ELEMENTIS

A global specialty chemicals company

Application Leaflet

BENTONE® and BENTONE® SD

Hectorite and Bentonite based organoclay grades

Optimum activation of organoclays by ideal organoclay for highest effectivity

Correct activation for highest efficiency

- Optimum shear applied for proper delamination
- Correct use of polar activator for conventional grades
- Right order of addition for best processing result

Introduction

The effectivity of BENTONE® organoclays can be optimized by improved process parameters including a review of the process temperature. However, temperature control during organoclay dispersion in solvent based systems is not as important as with e.g. organic thixotropes.

Various methods used in manufacturing formulations and procedures sometimes suffer in efficiency when order of addition and mixing conditions are less than optimum. This leaflet will provide information and data such as changes to the order of addition plus or correct use of polar/chemical activator in order to obtain the best and most effective result and gel strength. Further, the effects of solvent resin temperature on process development and final results will be discussed.

Mineralogy and mechanism

BENTONE® organoclay materials are based on either bentonite or Hectorite, both minerals from the smectite group. They consist of microfine platelet stacks that, due to their mineralogical structure, expand in water in their natural form. In order to make them compatible with non-aqueous media such as organic solvents, however, it is necessary to modify the surface of their silicate plates with quaternary ammonium compounds. The choice of this modification and processing conditions also plays an important role in the practical applicability and performance capabilities of the finished end systems. The resulting organoclay will be dried and milled to achieve a powdered material. To be most rheologically effective, the size of the individual platelets and the total combined edge length following their successful activation is decisive.

As visualized in *Figure 1*, the Hectorite platelets are significantly smaller than the bentonite ones, the resulting edge length per gram of silicate in the Hectorite is much larger. This makes Hectorite additives able to build up a much denser and more rheologically effective network. In order to be activated, organoclays must first be exposed to high shear forces over a defined swelling period.

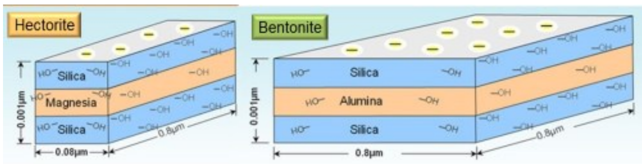


Figure 1: Hectorite/Bentonite comparison

During the activation process, the platelet stack is first subjected to swelling and then smashed with strong shear. As it can be seen in figure 2, the delaminated, organically modified silicate platelets that result can then effective rheologically via intermolecular forces, e.g. hydrogen bonds with the water molecules of a polar activator. These are usually short-chain alcohols combined with small amounts of water or special additives such as DAPRO® FX 2060 or DAPRO® BEZ 75.

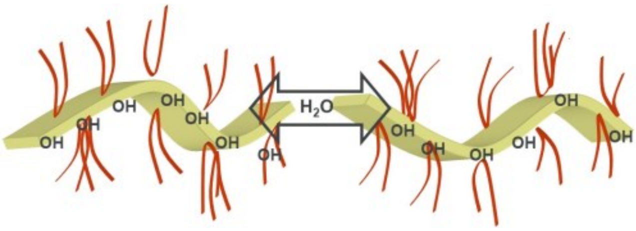


Figure 2: Hydrogen bonding

The smaller particle size of the hectorite-based products requires higher shear forces than their bentonite-based counterparts in order to achieve the high performance level described. For the organoclays to be activated completely – and especially the hectorite based grades – the use of correspondingly powerful production equipment is necessary. Such machinery is, however, not available in every manufacturing facility.

With the fully-activated BENTONE® P organoclay pastes, the need for this type of activation is eliminated. Using a special process carried out by Elementis, the clays in the products are made available in various solvents and in a fully activated

Order of addition

In *figure 3*, the recommended procedure to achieve optimum efficiency is visualized. Initial wetting and deagglomeration of the BENTONE® organoclays in only solvent prior to the addition of any chemical activators or resins is recommended for all systems. This procedure enables thorough wetting of the clay platelet stacks before they are exposed to any additive (or chemical activator) which will cause them to swell (or gel) prematurely. Low viscosity development and poor fineness of grind often results from encapsulation of the BENTONE® by either the resin or premature gel development on the surface of the platelet stacks.

The next step is to incorporate a chemical activator using high shear dispersion. Optimal viscosity development is only possible when enough water is available to engage in hydrogen bonding which creates the end-to-end bridging mechanism of organoclay gel structure (*Figure 2*).

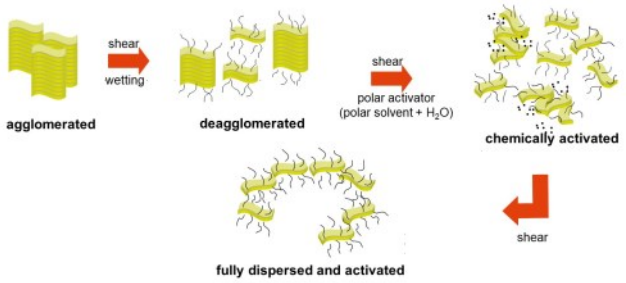


Figure 3: Activation process

Ideal processing is key to provide excellent fineness of grind and viscosity development of organoclays in non -aqueous systems.

Correlation solvent polarity

In figure 4 it can be seen that all individual organoclays are covering a certain range of solvent polarity. As unfortunately no product is covering the entire range of polarity, are careful selection of a suitable organoclay grade is necessary.

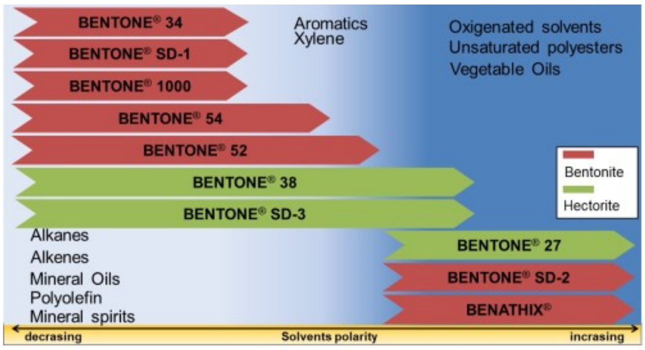


Figure 4: Selection chart organoclays

The grades with the widest solvent polarity acceptance are BENTONE® 38 and BENTONE® SD-3. These products are able to be used over a wide range of aromatic and aliphatic solvents. Even solvent blends with solvents of higher polarity can be rheologically modified by the use of BENTONE® 38 and BENTONE® SD-3. BENTONE® 54 and BENTONE® 52 are limited to the use in aliphatic and aromatic systems. All other grades are covering a smaller range of polarities.

Chemical/polar activators

As already mentioned, polar activators are having a functional role in the activation process of organoclays. Suitable chemical activators can be found in *table 1*.

Chemical/polar activator	Concentration related to BENTONE® clay [%]
Ethanol/water (95/5)	50
Propylene carbonate	33
Acetone/water (95/5)	60
DAPRO® FX 2060	30
DAPRO® BEZ 75	30

Table 1: Polar/chemical activators

As it can be seen, polar activators typically consist of small molecule size but highly polar molecules, e.g. alcohols, blended with small amounts of water. In case the proposed system necessarily needs to be free of water, propylene carbonate is a suitable alternative. Further certain surfactant products such as DAPRO® FX 2060 and DAPRO® BEZ are suitable to especially create low viscous, better pumpable, pregels.

The chemical activators are essentially responsible for two functions. The first is to carry available water into the morphological structure of the organoclay to make it available for hydrogen bonding at the platelet edges. Most activators (e.g. low molecular weight alcohols) are reducing the surface tension of water which allows better distribution of the hydrophilic water into the hydrophobic organoclay matrix. Additionally activators are solvating and swelling the organic component in order to keep the platelet farther apart from each other. The second function is given by the water migrated between the hydroxyls on adjacent platelet edges, completing and strengthening the hydrogen which results at the end in optimum rheological structure.

It is also very important to keep the correct concentration of polar activator related to the organoclay portion in order achieve optimum effectivity. Too little activator will result in only partial delamination; excessive amounts will weaken the hydrogen bonding in non-polar systems.

Premature swelling

In case chemical activators and surfactants are present in the critical wetting phase, the clay powder particles stack and have a tendency to swell and become gel coated before they fully wet out. As result in such case, dry-centered agglomerated form which are very difficult to be dispersed even with high shear.

Therefore it is crucial to expose and disperse the BENTONE® organoclays always first into the solvent before polar activator and surfactants are being added.

Processing and results

In *table 2* the recommended pregel manufacturing process is listed:

Component	Procedure	Concentration [%]
Solvent	begin mixing	90-X
BENTONE® organoclay	Disperse for 10 minutes	10
Chemical activator	Mix for 5-15 minutes	X

Table 2: Recommended pregel procedure

In this example the organoclay, BENTONE® 34 , has been subjected to an aliphatic hydrocarbon based solvent and pregelled at a concentration of 10%. The used polar activator was a blend of Ethanol and water (blending ratio 95/5).

In *figure 5* the pregel viscosities with and without the use of a chemical activator is displayed.

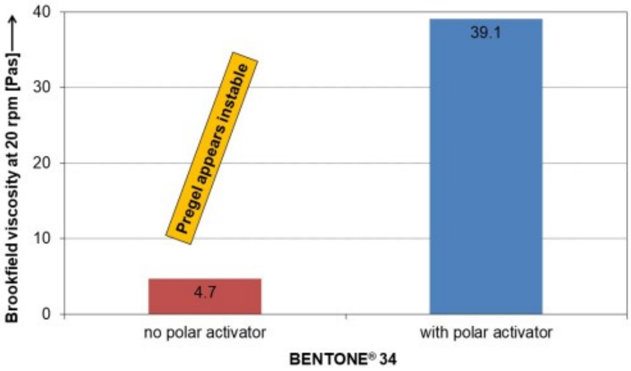


Figure 5: Pregel viscosity

The use of Ethanol/water blend as chemical activator guides to significantly higher pregel viscosities than when formulating without. Further, the pregel shows optimum stability whilst the lower viscous material without polar activation shows severe instabilities. The differences are becoming obvious in *figure 6*.

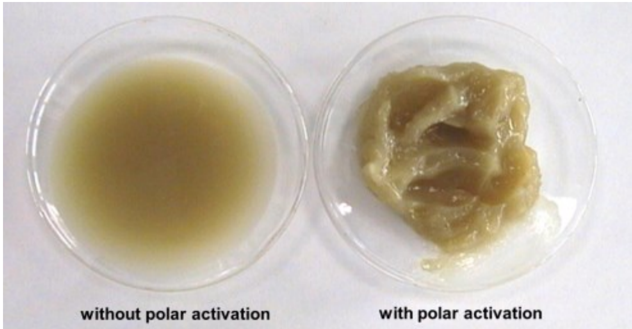


Figure 6: Pregel appearance

The other important point is the fineness of grind. This is usually better with polar activation rather than without. The individual values are displayed in *figure 7*.

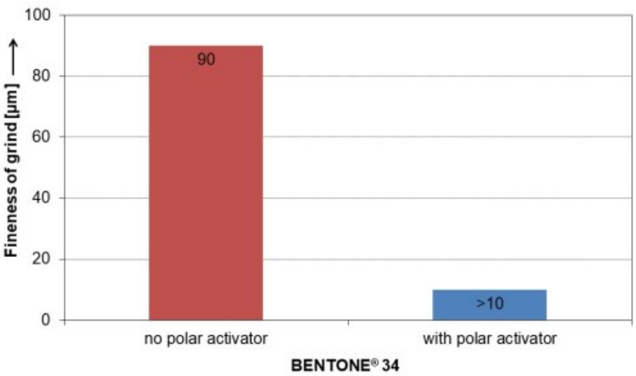


Figure 7: Pregel fineness of grind

The pregel without polar activation shows the poorest fineness of grind values. Whilst the organoclay with polar activator milled down to a maximum particle size of <10 µm, was in case of the unactivated sample 90 µm the optimum.

However, it is also important that a BENTONE® pregel needs further shear for full gel development. Therefore, a pregel of a conventional organoclay should always be added to the pigment dispersion/ millbase step of manufacturing. If this is not possible, e.g. no millbase is made, it is beneficial to select our preactivated organoclay pastes BENTONE® P 380 MS or BENTONE® P 270 CO alternatively. Here the organoclays have been activated by a unique process so that they can be used as a post-add additive.

Using the previously described BENTONE® 34 in an aromatic free alkyd paint, the in *figure 8* shown the real benefit of Pregelling and polar activation is shown.

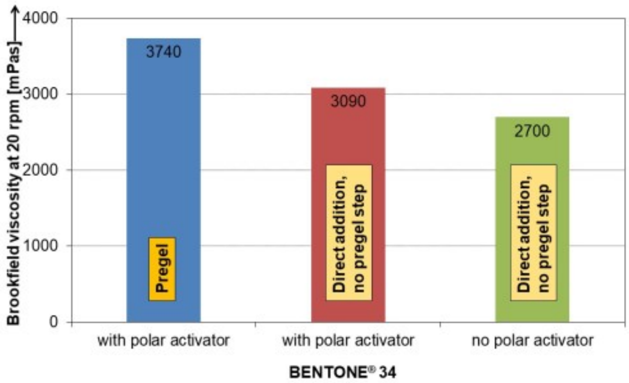


Figure 8: Alkyd paint viscosity

In all the displayed case the BENTONE® 34 content is with 1% identical. In the case were the BENTONE® 34 was added directly, so that no pregel step was performed, the clay first was exposed to the solvent portion of the formulation to ensure proper wetting.

It is obvious, that when added as a polar activated pregel, the effectivity is by far the highest. The direct addition, is another potential way of application, however, with a lower viscosity effect. No polar activation guides to even lower viscosities. The effect of the sagging stability is following the same trend and can be seen in *figure 9*.

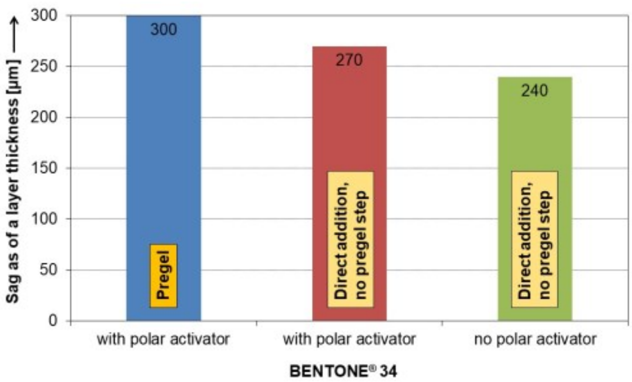


Figure 9: Sagging stability

It can be concluded, that it is always beneficial to prepare a pregel conventional organoclays with polar activation as this is providing the most effective viscosity, optimum sag stability and grinding result. When directly added, the use of a polar activator is always recommended. Without polar activator, the effectivity is by far the lowest. The effect of the fineness of grind is with direct addition not as worse as in case of preparing a pregel with polar activator in case of pigmented systems. The reason is that due to pigments and extenders the applied shear forces are significantly higher than in a clear system.

In case pregel step and polar activation should be avoided, the BENTONE® SD grades are the products of choice.

BENTONE® SD products

BENTONE® SD are so called super-dispersible organoclays. This group currently covers three products. These are BENTONE® SD-1 which is covering the similar lower polarity range as BENTONE® 34 and BENTONE® 1000. BENTONE® SD -3 has designed for the low to medium polarity range like BENTONE® 38, BENTONE® 52 and BENTONE® 54. The third product BENTONE® SD-2 is together with BENTONE® 27 dedicated for systems of high polarity.

Due to the differences in the platelet agglomerate structure, BENTONE® SD grades are significantly better to disperse and do neither require the preparation of an intermediate pregel not a polar activation in the typical solvent borne systems. The improved dispersibility of the superdispersible grade is given by a larger platelet distance within the undispersed stack due to a higher quat content in comparison to conventional organoclays out of the BENTONE® range. This is visualized in figure 10.

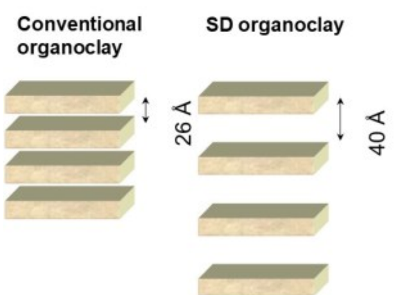


Figure 10: Platelet structure

However, in special cases e.g. in high solids and solvent less systems, chemical activation might be beneficial.

The activation of BENTONE® SD grades follows in general the recommendations for the of conventional BENTONE® SD organoclays. The clay portion should be first immersed and dispersed to the solvent portion to ensure proper solvation. Afterwards the process continues as usual with all other raw materials so that the BENTONE® SD organoclay dispersed alongside with the fillers and extenders.

However, a visible in *figure 11*, due to the larger amount of quaternary ammonium components in the BENTONE® SD product, less rheological active clay platelets a present per certain quantity up on optimum activation.

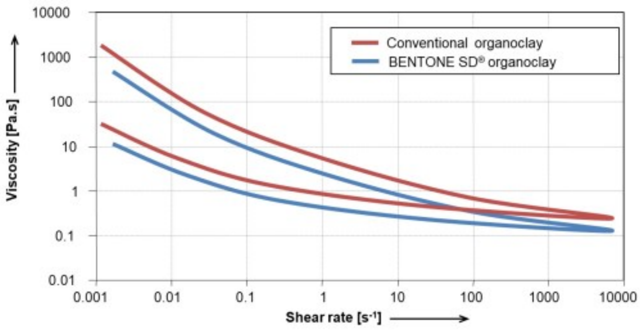
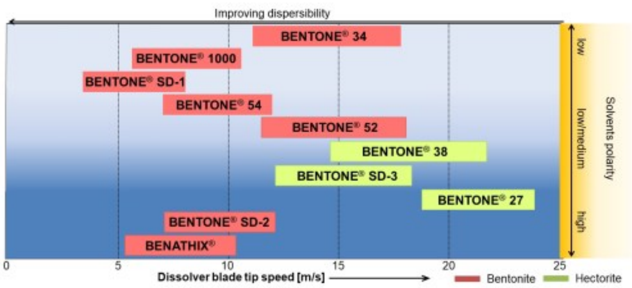


Figure 11: Efficiency comparison

Shear requirements

In general all BENTONE® and BENTONE® SD organoclays are having various shear requirements in order to be properly delaminated and activated. The differences visualized as various tip speed can be found in *figure 12*.



It can be seen that with decreasing requirements of tip speed the dispersibility is improving. Tendencially all clay products based on Hectorite require high shear forced. However, this can be explained by the significantly smaller size of the individual platelet. On the other hand, Hectorite based grades such as BENTONE® 27, BENTONE® 38 and BENTONE® SD-3 are providing remarkably higher effectivity than the relevant Bentonite based product. The graph also displays the lower shear demand of the BENTONE® SD in comparison to the conventional organoclay which is covering the same range of polarity. This means that BENTONE SD-1 can be activated utilizing less dispersing speed than BENTONE® 34. The same is relevant for BENTONE® SD-3 with BENTONE® 38 as well as BENTONE® SD-2 and BENTONE® 27. BENTONE® 54 is acting in between BENTONE SD-1 and BENTONE 34.

BENTONE® SD-1 application

A special case is the application of BENTONE® SD-1 in aromatic-free system of very low polarity.

As discussed, BENTONE® SD-1 can be used, as any other BENTONE® SD grade without Pregelling and polar activation directly in the production of the end system. As with all organoclays, it is recommended to expose and disperse the clay powder first in the solvent portion before adding further components.

However, experience has shown that in systems which are based on dearomatised aliphatic hydrocarbons the efficiency is often insufficient. In such case, the use of a chemical activator can help significantly. In *figure 13* these differences in viscosity build and flow character of BENTONE® SD-1 dispersed at a concentration of 7.5% in an aromatic free aliphatic hydrocarbon is illustrated in manufacturing process of an alkyd paint.

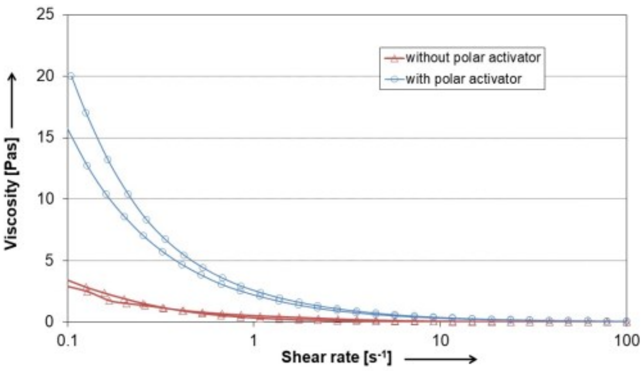


Figure 13: BENTONE® SD-1 efficiency

In this phase of the production the viscosity of the unactivated material is remarkably lower. A polar activation, in this case with propylene carbonate, increases the viscosity and generates in the flowing higher friction which is beneficial for the entire manufacturing process of manufacturing.

Temperature effect

Changing temperature conditions are always affecting the paint manufacturer in all areas. As temperature is directly related to solvency, it will also play a significant role in the reproducibility of solvent pregels of organoclay.

In the following temperature effects on the gel development of BENTONE SD® 1 in a system based on aromatic free aliphatic hydrocarbon is illustrated. Each of the following set of samples have been manufactured at various temperatures of 15°C, 22°C and 40°C. The dispersion took place in the solvent itself and directly in the used long oil alkyd resin, with and without a chemical activator.

In *figure 14* the results are illustrated.

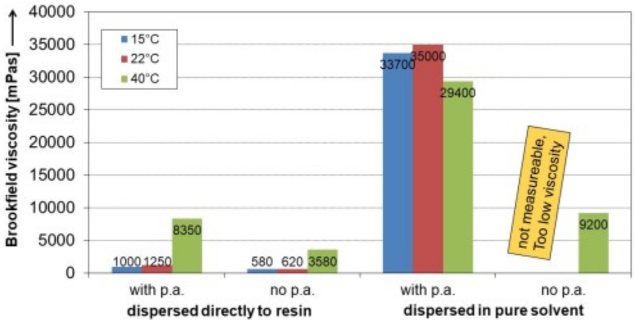


Figure 14: Temperature effect

All samples show a clear effect of the temperature on the dispersibility of BENTONE® SD-1. The highest Brookfield viscosities at 20 rpm could be achieved when dispersed at the highest temperature of 40°C.

When dispersed directly into the resin, the viscosities are generally lower than in the solvent. The use of a chemical activator generally results in higher viscosity build than without.

The polar activator has been necessary to achieve sufficient structure of the gel in solvent. In such case, the dispersing process results in similar high viscosities. A solvent based produced at lower temperature without polar activation results in poor gel structure. In this case elevated temperature of around 40°C can compensate to a certain extend.

It can be summarized, that the dispersion of an organoclay also depends on the temperature. However, not as much as known from organic thixotropes. Lower temperatures, generally guide too less gel structure. This difference can be compensated by the use of a polar activator.

Conclusion

- Hectorite based grades are acting more effective than those based on Bentonite clay.
- Conventional organoclays exhibit the greatest efficiency and improved fineness of grind when initially wet out in only solvent, followed by the proper level of chemical
- Adding the chemical activator after the organoclays is fully wet out and swollen is crucial for optimum effectivity. A stabilizing resin should be added as the last ingredient to the pregel.
- Temperature plays an important role in the dispersion and viscosity development process. However, this temperature control is not as important as in case of organic thixotropes.

- In case of BENTONE® SD-1 the use of a polar activator is beneficial when used in dearomatised systems.

BENTONE® overview

Organoclay based on	
Hectorite	**Bentonite**
BENTONE® 38	BENTONE® 34
BENTONE® 27	BENTONE® 52
BENTONE® SD-3	BENTONE® 54
	BENTONE® 1000
Preactivated	BENTONE® SD-1
BENTONE® P 270 CO	BENTONE® SD-2
BENTONE® P 380 MS	BENATHIX®

Table 3: Overview available organoclay grades

North America
Elementis
469 Old Trenton Road
East Windsor,
NJ 08512, USA
Tel:+1 609 443 2500
Fax:+1 609 443 2422

Europe
Elementis UK Ltd.
c/o Elementis GmbH
Stolberger Strasse 370
50933 Cologne, Germany
Tel:+49 221 2923 2066
Fax:+49 221 2923 2011

Asia
Deuchem (Shanghai) Chemical Co., Ltd.
99, Lianyang Road
Songjiang Industrial Zone
Shanghai, China 201613
Tel:+86 21 5774 0348
Fax:+86 21 5774 3563