invariably unsupportive of insoluble particulates. Formulators are therefore forced to adjust water to suit their needs. Fortunately, this can be readily accomplished through the use of rheology modifiers.

Specific control of water is enabled by the careful application of one or more of the rheology modifiers available for use in aqueous compositions. Familiarity with the rheological nuances of a particular modifier can at times make the difference between an exceptional formulation and a routine one. What follows is an overview of the clay, gum and polymeric additives most commonly used to control water. The intent is to make the formulator sufficiently familiar with the fundamental nature of each of these materials, so as to facilitate proper selection.

The terms used to characterize rheology are defined as follows:

Pseudoplastic – Pseudoplastic fluids are generally considered to be simply shear-thinning. Specifically, they show decreasing viscosity in response to increasing shear rate. Moreover, they immediately recover their non-sheared viscosity once shear is removed.

Thixotropic – Thixotropic fluids show a time-dependent response to shear. When subjected to a fixed shear rate, they will decrease in viscosity over time. Often this is seen as a large initial viscosity loss, followed by gradual further loss. Once shear is removed, thixotropic fluids recover their viscosity, but over a period of time, not instantaneously. These fluids are also considered to be pseudoplastic, but only in that they show decreasing viscosity in response to increasing shear rate.

Yield Value – Yield value indicates the minimum force (the yield stress) that must be applied to a liquid to start disrupting the structure imparted by the rheology modifier, so that flow can occur. In practical terms, solids, oils and gases are trapped and segregated by this structure unless gravity or buoyancy can exert a force greater than the yield stress.

In addition, the term “synergism” is used to indicate that a combination of two rheology control additives provides a stronger rheological effect (e.g., viscosity or yield value) than would be anticipated by adding the individual contribution of each additive.

Smectite Clay

Description: The smectites are a family of water-swallowable clays having a lattice sheet structure. Smectite clays are more commonly known as bentonite or magnesium aluminum silicate. Once hydrated, most smectites form an alkaline dispersion. Water-washed smectite clays are often preferred because they are controlled for purity, bacteria, whiteness, heavy metals and performance efficiency.

Rheology: A macroscopic particle of smectite clay is composed of many thousands of stacked and/or overlapped submicroscopic flakes. These are approximately 1 nanometer thick by several hundred nanometers across and are separated by a highly oriented layer of water. The flake faces carry a negative charge, while edges have a slightly positive charge. The overall negative charge is balanced by exchangeable sodium ions. When the clay and water are mixed, water penetrates the area between the flakes, forcing them farther apart. The exchange ions then begin to diffuse away from the flake faces. Further penetration of water between the flakes then proceeds in an osmotic manner until they are completely separated. For most smectites, the speed with which flake separation occurs is directly related to the amount of energy introduced during hydration. Mechanical and thermal energy accelerate delamination.

The smectites produce thixotropic, pseudoplastic dispersions with yield value. These clays are available in a range of viscosities, although their primary function is to impart yield value and thereby stabilize emulsions, suspensions and foams. They are often used in combination with anionic and nonionic organic thickeners to finely tailor rheology and for advantageous synergism in viscosity and/or yield value.

Compatibilities: Electrolytes and most other water-soluble ingredients inhibit the hydration of the smectites. However, these same solutes often exert a beneficial viscosity enhancing effect when added in limited amounts after the clay is well hydrated. The smectites are generally stable in systems between pH 3 and pH 12, but have a limited tolerance of electrolytes due to the ionic nature of their colloidal structure. This is compensated for by their use in combination with electrolyte-tolerant organic rheology modifiers. Smectites are synergistic in viscosity and yield value with most

common organic thickeners. The viscosity and yield value of smectite dispersions are unaffected by temperature, microorganisms, enzymes or UV light.

Hormite Clay

Description: The hormites are water dispersible clays with a chain structure that results in microscopic, needle-like particles. The commercial varieties are palygorskite, more commonly known as attapulgite, and sepiolite. The primary commercial palygorskite, attapulgite, has typically short (< 2 μm) and low aspect ratio (< 10:1) needles. The primary commercial sepiolite, from Spain, has longer and more flexible needles. Most hormite clay is dry processed for absorbent and rheological uses. Small quantities are hydroclassified for personal products and pharmaceutical applications. Although there are differences in the performance of attapulgite and sepiolite, they are relatively minor. The choice between the two is usually decided by local availability. Hormite dispersions are alkaline in pH, with less cohesive colloidal structures than produced by smectites since these structures are not based on ionic bonds.

Rheology: When hormite clays are dispersed in water, they do not swell like smectites, but deagglomerate in proportion to the amount of shear applied, and form a random colloidal network. This loosely cohesive structure offers rheological properties similar to those of smectite clays but often with somewhat less physical stability.

Compatibilities: Because a dispersion of hormite clay is mechanically rather than osmotically driven, it is unaffected by the presence of solutes. Likewise, since the hormite colloidal structure does not depend on ionic attraction, it is insensitive to subsequently added solutes and exhibits broad pH stability. The viscosity and yield value of hormite dispersions are unaffected by temperature, microorganisms, enzymes or UV light.

Xanthan Gum

Description: Xanthan gum is an anionic polysaccharide derived from the fermentation of the plant bacteria *Xanthomonas campestris*. It is soluble in hot or cold water and gives visually hazy, neutral pH solutions. Grades that provide

high light transmittance are available. Xanthan gum will dissolve in hot glycerin.

Rheology: Xanthan gum solutions are typically in the 1500 to 2500 cps range at 1%; they are pseudoplastic and especially shear-thinning. In the presence of small amounts of salt, solutions show good viscosity stability at elevated temperatures. Solutions possess excellent yield value.

Compatibilities: Xanthan gum is more tolerant of electrolytes, acids and bases than most other organic gums. It can, nevertheless, be gelled or precipitated with certain polyvalent metal cations under specific circumstances. Solutions show very good viscosity stability over the pH 2 to pH 12 range and good tolerance of water-miscible solvents (30 to 50% of solution weight). Xanthan gum is compatible with most nonionic and anionic gums, featuring useful synergism with galactomannans. It is more resistant to shear, heat, bacterial, enzyme, and UV degradation than most gums.

Sodium Carboxymethylcellulose

Description: Sodium Carboxymethylcellulose (CMC) is an anionic polymer made by swelling cellulose with NaOH and then reacting it with monochloroacetic acid. It is soluble in hot or cold water and gives neutral solutions. Solutions of refined grades are clear and colorless.

Rheology: CMC is available in grades ranging from 10 cps at 2% to 4500 cps at 1%. Most CMC solutions are slightly thixotropic; some strictly pseudoplastic grades are available. All solutions show a reversible decrease in viscosity at elevated temperatures. CMC solutions lack yield value.

Compatibilities: In general, stability with monovalent salts is very good; with divalent salts good to marginal; with trivalent and heavy metal salts poor, resulting in gelation or precipitation. CMC solutions offer good tolerance of water-miscible solvents (30 to 50% of solution weight), good viscosity stability over the pH 4 to pH 10 range, compatibility with most water-soluble nonionic gums, and synergism with hydroxyethylcellulose and hydroxypropylcellulose. Solutions are susceptible to shear, heat, bacterial, enzyme, and UV degradation.

Methylcellulose, Hydroxypropylmethylcellulose

Description: Methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC) are nonionic polymers made by swelling cellulose with NaOH and then reacting it with methyl chloride alone (MC) or methyl chloride and propylene oxide (HPMC). Both are soluble in cold water and give clear, colorless, surface-active solutions of neutral pH.

Rheology: MC is available in grades from very low to high viscosity. HPMC is available in grades from very low to extremely high viscosity. Solutions are pseudoplastic and have characteristic gelation temperatures between 50°C and 85°C, depending upon the grade. These gels are reversible with return to fluidity on cooling. Below the gelation temperature, solutions show a decrease in viscosity as temperature increases. Non-gelled solutions lack yield value.

Compatibilities: MC and HPMC are compatible with most inorganic salts, limited only by the electrolyte concentration at which the polymers are salted out. HPMC will tolerate somewhat higher electrolyte concentrations than MC. Both polymers show good viscosity stability in the pH 3 to pH 11 range, and good tolerance of water-miscible solvents. Some grades are soluble in specific polar organic liquids. MC and HPMC are more resistant to bacterial and enzyme degradation than most cellulose derivatives.

Hydroxyethylcellulose

Description: Hydroxyethylcellulose (HEC) is a nonionic polymer made by swelling cellulose with NaOH and reacting with ethylene oxide. HEC is soluble in hot or cold water and gives clear, colorless, neutral pH solutions.

Rheology: HEC is available in grades ranging from 2 cps to 800,000 cps at 2%. Solutions are pseudoplastic and show a reversible decrease in viscosity at elevated temperatures. HEC solutions lack yield value.

Compatibilities: HEC solutions are compatible with most inorganic salts, limited only by the electrolyte concentration at which the polymer is salted out. Polyvalent inorganic salts will salt out HEC at lower concentrations than monovalent salts. HEC solutions show only a fair tolerance of

water-miscible solvents (10 to 30% of solution weight), but good viscosity stability over the pH 2 to pH 12 range. They are compatible with most water-soluble gums and resins, and are synergistic with CMC and sodium alginate. HEC solutions are susceptible to bacterial and enzyme degradation.

Hydroxypropylcellulose

Description: Hydroxypropylcellulose (HPC) is a nonionic polymer made by swelling cellulose with NaOH and then reacting it with propylene oxide. HPC is soluble in cold water at <40°C and gives clear, colorless, surface-active solutions of pH 5 to pH 8.5.

Rheology: HPC is available in grades ranging from 4 cps to 25000 cps at 1%. Solutions are pseudoplastic and lack yield value. HPC will precipitate from water solutions above 45°C.

Compatibilities: HPC is compatible with most inorganic salts, limited only by the electrolyte concentration at which the polymer is salted out. Polyvalent inorganic salts will salt out HPC at lower concentrations than monovalent salts. HPC has better solubility in most polar liquids than in water. Aqueous solutions can tolerate unlimited dilution with most water-miscible solvents. The best viscosity stability is achieved in the pH 6 to pH 8 range. HPC is compatible with most water-soluble gums and resins, and it is synergistic with CMC and sodium alginate. Solutions are susceptible to shear, heat, bacterial, enzyme and UV degradation.

Carageenan

Description: Carageenan is an anionic polysaccharide, extracted principally from the red seaweed *Chondrus crispus*. Carageenan is available in sodium, potassium, magnesium, calcium and mixed cation forms. Three main structural types exist: Iota, Kappa, and Lambda, differing in solubility and rheology. The sodium form of all three types is soluble in both cold and hot water. Other cation forms of Kappa and Iota are soluble only hot water. All forms of Lambda are soluble in cold water. Carrageenan solutions are typically clear, and of alkaline pH.

Rheology: All solutions are pseudoplastic with some degree of yield value. Certain Ca-Iota solutions are thixotropic. Lambda is non-gelling.

Kappa can produce brittle gels; Iota can produce elastic gels. All solutions show a reversible decrease in viscosity at elevated temperatures.

Compatibilities: Iota and Lambda carageenan have excellent electrolyte tolerance, Kappa's being somewhat less. Electrolyte will, however, depress solution viscosity. Solutions show a fair to good tolerance of water-miscible solvents (10 to 30% of volatile solvents; up to 80% of glycerin). The best solution stability occurs in the pH 6 to pH 10 range. Carageenan is compatible with most nonionic and anionic water-soluble thickeners. It is strongly synergistic with locust bean gum and strongly interactive with proteins. Solutions are susceptible to shear and heat degradation.

Hydroxypropyl Guar

Description: Hydroxypropyl Guar (HPG) is a nonionic derivative of guar gum. Guar is the refined endosperm of the guar (*Cyamopsis tetragonolobus*) seed. HPG is made by reacting guar gum with propylene oxide. It is soluble in hot or cold water and gives clear solutions.

Rheology: HPG gives high viscosity, pseudoplastic solutions that show a reversible decrease in viscosity at elevated temperatures. HPG solutions lack yield value.

Compatibilities: HPG is compatible with high concentrations of most salts. It shows good tolerance of water-miscible solvents (up to about 60% by weight) and much better compatibility with minerals than does guar. HPG offers very good viscosity stability in the pH 2 to pH 13 range, and is more resistant to bacterial and enzyme degradation than underivatized guar and many other organic thickeners.

Gum Arabic (Acacia)

Description: Gum Arabic is an anionic polysaccharide collected as the dried exudate from the acacia tree (*Acacia senegal*). Sold as the naturally occurring mixed Ca, Mg, and K salt, it is soluble in hot or cold water and gives clear solutions of neutral to acidic pH.

Rheology: Gum Arabic is a very low viscosity gum, with possible concentrations of up to 50% in water. Below a 40% concentration, solutions are Newtonian; above 40% they are pseudoplastic.

Solutions show reversible viscosity loss at elevated temperatures and possess yield value at sufficient concentration.

Compatibilities: Gum Arabic is compatible with moderate amounts of most salts, acids and alkalis, as well as with most water-soluble thickeners. Solutions are stable between pH 1 and pH 14; viscosity peaks at pH 6, dropping sharply below pH 5 and above pH 7. Electrolytes depress solution viscosity. Solutions are tolerant of water-miscible solvents to about 50% of solution weight, and are susceptible to bacterial, heat and UV degradation.

Gum Tragacanth

Description: Gum Tragacanth is an anionic polysaccharide collected as the dried exudate from shrubs of the genus *Astragalus*. It is composed of two major components: water-swelling bassorin and water-soluble tragacanthin. It produces hazy, surface active solutions of slightly acidic pH in hot or cold water. Its ability to lower surface tension and interfacial tension, in addition to thickening, makes Gum Tragacanth an effective emulsion stabilizer

Rheology: Gum Tragacanth is available in grades of varying quality and refinement with 1% viscosities of about 300 cps to 3000 cps. Solutions are pseudoplastic, show a reversible decrease in viscosity at elevated temperatures and possess good yield value.

Compatibilities: Gum Tragacanth solutions are tolerant of monovalent and divalent cations, but are precipitated by trivalent species. They show a limited tolerance of water-miscible solvents, but provide synergistic viscosity with glycerin. Solutions are stable between pH 2 and pH 11, with some loss in viscosity at pH <5. Gum Tragacanth is compatible with most water-soluble thickeners. Solutions are unusually resistant to bacterial growth and degradation.

Sodium Alginate

Description: Sodium alginate is an anionic polysaccharide extracted principally from the giant kelp *Macrocystis pyrifera* as alginic acid and neutralized to the sodium salt. It is soluble in hot or cold water and gives somewhat hazy solutions of neutral pH.

Rheology: Sodium alginate is available in grades ranging from about 20 cps to about 1000 cps at 1%. Solutions are pseudoplastic and show a reversible decrease in viscosity at elevated temperatures. Sodium alginate solutions lack yield value.

Compatibilities: Sodium alginate has limited compatibility with monovalent salts. Polyvalent cations tend to cause gelation or precipitation. Solutions show a fair to good tolerance of water-miscible solvents (10 to 30% of volatile solvents, 40 to 70% of glycols). Highly refined sodium alginate shows good stability over the pH 3 to pH 10 range; residual Ca raises the pH minimum to 5. Sodium alginate is compatible with most water-soluble thickeners and resins. Its solutions are more resistant to bacterial and enzyme degradation than those of many other organic thickeners.

Polyacrylates

Description: The polyacrylates are anionic polymers typically produced by emulsion polymerization of acrylic acid or substituted acrylic acid. They are most often sold as thin emulsions of poly(acrylic acid) which upon neutralization give clear solutions.

Rheology: Sodium polyacrylates usually give pseudoplastic solutions with some yield value. With the multitude of variations of sodium polyacrylate and copolymers containing polyacrylate, almost any desired rheology can be found. Solutions usually show a reversible decrease in viscosity at elevated temperatures.

Compatibilities: Many organic and inorganic bases can neutralize poly(acrylic acid) to produce viscous, clear solutions. Neutralized solutions have limited compatibility with excess alkali or electrolytes before salting out. Electrolytes tend to depress solution viscosity. Sodium polyacrylates are compatible with many water-soluble thickeners and resins. Solutions are resistant to bacterial degradation, but susceptible to shear degradation.

Carbomer

Description: Carbomers are anionic carboxyvinyl polymers made by chemically crosslinking poly(acrylic acid). They are dispersible in hot or cold water and give acidic solutions; they must be

neutralized to develop desired rheological properties.

Rheology: Carbomers are typically neutralized with sodium hydroxide (NaOH) or triethanolamine (TEA) to give extremely high viscosity, clear, colorless gels at >0.5% (depending on the grade) or smooth-pouring viscous solutions at lower levels. Solutions are pseudoplastic, possess excellent yield value and show some reversible viscosity loss at elevated temperatures.

Compatibilities: Electrolytes depress the viscosity of neutralized solutions of carbomers, usually in proportion to the valence of the cation. NaOH or TEA neutralized solutions show good viscosity stability over the range of approximately pH 5 to pH 11. Carbomer solutions typically show excellent tolerance of water miscible solvents. A number of polar liquids can be effectively thickened in the anhydrous state by the proper choice of neutralizing agent. Water solutions are generally resistant to shear, heat, bacterial and enzyme degradation, but are susceptible to UV degradation.

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