

# NANOCLAYS: MULTIDIMENSIONAL NEW NANO-TOOLS IN THE POLYMER DEVELOPMENT TOOLBOX

*Karl Kamena*

*Southern Clay Products*

## **Abstract**

Layered smectite nanoclays, particularly of the montmorillonite type, have interesting structural characteristics making them suitable for converting the planar surfaces from hydrophilic to hydrophobic, thereby rendering them more suitable for incorporation into organic polymer matrices. Since surface areas of these clays are very large, on the order of 750 m<sup>2</sup>/gram, a small percentage of the clays when fully dispersed and exfoliated can saturate the host polymer (or monomer) system. Nanoscopic phase distribution can impart enhanced stiffness and strength with substantially less inorganic content than conventional mineral fillers. Furthermore, additional properties such as improved barrier properties, abrasion resistance, and modified flame retardancy can result.

Traditionally, the focus has been on the development and preparation of nanocomposites with nanoclays being the principal non-polymer ingredient. Increasingly, however, we're seeing the development of polymer systems combining a variety of modifier agents combining to generate the desired properties and cost/performance characteristics. Nanoclays are demonstrating unique, multi-dimensional capabilities to synergistically enhance overall polymer system performance, and constitute a powerful new nano-tool in the polymer development toolbox.

Thermoplastic polyolefin (TPO) formulations based on nanoclays are being used in exterior automotive trim applications, and a variety of polyolefin-based products are being used in the interior. Nano-modified nylons have been specified for under-the-hood applications. Unsaturated polyester formulations utilizing nanoclays and microspheres are also being developed for SMC applications.

## **Background**

During the past ten years, hundreds of academic, government and industrial research programs have focused on the identification and development of clay-polymer "nanocomposites", a term popularly used to refer to a polymer composite having as one component an inorganic particle with nanometer dimensions in at least one direction.

Layered smectite nanoclays, particularly of the montmorillonite type, have interesting structural characteristics making them suitable for converting the planar surfaces from hydrophilic to hydrophobic, thereby rendering them more suitable for incorporation into organic polymer matrices. Since surface areas of these clays are very large, on the order of 750 m<sup>2</sup>/gram, a small percentage of the clays when fully dispersed and exfoliated can saturate the host polymer (or monomer) system. Nanoscopic phase distribution can impart enhanced stiffness and strength with substantially less inorganic content than conventional mineral fillers. Furthermore, additional properties such as improved barrier properties, abrasion resistance, and modified flame retardancy can result.

The nanocomposite concept appears to have had its origin in pioneering research conducted in Japan by Unitika, Ltd. in the 1970s and separately by Toyota Central Research and Development Laboratories, Inc. (CRDL) in the late 1980s. The theory was that if nanoclays could be fully dispersed or exfoliated to high aspect ratio platelets into polymers at relatively low levels (2-5 wt%), a number of mechanical and barrier properties would be enhanced. The original work at both Unitika and Toyota CRDL was based on an *in-situ* process for the preparation on nylon 6 nanocomposites. According to this method, a nanoclay is introduced into the caprolactam monomer stage of the process, and the caprolactam is intercalated into the clay galleries. Under appropriate reactor conditions, the caprolactam polymerizes and the platelets are further expanded and become exfoliated to become an integral part of the bulk polymer. Toyota reported that NCH (nanocomposite nylon 6-clay hybrid) materials provided significant improvements in mechanical, thermal, and gas barrier properties at loadings of 2-5 wt % montmorillonite. Toyota CRDL has also prepared nylon 6-clay nanocomposites (NCC) by melt compounding techniques.

Unitika became one of the first commercial producers of nano nylon 6, which has been used primarily for under-the-hood automotive engine covers requiring substantially higher heat distortion temperatures (HDT) than achieved with nylon 6. At a 4-wt% loading of synthetic mica (an alternative to montmorillonite), HDT (at 1.8 MPa) increased to 152°C from 70°C for neat nylon 6. Also, flexural strength increased from 108 to 158 MPa and flexural modulus from 3.0 to 4.5 GPa.

Other methods to prepare nanocomposites include a solvent assist process, whereby a co-solvent is employed to help carry the monomer into the galleries and is subsequently removed from the polymer system, and direct polymer melt intercalation methods which depend on nanoclays being directly added to a polymer melt under temperature and shear conditions to be directly exfoliated into the polymer.

Following on the Unitika and Toyota CRDL work, there has been a large amount of investigation in many industrial and academic environments, and much of the effort has been targeted at achieving exfoliation in a technologically and economically feasible manner.

A broad range of other government, academic and industrial research laboratories have investigated and continue to develop nanocomposites of seemingly every thermoplastic and thermoset type having commercial significance. Of particular interest have been those based on polyolefins, more specifically polypropylene TPOs and thermoplastic elastomers (TPEs). TPOs have been increasingly used for exterior trim parts on cars and light trucks, and TPO-based nanocomposites hold promise for an attractive property profile.

## **Clay Raw Materials**

The specific clay (nanoclay) of interest is montmorillonite, a natural clay mineral of the smectite family that traces its origins to volcanic ash deposited millions of years ago in ancient brine seas where it slowly underwent alteration processes. Although montmorillonite is found in vast deposits around the world, it is always found with impurities such as gravel, shale, limestone, quartz, feldspar, etc. The mixture of materials is known as bentonite.

The unique characteristic of smectite or montmorillonite that sets them apart from other clay minerals is their ability to swell in water. They disperse and swell in water thus controlling the rheology of the water system in which they are used.

Montmorillonite is classified as magnesium aluminum silicate and each individual crystal has a flat thin sheet morphology. They are irregular in overall shape and can be up to 1,000 nanometers in the largest dimension. A side view of the crystal reveals a uniform size of 0.92-nm thickness. The result of this morphology is an extremely large surface area of 750-800 square meters per gram.

Each montmorillonite crystal or sheet is a 2:1 layered structure consisting of silica tetrahedra layers bonded to an inner alumina octahedral layer. Other metals such as magnesium or iron can replace some of the aluminum atoms in the structure and establish a charge deficiency. The resulting negative charge on the surface will attract any positive ions (cations), such as calcium or sodium ions, to neutralize the charge. On the other hand, the edge of the crystal has a few positive charges thus attracting negatively charged ions or molecules.

The cations on the clay surface can be easily exchanged for other cations. A measure of this capacity is commonly referred to as the cation exchange capacity (CEC) and is usually expressed as milliequivalents of cations per hundred grams of clay.

Stating the obvious, it should be understood that each montmorillonite deposit prepared by Mother Nature is unique unto itself. Particle size, shape, and charge are different, and the replacement ions and positioning in either the octahedral or tetrahedral layers can have a significant effect on the characteristics and performance of the specific montmorillonite. Also, the impurities making up the overall bentonite deposit can be very different, and removing non-montmorillonite impurities is essential to overall performance of the montmorillonite in a nanocomposites formulation on the basis that impurities cannot be reduced to nanoscopic particle sizes.

## **Organo Nanoclays**

Unmodified, natural and purified montmorillonite clays are extremely hydrophilic and fundamentally incompatible with hydrophobic organic polymers.

The conventional way to prepare an organoclay is to replace the sodium ions on the surface of the sheets with an organic cation, such as a quaternary ammonium chloride (quats). This is typically done in a very dilute, purified aqueous solution. During the reaction, the clay loses its hydrophilicity and becomes oleophilic, at which point it precipitates from the aqueous phase, is filtered, dried, ground and packaged.

Quat chemistry can be modified to produce dozens of iterations. By modifying the surface polarity of the clay, the function of the onium ions is to allow thermodynamically favorable penetration of the polymer into the interlayer region. The ability of the onium ion to assist in delamination of the clay is critical to achieving exfoliation. In non-polar polyolefin systems, a primary issue yet to be fully resolved is identification of a chemistry (or combination of chemistries) that will provide a thermodynamic driving force. In the world of chemistry and polymers, "like attracts like" is a truism that we must deal with.

Another function of the quat chemistry is to pry open the individual sheets of montmorillonite to reduce the inherent Van der Waals forces attracting adjacent sheets and facilitate delamination. Although there is reason to believe that increasing the d-spacing between the sheets is desirable, empirical evidence would suggest a larger d-spacing is less important than improving compatibility between the polymer and the chemistry.

Representative quat chemistries shown in the appendix are selected depending on compatibility with the host polymer matrix.

## Nanoclay Functionalities

Historically, nanoclays based on montmorillonite have been used in aqueous and organic solvent formulations to modify rheology. Typical application areas include paints and coatings, consumer care products, inks, ceramics and refractories, drilling fluids, greases, and polyester and epoxy composites. Because of the tremendous surface area of 750 m<sup>2</sup>/gram, just a few percent of completely dispersed platelets “solvate” in the liquid creating a functional network and imparting the desired rheological properties to the system.

In thermoset composites, nanoclays can be considered for a variety of functionalities:

- Improved Syneresis Control:
  - Improved dispersion of low-profile additive (LPA) in resin,
  - Decreased settling of fillers;
- Improved Surface Appearance:
  - Decreased surface roughness,
  - Class-A surface achieved;
- Improved Processability:
  - Better flow despite increased viscosity,
  - Lower Shrinkage;
- Enables Lower Density Formulations to be Achieved:
  - Decreased CaCO<sub>3</sub> levels,
  - Uniform distribution of glass beads.

Interestingly, thermoset formulations have always been a cocktail of chemistries, fillers, additives and curing agents, and have tended to consider nanoclays as one more synergistic ingredient, to be used as a part of the whole. Ashland, for example, has been issued two recent patents on “Thermosetting inorganic clay nanodispersions and their use”. The primary function of the nanoclays are to complement and enhance the use of other conventional fillers such as fibrous reinforcing agents or low density fillers, such as hollow glass microspheres.

On the other hand, the development mindset on thermoplastic nanocomposites seems to have started with nanoclays as providing the single or primary inorganic additive. More recently, however, researchers are reporting developments based on synergy and combinations of additives. Honeywell, for example, is one of the pioneers in developing clay/nylon nanocomposites, and has recently announced the commercialization of AEGIS™ Barrier Nylon Resins. Products offered include a passive resin with nanoclay as the primary barrier, and an active/passive resin that includes an active oxygen-scavenging agent working in combination with nanoclays.

Similarly, early developments on flame retardant polymers focused on the use of nanoclays as the primary additive to impart flame retardant performance to the host polymer. Products that have been commercialized and are in late stages of the development process, however, employ a small amount of nanoclays (up to 5%) in combination with conventional additives such as magnesium hydroxide or aluminum trihydrate. The synergies resulting provide a flame retardant polymer system with enhanced mechanical performance. Several companies are employing this approach in the wire & cable market.

One of the more remarkable but perhaps unappreciated characteristics of nanoclays is their effect on improving the melt strength of thermoplastics. As is the case with thermosets, a higher melt strength of a given thermoplastic may allow for the incorporation of other beneficial additives, and perhaps unique processing techniques and parameters.

In addition to thermoset and thermoplastics, rubber formulations are being developed based on nanoclays in combination with other additives. As is the case with thermosets, rubber formulations are a complex recipe and nanoclays are perceived more as synergistic additives than replacements.

## **Clay / Polyolefin Nanocomposites**

Many organizations are in the process of developing clay/polyolefin nanocomposites with varying degrees of success. A number of commercial products have been introduced which are in effect moving the concept down the nanoroad. While nobody is yet claiming full exfoliation and complete technical success, competitive products are evolving, and newer and improved products are certain to come.

Basell Polyolefins has been a leader in developing TPO nanocomposites in conjunction with General Motors R&D and Southern Clay Products. The first product produced was for a GM M-Van step assist in August 2001. In February 2004, GM announced a second application: side-trim moldings for their Impala line; this was quickly followed with additional trim and panel applications for the Hummer H2 SUV.

GM R&D has been a visible and active promoter of polyolefin as well as other types of nanocomposites. Their interest is based on a variety of factors:

- Mass savings,
- Lower specific gravity,
- Lighter weight reduces cost and requires less adhesive for attachment,
- Large processing window,
- Consistent physical and mechanical properties,
- Elimination/reduction of tiger striping,
- Improved appearance,
- Improved knit line appearance,
- Improved colorability and painting,
- Sharper feature lines and grain patterns,
- Improved scratch/mar resistance,
- Low temperature ductility, and
- Improved recyclability.

TPO nanocomposites used in GM applications were prepared via a compounding method. Although specific details are proprietary, a number of processing issues and challenges were addressed.

## Processing Nanocomposites

Preparing a TPO nanocomposite is certainly similar to preparing other types of nanocomposites, but more difficult because of the polar nature of polyolefins and the lack of a thermodynamic driving force. Studies at Southern Clay Products and with other researchers and organizations suggest that a combination of chemistries used to modify the clay surface, compatibilizers such as maleated polypropylene, and processing conditions will markedly affect the degree of dispersion and exfoliation of the nanoclay and, therefore, the properties and performance characteristics of the TPO nanocomposites.

Nanoclays in their dry form are approximately 8-10 micron particles containing over 1 million individual montmorillonite platelets. Conventional theory supposes that during the extrusion process, polymer gradually enters the galleries between the platelets, and the distance between the platelets, the d-spacing, begins to expand until finally the Van der Waals forces are overcome and the platelets are no longer linked together.

We would propose, however, that the exfoliation mechanism is more of a shearing process whereby hundreds or thousands of tactoids comprising the 8-10 micron particles are separated by a combination of mechanical and chemical forces, reducing them to smaller ribbons. Individual platelets peel from the ribbons to complete the exfoliation process. The maleated polypropylene in the formulation appears to aid in the dispersion and exfoliation process, apparently by acting as a compatibilizing agent with the clay edges, which are very different in character from the clay surfaces.

During commercial scale-up of the TPO nanocomposite product, we encountered a number of production issues, many of which were related to feeding a small amount of nanoclay (3-5% by weight of the bulk polymer) to attempt good distribution and dispersion.

During the specification process for a painted trim application, we experienced an unacceptable surface defect problem. The defects were found to be caused by 100-200 micron clumps of clay. The cause was initially thought to be a problem with the incoming clay, but exhaustive sieving analyses ruled this out. A thorough investigation of the causes determined that clay agglomeration was occurring during the processing to prepare the nanocomposites. A combination of the clay feed position, the screw design, temperature and pressure caused clay to agglomerate, and no manner of subsequent processing would break up the clumps.

We also found that adjusting the processing conditions and establishing an acceptable processing window could resolve the problem. In general, our recommendations to prevent clay agglomeration:

- Top downstream feeding best, not side feeding;
- Feeder needs to have smooth delivery;
- Don't use a vibrator and screen between the feeder and screw;
- Lower temperatures are better;
- Lower degree of fill in the screw gives less clumping;
- Screw configuration is important-high shear is not necessarily desirable;
- Where to feed downstream is important.

An important note on clay agglomeration is that not only can agglomeration cause surface defects, but agglomerates can tie up a tremendous amount of individual clay platelets that can not be exfoliated and benefit the overall polymer matrix. It cannot be stressed enough that when adding a small amount of nanoclay to a polymer, all steps must be taken to maximize homogeneous distribution, micro dispersion to facilitate separation of tactoids, and proper temperature and pressure to create shear conditions favoring exfoliation. Studies tend to suggest that exfoliation happens early in the extrusion process, and conditions should be encouraged to assure that exfoliation continues until completion.

The production of commercial nanocomposites from a concept and laboratory curiosity is taking hold, especially as production engineers develop the necessary handling and processing parameters required to consistently prepare the same product, time after time.

### **Next Generation Nanocomposites**

Although it is likely that in the next several years a number of nanocomposites will be developed and introduced as commercial products, it is also apparent that conventional technologies using natural clays, quaternary amine chemistries and existing polymer bases have some limitations.

Concurrent with the development of first generation polyolefin nanocomposites, Southern Clay Products as well as other industry and research-based organizations are studying the fundamentals of nanocomposites. While Mother Nature has provided us with an excellent starting point, natural montmorillonite clays, they can lack consistency in terms of particle shape, charge density, and charge positioning. Programs are underway to develop synthetic smectite clays where we can define more precisely how to build clays that are more compatible with polyolefin matrices. By the same token, polyolefins can be prepared to be more receptive to nanoclays. The quaternary amine chemistries required to modify the natural clay surfaces to make them more compatible with non-polar polyolefin structures have inherent thermal stability limitations, and once they have served the purpose of helping to exfoliate the individual clay platelets, the chemistry has no further function and can have deleterious effects on the final nanocomposite. Designing clays that would not require large quantities of added compatibilizing chemistries would have obvious benefits.

### **Conclusions**

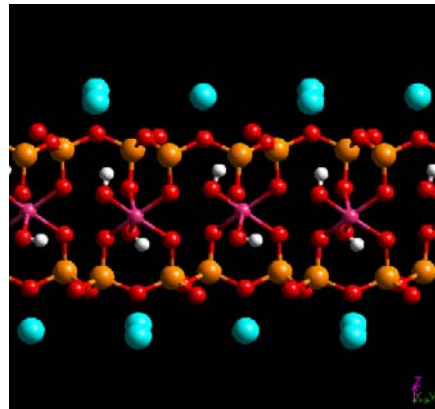
Clay/polymer nanocomposites are in the early stages of technology development, and are beginning to take hold commercially. While there are some limitations to current technologies and products, R&D programs are accelerating and are expected to foster a number of new approaches.

Traditionally, the focus has been on the development and preparation of nanocomposites with nanoclays being the principal non-polymer ingredient. Increasingly, however, we're seeing the development of polymer systems combining a variety of modifier agents combining to generate the desired properties and cost/performance characteristics. Nanoclays are demonstrating unique, multi-dimensional capabilities to synergistically enhance overall polymer system performance, and constitute a powerful new nano-tool in the polymer development toolbox.

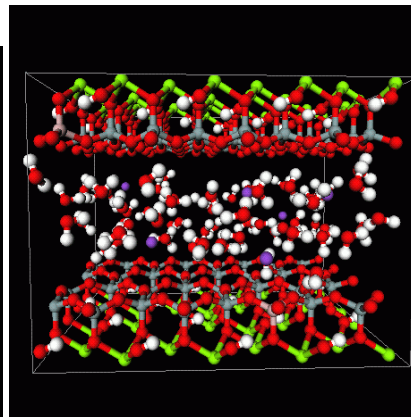
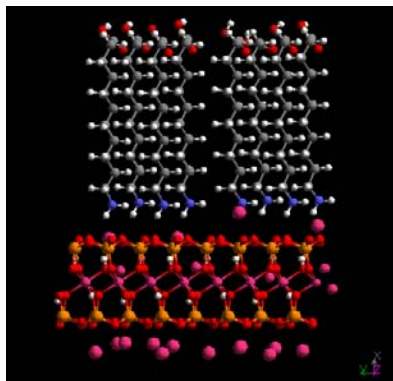
It had been earlier suggested that nanoclays promised a quick route to breakthrough product performance, but as we learn time and again, there is no shortcut to success. Developments with current nanocomposite formulations are leading the way for future discoveries and developments.

## Smectite Clay Chemistry

- **Smectite (dioctahedral)**
  - 2-dimensional arrays of silicon-oxygen tetrahedra and 2-dimensional arrays of aluminum- or magnesium-oxygen-hydroxyl octahedra

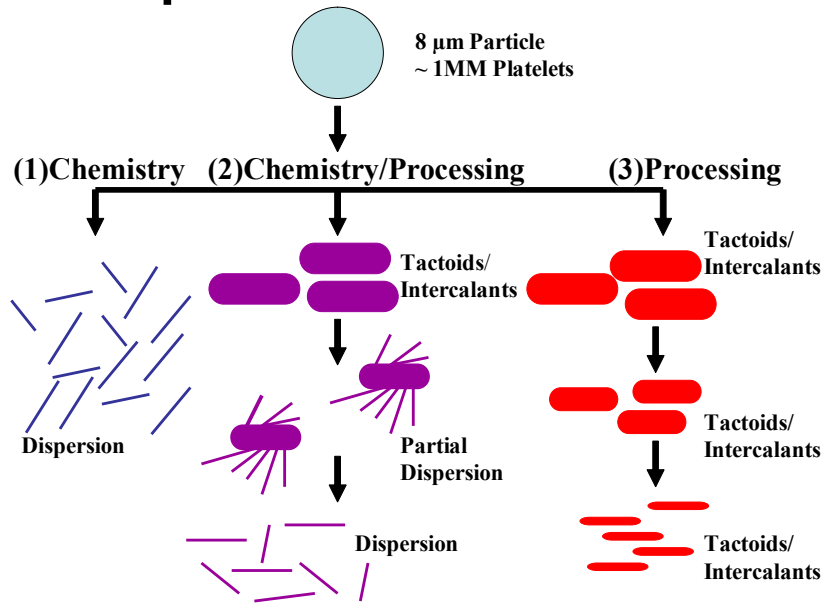


## Quat Ion Exchanged Montmorillonite

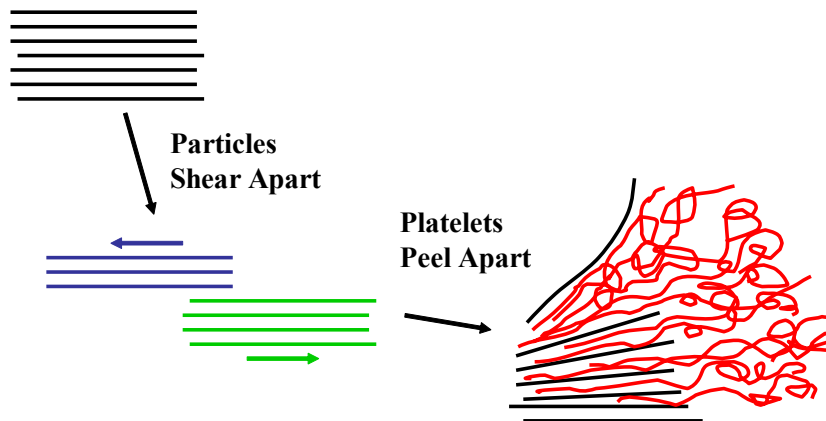




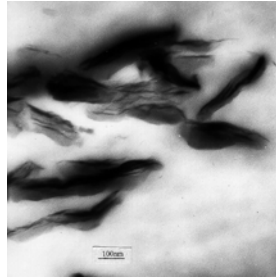
# Dispersion Mechanisms



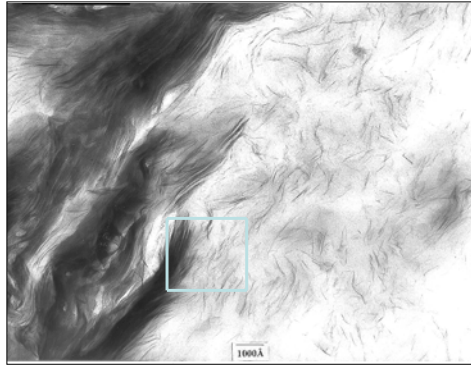
## Dispersion Mechanism



# Dispersion: Particles Shear Apart Platelets Peel Apart

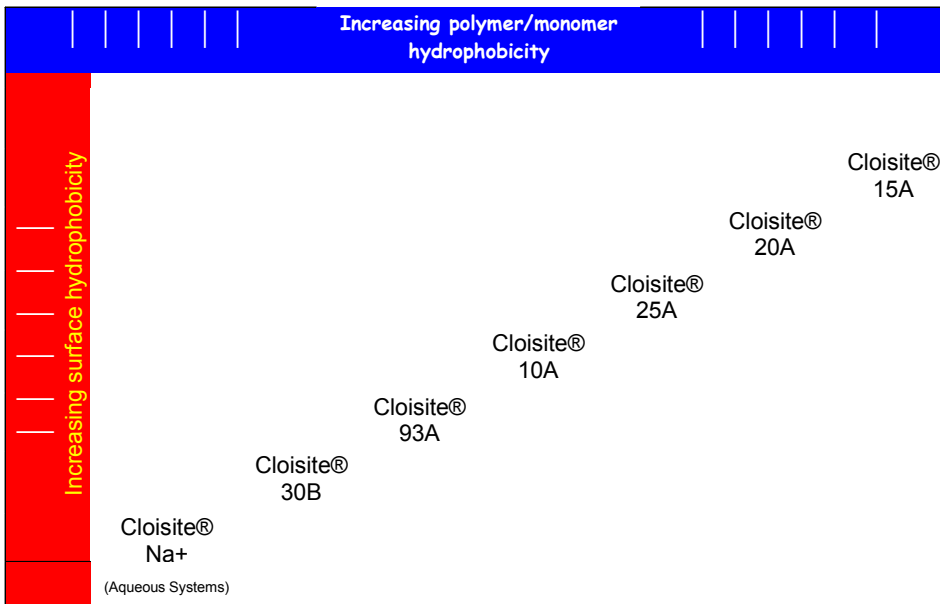


Particles Shear Apart

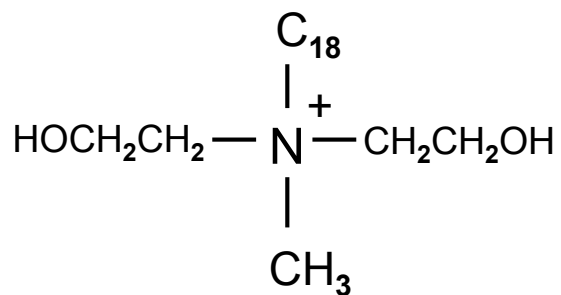


Platelets Peel Apart

## SCP CLOISITE Products

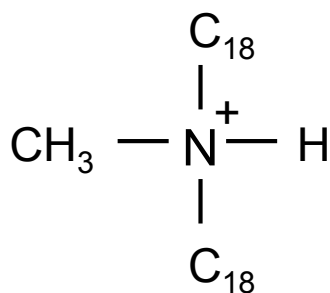


**Cloisite 30B 90 meq/100g**



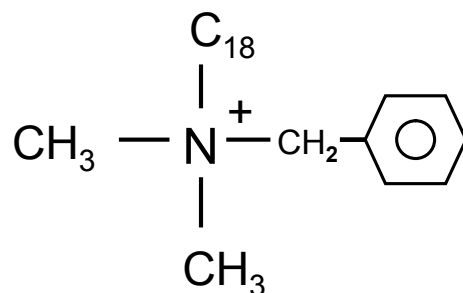
Methyl, Tallow, bis-2-Hydroxyethyl, Quaternary Ammonium X

**Cloisite® 93A 90 meq/100g)**



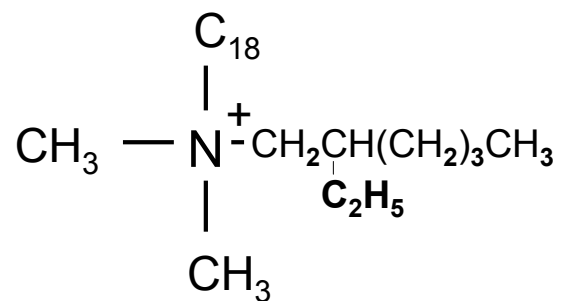
Methyl, Dihydrogenatedtallow, Ternary Ammonium X

**Cloisite 10A 125 meq/100g**



Dimethyl, Hydrogenated tallow, Benzyl, Quaternary Ammonium X

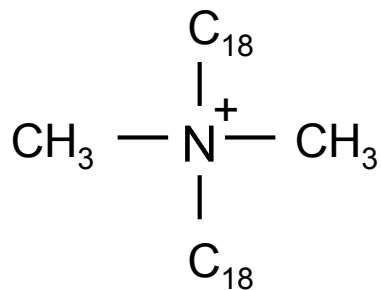
**Cloisite 25A 125 meq/100g**



Dimethyl, Hydrogenated tallow, 2-Ethylhexyl, Quaternary Ammonium X

**Cloisite 15A 125 meq/100g**

**Cloisite 20A 95 meq/100g**



Dimethyl, Dihydrogenated tallow, Quaternary Ammonium X