



Vanderbilt Minerals, LLC

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VAN GEL® Magnesium Aluminum Silicate For Industrial Applications



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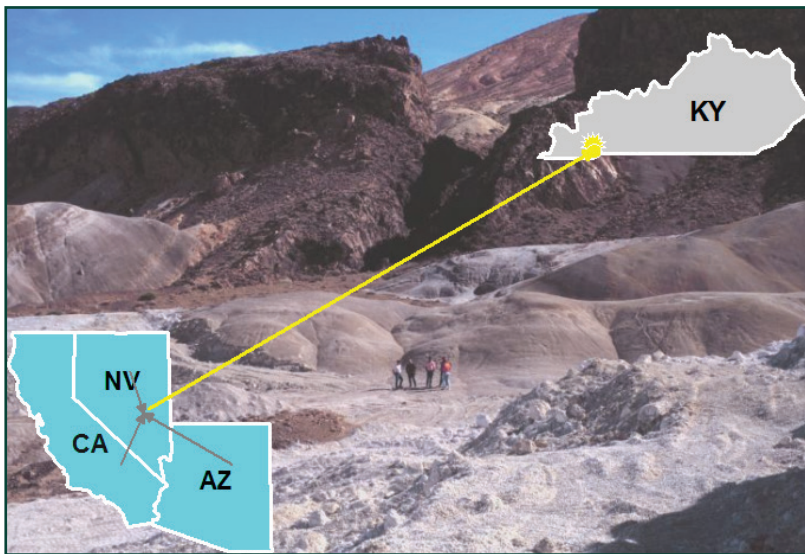
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VAN GEL® Magnesium Aluminum Silicate For Industrial Applications

VAN GEL products are natural smectite clays that have been water-washed to optimize purity and performance. Vanderbilt Minerals' diversified reserves in the U.S. southwest are the foundation of our clay's reputation for uniformity and quality. This secure resource base also enables the continuing development of new grades in response to customer needs.

The ores used to make **VAN GEL** clays are mined in Nevada, Arizona and California. They are milled in Nevada and shipped to the clay processing plant in Murray, KY.



VAN GEL smectite clay products are offered for industrial applications, such as agricultural suspensions, waterborne coatings, ceramic bodies and glazes, cleaning products and polishes. All **VAN GEL** clays undergo the same water-washing process and meet the same standard of clay purity as our personal care and pharmaceutical grade smectite clays.



FORMULATION BENEFITS

Formulators of nearly every type of water based product – from cleaners, polishes and suspension concentrates to coatings and ceramics – depend on **VAN GEL®** Magnesium Aluminum Silicate clays to:

- **Stabilize Suspensions** — The colloidal structure of these natural clays provides excellent suspension of fine particles in aqueous systems. These clays:
 - Suspend even high density particulates
 - Prevent hard packing; suspensions that tend to settle are easily re-dispersed
 - Ensure suspensions of uniform concentration
 - Achieve maximum suspension without losing flowability
 - Maximize pigment color value
 - Offer better suspension efficiency than most organic gums at equal viscosity
- **Stabilize Emulsions** — Like its suspension stabilizing property, the smectite clay colloidal structure effectively keeps the internal phase droplets suspended and separated. Since this structure is not affected by heat, these clays reduce the tendency of emulsions to thin out, cream, or break at elevated temperatures.
- **Modify Rheology** — Shear-thinning products with controlled thixotropy can be formulated. Suspensions, emulsions and thickened solutions freely spread, pump or pour without losing stability.
- **Modify Organic Thickeners** — These clays are often used with organic thickeners to enhance the best characteristics of each. The clays contribute synergistic viscosity and yield value. Gums and polymers provide a protective colloidal action that improves the clay's stability in the presence of electrolytes, surfactants, and other water-solubles.



VAN GEL® (left) preventing pigment settling.



VAN GEL® (left) preventing emulsion separation and creaming.

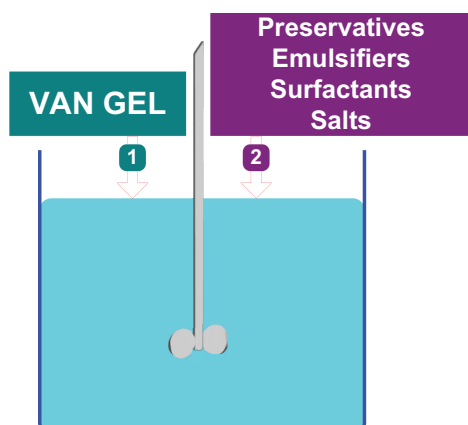
- **Perform at High and Low pH** — **VAN GEL**® Magnesium Aluminum Silicate clays are routinely used in products spanning the pH 2 to pH 13 range - from acid metal cleaners to caustic oven cleaners. Certain grades are particularly effective at pH extremes, where their pH stability is further extended by protective colloids such as xanthan gum.
- **Function with Most Additives** — These anionic clays are compatible with most anionics and nonionics; they are incompatible with most cationics.
- **Resist Degradation** — Because they are minerals, **VAN GEL** clays are not decomposed by bacteria, heat or excess mechanical shear.

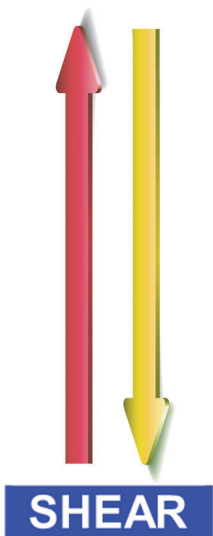
PREPARATION of DISPERSIONS

For most suspension stabilization, emulsion stabilization and thickening applications, **VAN GEL** clays must be properly dispersed in water and hydrated to provide the desired performance properties. The two guides to successful hydration are:

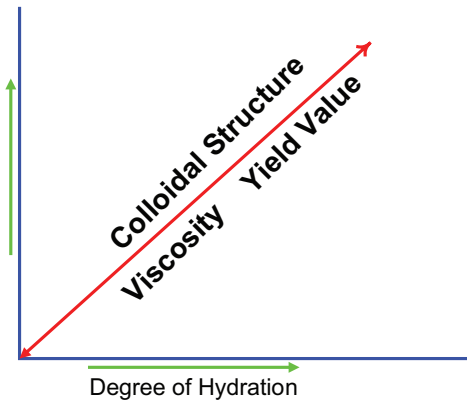
- ✓ **THE BEST DISPERSIONS ARE PREPARED IN WATER FREE OF ADDITIVES.**
- ✓ **MORE ENERGY INPUT GIVES QUICKER HYDRATION.**

Any materials present in the water when the clay is added, including preservatives, chelating agents or other minor additives, will interfere with hydration and inhibit the formation of the desired colloidal structure.





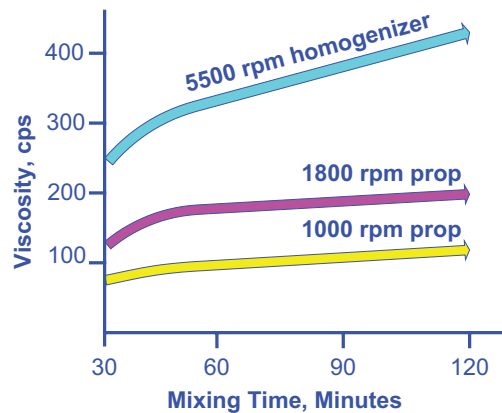
Dry clay particles are actually multiple layers of individual platelets, each separated by a layer of water. The extent to which these particles are delaminated into individual clay platelets is referred to as the degree of hydration. The greater the degree of hydration, the stronger the colloidal structure and the greater the viscosity and yield value of the dispersion.



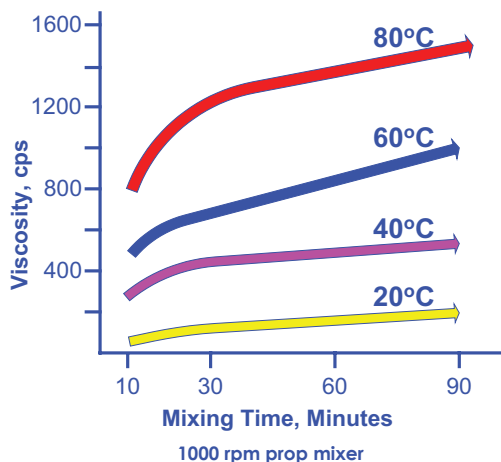
For most clay grades the degree of hydration is directly proportional to the amount of energy used to disperse the product, and therefore increases in proportion to the following factors:

- **Shear, or mixing intensity**
- **Heat input, or water temperature**
- **Mixing time**

Using greater shear, or mixing for a longer time, will provide better hydration, which is measured as higher viscosity, as seen here with a 5% dispersion of **VAN GEL® R** Magnesium Aluminum Silicate, and greater yield value.



Heat input in the form of heated water has an even more pronounced beneficial effect on hydration than does the mechanical energy contribution of shear.



Any modification of mixer intensity (e.g., speed, propeller to vessel ratio) or water temperature will affect the degree of hydration and the hydration time. Whichever mixing conditions are used, it is very important that they be consistently controlled to achieve reproducible results in the laboratory, during scale-up and in production.

VAN GEL® SX Magnesium Aluminum Silicate is an exception. This blend of clay and xanthan gum is relatively unaffected by changes in hydration parameters. Adequate hydration will be achieved in most cases in no more than 15 minutes. Increasing mixing intensity, mixing time or water temperature will not significantly affect degree of hydration.

The following table provides guidelines for the minimum amount of time suggested for the hydration of the various clay grades. They are based on laboratory scale preparations: 1 kg batches using distilled, deionized water at specification concentrations under practical formulating conditions. Actual hydration times in the laboratory or in production will depend on the particular combination of batch size, mixer shear, and water temperature used. In the laboratory or during production, the key to consistent performance of these clays is consistent hydration conditions. Changes in hydration time, mixer shear, vessel size or water temperature will change results.



Minimum Suggested Hydration Times for VAN GEL® Magnesium Aluminum Silicate

Hydration Rate

Normal	Fast	Ultra
VAN GEL® B VAN GEL R VAN GEL K	VAN GEL ES	VAN GEL SX

Propeller Mixer:

800 rpm, 25°C water	120 Minutes	30 Minutes	15 Minutes
800 rpm, 75°C water	45 Minutes	20 Minutes	10 Minutes

Homogenizer:

3000 rpm, 25°C water	30 Minutes	20 Minutes	10 Minutes
3000 rpm, 75°C water	15 Minutes	10 Minutes	10 Minutes

DRY ADDITION

In certain applications **VAN GEL®** Magnesium Aluminum Silicate clays are incorporated dry instead of being first dispersed and hydrated. For example:

- Wet milled suspension concentrates of agricultural actives, biocides and pigments
- Waterborne Coatings
- Ceramic Slips

In these applications, shear or impact milling is used to adequately delaminate the clay.

SYNERGY WITH ORGANIC GUMS AND POLYMERS

VAN GEL[®] Magnesium Aluminum Silicate clays are often used synergistically with gums and organic thickeners. The stability or viscosity of formulations containing these mixtures will be greater than that of the same formulation made with each individual component of the mixture. These combinations allow the formulator to fine-tune viscosity, stability, and flow properties beyond what is possible with either the clay or organic thickener alone.

For example, these clays are frequently used with xanthan gum in agricultural suspension concentrates or cellulose gum in ceramic glazes to provide a balance of suspension stability and uniform flow properties.

Other advantages of combining **VAN GEL** clays with an organic thickener are:

- **VAN GEL** clays can impart yield value to systems thickened with high efficiency organic polymers or gums.
- Because the colloidal structure of these clays is not sensitive to heat, it can compensate for the loss of viscosity at elevated temperatures common to many organic thickeners.
- The combination may be more economical than the use of either component alone.

Because of the benefits of such clay/thickener combinations, Vanderbilt Minerals offers **VAN GEL SX**, a pre-blended product of smectite clay and xanthan gum, for industrial applications.



The table below provides suggested weight-to-weight ratios of **VAN GEL®** Magnesium Aluminum Silicate clays that will produce beneficial synergistic effects. Mixing procedures to introduce the two ingredients into the formulation are also recommended.

Suggested Starting Weight to Weight Ratio Ranges of VAN GEL® Magnesium Aluminum Silicate to Organic Thickener^{1,2}

Organic Thickener	Weight to Weight Ratio Range	Recommended Mixing Procedure
Polyacrylates		
Polyacrylates	5:1 to 1:1	A
Carbomers	10:1 to 1:1	A
Cellulosics		
Sodium Carboxymethylcellulose	10:1 to 1:1	B
Hydroxyethyl Cellulose	1:1	A,C
Hydroxypropyl Cellulose	1:1	A,C
Hydroxypropylmethylcellulose	1:1	A,C
Methylcellulose	1:1	A,C
Natural Gum		
Xanthan Gum	10:1 to 1:1	B
Sodium Carrageenan	10:1 to 1:1	B
Sodium Alginate	2:1 to 1:1	B
Hydroxypropyl Guar	1:1	A
Gum Arabic (Acacia)	4:1 to 2:1	B
Gum Tragacanth	9:1 to 2:1	B

¹For initial evaluations. Ratios are based on rheological studies in water, alone. Preferable or optimum ratios may be different in formulated products.

²Does not apply to **VAN GEL SX**, which is already blended with a gum.

Recommended Mixing Procedures

A. Divide the available water and prepare the hydrated clay dispersion and the organic thickener solution separately. Slowly add the thickener solution to the clay dispersion with good agitation. Mix until uniform before adding other formula ingredients.

B. Add the clay and organic thickener simultaneously or as a dry blend to the available water. Hydrate thoroughly before adding other formula ingredients.

C. For nonionic cellulosics that are insoluble in hot water: hydrate the clay in hot water. Add the gum to the hot clay dispersion with good agitation. Cool the dispersion with continued agitation until the gum is completely dissolved.

NATURAL SMECTITE CLAYS - A GRADE FOR EVERY USE

VAN GEL® B Magnesium Aluminum Silicate	Most economical grade for general industrial applications: as suspension and emulsion concentrates, waterborne coatings, household and institutional cleaners, polishes, and caustic cleaners. Typical use levels: between 0.5% and 3%.
VAN GEL ES	Maximum electrolyte stability and optimum pH stability in acidic compositions. Typical use levels: between 1% and 3%.
VAN GEL K	A low acid demand and high acid and electrolyte compatibility product. Used in acid pH suspensions and cleaners. Typical use levels: between 0.5% and 3.0%.
VAN GEL R	A useful, economical grade for a wide range of applications. Typical use levels: between 0.5% and 3.0%.
VAN GEL SX	High thickening, suspension stabilizing and emulsion stabilizing efficiency. A blend of smectite clay and xanthan gum. Typical use levels: between 0.5% and 3%.

Industrial grades of **VAN GEL®** Magnesium Aluminum Silicate clays, including **VAN GEL B**, **VAN GEL ES**, **VAN GEL R**, **VAN GEL K**, and **VAN GEL SX**, are intended for industrial use only. These products are not intended for other uses, such as for pharmaceutical or cosmetic use.





SMECTITE CLAYS

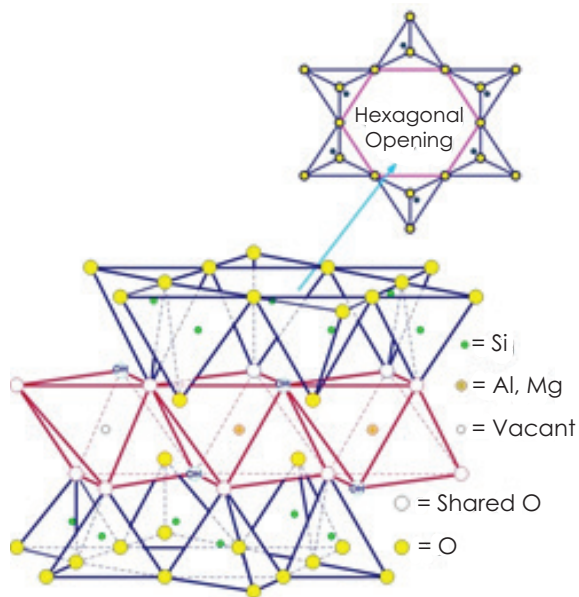
VAN GEL® Magnesium Aluminum Silicate

What They Are

Smectite is the mineralogical term for a group of trilayer clays which include the commercially significant varieties montmorillonite, hectorite and saponite. At one time this group was referred to generically as montmorillonite clay. The group name was changed to smectite clay to avoid confusion with the mineralogically distinct montmorillonite member, but the generic use of the term montmorillonite has persisted among some researchers. Smectite clays are also, by tradition, known under the geological term bentonite. Bentonite is an ore or product with substantial smectite content, most often montmorillonite.

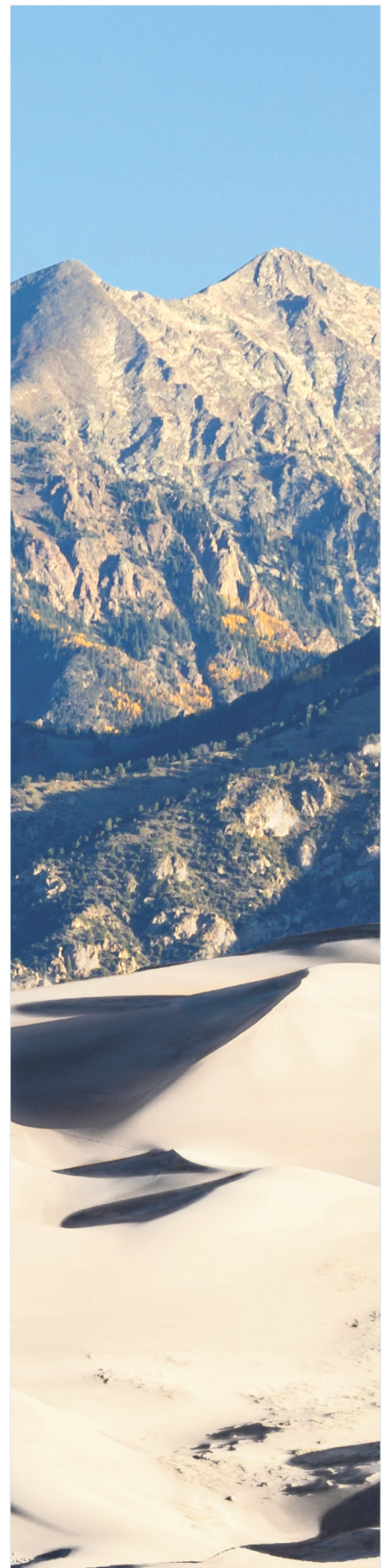
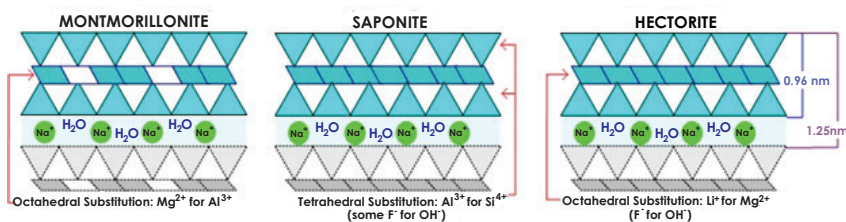
Smectite clays have characteristic layered structures and consequently individual crystals have a flake or platelet shape. They contain a continuous alumina or magnesia octahedral layer that is bound on both sides by a continuous silica layer. The silica layer is composed of tetrahedra with three shared oxygens, forming linked rings with hexagonal openings. When the predominant octahedral cation is Al^{3+} , as in montmorillonite, charge balancing within the clay lattice requires that only two of every three octahedral positions are filled, and the clay is described as dioctahedral. If Mg^{2+} predominates, as in saponite and hectorite, all octahedral positions must be filled, and the clay is called trioctahedral. A single smectite clay crystal is 0.96 nanometer thick and up to several hundred nanometers across.

The smectite clays are characterized by metal ion substitutions within their lattice structures, so that they are electrically unbalanced. Substitutions within the crystal lattice result in negatively charged platelet faces. Lattice discontinuities account for a very slight positive charge on edges. The net platelet charge is negative.



Montmorillonite is characterized by the substitution of a limited number of octahedral Al^{3+} with Mg^{2+} , which accounts for its negative charge. This is naturally balanced by Na^+ between the clay platelets, partially sunk in the hexagonal openings of the silica layer. Because the sodium ions are not structural they can be easily replaced by other positively charged elements or molecules, and are called exchangeable cations. In addition to the charge balancing cations, a tightly held layer of oriented water, about 0.29 nanometers thick, occupies the space between individual flakes. This water requires temperatures well in excess of 100°C for removal. A single **VAN GEL**[®] Magnesium Aluminum Silicate particle is composed of thousands of these sandwiched platelets with exchangeable cations and a layer of water between each.

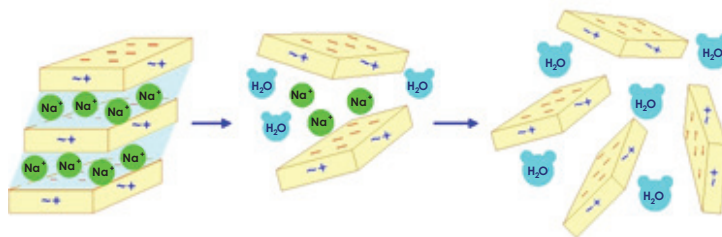
The trioctahedral analogues of montmorillonite are saponite and hectorite. Saponite has limited substitution of tetrahedral Si^{4+} by Al^{3+} , while hectorite has limited substitution of octahedral Mg^{2+} by Li^+ and OH^- by F^- . As with montmorillonite, the resulting charge imbalance is naturally compensated for by exchangeable Na^+ .





Clay Hydration

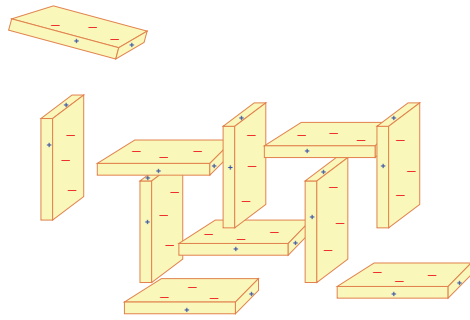
The binding effect of inter-platelet water and counterions makes mechanical delamination of smectite clays very difficult, but swelling by intercalation with polar liquids and solutions is quite easy. Likewise, in cases where the full surface area of the clay needs to be exposed and/or its rheological properties exploited, hydraulic delamination is relatively simple. When clay and water are mixed, water penetrates between platelets forcing them further apart. The cations begin to diffuse away from platelet faces. Diffusion (the movement of cations from between platelets out into the water) and osmosis (the movement of water into the space between platelets) then promote delamination until platelets are completely separated.



For most **VAN GEL**[®] Magnesium Aluminum Silicate grades, the speed with which platelet separation occurs is directly related to the amount of energy introduced during hydration. Both mechanical and thermal energy accelerate hydration: high shear mixing or the use of warm water will reduce hydration time. The presence of dissolved substances in the water will prolong hydration time by inhibiting the diffusion and osmosis essential to platelet separation.

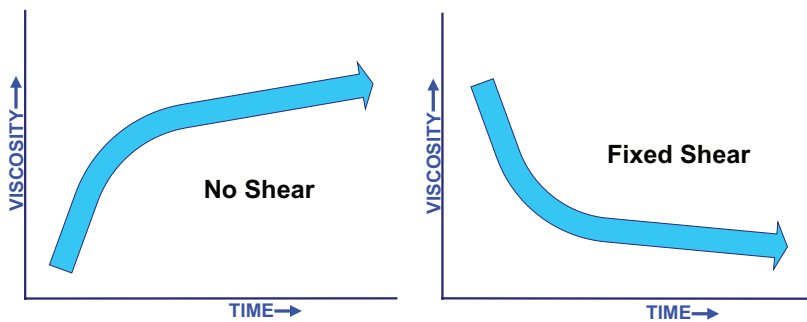
Clay Rheological Properties

Once the clay is hydrated (i.e., the platelets are separated) the weakly positive platelet edges are attracted to the negatively charged platelet faces. A three dimensional colloidal structure forms, commonly called the “house of cards”. The formation of this colloidal structure accounts for the characteristic rheology imparted by these clays. Dispersions of **VAN GEL** clays are pseudoplastic and thixotropic, in addition to contributing useful yield value.

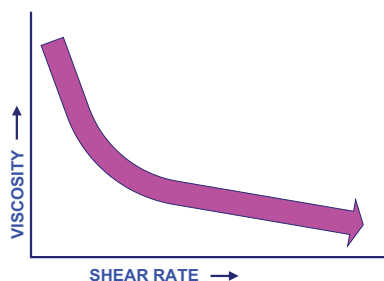


This colloidal structure is particularly valued for its ability to trap and segregate solids, as in a suspension, oils, as in an emulsion, and gases, as in a foam or mousse.

Rheology - After the clay is hydrated, the colloidal structure builds rapidly at first, giving a quick increase in viscosity. As time passes, the remaining free platelets take a longer time to find an available site in the structure, so viscosity increases at a progressively slower rate. Conversely, when a given shear is applied, most of the structure is disrupted quickly, with subsequent breakdown becoming more gradual. The dispersions are therefore thixotropic: undisturbed they increase in viscosity over time, and under a constant shear rate they decrease in viscosity over time.

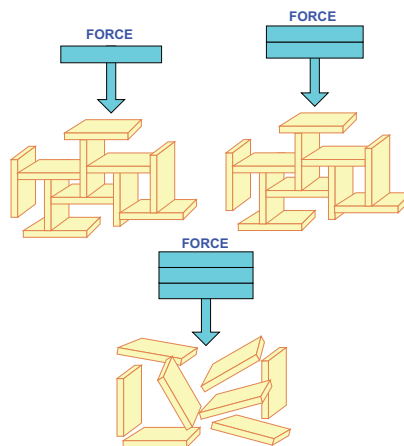


Smectite dispersions are also pseudoplastic, because increasing the rate of applied shear (thereby increasing structure breakdown) results in decreasing viscosities.



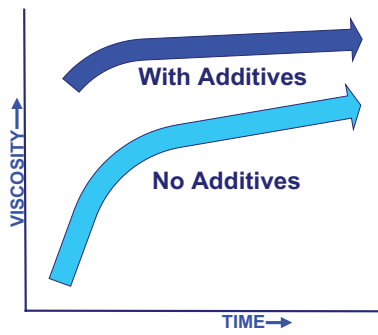


Yield Value - The colloidal structure also provides the clay's most useful property - yield value. This is a measure of the resistance of the structure to breakdown. A certain minimum force, the yield value, must be applied to start disrupting the structure. Solids, oils and gases are trapped and segregated by the structure. They must exert a force greater than the yield value to be able to move through the liquid. This means that the greater the yield value, the more stable the suspension, emulsion or foam.

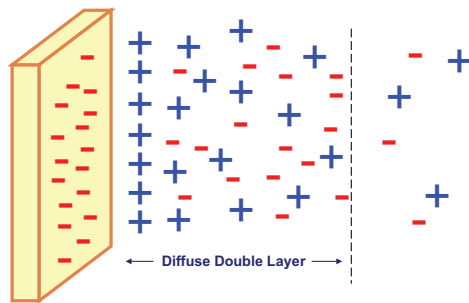


A unique and valuable feature of **VAN GEL®** Magnesium Aluminum Silicate clays is their ability to impart yield value at low viscosity. Stabilization of the dispersed phase is possible even in thin, fluid systems where flowability is important. Most common organic thickeners possess little or no yield value and can only stabilize suspensions, emulsions or foams at high viscosity.

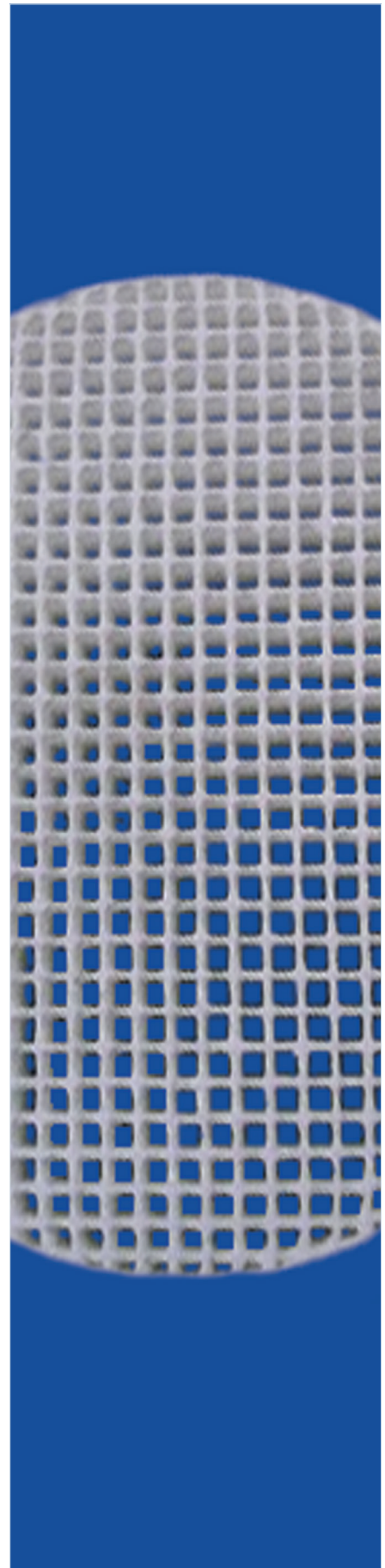
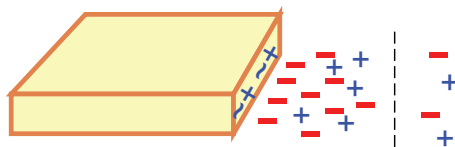
Rheology Modifiers - Formulators are more concerned with the behavior of **VAN GEL** clays in the presence of other ingredients, rather than that in water alone. Most water-soluble components will modify the rheological properties of smectite clay, usually beneficially. Salts, surfactants and water-miscible solvents will increase the clay's viscosity and yield value contribution and decrease thixotropy, but still enable a shear-thinning composition.



Excess water solubles will destabilize the clay's colloidal structure. This may appear as a relatively stable thick gel or as flocculated masses with syneresis. The effect of electrolytes and water miscible solvents can be explained in relation to double layer theory. According to this model, most of the exchangeable ions in the clay dispersion tend to accumulate, due to electrostatic attraction, near the negative faces of the platelets, but simultaneously have a tendency to diffuse away from platelet surfaces toward the bulk of the water where their concentration is low. The equilibration of these opposing effects causes the formation of a diffuse atmosphere of counterions, with concentration diminishing with distance from the platelet face. A negative "double layer" is thus established, consisting of the negative surface charge plus the diffuse counterions.

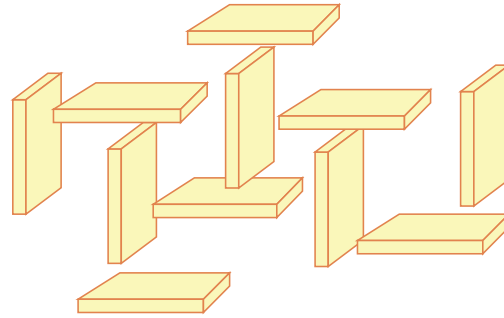


The analogous positive double layer is established in association with platelet edges.

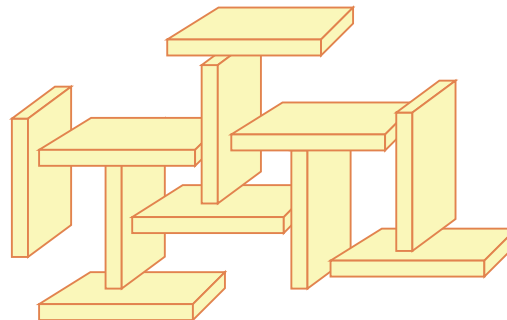




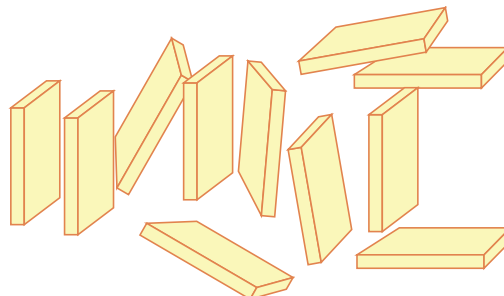
The house of cards colloidal structure is therefore actually based on the interaction of smectite platelet edge and face double layers.



When electrolyte or polar solvent is added to the dispersion, the double layers are compressed. This allows the platelet edges and faces to more closely approach, resulting in a more rigid structure and consequently higher viscosity and yield value.



If the double layers become sufficiently compressed, face-face van der Waals attraction will predominate and the house of cards colloidal structure will be lost, as will thickening and suspending efficiency.



The effect of electrolytes on the clay dispersion depends on cation valence and size as well as concentration. Cations with greater positive charge and/or smaller hydrated radius are more strongly attracted than cations with lower positive charge and/or larger hydrated radius because they can get closer to the clay surface and/or satisfy more negative charges. The higher the cation valence, the less electrolyte the clay can accommodate before the colloidal structure collapses. In short, monovalent cations have the weakest flocculating effect and are the most compatible with **VAN GEL**[®] Magnesium Aluminum Silicate clays. Divalent cations have a stronger flocculating effect, and trivalent cations the strongest. The following lyotropic series indicates the relative ability of cations to replace one another if present in equivalent quantities based on ionic charge and size (hydrated radius).



By the Law of Mass Action, nevertheless, adding large amounts of one cation will replace others, regardless of their position in the lyotropic series.

The properties of individual smectite clays – e.g., viscosity, hydration rate, electrolyte tolerance – vary according to their particular structure, exchange cations and exchange capacity. Each of these properties can be manipulated by the choice of smectite clay, based on location and type, and by blending clays from different locations so as to obtain the desired balance of properties. For example, the blend of smectite clays that make up **VAN GEL K** enable this product to provide greater electrolyte tolerance than **VAN GEL R** while the blend of clays in **VAN GEL R** provide greater viscosity and yield value than **VAN GEL K**. In addition, certain gums, such as xanthan gum and CMC, act as synergists and protective colloids when used together with **VAN GEL** clays. They can significantly improve the compatibility of the clay with relatively high levels of water solubles.





Vanderbilt Minerals, LLC

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