A Comparison of Smectite Clays in Underarm Products

ELEMENTIS SPECIALTIES

Introduction

The functionality of smectite clays (primarily Hectorite or Bentonite in origin) as rheology modifiers and especially as suspension aids for Aluminium salts, which are the active ingredients in antiperspirants, is well appreciated. Even a casual review of ingredient labels on store shelves will reveal their usage in most aerosol and roll-on antiperspirant products. They are also used in antiperspirant sticks as an in-process suspension aid, so that the Aluminium salts do not settle out while the sticks are still in their molten state before the fatty alcohols have an opportunity to solidify during cool-down. Once the stick has formed they provide an internal matrix that enhances structural integrity, smooths application, controls payout rate and provides a soft skin feel. Request a copy of our 'Antiperspirants Formulary' for examples of a wide range of underarm antiperspirant prototypes that have been stability tested.

A comparison of the fundamental properties of Hectorite are an indication of its key performance advantages over Bentonite. Hectorite offers the general benefits of higher rheological efficacy (viscosity and yield value), lower iron content and lighter colour(1). 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 and significantly less staining potential of cotton fabrics than Bentonites, due to contact with low pH Aluminium salts. Thus the usage of Hectorite reduces the objectionable and unsightly appearance of dark yellow armpit staining of shirts. The use of Bentonite is more likely to require EDTA and other chelating agents to sequester its higher iron content. The phenomenon of armpit staining of white cotton shirts and undergarments associated with Aluminium salts is likely only to be enhanced in-vivo with the presence of sweat and sebaceous secretions. Using products containing the INCI names of either "Hectorite" and/or "Disteardimonium Hectorite" on the ingredient labels is a consumers best assurance that the level of staining potential due to the presence of Aluminium salts is at a minimum.

What are Smectite Clays?

Smectite clays belong to a family of layered minerals that are comprised of individual platelets with a metal oxide center sandwiched between two Silicone Dioxide outer layers. Included in this group of minerals are Hectorite, Bentonite (Montmorillonite), Saponite, Sepiolite, Beidellite, Nontronite and Sauconite. Of these, Hectorite and Bentonite are the most important because of their swelling properties and availability.

Because of the structure these clays build after they swell in water, they have become commercially important as rheological additives, or flow control agents. In the cosmetics industry, clay based products are used to improve properties such as suspension, emulsion stability, viscosity, thermal stability and spreadability.

Structurally, Bentonite is a dioctahedral, Aluminium based clay, while Hectorite is a trioctahedral, Magnesium based clay. This structural difference leads to differences in the chemistry and physical properties of the two clays. In addition, Hectorite does not contain any crystalline Silica.

Both Bentonite and 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 reacted hydrophilic bases; i.e., Hectorite based organoclays have a lighter colour, lower iron content and greater viscosity efficiency. In Table 1 we can see the general properties of Hectorite and Bentonite.

	Hectorite	Bentonite
Chemistry	$Na_{0.33}[Mg_{2.67}Li_{0.33}]Si_4O_{10}[OH]_2$	$Na_{0.33}[Al_{1.67}Mg_{0.33}]Si_4O_{10}[OH]_2$
Platelet Shape	Elongated	Equidimensional
Platelet Size (dispersed)	0.8 x 0.08 x 0.001 microns	0.8 x 0.8 x 0.001 microns
Type	Trioctahedral	Dioctahedral
Swelling Ability	35 x	15 x
Colour	Light Pink to Tan	Grey to Green
Iron (typical)	0.2%	2.3%
Viscosity (5% concentration)	10000 mPa.s	750 mPa.s

Table 1. Typical properties of Hectorite and Bentonite

Morphology of Hectorite and Bentonite

The structural differences result in different platelet shapes and sizes for Hectorite and Bentonite. The Hectorite platelets are much smaller and elongated compared to the more equidimensional Bentonite platelets. Therefore, Hectorite clay has more platelets per gram providing greater swelling capacity and improved rheological efficiency compared to Bentonite. The relative sizes of Bentonite compared to Hectorite are shown in Figure 1. Figure 2 and 3 show Bentonite and Hectorite, respectively, under atomic force microscopy.

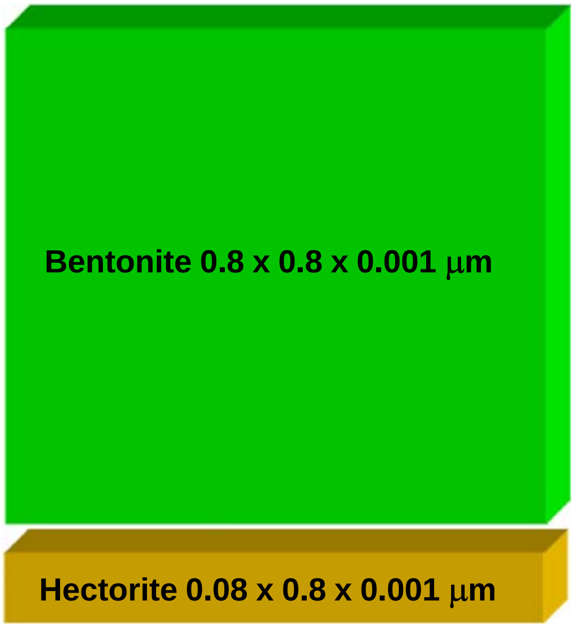


Figure 1. Relative dimension of platelet sizes

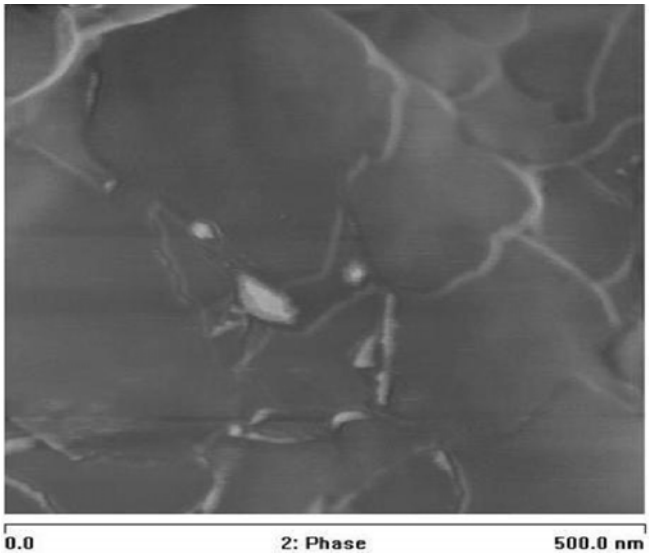


Figure 2. Close-up of Bentonite platelets, using atomic force microscopy

Figure 3. Close-up of Hectorite platelets, using atomic force microscopy

Iron Content of Hectorite and Bentonite

Hectorite clay typically contains ten times less iron than Bentonite clays. Iron content in formulations can be a very important aspect in fragrance stability and antiperspirant staining potential. Figure 4 compares the iron content of Hectorite and Bentonite.

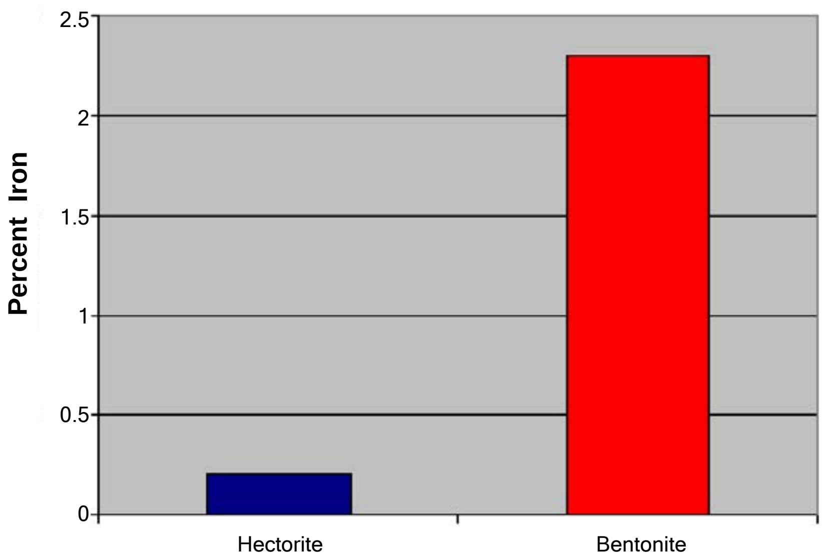


Figure 4. Iron content of Hectorite and Bentonite

Colour of Hectorite and Bentonite

Hectorite is a lighter colour than Bentonite clay, as seen in Figure 5. Since this colour difference carries over to the dispersed state, it means that products using Hectorite will be lighter in colour and more cosmetically acceptable. This colour difference can be seen in certain antiperspirant roll-ons, sticks and emulsions.

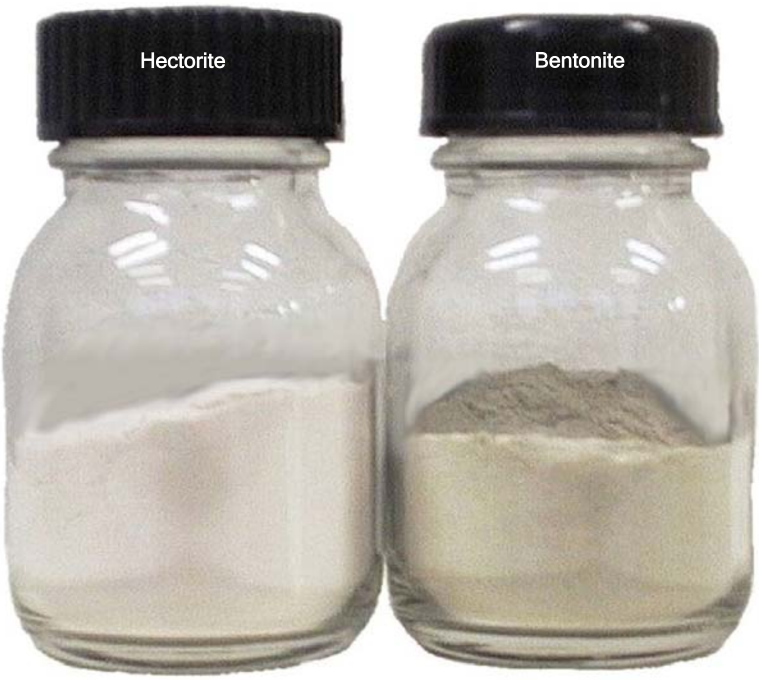


Figure 5. Visual comparison of Hectorite and Bentonite

Viscosity and Yield Value of Hectorite vs Bentonite in Water

Hectorite and Bentonite were compared at various concentrations in water. The results are shown in Figure 6. The smaller particle size of Hectorite clay means that there are a greater number of particles and it has a larger surface area per gram. As we would expect, due to the smaller particle size, the viscosity profile for Hectorite clay in water shows it to be much more efficient than Bentonite clay. In fact, to get the same viscosity as Hectorite, approximately twice as much Bentonite must be used.

In Figure 7 we can see that the yield value for Hectorite is much higher than the yield value of Bentonite. In antiperspirant roll-ons and emulsions the higher viscosity of Hectorite means that smaller amounts of Hectorite are needed than Bentonite 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 Bentonite.

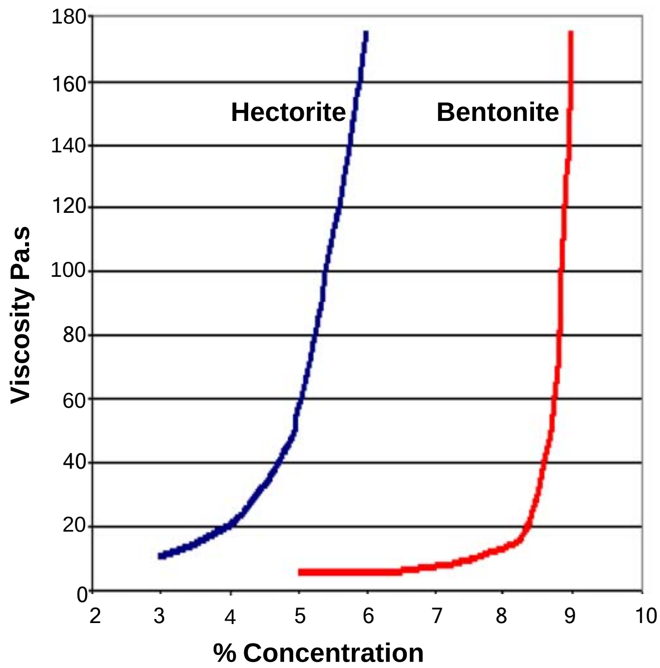


Figure 6. Viscosity vs concentration of Hectorite and Bentonite in aqueous solution

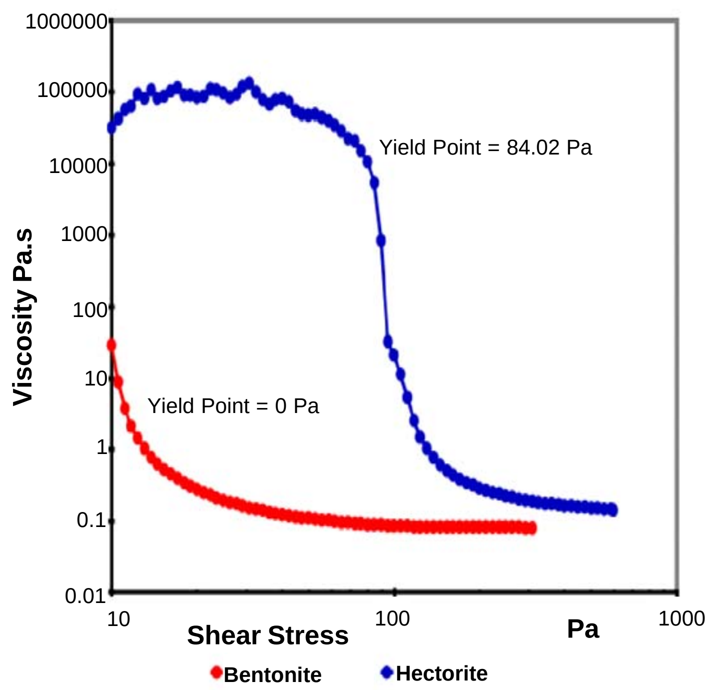


Figure 7. Yield values of 5% Hectorite and Bentonite in aqueous solution

Viscosity and Yield Value Hectorite vs Bentonite Organoclays in Cyclopentasiloxane

Hectorite and Bentonite organoclay (Disteardimonium Hectorite or Disteadimonium Bentonite) were compared at various concentrations in Cyclopentasiloxane. The results are shown in Figure 8. The viscosity profile for Hectorite organoclay in Cyclopentasiloxane shows it to be much more efficient than Bentonite organoclay. In Figure 9 we can see that the yield value for Hectorite organoclay is higher than that of Bentonite organoclay. In anhydrous antiperspirants the higher viscosity and yield value provided by Disteardimonium Hectorite offer a potential cost saving advantage because less organoclay is required to achieve the required suspension stability of Aluminium salts.

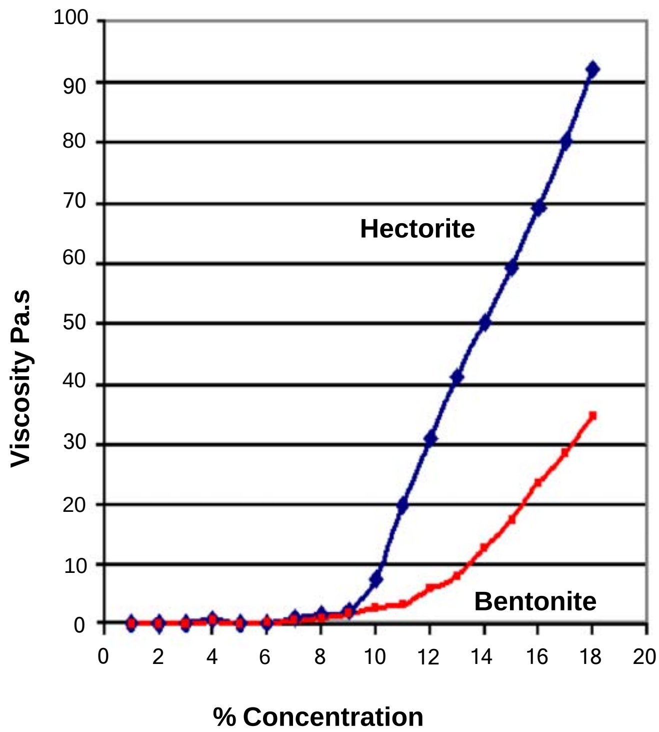


Figure 8 Viscosity vs concentration of Hectorite and Bentonite organoclay in Cyclopentasiloxane

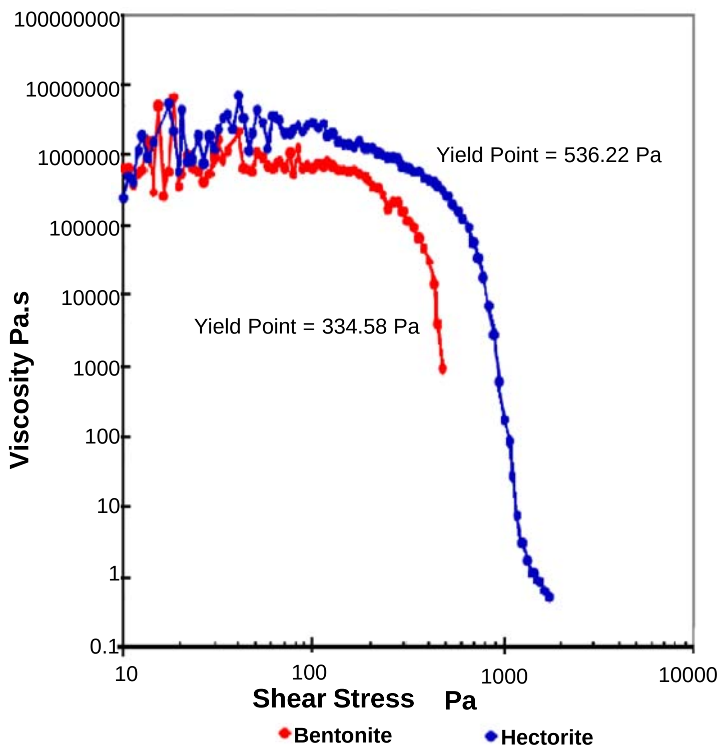


Figure 9. Yield values of 18% Hectorite and Bentonite organoclay in Cyclopentasiloxane

Suspension of Particles in Antiperspirant Sprays

Aluminium Chlorohydrate is a heavy salt which is used as an antiperspirant. It diffuses into the sweat duct, where the acidic metal salt (pH4) is neutralised and forms a polymeric Aluminium Hydroxide gel. This partially blocks the sweat duct, reducing the amount of sweat released onto the skin[(2)]. Without addition of organoclay rheological additives the Aluminium Chlorohydrate settles within seconds, making it impossible to deliver a uniform concentration, or dose, of drug active ingredient. Organoclays are not only excellent suspension agents in non-aqueous antiperspirants, but they also prevent hard packing of Aluminium salts at the bottom of the container. This makes it much easier to return the active ingredient to a homogeneous dispersion with minimal shaking before use and reduces the potential for blockage of the spray-valve actuator[(2)]. The higher yield value means that it is more effective at suspending Aluminium Chlorohydrate than Bentonite clay. In Figure 10 we can see antiperspirant sprays containing no additive, BENTONE® 38 V, BENTONE GEL® VS-5PC V and BENTONE GEL® IPM V 16 seconds after shaking. The sample with no additive has the worst suspension. BENTONE® 38 V improves this, with BENTONE GEL® VS-5PC V and BENTONE GEL® VS-IPM V offering superior suspension. After 1 minute the Aluminium Chlorohydrate in the samples with no additive and BENTONE® 38 V has completely settled to the bottom of the container, whereas the samples with BENTONE GEL® show good to almost complete suspension even after 1 minute, see Figure 11. Optimal performance of any organoclay requires addition of chemical activator (typically Propylene Carbonate or Ethanol/Water) and high energy homogenisation to fully delaminate individual clay platelets. Adding BENTONE® 38 V powder and the desired chemical activator using standard homogenisation does not work as efficiently as using the corresponding BENTONE GEL®. Whenever using a BENTONE GEL® the experience and know-how of Elementis Specialties garantees the formulator that the organoclay is fully dispersed. This is because we use the optimal organoclay:chemical activator ratio and specialised high pressure/high shear homogenisation under tightly controlled processing parameters.

Figure 10. Antiperspirant sprays 16 seconds after shaking

Figure 11. Antiperspirant sprays 1 minute after shaking

Methodology to Determine Staining

Staining tests were carried out by first applying 2.5g of test sample to marked-off areas (5cm x 5cm) on white 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 shift from the original untreated fabric with a spectrophotometer.

We used a Microflash V4.0 spectrophotometer from Data Color International 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(5). 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 white cotton. The human eye can perceive colour differences when ΔE is 1, and for certain tones it is even lower(6).

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

Figure 12. Spectrophotometer

Low Staining Potential of Hectorite Clay and Organoclay Dispersions

Everybody is aware of the common problem of armpit (axillary) staining of shirts. This is caused by two effects, firstly the acidic nature of the antiperspirant active Aluminium Chlorohydrate in combination with the eccrine component of sweat causes a reaction to occur, resulting in yellowing of fabric. This is generally not visible immediately. The Aluminium Chlorohydrate is extremely effective at blocking perspiration, so this yellowing occurs only due to repeated wear, and therefore prolonged exposure to small levels of perspiration in combination with the Aluminium salt(3). Previously Aluminium Chloride was used, but due to its lower pH, which caused fabric staining and eventual disintegration of the material it was replaced with the less harsh Aluminium Chlorohydrate(4). The second cause is due to the iron present in formulation ingredients, including Aluminium salts themselves, as well as in the laundry detergent and wash water. The deposition of iron onto the fabric causes an almost instant yellowing effect which can be followed by reactions with organic acids in skin secreations producing red/brown stains(4). Hectorite clay only contains traces of iron, whereas Bentonite clay contains high levels of iron. Hectorite clay and Hectorite organoclays have been shown to have less antiperspirant stain potential than Bentonite products, both as raw materials and in combination with Aluminium Chlorohydrate. While only one representative photograph is shown, each test was run in triplicate for statistical analysis of the measured CIE L*a*b* values.

The fabric was treated with either 5% hydrophilic clay (INCI: either Hectorite or Bentonite) in water or 18% hydrophobic organoclay (INCI: either Disteardimonium Hectorite or Disteardimonium Bentonite) in Cyclopentasiloxane, as indicated in the captions on Figure 13 and 14. Visual assessment of the stain intensities correlated well with the numerical differences found by using a portable spectrophotometer.

Figure 13. Stain intensity of aqueous dispersions of hydrophilic clays following six (6) treatment cycles

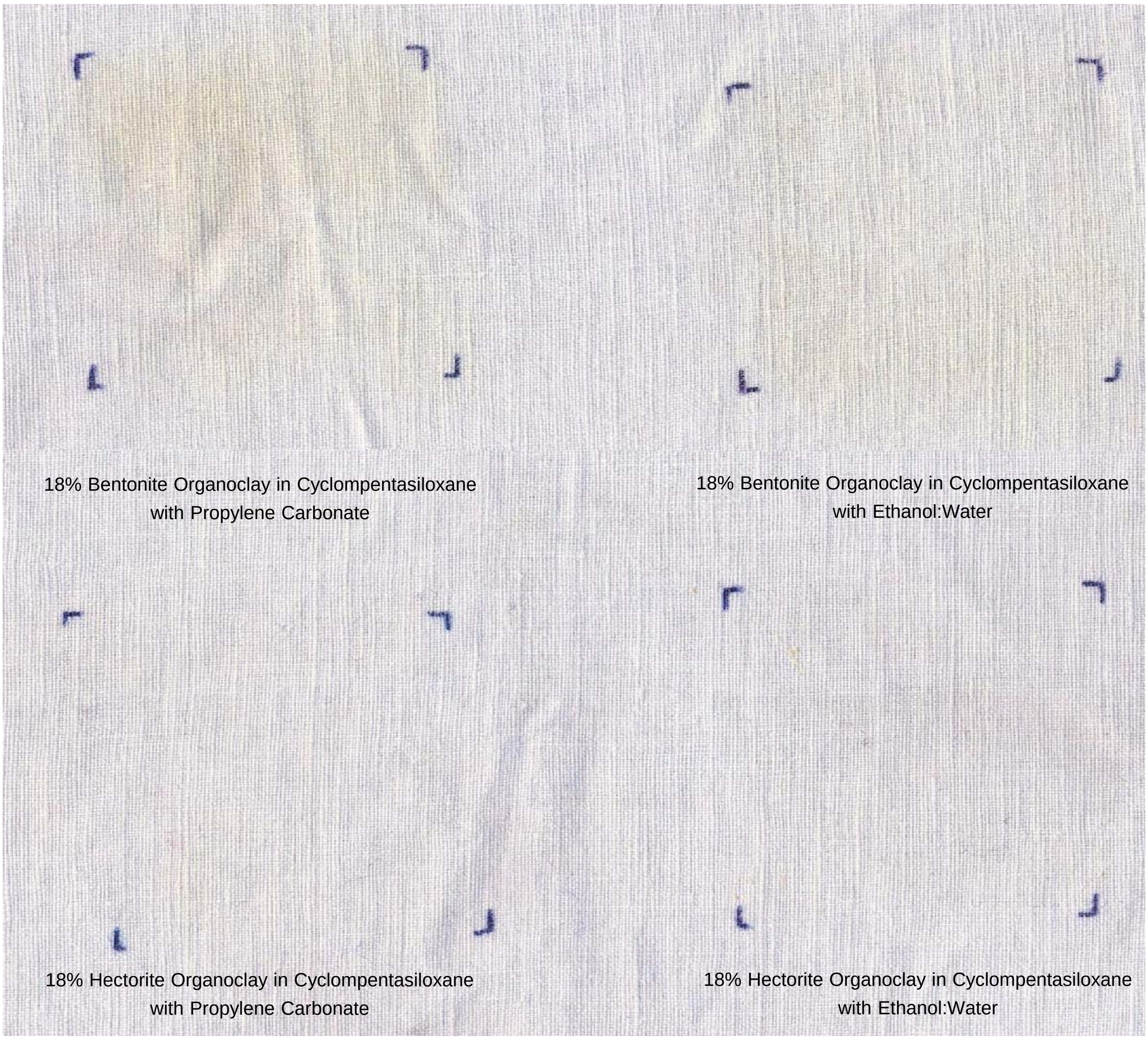


Figure 14. Stain intensity of hydrophobic organoclays in Cyclompentasiloxane following six (6) treatment cycles

CIE L*a*b* Measurements of Hectorite Clay and Organoclay Dispersions

The difference in colour (ΔE) between the test materials and white cotton was measured using the equation on page 8 and plotted in Figure 15.

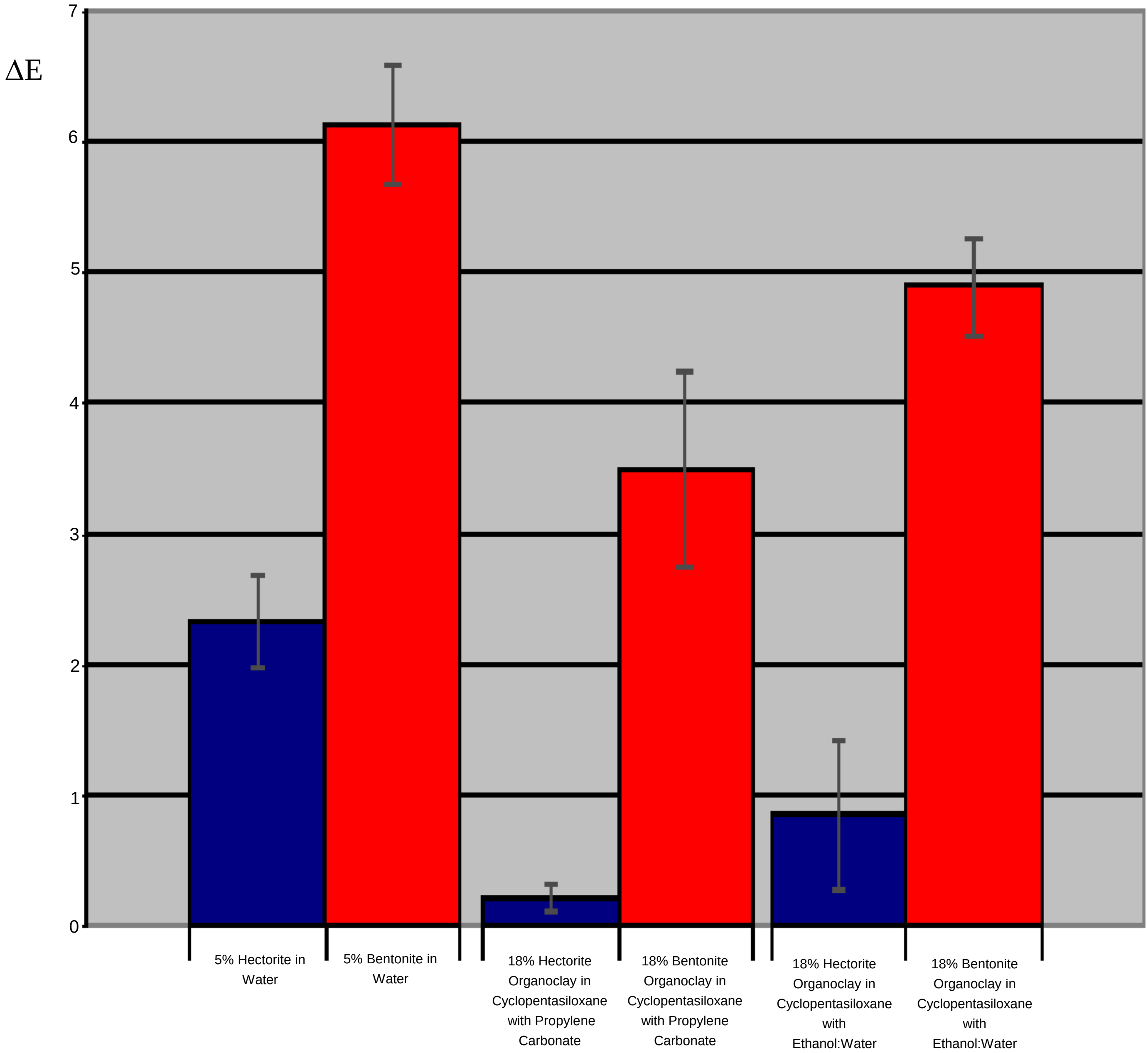


Figure 15. Difference in overall colour from white cotton

Low Staining Potential of Clays and Organoclays in Combination with Aluminium Chlorohydrate

Tests were carried out to see the effect of clay and organoclay on white cotton when used in combination with Aluminium Chlorohydrate. The photos are shown in Figure 16 and 17. The iron present in clay is thought to form complexes with the Aluminium Chlorohydrate. This effect can lead to increased staining of the white cotton. Hectorite contains less iron than Bentonite, so therefore causes less staining.

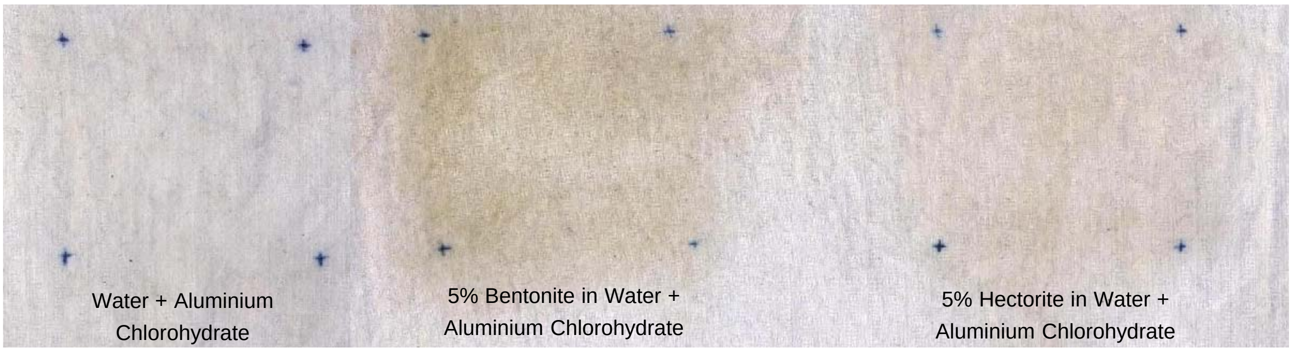


Figure 16. Stain intensity of aqueous dispersions of hydrophilic clays with Aluminium Chlorohydrate following six (6) treatment cycles

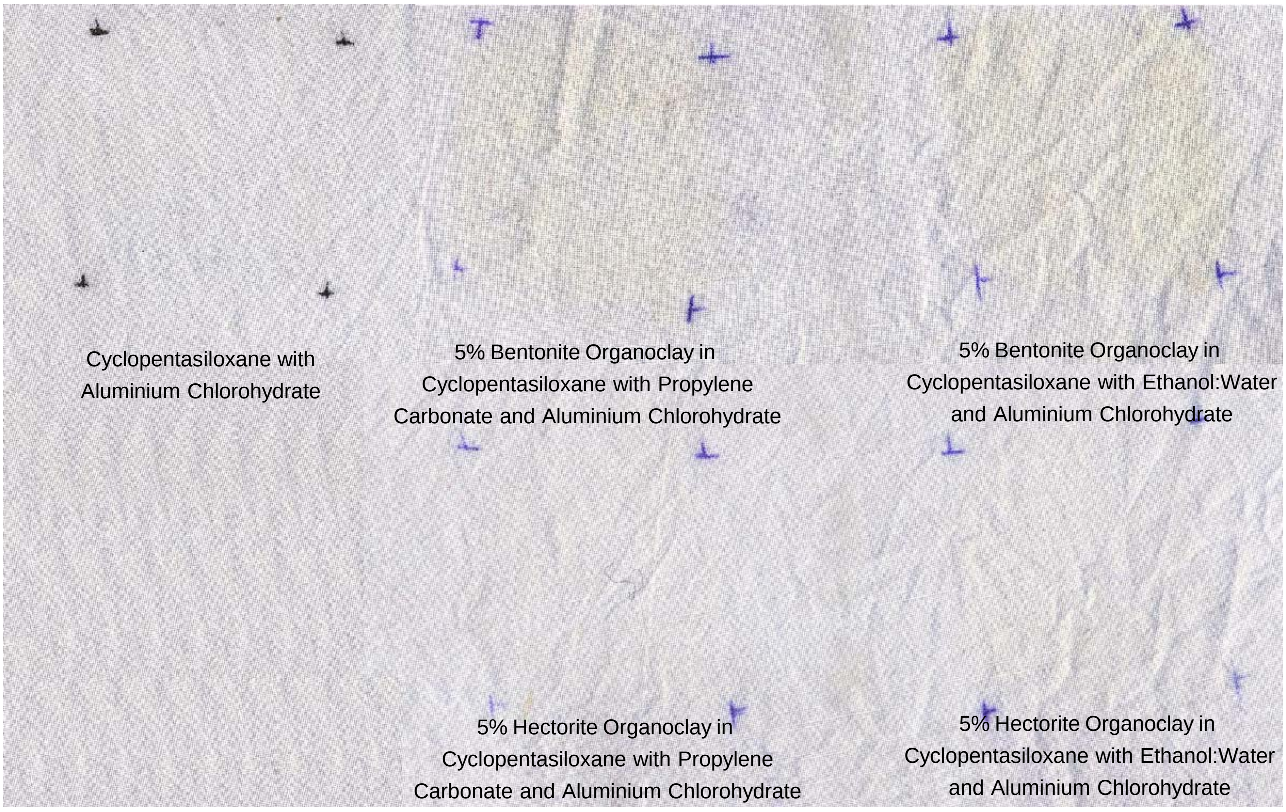


Figure 17. Stain intensity of hydrophobic organoclays in Cyclopentasiloxane with Aluminium Chlorohydrate following six (6) treatment cycles

CIE L*a*b* Measurements of Clays and Organoclays in Combination with Aluminium Chlorohydrate

The spectrophotometer was used again to take tristimulus CIE L*a*b* readings to determine the difference in colour between the test materials and white cotton when used in combination with Aluminium Chlorohydrate. The same equation, as used previously, was used to determine the change in colour (ΔE) and plotted in Figure 18.

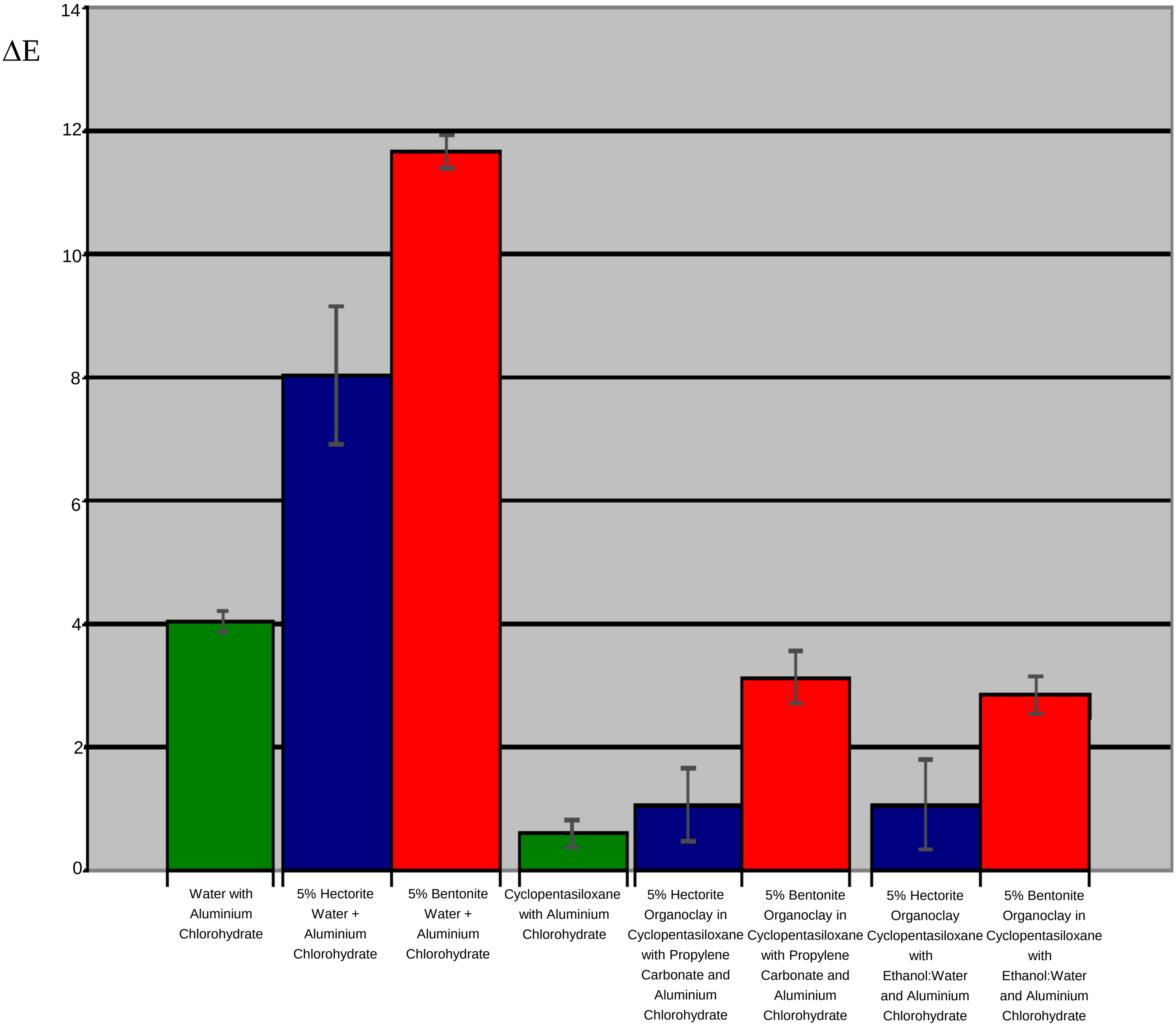


Figure 18. Difference in overall colour from white cotton

Summary

Hydrophilic Hectorite clay (used in water-based systems) and hydrophobic Hectorite organoclay (such as Disteardimonium Hectorite used in anhydrous systems like Cyclopentasiloxane) deliver the following advantages over Bentonite clays

Improved Formula Stability

- Smaller platelet size results in enhanced rheological properties (higher 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
    4. Improved suspension of particles

- Lower Iron Content:

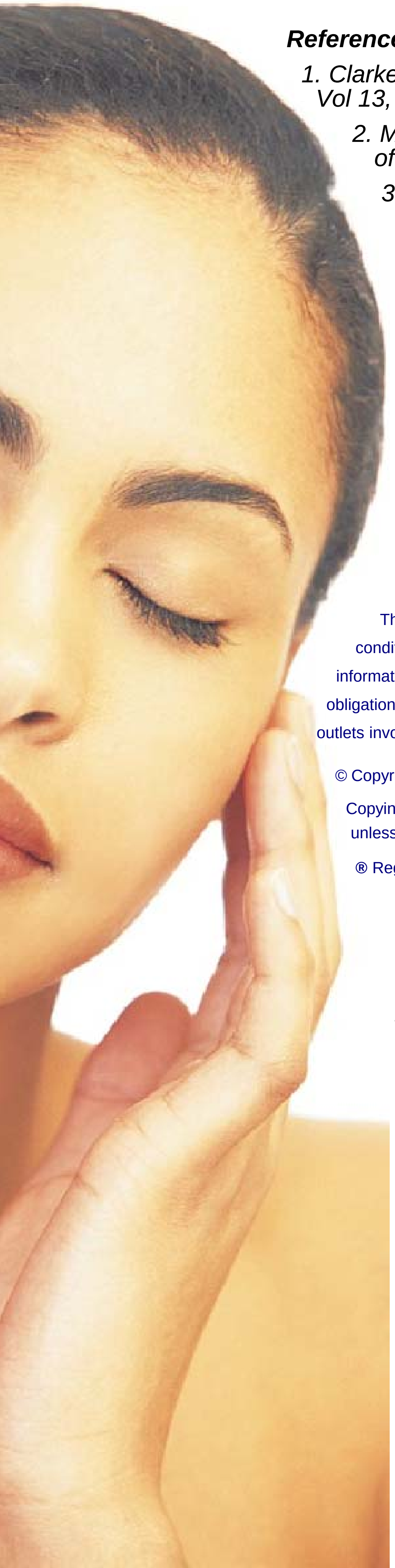
    1. Results in lighter colour
    2. Provides better compatibility with fragrances and other sensitive materials so colour, odour and appearance will not change

Improved Performance

- Uniform distribution of active ingredients
- Softer skin feel
- Lower iron content means less potential for staining of cloth fabrics like white cotton shirts
- Significantly less staining of underarm areas of white cotton shirts due to presence of Aluminium Chlorohydrate

Improved Work Place Safety

- No crystalline Silica dusting which can be a problem with Bentonite



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6. R. W. G. Hunt, 'The Reproduction of Colour', Sixth Edition, Voyageur Press, 2004

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