

## HYDROCOLLOIDS

### *Efficient Rheology Control Additives*



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heology is defined as "the study of the change in form and the flow of matter embracing elasticity, viscosity and plasticity." We concern ourselves with viscosity, further defined as "the internal friction of a fluid

caused by molecular attraction, which makes it resist a tendency to flow."

Water is an invaluable solvent and vehicle but it is not without certain deficiencies. It is, above all, watery. The exercise of rheological control over water is a significant challenge for formulators. It is often too thin, it is generally runny and it is invariably unsupportive for 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 hydrocolloids based 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:**

**Newtonian** - The viscosity of such fluids will not change as the shear rate is varied. Water and thin motor oils show typical Newtonian behavior.

**Non-Newtonian** - The viscosity of such fluids will change as the shear rate is varied. There are several types of non-Newtonian flow behavior, characterized by the way a fluid's viscosity changes in response to variations in shear rate. The most common types of non-Newtonian fluids you may encounter include:

- **Pseudoplastic** - This type of fluid will display a decreasing viscosity with an increasing shear rate. Probably the most common of the non-Newtonian fluids, pseudo-plastics include paints, emulsions and dispersions of many types. This type of flow behavior is sometimes called "shear-thinning." Moreover, they immediately recover their non-sheared viscosity once shear is removed.
- **Dilatant** - Increasing viscosity with an increase in shear rate characterizes the dilatant fluid. Although rarer than pseudoplasticity, dilatancy is frequently observed in fluids containing high levels of deflocculated solids such as clay slurries, candy compounds, corn starch in water and sand/water mixtures. Dilatancy is also referred to as "shear-thickening" flow behavior.
- **Plastic** - This type of fluid will behave as a solid under static conditions. A certain amount of force must be applied to the fluid before any flow is induced; this force is called the "yield value." Tomato ketchup is a good example of this type of fluid; its yield value will often make it refuse to pour from the bottle until the bottle is shaken or struck, allowing the ketchup to gush freely. Once the yield value is exceeded and flow begins, plastic fluids may display Newtonian, pseudoplastic or dilatant flow characteristics.

**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.

Some fluids display a change in viscosity with time under conditions of constant shear rate. There are two categories to consider:

**Thixotropy** – Thixotropic fluids show a time-dependent response to shear. When subjected to a constant 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. Thixotropy is frequently observed in materials such as greases, heavy printing inks and paints.

**Rheopexy** - This is essentially the opposite of thixotropic behavior, in that the fluid's viscosity increases with time as it is sheared at a constant rate. Rheoplectic fluids are rarely encountered.

Both thixotropy and rheopexy may occur in combination with any of the previously discussed flow behaviors or only at certain shear rates. The time element is extremely variable; under conditions of constant shear, some fluids will reach their final viscosity value in a few seconds, while others may take up to several days.

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.

### **Rheology Control Additives**

#### **Guar Gum**

**Description:** Guar gum is a nonionic hydrocolloid obtained from the ground endosperm of the legume *Cyamopsis tetragonolobus*, an annual plant which grows mainly in arid and semi-arid regions. It is soluble in cold water and gives visually hazy, neutral pH solutions.



**Rheology:** Guar gum shows pseudoplastic or “shear thinning” behavior in solution. The degree of pseudoplasticity increases with concentration and molecular weight. Solutions of guar gum do not exhibit yield stress properties.

**Compatibilities:** Guar gum is compatible with most nonionic and anionic gums, featuring useful synergism with some microbial gums. It is soluble in salt solutions that contain up to 70% by weight of monovalent cation salts. Tolerance decreases as the valency of cations increases. Solutions are stable between pH 4 to 11; viscosity peaks between pH 6 to 8. Solutions are susceptible to bacterial, heat, enzyme and UV degradation.

### 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 12 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.

### Carrageenan

**Description:** Carrageenan is an anionic polysaccharide, extracted principally from the red seaweed *Chondrus crispus*. Carrageenan 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-lota 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 carrageenan 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 between the pH 6 to 10. Carrageenan 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.

### 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 to 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 to 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 10. Sodium alginate is compatible with most water soluble thickeners and resins. Its solutions are more resistant to bacterial and enzymatic degradation than those of many other organic thickeners.

### Sodium Carboxymethyl Cellulose

**Description:** Sodium carboxymethyl cellulose (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 5000 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 10, compatibility with most water-soluble nonionic gums and synergism with hydroxyethyl cellulose and Hydroxypropyl cellulose. Solutions are susceptible to shear, heat, bacterial, enzyme, and UV degradation.

### Methyl Cellulose, Hydroxypropylmethyl Cellulose

**Description:** Methyl cellulose (MC) and hydroxypropylmethyl cellulose (HPMC) are nonionic and anionic polymers respectively 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 and 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 between the pH 3 to 11 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 enzymatic degradation than most cellulose derivatives.

### Hydroxyethyl Cellulose

**Description:** Hydroxyethyl cellulose (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 80000 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 12. 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 enzymatic degradation.

### **Hydroxypropyl Cellulose**

**Description:** Hydroxypropyl cellulose (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 9.

**Rheology:** HPC is available in grades ranging from 10 cps to 5000 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 8. 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.

### **Hydroxypropyl Guar**

**Description:** Hydroxypropyl guar (HPG) is a nonionic derivative of guar gum. 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 range 4 to 10 and is more resistant to bacterial and enzyme degradation over native guar and many other organic thickeners.

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