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VANDERBILT *Technical Data*

Stabilizing Concentrated Suspensions with VAN GEL® and VEEGUM® MAGNESIUM ALUMINUM SILICATE CLAYS

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STABILIZING CONCENTRATED SUSPENSIONS WITH VAN GEL® AND VEEGUM® MAGNESIUM ALUMINUM SILICATE CLAYS

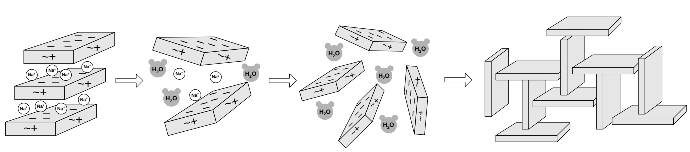
Stabilizing aqueous suspensions of fine particulates can be a considerable challenge, particularly if the concentration of particulates is high and the suspension needs to be sufficiently fluid to be easily poured or pumped. **VAN GEL** and **VEEGUM** smectite clays form a colloidal structure in water that is well-suited for suspension stabilization. The utility of these clays as suspending agents is further enhanced by their synergistic interaction with thickening agents. Common thickeners may efficiently increase viscosity, but are often poor suspending agents. **VAN GEL** and **VEEGUM** clays are used with these thickeners to impart suspension stabilization and allow finer adjustment of rheological properties than would be possible with the thickener alone. These clays are also used with other thickeners that function as suspension stabilizers, such as **VANZAN**® xanthan gum, for optimum control over stability, viscosity and flow properties.

HOW VAN GEL AND VEEGUM CLAYS WORK

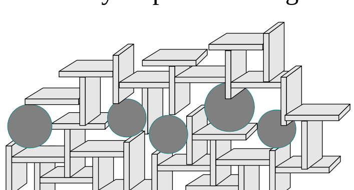
Each clay granule is composed of millions of flake-shaped particles stacked in sandwich fashion with a layer of water between each. A single flake is one nanometer thick and up to several hundred nanometers across. The faces of these flakes carry a negative charge, while edges have a slightly positive charge. The net negative charge is balanced by sodium ions.

When clay and water are mixed, water penetrates between the flakes forcing them further apart. Diffusion, the movement of cations from between flakes out into the surrounding water, and osmosis, the movement of water into the spaces between flakes, then promote delamination until the flakes are completely separated. The speed with which flake separation occurs is directly related to the amount of energy introduced during hydration. Both mechanical and thermal energy accelerate hydration: high shear mixing or warm water reduce hydration time. The presence of dissolved substances will prolong hydration time by inhibiting the diffusion and osmosis essential to flake separation.

Once the clay is hydrated (delaminated), the weakly positive flake edges are attracted to the negatively charged faces. A three dimensional colloidal structure forms that accounts for the characteristic thickening and stabilizing properties imparted by these clays.



This structure effectively traps particulates, keeping them segregated and uniformly dispersed throughout the water.



SUSPENSION TECHNIQUES

There are three techniques commonly used to produce stable concentrated suspensions with **VAN GEL** and **VEEGUM** clays.

1. When the particulates (pigments, pesticides, abrasives, drugs) are already of the desired particle size, the clay and the organic thickener (if used) are first thoroughly hydrated before the other ingredients are added with a dispersing mixer.
2. When the particulates need to be milled, a pre-suspension can be formed as above, but omitting the thickener. This is then media milled (attritor, ball mill, sand mill) until the particulates are reduced to the desired size. The organic thickener is usually reserved until the end of the milling cycle to avoid shear degradation.
3. All ingredients except the thickener are added directly to the media mill without pre-dispersion. The dispersion is formed as the particulates are milled, with the thickener added at the end of the milling cycle. The clay is generally not as well delaminated as when it is pre-hydrated, but the shear imparted by the mill is usually sufficient. This method was used to prepare the model suspension shown below in a ball mill, with sulfur as the particulate.

MODEL SUSPENSION	
VAN GEL B, clay suspending agent	0.25%
Polynaphthalene sulfonate, dispersant	2.50
Water	22.87
Propylene glycol, antifreeze	10.00
Surfynol® 104H[1], wetting agent	0.05
Triton® X114[2], wetting agent	0.20
Preservative	0.20
Flour Sulfur	64.00
VANZAN® xanthan gum suspending agent	0.03
Sulfur average particle size, μm[A]	2.7
Viscosity, cps[B]	
1 Day	880
1 Month	1010
3 Months	1080
Stability, 3 months	
Gelation/ Syneresis/ Packing	none

[A]Coulter [B]Brookfield, 60 rpm
[1]Air Products and Chemicals, Inc., Allentown, PA
[2]Dow Chemical Company, Midland, MI

CLAY GRADES

The clays most often used for suspension stabilization are:

VAN GEL B	The most economical grade for most suspensions.
VAN GEL ES	The most electrolyte-tolerant grade
VEEGUM	The standard grade for a wide range of applications.
VEEGUM CER	A smectite clay/CMC blend; a high efficiency suspension stabilizer.

Several additional clay grades are available to best match the **VAN GEL** or **VEEGUM** clay to formulation requirements.

RHEOLOGY

The terms used in this publication to characterize rheology are defined as follows:

Pseudoplastic: Pseudoplastic fluids are shear-thinning, with decreasing viscosity in response to increasing shear rate. They immediately recover their initial viscosity once shear is removed.

Thixotropic: Thixotropic fluids show a *time-dependent* response to shear. When subjected to a fixed shear rate, they decrease in viscosity over time. Often this is seen as a large initial viscosity loss, followed by gradual further loss. When shear is removed, viscosity recovers over a period of time. These fluids are usually also pseudoplastic.

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. For example, a particulate is trapped and segregated by this structure unless gravity can exert a force on it that exceeds the yield stress. In practical terms, yield value is indicative of the clay's ability to stabilize suspensions.

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 adding the individual contributions of each additive.

THICKENERS USED WITH VAN GEL AND VEEGUM CLAYS

Included below are descriptions of thickeners that are used in combination with **VAN GEL** and **VEEGUM** clays to adjust rheological properties and optimize suspension stability. In cases where a formulation relies solely on one of these thickeners for suspension stability, a more favorable balance of flow and stability, particularly at temperature extremes, is often attained by addition of a **VAN GEL** or **VEEGUM** clay.

Anionic Naturally-Derived Thickeners

Anionic naturally-derived thickeners generally show the best compatibility and synergism with **VAN GEL** and **VEEGUM** clays. Smectite:thickener ratios in the 9:1 to 2:1 range are recommended for a favorable balance of viscosity, yield value and flowability.

Xanthan Gum: Xanthan gum is soluble in hot or cold water and gives neutral pH, pseudoplastic solutions with yield value. In the presence of small amounts of salt, solutions show good viscosity stability at elevated temperatures and over the pH 2 to pH 12 range. Solutions are more tolerant of electrolytes, acids and bases, and more resistant to shear, heat, bacterial, enzyme and UV degradation than are most thickeners.

Xanthan gum enhances the flow properties, suspension efficiency, and the electrolyte, acid and alkaline compatibility of smectite clay dispersions. Smectite/xanthan gum combinations are particularly useful for stabilizing concentrated suspensions and emulsions that must remain flowable.

Sodium Carboxymethylcellulose: Sodium CMC is soluble in hot or cold water and gives neutral pH, slightly thixotropic solutions without yield value. Solutions provide good viscosity stability over the pH 4 to pH 10 range, but a reversible decrease in viscosity at elevated temperatures. CMC solutions are susceptible to shear, heat, bacterial, enzyme, and UV degradation.

CMC is strongly synergistic with **VAN GEL** and **VEEGUM** clays: high yield value, high viscosity, good electrolyte compatibility and good high temperature viscosity stability result. **VEEGUM CER**, a smectite/CMC blend, is a high efficiency suspension stabilizer, although somewhat less versatile than smectite/xanthan gum combinations in balancing suspension stability with flowability.

Carrageenan: Carrageenan is a seaweed-derived polysaccharide available in three main structural types - Iota, Kappa, and Lambda - that differ in solubility and rheology. The sodium form of all three types is soluble in both cold and hot water, providing alkaline, pseudoplastic solutions with yield value. Solutions show good viscosity stability in the pH 6 to pH 10 range, but a reversible decrease in viscosity at elevated temperatures. Solutions are susceptible to shear and heat degradation.

Sodium carrageenans are synergistic in viscosity and yield value with smectite clays, resulting in dispersions that are thixotropic but with good flowability.

Gum Tragacanth: Gum tragacanth is a plant-derived polysaccharide that is soluble in hot or cold water and produces slightly acidic, surface-active, pseudoplastic solutions with yield value. Its ability to lower surface tension and interfacial tension makes gum tragacanth an effective emulsion stabilizer. Solutions provide good viscosity stability over the pH 2 to pH 11 range, but with some loss in viscosity at pH <5 and a reversible decrease in viscosity at elevated temperatures. Gum tragacanth solutions are unusually resistant to bacterial growth and degradation.

Gum tragacanth is generally synergistic in viscosity and yield value with smectite clays, resulting in dispersions that are thixotropic but with good flowability.

Anionic Synthetic Thickeners

Polyacrylates: The polyacrylates are polymers 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. 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 and are resistant to bacterial degradation, but susceptible to shear degradation.

Combinations of sodium polyacrylates with **VAN GEL** and **VEEGUM** clays are strongly synergistic in viscosity and yield value at ratios in the 4:1 to 1:1 range. Rigid gels or thick pourable systems are possible.

Carbomer: Carbomers are chemically crosslinked poly(acrylic acid). They are dispersible in hot or cold water and give acidic solutions that must be neutralized to develop desired rheological properties. Depending on the grade, neutralized solutions can provide gels at >0.5%, or smooth-pouring viscous solutions at lower levels. Neutralized solutions provide good viscosity stability over the range of approximately pH 5 to pH 11. They are pseudoplastic, with yield value, and show some reversible viscosity loss at elevated temperatures. Neutralized solutions are generally resistant to shear, heat, bacterial and enzyme degradation, but are susceptible to UV degradation.

Carbomers generally demonstrate limited compatibility with **VAN GEL** and **VEEGUM** clays, and tend to cause flocculation. Useful, stable, synergistic combinations are obtained with some grades at low levels (<0.5%) and at approximately a 1:1 ratio. The smectite clay contributes improved high temperature viscosity stability.

Nonionic Naturally-Derived Thickeners

The common nonionic thickeners are more limited than anionic thickeners in their compatibility with **VAN GEL** and **VEEGUM** clays. Useful, stable, synergistic combinations are obtained at approximately a 1:1 ratio. The smectite clay contributes yield value and good high temperature viscosity stability; the thickener contributes smooth pour properties and good electrolyte tolerance. Lower thickener molecular weight generally provides better compatibility with smectite clays.

Methylcellulose, Hydroxypropylmethylcellulose: MC and HPMC are soluble in cold water to give surface-active, neutral pH, pseudoplastic solutions that gel between 50^{o}C and 85^{o}C, depending upon the grade. These gels are reversible, with return to fluidity on cooling. Below the gelation temperature, solutions lack yield value and decrease in viscosity as temperature increases. Both polymers show good viscosity stability in the pH 3 to pH 11 range, and are more resistant to bacterial and enzyme degradation than most cellulosics.

Hydroxyethylcellulose: HEC is soluble in hot or cold water and provides neutral pH, pseudoplastic solutions without yield value. Solutions provide good viscosity stability over the pH 2 to pH 12 range, but a reversible decrease in viscosity at elevated temperatures. HEC solutions are susceptible to bacterial and enzyme degradation.

Hydroxypropylcellulose: HPC is soluble in cold water at <40^{o}C and gives pseudoplastic surface-active solutions without yield value. HPC will precipitate from water solutions above 45^{o}C. 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. Solutions are susceptible to shear, heat, bacterial, enzyme and UV degradation.

Hydroxypropyl Guar: HPG is soluble in hot and cold water and gives pseudoplastic solutions without yield value. Solutions provide good viscosity stability in the pH 2 to pH 13 range, but show a reversible decrease in viscosity at elevated temperatures. HPG solutions are more resistant to bacterial and enzyme degradation than many other organic thickeners.

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