Application Leaflet

Next stop Hector... Part 2

Benefits and applications with BENTONE® Hectorite clay based rheology modifiers

Unique chemistry, sustainable solutions

Key Benefits

- Effective viscosity build in aqueous and non-aqueous applications
- Significantly higher efficiency than other mineral based rheology modifiers
- Strong adsorptive effect due to large surface area or applications in water treatment
- Applicable in manifold applications

Introduction

Detailed explanations on the chemistry and properties of natural Hectorite clay can be found in the leaflet "Chemistry and properties of BENTONE® Hectorite clay based rheology modifiers". In this second part, the technical benefits are shown based on some typical applications of this unique mineral.

Hectorite is a smectite clay mineral (sodium lithium magnesium silicate) that swells after immersion and dispersion in water. Under the correct conditions it imparts shear-thinning flow and thixotropy, as well as controlling sedimentation efficiently. It is a naturally occurring, lightly-colored mineral and can be found in very few locations globally, primarily in Hector, near Newberry Springs in California. It is in a wet process refined to provide an additive of very high purity. In its normal form Hectorite is hydrophilic and can either be used pure or combined with polymers or dispersants to give exactly the required flow properties to aqueous formulations. Reaction with quaternary ammonium compounds converts the clay to a hydrophobic form that is used for solvent-borne systems – an organoclay. Depending on the type of quaternary ammonium species used, products can be designed for all different polarities and chemistries of solvents. All these products are commercially available under the registered BENTONE® name and are considered the industry bench-mark.

The commonly used montmorillonite, or also called bentonite, is also an effective rheological additive but differs from Hectorite in some key properties. Often the bentonite clays have high levels of iron in their structure leading to a darker color that is not desirable for top quality coatings. Also, the bentonite ores usually contain significant amounts of crystalline silica which has raised health concerns around dust problems during handling. However one fundamental property more than anything else gives the Hectorite from Hector unique characteristics: its crystal morphology. This Hectorite has a thin, lath-like shape (ca 50 x 250 x 1.0 nm when fully dispersed). A typical montmorillonite crystallite, on the other hand, has a more flake-like morphology with dimensions of ca 300 x 300 x 1.0 nm, so much less edge area is exposed after dispersion. As the rheological activity is mainly caused by edge interactions, the Hectorite is much more efficient in building structure at rest. This gives excellent

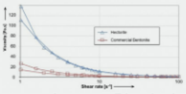

FIGURE 1: Rheological efficiency

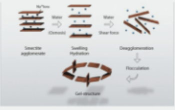

FIGURE 2: Delamination and gel formation

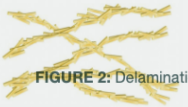

FIGURE 3: Schema of Hectorite ribbon structure

suspension properties and sag control. As less material is required, the Hectorite does not tend to over-build viscosity at mid-shear rates. This means that a paint's in-can structure is not adversely affected, avoiding any puffy appearance, and the strongly shear-thinning properties are ideal for industrial spray applications. (**FIGURE 1**)

Rheology and viscoelasticity

Hectorite clay, either in its pure state, combined with polymers, or surface modified to a hydrophobic organoclay is a unique, multi-purpose rheological additive. In the following examples of applications we shall demonstrate its use to achieve diverse rheological benefits.

It is useful to understand how Hectorite builds viscosity and imparts sag control and suspension properties. As described in the leaflet "Chemistry and properties of BENTONE® Hectorite clay based rheology modifiers", in the dry state the lithium magnesium silicate crystal platelets are stacked together into so-called tactoids much like cards in a pack. Due to isomorphous substitution in the crystal structure, the individual platelets carry a negative charge imbalance that is countered by sodium ions which are located on each plate face. When wetted out by water, the sodium ions hydrate, pushing the platelets apart and the clay starts to swell. With high shear the platelets can move away from each other and as colloidal, slightly charged particles they are subjected to double-layer effects, van der Waals attraction forces and electrostatic repulsion. When shear is removed, the platelets will align themselves into the most energy favorable arrangement, flocculating into an energy minimum as illustrated in **FIGURE 2**.

It has been shown that the preferred alignment involves edge contacts which is why the much greater edge area available from the fine, narrow, hectorite crystallites is so important for its rheological performance. At rest, the platelets align in this way into "bands" or a ribbon structure forming a 3-dimensional network (**FIGURE 3**) that extends throughout the suspension. In the case of the organoclays, swelling is caused by solvation and extension of the organic species from the surface. Structuring is again an edge- driven effect.

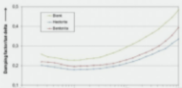

FIGURE 4: Viscoelasticity of latex paint

Influence on rheology

In the following, data determined by oscillatory measuring techniques are shown which allows us to visualize viscoelastic characteristics. This technology enables us to study the structural relationships of a suspension at rest and under different degrees of applied stress in detail. Viscoelasticity explains the ratio between the elastic or storage modulus (G') and the loss or viscous modulus (G"). These properties are very useful to predict suspension, storage stability, syneresis, sag, levelling and thixotropic recovery. In general, the more G' dominates, the stronger a gel structure is and the greater the suspension and sag control. If G" dominates, the system will tend to flow under the applied stress, including that caused by gravity and transportation. The ratio G"/G' is known as the loss function and is represented by tan delta. If tan delta >1, then G" dominates and vice versa.

In **FIGURE 4** the tan delta values are shown as a function of frequency of oscillation for a latex paint containing hectorite clay to control settling. The value remains well below 1 indicating the high degree of elasticity imparted by the mineral even under stress.

This is to be expected from the gel structure as the hectorite particles are positioned in an energy favourable state. They resist flow under the stress forces typically experienced during storage. A bentonite clay under the same test conditions is shown for comparison. Although the elastic modulus still dominates, it is clearly not as strong as with the hectorite. In the paint itself, the hectorite is indeed found to be much more effective for sag control and suspension.

However, a lot of other thickener technologies are used in the market as well. Most of the different types of polymers often used for thickening aqueous systems function by volume filling or chain entanglement. In the absence of the colloidal electrostatic effects, they do not offer such high relative elasticity (the loss modulus gains importance and tan delta is greater) and give suspension simply by blocking free flow. This leads to higher viscosity build under moderate shear conditions and can often cause "heavy" or "puffy" in-can paint appearance.

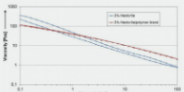

FIGURE 5: Flow curves of aqueous gels

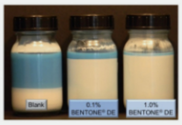

FIGURE 6: Paint stability after 1 week at 50°C

FIGURE 7: Stability of aqueous wood stain system

On the other hand, once the natural hectorite gel structure has been broken by shear, the platelets can move freely through the medium and the viscosity drops rapidly. This allows much greater flexibility in achieving the ideal flow properties by combining the clay with other types of rheological additives. It also gives excellent conditions for spray application where a very low viscosity is normally required under the high shear generated at the nozzle. (**FIGURE 5**)

Aqueous decorative systems

In the following examples, the Hectorite clay is incorporated into decorative coating systems typically under strong dispersing conditions during millbase processing. The clay is allowed to wet-out in water first and then sheared together with the pigments and fillers. In case of BENTONE® DE, the Hectorite has been made available in a form that has been beneficiated with a special modification in order to make it very easy to disperse so that it can even be incorporated at the start of the let-down, e.g. in the shown example, BENTONE® DE was incorporated into a low PVC acrylic paint in the formulation shown in **TABLE 2** at two different loadings.

Results after storage at an elevated temperature of 50°C are shown in **FIGURE 6** (note a dye was added to show the phase separation clearly). Without BENTONE® DE, severe settling occurred even after a few days storage. With 0.1%, stability was greatly improved and with 1% modified clay, settling showed strong improvement.

In a second example, the BENTONE® EW was used to stabilise a commercial wood-stain formulation (refer to **TABLE 2**) that also showed poor settling properties in its original composition. BENTONE® EW is based on pure natural hectorite with a beneficiation to optimize the ease dispersion. BENTONE® EW was first dispersed in water to form a pregel of 3% concentration. This was then used at the desired loading to substitute a part of the original water content. In this case, a commercial hydroxyl ethyl cellulose was used in comparison. Results of storage are given in **FIGURE 7**.

Again the blank showed complete sedimentation of the pigment. The HEC at 0.5% loading offered some suspension but the hectorite clay at 1% gave a totally stable formulation.

Both of these examples show the value of the hectorite clay as an anti-settling agent in waterborne decorative coating formulations. For this reason it is also used commercially in many aqueous tint bases and colorants.

Hectorite based organoclays

Organically modified smectites have been available for over 50 years. As already mentioned, the polarity of the solvent used determines the choice of organoclay. Those modified with long-chain alkyl quaternary ammonium compounds are suitable for non-polar systems whereas those modified with short-chain or more aromatic species are best for mid-to-high polarity systems. However, the choice of clay also has a strong influence on the performance. Just as in aqueous systems, the particle morphology makes organoclays based on Hectorite much more efficient at building structure at low shear than those based on bentonites. Due to the global abundance of bentonite, most organoclays commercially available are in fact made from this mineral. However for the most efficient performance and the ultimate rheological properties, the hectorite-based products are preferred.

In the following example, the performance of organoclays based on these two minerals, Hectorite and bentonite, are compared in an aromatic-free alkyd formulation. The formulation is given in **TABLE 4**. The Hectorite based material is BENTONE® 38, while the bentonite based grade is BENTONE® 34. This product selection was made as both grades are similar in amount and type of the quaternary ammonium component used. The main difference is the smectite clay.

TABLE 1: Result overview alkyd test paint

	BENTONE® 34 (bentonite)	BENTONE® 38 (Hectorite)	Blank
Hegman after			
10 Minutes	6.5 B	6.5 B	6.5 B
20 Minutes	7.0 A	7.0 A	7.0 A
30 Minutes	7.0 A	7.0 A	7.0 A
Brookfield Viscosity [mPA.s] at			
10 rpm	2200	3840	720
20 rpm	2100	3140	700
50 rpm	1920	2360	690
100 rpm	1670	1930	690
Sag resistance [µm wet]	210	300	30
Levelling blade 419 0 = poor; 10 = excellent	7	6	10
Gloss			
20°	77	76	82
60°	88	87	91

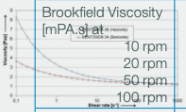

FIGURE 8: Flow curves of aqueous gels

The organoclay was incorporated into the resin and solvent blend and dispersed before a polar activator was added. (This helps the organoclay to delaminate into its active form and provides the chemistry to encourage hydrogen bond bridges between the platelets). Then the pigment was added and the mill- base fully dispersed.

The paint characteristics are shown in **TABLE 1**. Paints with either organoclay showed excellent fineness of grind. Although both also developed Brookfield viscosity, the hectorite-based product was much more effective. This in turn contributed to a better sag resistance without significantly affecting either levelling or gloss.

The rheological characteristics of the paints were also determined and are shown in **FIGURE 8**. clearly demonstrating the higher efficiency of the hectorite- based formulation and its more shear-thinning character for improved application.

This example demonstrates the value of Hectorite clay organoclays for efficiency of performance and excellent sag control without negatively affecting other coating characteristics. For either solvent or water- borne applications, the Hectorite based products offer significant advantages over the bentonite equivalents.

Aqueous metallic coatings

Traditional solvent-borne metallic basecoats and other effect coatings owe their pigment alignment and optical effects to evaporation and film shrinkage during the drying process. This forces the metallic pigment flakes to lie parallel to the surface and gives the flip- flop effect (also known as travel or two-tone effect). For environmental reasons, water-borne metallic coatings are now preferred. However, these systems tend to show less flip-flop effect so that considerable effort are made to improve this property.

In water-borne systems, the pigment alignment is not driven by solvent loss but by the rate of structural recovery.

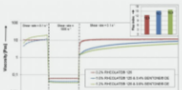

FIGURE 9: Viscosity recovery and optical properties

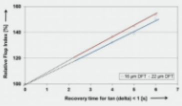

FIGURE 10: Recovery time tan delta vs flop index

In this example, a one-coat metallic television cabinet coating was studied. The formulation used two different types of rheological additive. RHEOLATE® 125, an alkali-swellable emulsion that provide the so- called spray-viscosity, is combined with BENTONE® DE, a natural hectorite clay that had been modified to be easy dispersible. The formulation is shown in **TABLE 5**. Both the hectorite clay and the alkali-swellable thickener were first dispersed in water as 10% active pregels and then added at a mentioned concentrations. The hectorite clay greatly increased the thixotropy of the formulation as shown in the structure recovery diagram, **FIGURE 9**. In this experiment the viscosity was measured at a constant, low shear rate of $0.1 s^{-1}$, then the shear increased to $1000\ s^{-1}$ and finally stepped-back to $0.1 s^{-1}$ again. Furthermore the data shown compare the rheological characteristics with the measured flop effect.

Whereas the control without the hectorite recovered its structure almost immediately, the samples containing the Hectorite clay based BENTONE® DE showed a slight delay. This element of thixotropy allowed the metallic pigment flakes to align themselves parallel to the substrate surface and hence give a higher flop index that is also visible. Increasing the quantity of hectorite increased the flop index significantly. Two different dry film thicknesses were applied and the effect was seen in both cases. The recovery was also investigated using viscoelastic measurements. As the structure re-built at rest, the elastic modulus rose and the loss function, tan delta, decreased. The point at which tan delta = 1.0 marks when the elastic and viscous moduli are equal. Flop indexes for both series of film thickness were plotted against the time required for tan delta to drop below 1.0 (**FIGURE 10**).

For both, a perfect relationship between these parameters was found. The flop index was directly dependent on the time of recovery of the elastic modulus. The higher the ratio of natural hectorite used, the longer the recovery time and the better the flop effect.

This example shows how addition of hectorite based rheology modifiers to a formulation can improve the thixotropic flow character and delay structural recovery. The effect is enough to allow pigment alignment but not so much to cause film sag. A clear relationship is found between the viscoelastic recovery rate and the metal flop index.

Other application

Hectorite clay is used in a very large number of applications that cannot possibly be described in a single paper. However, it is of value to highlight some of the more important ones.

Water treatment

In water sprinkle spray cabinets the paint over-spray is often collected in water that then has to be cleaned for recycling. The dispersed paint is flocculated with a polymer and separated out. A dual system using the polymer together with hectorite clay is much more efficient. This is because the hectorite adsorbs on the paint droplet surfaces and forms strong anchor points for the polymer then to bridge. Again, the high edge area of the clay platelets is the key to this technology. This can effectively reduce the quantity of polymer required and also the volumes of paint sludge destined for land-fill.

Construction

Natural hectorite clay can partially replace cellulose- based products used in plasters both to assist sag resistance and ease application. The shear-thinning flow makes pumping the plaster much easier, reducing energy costs, and also makes manual application on the wall less strenuous, which cuts down the time required for any project. In tile adhesives, use together with a cellulose-based thickener improves the sag resistance to avoid slippage during drying, without reducing the open-time.

PICTURE 1: Hectorite mine

Ceramic glazes

Due to its high efficiency and absence of paramagnetic impurities, hectorite clay is ideal for use in ceramic glaze formulations. It provides settling control and good sag resistance, maintaining the structure during firing. This also improves edge-coverage and avoids the bubbling caused by organic thickeners.

Cosmetic & Personal care

Organoclays based on hectorite are particularly useful to stabilise cosmetic and toiletry formulations. Their main function is to prevent settling and phase separation but the shear-thinning flow they provide also gives smooth and pleasant application and rub-in properties.

Oil drilling

Hectorite-based organoclays show unique stability at elevated temperatures (above 150°C). They are used in drilling muds to provide the necessary suspension for the dense barites mineral. Many oil-fields nowadays are at great depths below the surface where the temperature rises significantly. Under these conditions, bentonite-based organoclays can fail as their structure starts to break down. The chemistry of the hectorite adds a vital amount of extra stability making it highly prized for this application.

Conclusion

The unique chemistry and particle morphology of natural hectorite clay from the Hector deposit in California provide it with a wide range of useful characteristics for coatings and other applications and is therefore the base for many rheology modifiers. The several practical examples described have demonstrated the many facets of this material whether used in its pure state, beneficiated or modified, or converted to a hydrophobic form as an organoclay.

The shear-thinning and thixotropic flow it provides ensure good and easy application characteristics, including spraying, whereas the viscoelastic properties it gives to a system at rest make it a highly efficient suspending agent and encourage the best sag control. These rheological properties also have important secondary effects such as a significant improvement in metallic pigment alignment in waterborne basecoats and indeed optical properties in general. On the other hand, its efficiency in use ensures reduced production costs while unwanted side-effects are avoided, such as too high in-can viscosity or severely shortened open-times. In all these aspects Hectorite clay significantly out-performs the more common bentonite- based products. Hectorite clay is indeed a unique, multi-purpose rheological additive.

Formulations

TABLE 2: Low pvc acrylic decorative paint

Raw material	Concentration [%]
Demin-water	15.6
Hectorite clay product	x
Defoamer (DAPRO® DF 52)	0.2
Biocide	0.2
Dispersant (NUOSPERSE® FX 605)	2.0
Dispersant (NUOSPERSE® FX 600)	1.0
Titanium dioxide	23.0
Acrylic binder emulsion	58.0

TABLE 3: Aqueous wood stain

Raw material	Concentration [%]
Acrylic binder emulsion	38.8
Neutralizing agent (AMP 90)	0.2
Propylene glycol	2.7
Coalescing agent (DAPRO® FX 511)	0.5
Defoamer (DAPRO® DF 17)	0.2
Yellow colorant paste	0.7
Red colorant paste	0.4
Black colorant paste	0.3
Water	56.2

TABLE 4: Low pvc acrylic decorative paint

Raw material	Concentration [%]
Long-oil alkyd; 75% resin diluted in isoparaffin	52.5
Isoparaffin	10.0
BENTONE® Organoclay	1.0
Polar activator	0.3
Titanium dioxide	30.4
Siccative	2.8

TABLE 5: Aqueous metallic coating

5.1. Aluminum pigment preparation

Raw material	Concentration [%]
Aluminum pigment	40.5
Butylglycol	40.5
Dispersant (NUOSPERSE® W30)	4.1
Butanol	14.9

Ratio Base varnish /Pigment preparation = 5.4:1

DMEA has been added to adjust the pH to a ratio of ~9. Both rheological additive have been added in the concentration mentioned in **FIGURE 9** replacing the relevant amount of formulation water.

5.2. Base varnish

Raw material	Concentration [%]
Styrene acrylic binder emulsion	66.1
Substrate wetting agent (SUPREAD® 2059)	0.5
BENTONE® DE (added as a 10% pregel in water)	X
Purified water	30.5
Butylglycol	1.0
Butanol	1.9
DMEA (added as a 10% solution in water)	X
RHEOLATE® 125 (added as a 10% solution in water)	X

BENTONE® Hectorite grades

Aqueous Application	Non-aqueous application
BENTONE® EW	BENTONE® 27
BENTONE® LT	BENTONE® 38
BENTONE® HC	BENTONE® SD-1
BENTONE® DE	BENTONE® P 270 CO
BENTONE® DH-CE*	BENTONE® P 380 MS
BENTONE® CT	
BENTONE® OC	
BENAQUA® 4000	

* available only in the USA

References

- W. L. Ijdo, D.N. Smith, Hectorite a unique multi- purpose additive—Chemistry and properties, **2011**
- R.E. Grim, Clay Mineralogy, McGraw Hill, New York, **1968**
- Rheology Handbook, A practical guide to rheological additives, PB113 5/08, Elementis Specialties Inc, **2008**
- G. Lagaly, S. Ziesmer, Colloid chemistry of clay minerals: the coagulation of montmorillonite dispersions, Advances in Colloid and Interface Science, **2003**, 100 – 102, 105
- H. van Olphen, Clay colloid chemistry, Wiley, New York, **1977**
- H. Vali, L. Bachmann, Ultrastructure and flow behaviour of colloidal smectite suspensions, J. Colloid and Interface Science, **1988**, 126, 278
- U. Brandenburg, G. Lagaly, Rheological properties of sodium montmorillonite dispersions, Applied Clay Science, **1988**, 3, 263
- G. Lagaly, Principles of flow of kaolin and bentonite dispersions, Applied Clay Science, **1989**, 4,105
- I.C. Callaghan, R.H. Ottewill, Interparticle forces in montmorillonite gels, Discussions of the Faraday Society, **1974**, 57,110
- T.G. Mezger, Das Rheologie Handbuch, Vincent Network, Hannover, **2010**
- P. Wissling, Metallic effect pigments, Vincent Network, Hannover, **2006**
- D. van Peij, D.N. Smith, Correlation of a coating's performance with its viscoelastic properties, European Coatings Show presentation, Nuremburg, **2007**

August 2024

For more details
please contact:

North America
Elementis
469 Old Trenton Road
East Windsor,
NJ 08512, USA
Tel: +1 609 443 2500

Europe
Elementis UK Ltd c/o
Porto Business Plaza
Santos Pousada Street, 290
4300-189, Porto, Portugal

Asia
Deuchem (Shanghai) Chemical
Co., Ltd.
99, Lianyang Road
Songjiang Industrial Zone
Shanghai, China 201613
Tel: +86 21 577 40348

elementis.com