

Next stop Hector....

Chemistry and properties of BENTONE[®] Hectorite clay based rheology modifiers



Key Benefits

- ❖ Unique platelet shaped clay material
- ❖ Platelets are remarkably uniform in terms of composition, charge density and charge location
- ❖ Significant benefits in applications and provided rheology

Introduction

The earliest applications utilizing clays go back to a long time ago in history. These were clay tokens for record keeping purposes, clay bricks and pottery. Further practical uses of clays include bleaching, laundry, cosmetics, medicine, porcelain as well as special decorative applications. A couple of these uses are still relevant today. Although old, the sophisticated nature of these clay applications should not be underestimated. The ancient Maya blue pigment is a good example of early nanotechnology where clay is used to stabilize an indigo dye. An organic – inorganic surface complex is formed when indigo dye binds to the clay surface during pigment preparation. Unlike the dye alone, this combined clay-dye complex is remarkably stable and does not fade when exposed to harsh weathering conditions. Furthermore, the clay-indigo color is resistant to acids, bases, chemical solvents and does not biodegrade. Other pigment systems can be formulated for use in coatings based on such dye-clay complexes and as such might offer an environmentally friendly alternative next to the pigments currently used in the coatings industry.

Clays are abundant in nature and this is not surprising since they are essentially composed of some of the eight most common elements found in the Earth's crust. Clay minerals are crystalline, layered hydrous aluminum- or magnesium silicates and have two-dimensional building blocks. Hence, a clay layer is a platelet of nanosomic thickness, which stacks to form a three dimensional solid material. These stacks of platelets are referred to as tactoids, and these tactoids aggregate into particles. The platelet itself (also often referred to as a layer) has a length and width in the microscopic size scale. The space between stacked platelets is either empty, or is occupied by a cationic species in the event that the platelet carries a net negative charge.

Classification

Clays can conveniently be classified based on the composition of the clay platelet. One can identify elementary sheets within a clay platelet, which typically contains either one or two silicate sheets condensed on a (central) magnesium or aluminum hydroxide sheet. Thus, a 1:1 clay platelet is built from one silica sheet and one other magnesium or aluminum hydroxide sheet. A 2:1 clay platelet layer contains two silica sheets and one central magnesium hydroxide or aluminum hydroxide sheet. *Figure 1* provides an overview of the most important clay minerals.

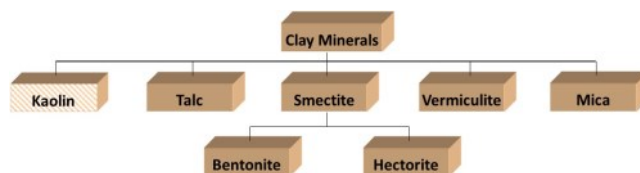


Figure 1: Clay minerals family

Kaolinite $[Al_4](Si_4)O_{10}(OH)_8$ is a well known lower cost functional extender in paint formulations that can affect opacity, gloss and color. The 1:1 kaolinite aluminum silicate composition is comprised of one tetrahedral silicate sheet and one octahedral gibbsite-like sheet. The sheets are linked together through shared oxygens so that an asymmetrical platelet remains with hydroxyl groups on one side of the platelet surface and silicate oxygens on the other side of the surface. Although the space between platelets is empty, strong interactions exist between them because of hydrogen bonding between the surface functionalities, *Figure 2a*. As such, the platelets do not de-stack and as a rule, other species do not intercalate between the platelets, i.e. other compounds cannot penetrate the interlayer region. **Serpentines** $[Mg_6](Si_4)O_{10}(OH)_8$ have a similar 1:1 structure but rather than an aluminum hydroxide sheet, a magnesium hydroxide sheet is condensed on a silicate sheet. However, these last two sheets do not fit perfectly together, and this mismatch has the effect of bending the platelets, which results in a fibrous particle morphology and some polymorphs form serpentine asbestos.

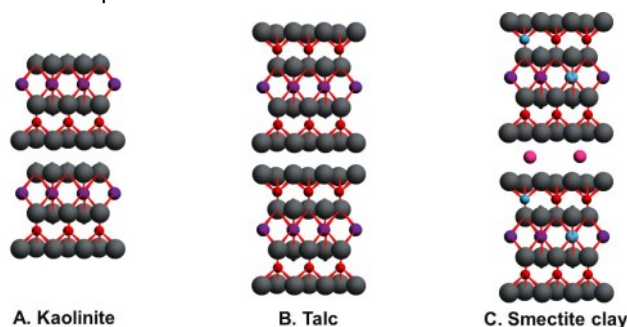


Figure 2: Structure and sticking of clay platelets

Talc $[Mg_6](Si_4)O_{10}(OH)_4$ is used as a functional filler in the coatings industry. This 2:1 structure is comprised of two tetrahedral silicate sheets that sandwich a central octahedral magnesium hydroxide sheet, *Figure 2b*. The platelet does not carry any net overall electrical charge. Both platelet surfaces (top and bottom) are identical and weak van der Waals interactions between the silicate surfaces keeps the platelets together. The talc platelets do not normally de-stack but the van der Waals forces are weak enough so the platelets can readily slide over each other and this provides talc with the soft feel. Functional extenders based on talc are also available at Elementis under the brand names FINNTALC® and PLUSTALC®.

Pyrophyllite $[Al_4](Si_8)O_{20}(OH)_4$, which is similar in structure to talc, finds relatively minor use in coatings applications as functional extender.

All positions in the crystalline lattice structure of talc are occupied, i.e. there are no vacancies and the clay platelet is electrically neutral. In **smectite** clays, a charge deficiency occurs in the crystalline structure when a number of metal cations take up positions that are normally occupied by cations of higher valence. These isomorphous substitutions leave a net negative charge on the clay platelet which is neutralized with exchangeable cations positioned on the surfaces of the clay platelets, *Figure 2c*. Electrostatic forces now control the interlayer region between the clay platelets as these are significantly more powerful than the van der Waals interactions between platelets. Clay layer charge density, type and the number of interlayer cations determine if the clay can swell and expand in water. The average distance between platelets increases when water penetrates the interlayer space. For certain clays, hydration can be so powerful that all registration between clay platelets is lost. The clay is said to be exfoliated, i.e. the clay tactoids have de-stacked (delaminated). A clay that is in the calcium exchanged form generally will only swell in water but cannot delaminate, yet hydration and electrostatics can allow the same clay to delaminate in water when it is in the sodium exchanged form. In fact, only clays that are in the lithium or sodium exchanged form will delaminate in water. All other clays remain flocculated (aggregated); even those that have been converted into the proton (H^+) or potassium exchanged forms. This ability to exchange platelet counter ions to control clay dispersion characteristics, is a key feature of smectites. Smectite clays are defined to be swellable due to delamination in water. Hectorite and bentonite are different clay minerals but they both are members of the smectite clay family.

A Hectorite clay is obtained when some magnesium cations are substituted by lithium in the layer structure. The negative charge on the platelet thus resides within the central octahedral sheet of the clay structure. Still, exchangeable counter ions are necessary to maintain neutrality and these can be positioned on any face side of the clay platelet. On the other hand, a saponite clay is obtained when tetravalent silicon is replaced with trivalent aluminum in the tetrahedral sheets of the clay structure. The platelets thus have charged sites directly on their surface, and cationic counter ions usually are located close by. The different charge locations have a significant influence on the effect of hydration of both clay types.

Hectorite clay hydrates more homogeneously as it lacks the tetrahedral charge location. The hydration preferentially occurs at the tetrahedral charge location.

Similarly, starting with variations on the pyrophyllite structure, which has vacancies in the octahedral sheet, a **bentonite** (also called **montmorillonite**) is obtained when the central octahedral lattice carries a negative charge and a beidellite clay is based on a composition where tetrahedral substitutions give rise to layer charge. Hence, a quaternary phase diagram exists between the four above-mentioned idealized end-member 2:1 clay structures and essentially all natural clays are positioned within this diagram, i.e. most natural clays have platelet charges that arise in both the central octahedral- as well as outermost tetrahedral- sheets. For instance, a Wyoming bentonite clay with an overall structural formula of $Na_{0.79}[Al_{3.00}Fe^{3+}_{0.42}Fe^{2+}_{0.01}Mg_{0.58}](Si_{7.80}Al_{0.20})O_{20}(OH)_4$ has about 25% of its charges arising from substitutions in the tetrahedral sheet, and 75% of the charges arise within the platelet.

Elementis Hectorite source



Hectorite clay, named in accordance with the sourcing location near Hector, California is an exceptionally pure clay. It essentially has no substitutions in the tetrahedral sheets. All charge arises from substitutions within the central octahedral sheet located in the platelet structure. This charge location is an important feature. It turns out that those charge centers located at the platelet surface can become catalytically active. That is why numerous papers have been published using bentonite clay as a catalyst, yet few publications deal with Hectorite as a catalyst.

Whereas catalyst activity might be desirable for certain applications, others benefit from a lack of it. Bentonite and Hectorite clays modified with similar quantities of organic ammonium as exchange ions show different thermal stability. Perhaps not surprisingly, the (tetrahedral) surface layer charge on bentonite clay promotes organic modifier decomposition at lower temperatures, i.e. the Hectorite based material shows enhanced thermal stability.

Note, the layer charge density for vermiculite clay is higher than that of smectite clays and even sodium vermiculite will only marginally swell in water but cannot delaminate. Micas have even higher charge densities and these clay layers are essentially joined together; micas will not swell in water. Mica tactoids can separate through cleavage along a platelet direction to give thinner, flexible, transparent stacks of layers.

Platelet charge density is usually expressing the cation exchange capacity (CEC), however, does not consider variations in platelet charge density for natural specimens. Hence, smectite clay platelets can have areas of higher charge density, similar to those of vermiculites and micas, and those areas would prevent total exfoliation. Similarly, certain clay platelets can have domains of low charge density allowing van der Waals forces to dominate those interlayer areas. It is thought that these anomalous areas that pin together clay layers can be broken up when clay dispersions are subjected to high levels of lateral shear. Such areas would not readily recombine once separated from each other. As most bentonites are products of weathering processes, such defects are more common in that clay and a significant fraction of bentonite clay platelets cannot easily delaminate. In contrast, hydrothermal clays, like Hectorite, are more uniform in size and the crystallization process does not readily yield such anomalous areas. Therefore, shearing of Hectorite clay does not yield further improvements in delamination character.

Hectorite geology

The Hectorite clay deposit in the Mojave desert near Hector, Newberry Springs, California is unique in occurrence and composition. A few other Hectorite deposits are known but none of these have the purity and platelet shape morphology that can rival the Hector material. This Hectorite clay is thought to be the alteration product from volcanic ash by hydrothermal means. The magnesium rich, lithium bearing water participating in this hydrothermal process yielded a unique clay mineral structure further distinguished from bentonite clays as this Hectorite contains fluoride in the lattice structure. A representative formula for this Hectorite clay mineral is: $\text{Na}_{0.67} [\text{Mg}_{5.33}\text{Li}_{0.67}](\text{Si}_8)\text{O}_{20}\text{F}_{2.69}(\text{OH})_{1.31}$. It should be pointed out that this fluoride is a structural part of the clay platelet and cannot be leached from it without total destruction of the clay phase under very acidic conditions. As such, fluoride cannot be made available in the solution in which the Hectorite clay is dispersed. The Hectorite clay ore is selectively mined in an open-pit mining operation.

In further wet processing, accompanying calcite, travertine, dolomite and other impurities are being removed in order to yield a purified spray dried Hectorite powder with a particle morphology suitable for easy dispersion in water. This refined clay has a white to light pink appearance. It is important to mention that the Hectorite clay is free of crystalline silica impurities. This is a distinct advantage over other smectite clays that typically have some crystalline silica associated with them. In practice, crystalline silica can only be removed via a difficult process.

The Hector clay is further unique in that the platelet has a lath-like shape, which differs from other Hectorite or bentonite clays that have flake-like morphologies. This fundamental difference in platelet morphology is shown in *Figure 3*. AFM analysis clearly reveals the

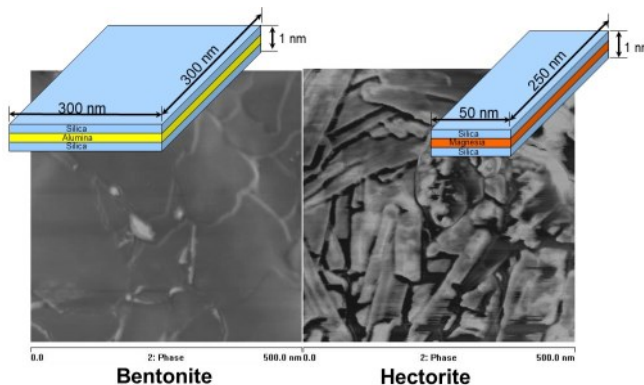


Figure 3: Visualization clay platelets

lath shape for Hectorite clay with dimensions of about 1 x 50 x 250 [nm]. In comparison, a Wyoming bentonite clay has a flake like structure of approximately 1 x 300 x 300 [nm]. At equal mass, the Hectorite clay has therefore about 3 – 4 times more edge area in comparison to the Wyoming bentonite. This is an important difference as the platelet edge is not only involved in network formation when clay is used as a viscosity modifier, but the various edge sites are also responsible for some unique chemical behavior.

Clay edge chemistry

As already explained, clay platelets carry a permanent negative charge on their facing sides, the edges may become positively charged at acidic pH values, or negatively charged in alkaline systems. This pH-dependent edge surface charging phenomena is complex, as the acidity of one edge group might be strongly influenced by the acidity of a neighboring group [13]. Furthermore, the familiar isomorphous substitutions on the face sites can also occur at edge sites, further complicating attempts to determine a point of zero edge charge as a function of pH.

Edge surface structure and resulting protonation / deprotonation schemes also depend on the crystallographic axis along which the crystal lattice is terminated. Similar edge reactivity is responsible for platelet degradation under specific conditions. It has been demonstrated that dissolution of both bentonite and Hectorite clays in acidic media occurs essentially at the platelet edges. Bentonite appears more resistant to degradation in acidic environments but conversely, Hectorite clay is much more stable in highly alkaline fluids.

Besides addition of alkali to raise the pH of a clay dispersion and to pass the point of zero charge into the negative charge region, specific electrolytes can be added that will become chemisorbed on the edges and alter the edge charge accordingly. For instance, metaphosphate dispersants and the like can chemisorb onto the broken edge sites and turn them into negatively charged complex sites. The platelet faces and edges then become negatively charged and the platelets repel each other. The viscosity building ability of the clay is then temporarily negated, but can be restored when other surfaces become available that compete for the dispersant. This approach not only greatly facilitates the wetting, dispersing and exfoliating of clays, but also allows high solids pre-gel dispersions to be made with them. The larger platelet edge area on Hectorite proves advantageous over bentonite when using these high solids clay pregels.

Synthetic Hectorite

Hectorite clay can also be synthesized but almost all processes use fluoride as a mineralizer. Hectorite can be manufactured in a solid state process when cooling a glass melt. A smaller laboratory version uses a flux approach but yields a similar fluor Hectorite material. Gaseous silicon tetrafluoride may form at elevated temperatures and this could present a significant environmental, corrosive and health problem. These solid-state derived clays, however, differ from the natural Hectorite clay in that they have larger platelet sizes and as such do not effectively build viscosity in water.

Synthetic hydrothermal Hectorite clays are also known but in these the platelet size is extremely small, with mean lateral dimensions of roughly 17 x 24 [nm] they approach quantum dot nanotechnology. Due to the extremely small platelet size synthetic Hectorite is suitable to be used in clear systems. This hydrothermal process requires high temperatures and pressure in order to couple the reactants. This process is very energy demanding and therefore commercially less effective

Organoclays

Organically modified clays were already mentioned earlier when discussing thermal stability. Hydrophilic Bentonite and Hectorite clays can be converted into hydrophobically modified materials by utilizing ion exchange with quaternary ammonium ions. These amine based compounds usually contain one or two long chain fatty alkyl groups, and polarity is further controlled by adding a benzyl- or methyl chloride methylating agent to obtain the quaternary cation. Although organoclays are hydrophobic, they often do require the use of a polar activator to disperse and exfoliate in organic solvent borne systems. Suitable polar compounds are small molecules such as acetone, ethanol, propylene carbonate. The use of these polar activating molecules is counter-intuitive as the solvent in which the organoclay is to be dispersed can be quite hydrophobic itself, as is the case for mineral spirits used in aliphatic alkyd paints. However, the polar activating material is attracted to the quaternary ammonium – clay surface interface and redirects the modifying alkyl chains away from the platelet surface increasing entropy and establishing a drive towards exfoliation of the platelet from the agglomerated tactoid state. Some organoclays are specifically engineered to function without polar activators and these usually contain additional organic compounds. Other organoclays, often those with only one alkyl chain on the quaternary cation, can make use of polar moieties from the resin formulation to achieve exfoliation, or in very rare circumstances even of polar character associated with the solvent. However, it may be advantageous still to use a polar activator with these organoclays for reliable and consistent results.

A highly significant portion of all organoclays that are commercially available on the market today are designed to function as rheological additives for solvent based systems, but they will also provide anti-settling. The exfoliated organoclay platelets “connect” with each other through an edge-edge interaction and the resulting 3D network will affect the viscosity and flow of the liquid system. Addition of a minute quantity of water can promote gelling as it partitions to the layer edges and facilitates reversible bonding between them. Hectorite has an advantage over bentonite because it has much more platelet edge area that is active in the network formation. Interestingly enough, organoclays based on synthetic Hectorite are not able to yield similar viscosifying ability despite the fact that the synthetic clay platelets are much smaller and thus have more edge area.

Clearly, there is a balance between platelet edge and face surface areas and natural hectorite has a more optimal ratio.

Conclusion

Hectorite clay certainly is a unique clay mineral. The platelets are remarkably uniform with respect to elemental composition, charge density distribution and charge location. The hydrothermal origin yielded platelets with a desirable lath shape, which also results in a favorable edge- to face- surface ratio. This provides significant benefits for applications such as rheology control in coatings. Essentially all the clay layers are defect free and can separate from each other easily when the clay is dispersed in water under moderate shear mixing. Hectorite offers substantial material advantages over bentonite clays that makes Hectorite clay a highly valued and sought-after product.

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BENTONE® Hectorite grades

Aqueous Application	Non-aqueous applications
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	
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