The Benefits of Hectorite vs. Silica in Underarm Products
Introduction

Underarm antiperspirants come in a variety of forms, but regardless of whether they are aerosols, sprays, roll-on emulsions or sticks, they all need rheological additives to suspend the Aluminium salts, which are the active ingredients in antiperspirants. Rheological additives provide uniformity in application and dosage of the product. In stick formulations they act as an in-process suspension aid, so that the Aluminium salts do not settle out while the sticks are still in their molten state. Once the stick has formed the rheological additives provide an internal matrix that enhances structural integrity, smooths application, controls payout rate and provides a soft skin feel.

Hectorite clay, Silica and modified Silica are often used as rheological additives in antiperspirants to help provide these desired effects.

An initial comparison of Hectorite shows that as well as providing an efficient, cost saving alternative in these applications it causes less dusting than Silica and is easier to store, due to increased density. In addition, test results presented in this brochure will show that Hectorite clay and organoclays offer benefits specifically for antiperspirant/deodorants, including anti-settling of actives, reduced coagulation, no clogging and significantly less whitening potential of dark fabrics than Silicas. Using products containing the INCI names of either "Hectorite" and/or "Disteardimonium Hectorite" on the ingredient labels is a consumers best assurance of stable and consistent formulations.

Request a copy of our ‘Antiperspirants Formulary’ for examples of a wide range of underarm antiperspirant prototypes that have been stability tested.
What are Hectorite, Silica and Modified Silica?

Hectorite is a smectite clay in the form of individual platelets with a Magnesium based centre between two Silicone Dioxide outer layers. Hectorite clay swells in water, building up a three-dimensional structure, making it commercially very important as a rheological additive and flow control agent. In the personal care industry, Hectorite is used to improve properties such as suspension, emulsion stability, viscosity, thermal stability and spreadability. Hectorite clays can be reacted with organic compounds to form organophilic clays. These swell in anhydrous media and maintain the same physical properties of the hydrophilic clays.

The Silica most commonly used in the personal care industry is fumed Silica. Fumed Silica is made via a vapour technology, which produces an extremely small particle size and high surface area. The fumed Silica thickens by forming a three-dimensional network in liquids. Silica can be modified in various ways to change its properties. Unmodified Silica is hydrophilic, but can also be used in hydrophobic systems, and modified Silica is hydrophobic.

Silica has a low density, making it difficult to use in production and it may contain crystalline Silica, which is carcinogenic. Silica can be drying on the skin, whereas Hectorite clay and organoclay leave a soft, dry and smooth feel on the skin.

Table 1 shows the general properties of Hectorite, fumed Silica and modified Silica.

<table>
<thead>
<tr>
<th></th>
<th>Hectorite</th>
<th>Fumed Silica</th>
<th>Silica Silylate</th>
<th>Silica Dimethyl Silylate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemistry</strong></td>
<td>Na(<em>{0.33})[Mg(</em>{2.67})(\text{Li}_{0.33})]Si(<em>4)O(</em>{10})[OH](_2)</td>
<td>Si(_2)O</td>
<td>Hydroxyl groups on silica replaced with Trimethylsiloxy groups</td>
<td>Hydroxyl groups on silica replaced with dimethyl silyl groups</td>
</tr>
<tr>
<td><strong>Particle Shape</strong></td>
<td>Elongated</td>
<td>Spherical</td>
<td>Spherical</td>
<td>Spherical</td>
</tr>
<tr>
<td><strong>Average Primary Particle Size, nm</strong></td>
<td>250</td>
<td>7-16 (varies depending on type)</td>
<td>7-16 (varies depending on type)</td>
<td>7-16 (varies depending on type)</td>
</tr>
<tr>
<td><strong>Specific Surface Area (BET), m(^2)/g</strong></td>
<td>0.8119</td>
<td>100 - 300 (varies depending on type)</td>
<td>100 - 300 (varies depending on type)</td>
<td>100 - 300 (varies depending on type)</td>
</tr>
<tr>
<td><strong>Tapped Density, g/l</strong></td>
<td>ca. 1700</td>
<td>ca 50 - 60 (varies depending on type)</td>
<td>ca 50 - 60 (varies depending on type)</td>
<td>ca 50 - 60 (varies depending on type)</td>
</tr>
<tr>
<td><strong>Colour</strong></td>
<td>Light Pink to Tan</td>
<td>White</td>
<td>White</td>
<td>White</td>
</tr>
</tbody>
</table>

*Table 1. Typical properties of Hectorite, fumed Silica and modified Silica*
Morphology of Hectorite Clay and Silica

Hectorite and Silica are structurally very different. Hectorite clay consists of small elongated platelets whereas Silica is in the form of agglomerates of small spherical particles. Fumed Silica has a very low density, which can make storage difficult and it is prone to form dust. Figure 1 shows a visual comparison of 1g of Hectorite clay and 1g of fumed Silica. Figures 2 and 3 show how Hectorite and fumed Silica appear under atomic force microscopy.

Figure 1. Visual comparison of 1 gram of Hectorite clay and 1 gram of fumed Silica

Figure 2. Close-up of Hectorite platelets, using atomic force microscopy

Figure 3. Close-up of fumed Silica using atomic force microscopy
Viscosity and Yield Value of Hectorite vs Fumed Silica in Water

Hectorite and fumed Silica were compared at various concentrations in water. The results are shown in Figure 4. The fumed Silica gave no to little viscosity increase even when the concentration was increased to 10%.

In Figure 5 the yield value for Hectorite is much higher than that of fumed Silica. In water based antiperspirant roll-ons and emulsions the higher viscosity of Hectorite means that smaller amounts of Hectorite are needed than fumed Silica to achieve the same viscosity and rheological performance. The higher yield value means that Hectorite is better at preventing the settling of suspended particles in formulations than fumed Silica. Overall fumed Silica is more expensive than Hectorite clay and less efficient in water.

![Figure 4](image1.png)  
*Figure 4. Viscosity vs concentration of Hectorite and fumed silica in aqueous solution*

![Figure 5](image2.png)  
*Figure 5. Yield values of 5% Hectorite and 10% fumed silica in aqueous solution*
Hectorite organoclay (BENTONE® 38 V, INCI:Disteardimonium Hectorite), fumed Silica, Silica Silylate and Silica Dimethyl Silylate were compared at various concentrations in Cyclopentasiloxane. The results are shown in Figure 6. The viscosity profile of the fumed Silica and the modified Silicas shows them to be more efficient thickeners than BENTONE® 38 V when compared at the same concentration. If the cost of modified fumed Silica is considered, the BENTONE® 38 V is more efficient. In Figure 7 the yield value for 5% BENTONE® 38 V in Cyclopentasiloxane is higher than the modified fumed Silicas at the same concentration, which means that BENTONE® 38 V offers a potential cost saving advantage because less BENTONE® 38 V is required to achieve the required suspension stability of Aluminium salts. The unmodified fumed Silica gave the highest viscosity and yield values in Cyclopentasiloxane.

**Figure 6. Viscosity vs concentration of BENTONE® 38 V and fumed and modified Silica in Cyclopentasiloxane**

**Figure 7. Yield values of 5% BENTONE® 38 V and fumed and modified Silica in Cyclopentasiloxane**
Coefficients of Friction

To measure the skin feel of the individual rheological modifiers, they were each dispersed at a concentration of 5% in Cyclopentasiloxane, with no other ingredients. A film thickness of 30 µm of test product was applied to a piece of black paper and left to dry. The coefficient of friction was measured using a friction/peel tester\(^1\). The coefficient of friction can be used to give an indication of the after feel of the product on the skin. A low coefficient of friction means that the product gives a smooth after feel with low dragging. The graph in Figure 8 shows the coefficients of friction for all of the additives tested. BENTONE® 38 V gave the smallest coefficient of friction, compared to the fumed Silicas and modified fumed Silicas, meaning that BENTONE® 38 V leaves a softer skin feel with less drag.

![Figure 8. Coefficients of friction for 5% rheological additives in Cyclopentasiloxane](image)
Comparison of Hectorite Organoclay with Fumed Silica and Modified Fumed Silica in an Antiperspirant Emulsion Formulation with Aluminium Chlorohydrate

The rheological additives were formulated into an antiperspirant emulsion formulation at 8% with 20% Aluminium Chlorohydrate. Figure 9 shows the samples after 1 month at 40°C. Here the modified fumed Silicas all showed stability problems, whereas the BENTONE® 38 V and fumed Silicas all gave good stability.

*Figure 9. Stability of roll-on formulations with Aluminium Chlorohydrate after 1 month at 40°C*
Comparison of Hectorite Organoclay with Fumed Silica and Modified Fumed Silica in an Antiperspirant Emulsion Formulation with Aluminium Chlorohydrate

The formulations from page 7 were applied to a piece of card with a levelling blade, see Figure 10. The blade contains gaps in two gap sets, which increase in size from left to right as follows: 0.25 mm, 0.5 mm, 1.0 mm, 2.0 mm and 4.0 mm. The product is placed inside the levelling blade, on a piece of card and moved down the card using a draw down machine. The uniformity of the lines show how good the spreading is and whether or not the product has experienced coagulation or instability after samples were kept for 1 month at 23°C. All samples, except for BENTONE® 38 V showed instability or inconsistent spreading patterns.

Figure 10. Coagulation of Aluminium Chlorohydrate and additive in antiperspirant roll-on formulations shown with levelling test blade
**Methodology to Determine Whitening**

Whitening tests were carried out by first applying 2.5g of test sample to marked-off areas (5cm x 5cm) on black cotton fabric. The treated fabric was dried at 40°C before washing with laundry detergent and drying again. This four-step procedure of product application, drying, washing and drying again was repeated 6 times before photographing and measuring the colour change from the original untreated fabric with a spectrophotometer.

A Microflash V4.0 spectrophotometer from Data Color International was used to measure tristimulus CIE L*a*b* readings. D75 North Sky Daylight at 7500K is used for visual evaluation of opaque materials as outlined by ASTM D1729\(^{(2)}\). Such readings give precise colour information in a numerical form. When L*=0 this represents black and when L*=100 this represents white. Negative a* numbers mean green, while positive a* values mean magenta. Negative b* readings represent blue and positive readings represent yellow. The testing was carried out in triplicate and error bars, from determinations made via the standard deviation were plotted on a graph. All results are based on comparing the test product with the results from black cotton. The human eye can perceive colour differences when \(\Delta E\) is 1, and for certain tones it is even lower\(^{(3)}\).

\[
\Delta E = \left[ \left( L_{\text{cotton}} - L_{\text{test}} \right)^2 + \left( a_{\text{cotton}} - a_{\text{test}} \right)^2 + \left( b_{\text{cotton}} - b_{\text{test}} \right)^2 \right]^{1/2}
\]

*Figure 11. Spectrophotometer*
Reduced Whitening of Hectorite Organoclay in an Antiperspirant Emulsion with Aluminium Chlorohydrate

Some antiperspirants leave a white mark on dark clothing, which is often caused by the antiperspirant active. The antiperspirant formulation can be modified to avoid this effect, but it is also desirable to select a rheological additive which does not contribute to any additional whitening.

The fabric was treated with the antiperspirant emulsions shown on page 7, which contained 8% rheological additive. Visual assessment of the whitening intensities, shown in Figure 12, correlated well with the numerical differences for the CIE L*a*b* values found by using a portable spectrophotometer.

Figure 12. Black cotton fabric whitening of antiperspirant emulsion formulations with Aluminium Chlorohydrate
Reduced Whitening of Hectorite Organoclay in an Antiperspirant Emulsion with Aluminium Chlorohydrate

The difference in colour ($\Delta E$) between the test materials and black cotton fabric was measured using the equation on page 9 and plotted in Figure 13.

Figure 13. Difference in overall colour from black cotton
**Comparison of Hectorite Organoclay with Fumed Silica and Modified Fumed Silica in an Antiperspirant/Deodorant Spray with Aluminium Chlorohydrate**

BENTONE® 38 V, the fumed Silicas of varying particle size and the modified fumed Silicas were formulated into a standard antiperspirant/deodorant spray at 0.28% with 9% Aluminium Chlorohydrate.

Samples were shaken for 30 seconds to disperse the Aluminium Chlorohydrate fully and left to settle. Figure 14 shows the samples 2 minutes after shaking. The fumed Silica products do not perform as well as the BENTONE® 38 V. The modified Silicas gave good suspension, which was similar to the performance of BENTONE® 38 V.

These samples were then stored for 1 month at 23°C. During the assessment of the samples it was clear to see that the Aluminium Chlorohydrate in the antiperspirant/deodorant sprays formulated with modified fumed Silicas had coagulated on storage, making it impossible to redisperse fully. The samples were shaken thoroughly and the liquid was decanted off. The coagulated residue compared to no residue from the sample with BENTONE® 38 V is shown in Figure 15.

**Figure 14. Suspension of Aluminium Chlorohydrate and additive in antiperspirant spray formulations 2 minutes after shaking**

**Figure 15. Coagulation of Aluminium Chlorohydrate and additive in antiperspirant spray formulations**
Comparison of 2.5% Hectorite Organoclay with Modified Fumed Silica in an Antiperspirant Roll-On Formulation

A roll-on antiperspirant formulation base was developed in a silicone system with Aluminium Zirconium Tetrachlorohydrate Gly. Suspending agents were added to the base at 2.5%. Figure 16 shows that the formulation with 2.5% BENTONE® 38 V gave better thickening than the modified Silicas. Figure 17 shows the percentage separation after undergoing 5 freeze/thaw cycles. Samples containing BENTONE® 38 V underwent the least separation. The samples are shown in Figure 18.

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**Figure 16. Flow comparison of roll-on formulations with Aluminium Zirconium Tetrachlorohydrate Gly and 2.5% rheological additive**

**Figure 17. Stability of roll-on formulations with Aluminium Zirconium Tetrachlorohydrate Gly and 2.5% rheological additive after 5 freeze/thaw cycles**

**Figure 18. Sedimentation of roll-on formulations with Aluminium Zirconium Tetrachlorohydrate Gly and 2.5% rheological additive after 4 weeks storage at room temperature**
Comparison of 5% Hectorite Organoclay with Modified Fumed Silica in an Antiperspirant Roll-On Formulation

Another roll-on antiperspirant formulation based on a silicone system was developed. Suspending agents are added to the base at 5%. Figure 19 shows the effect of aging on the viscosity. The sample with BENTONE® 38 V underwent the smallest change in viscosity. Figure 20 and 21 show the percentage separation after 4 weeks at 40°C and after 5 freeze/thaw cycles. BENTONE® 38 V caused the least separation in both cases.

Figure 19. The effect of aging on viscosity of roll-on formulations with Aluminium Zirconium Tetrachlorohydrate Gly and 5% rheological additive after 4 weeks at room temperature measured using a shear rate of 1 s⁻¹.

Figure 20. Stability of roll-on formulations with Aluminium Zirconium Tetrachlorohydrate Gly and 5% rheological additive after 4 weeks at 40°C.

Figure 21. Stability of roll-on formulations with Aluminium Zirconium Tetrachlorohydrate Gly and 5% rheological additive after 5 freeze/thaw cycles.
Summary

Hydrophilic Hectorite clay (such as BENTONE® EW, INCI: Hectorite, used in water-based systems) and hydrophobic Hectorite organoclay (such as BENTONE® 38 V, INCI: Distearidimonium Hectorite, used in anhydrous systems like Cyclopentasiloxane) deliver the following advantages over fumed Silica and modified fumed Silica:

**Improved Formula Stability**

- Hectorite clay and organoclay enhanced rheological properties (high viscosity and increased yield value) which collectively:
  1. Provides prolonged suspension of active ingredients and other particulates/droplets
  2. Prevents clogging of spray actuator-valves
  3. Facilitates redispersal of settled active ingredients

**Improved Performance**

- Uniform distribution of active ingredients
- Soft and dry skin feel with reduced drag
- Significantly less whitening of dark fabrics
- Better performance on a cost comparison

**Improved Work Environment**

- Less dust
- Less storage space needed
- No crystalline Silica
References:

