Hectorite, a natural clay: from formulation and instrumental tests to *in vivo* oil and sweat control efficient cosmetic products

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Abstract

Modern consumers expect from cosmetics ever more benefits such as naturalness and new sensorial experience without any trade-off in performance. Cosmetics dedicated to oily skin should ensure long lasting oil and sweat control while long lasting wetness and odor protection are expected from deodorants.

Hectorite is a specific natural clay of smectite-type, with a strong exfoliation ability that, in aqueous media, leads to the formation of gels which present some interesting features for cosmetic products. Indeed, after application of hectorite gels onto the skin, the dry films have the ability to absorb sebum; they show long lasting mattifying efficacy in *in vitro* and *in vivo* instrumental tests. However, formulating hectorite, especially in presence of some ingredients (such as salts), remains a highly challenging task. This is the case for magnesium containing compounds (ex. MgO, $Mg(OH)_2$) known for their anti-bacterial and anti-odor efficacy.

To overcome the formulation challenge and provide stable, safe and efficient cosmetic products we needed to understand both the interactions between hectorite and magnesium salts and the influence of other raw materials commonly used in cosmetics.
Then, different formulae, either for oily skin care or for deodorant, based on hectorite/MgO association were designed with the aim to demonstrate their efficacy.

They were evaluated first through instrumental tests, then through both clinical and consumer studies.

Thanks to the formulation understanding, *in vivo* efficacy of formulations based on hectorite/MgO association has been evidenced through different tests vs market products. Efficacy was also perceived by consumers when comparing tested product versus market references, highlighting that the hectorite/MgO association has high potential for cosmetic applications.

Keywords: hectorite; smectite; MgO; cosmetic; oily skin; deodorant; efficacy; clinical studies; consumer studies

Introduction

Hectorite clay

Hectorite belongs to the smectite family which belongs to the phyllosilicate class.
Smectites have a layered structure alternating tetrahedral and octahedral layers of minerals, linked by the vertices.
The tetrahedrons are SiO_4 units, formed by oxygen atoms at the vertices and occupied by silicon ions. They are thus organized in a hexagonal pattern (Figure 1).
The octahedra are formed by oxygen ions at the vertices and occupied in the middle by metal ions Al3+ or Mg2+. An octahedral layer is surrounded by two tetrahedral layers, forming an arrangement called TOT or 2:1 (Figure 1). This stacking forms the basic unit, a 10 Å thick sheet.

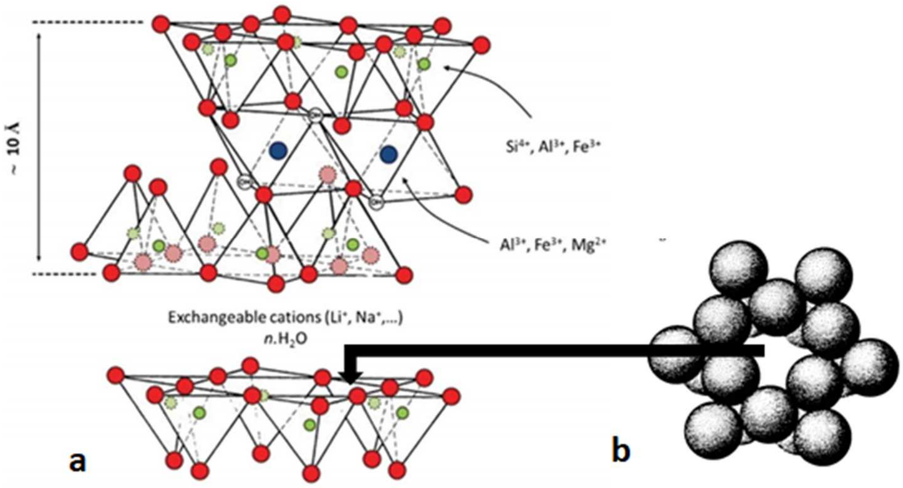


Figure1. Representation of the dioctaedric smectite structure (a) & representation of Si atoms forming a hexagonal pattern (b) [1], [2]

The interstitial sites of the layers are occupied by cations such as Al3+ or Si4+ but these cations can be substituted by other lower valence cations. Substitution of some cations by lower valence cations in the interstitial sites of smectites results in permanent charge deficits in the sheets, explaining their negative charge on the surface.

Smectites are also characterized by the presence of hydrated cations in the interleaf space (Figure 1); this compensates the permanent negative surface charges. The position of these cations affects the inter-foil spacing and therefore the spacing of the sheets [3].

The structural negative charge due to cations substitution is independent of pH and generates an electric field on the surface of the clay particles. On the other hand, the reactive groups present on the edges of the sheets (Figure 2), are capable of being protonated or deprotonated, thus being positively or negatively charged. The structure of the system is then dependent on pH and concentration.

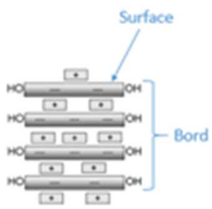


Figure 2. Stacking of smectite sheets [4]

This heterogeneity of charges affects the mode of association of the sheets. In fact, they can be associated in different ways: edge-to-surface, surface-to-surface, edge-to-edge. The obtained dispersion will therefore be dependent on the pH. (Figure 3) [4].

Figure 3. Association of clay sheets in aqueous dispersion (”house of cards” organisation)

When the pH is higher than the zeta potential, the surface and the edges of the clay are negatively charged, so there is no amphoteric character whatever the ionic concentration. However, when the pH is lower than the zeta potential, at low ionic concentration the electronic double layer compensates for the positive charges on the edges, so there can be no edge-surface attraction between the layers. However, at high ionic concentration, the positively charged edges emerge because the electronic double layer is no longer sufficient to screen the charges (Figure 4) [2].

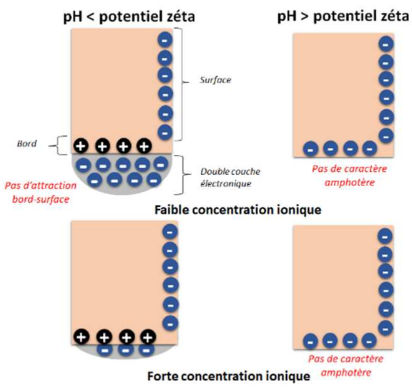


Figure 4. Representation of the charges of a clay sheet as a function of pH and ionic concentration

Due to the structure of smectites, solvents can diffuse into the interleaf space where cations exchange can occur. In the presence of water, the ions diffuse out of the interleaf space, creating an unoccupied site that will correspond to a negatively charged site on the surface. They can also exchange with an H+ ion [5], [6]. Hectorite delamination rate depends on its Cation Exchange Capacity (CEC) which is 70meq/100g.

Smectites are clays with a hydrophilic character which makes them dispersible in aqueous media. They are characterized by this high cation exchange capacity and by swelling when solvent or ions are inserted or exchanged in the inter-leaf space (Figure 5). In the presence of water, smectites hydrate causing a change in electrical forces. The water shrinks the electrostatic interactions, which reduces their strength, causing the sheets separation; this is the exfoliation mechanism [3]. The sheets will separate into small clusters of sheets called tactoids, which structure the medium according to the clay concentration. When the clay is activated, a clay gel is obtained. The exfoliation is more or less important according to the energy brought to the system.

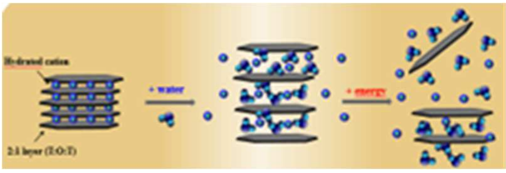


Figure 5. Exfoliation schema of smectites in water (internal source)

The aqueous gels formed by activated hectorite confer a particular texture to the formulas and can serve as a formulation base for many types of cosmetic products.

To design efficient products for oily skins as well as aluminum salt free deodorants we decided to associate this clay with MgO known for its anti-bacterial efficacy as well as malodors neutralization ability [7].

Challenges of hectorite and MgO formulation in the aqueous gels

Hectorite/MgO association presents several challenges in formulation, in terms of its stability over time and its sensoriality.

Electrostatic interactions occur between negatively charged hectorite sheets and positively charged MgO particles when introduced in aqueous media. This leads to the formation of a network of interconnected particles and gives a kind of “attractive” gel. The gel contraction phenomenon leads to the release of water, called syneresis. Moreover, the resulting gel tends to thicken and compact over time.

These issues present a major obstacle to the formulation of stable and robust products.

The modification of hectorite/MgO interactions may be an answer to this challenge. This can be done either by screening/distancing the charges of the hectorite and MgO particles or/and by delaying the hectorite/MgO interactions.

In the first case, glycols and polymers can be used. In the second case the introduction of an accurately chosen amount of acid allows to decrease the pH and thus, to change the edge charge from negative to positive. This leads to the possibility for the hectorite sheets to interact prior to the MgO introduction.

Another problem linked to the use of clay concerns its sensoriality. The hectorite/MgO gels easily break down into water during application, which gives a formula that is pleasant to the touch. However, the film formed after drying is rough. There is a need to introduce raw materials that will bring softness at the end of the application (for ex. fatty compounds, glycols, or fillers).

Thus, to satisfy all the requirements for efficient, stable and sensorial cosmetic products, the tested formulations contain between 3 and 5% of hectorite, between 0,9 and 2% of magnesium oxide, up to 20% of glycol (glycerin, propylene glycol), up to 4% of fatty compounds (for ex. vegetable oil, fatty alcohol, fatty acid and their combinations), up to 0,1% of natural polymer (for ex. sclerotium gum) in water.

Performance evaluation methods for skin care products

Instrumental In Vivo Study of Mattifying Efficacy

28 women with oily skin or combination skin on face

Mini-Areas protocol: 2 on forehead and 2 on cheeks

Mini Areas: ROI to exploitation (2x2,5 cm)

Randomization In Latin square of investigated products

2 mg/cm² with controlled mono-application in our facilities in ROI (3,5x4 cm)

T0, Timm and T2h after sweating in hammam conditions

Light-Cam : NTLC15009

Light-Cam: Contrast Gloss: In grey levels, calculated for each area

Clinical study

156 subjects aged from 18 to 40 years old, balanced between men and women were included. The study was conducted in New Delhi, India.

Subjects were included on mild (grade 2) to moderate acne (grade 3) severity without nodules on a IGA scale from 0 to 4, according to the investigator with an oily skin type measured by sebum casual level on forehead >120 µg/cm2.

It was a double blind, randomized, comparative, with 7 evaluations visits at the center. Investigational products and standard cleanser were applied on full face.

Study was divided into three phases:

- Investigational products application was made according as per Figure 6:

  -Pretreatment phase: D-14 to D-1

  -Treatment phase: D0 to D83

  -Relapse phase: D84 to D97
- Standard cleanser was used daily morning and evening during the 3 phases.

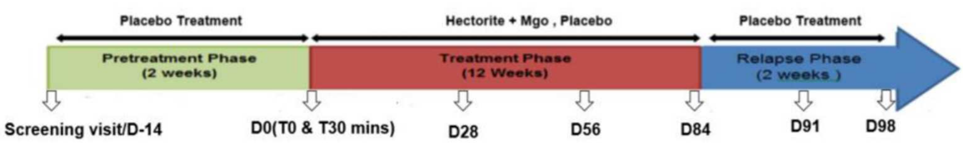


Figure 6. Study design

The dermatologist clinically counted the number of acne lesions on whole face (Forehead, Cheeks, Nose and Chin) during the study with:

-Non-Inflammatory acne lesions: Blackheads (Open comedones) & Microcysts (Closed comedones)

-Inflammatory acne lesions: Papules, Pustules & Nodules

Statistical analysis

For comparison of the two treatments with each other, the normality of the difference (from baseline) will be tested with Shapiro-Wilk test. The following statistical analyses will be performed for comparisons of the treatments:

-Parametric One way Analysis of Variance (ANOVA) in case of normality of differences

-Non-parametric One way Analysis of Variance on Ranks in the inverse case

For normality tests, the statistical significance level is set at $p \leq 0.01$. For all other statistical tests, the statistical significance level is set at $p \leq 0.05$.

Consumer study

30 women aged from 18 to 60 years with mixed or oily skin used the investigated product instead of their own in the morning for 7 days. The test was conducted as follows:

Exploratory phase: the panelists were asked to talk about their skin, how they feel about and take care of it – explaining their beauty routines, showing us their products, and the benefits they look for.

Product test phase: the members were asked to record their experience of the formula at three different moments of their trial: 1st day, 4th day and 7th day

Summary phase: at the end of the test the members were asked to give their final thoughts on the formula by summarizing the strengths and weaknesses.

Performance evaluation methods for deo products

Sniff Test Method (Anti-odor efficacy)

The deodorant efficacy was evaluated on different products within two different studies

- at 24 and 48 hours after a single standardized application to the treated armpit compared to the non-treated armpit by sensory evaluation.
- at 8 and 24 hours after a 4 applications standardized application to the treated armpit compared to the Bench armpit by sensory evaluation.

Study population

21 subjects in total analyzed

Female and male subjects; from 18 to 70 years old, Caucasian, phototype between I to IV, having an average perspiration smell intensity on armpits between 5 and 8 with an intensity difference between the two armpits ≤ (with a scale ranging from 0 to 10)

Methodology

Simple blind and intra-individual study

1st Study: Treated armpit *(5% of hectorite + 2% of MgO + 20% propylene glycol)* versus non treated armpit

2nd Study: Treated armpit *(3% of hectorite + 2% of MgO + 3% crystallized fatty compounds)* versus Bench

Kinetics:

1st study:

D-7 to D0: Use neutral shower gel at home, in normal condition use

D0 T0: Product application on one of the armpits

D0 T24h & T48h: Sniff test & sensory evaluation

2nd study:

D-7 to D1: pre-inclusion + wash out period

D1: 1st application

D2: 2nd application

D3: 3rd application

D4: 4th application

D5 T24 & T48h: Sniff test & sensory evaluation

Parameters evaluated:

Perspiration smell intensity *(scale 0: none -10: excessively strong)*

Hedonic value of the smell *(scale 1: extremely unpleasant – 9: extremely pleasant)*

Statistical analysis: *mean; standard deviation; percentage of variation*

At each time point, a paired t-test was carried out on the average jury assessors scores by subject, to assess whether the zones differ statistically significantly.

The underlying assumption of data normality was checked using Shapiro-Wilk tests (a=0.01).

The type I error was set at $\alpha=0.05$.

LUD Test [8] – Pure Monadic Home use test

The main objectives of this Consumer test are the following:

- Evaluate the appropriation of the new product,
- Validate the product performances at the usage and that there are no major weaknesses,
- Evaluate the deprivation after one week without using the product

Study Population

- 426 women aged from 18 to 60, regular users of deodorant in stick or roll on, natural - seekers having a profile of « eco-friendly / concerned with environmental issues
- deodorant users

Tested products:

Deodorant in tube

Deodorant in jar

Market roll on deodorant as reference

Protocol

Each woman tries 1 product, and the usage period is divided in 3 steps (Figure 7)

USE At the 1st, the 3rd and the 5th application – Online interviews

- Application assessment of the tested product

USE After 2 weeks of usage – Face to face interviews

- Evaluation of the tested product

DEPRIVATION 1 week after stopping the product – Online interviews

- Measure how much people miss the product

Recruitment – Face to face interviews

- Recruitment of the target
- Evaluation of usual product
- Product placement

Statistical analysis

Student test - Sig considered are at 95% for all decisions

Results

Skin Care products

Instrumental In Vivo Study of Mattifying Efficacy

The following formulations were investigated:

A: aqueous gel containing 5% of hectorite + 0.9% of MgO + 5% propylene glycol + polymer A

B: aqueous gel containing 5% of hectorite + 0.9% of MgO + polymer B

They were compared to the bare skin and to the technical reference C: aqueous gel containing 1% of ammonium polyacryloyldimethyl taurate + 2% of silica silylate.

Immediately after the application, both formulations containing 5% of hectorite + 0.9% of MgO lead to a significant decrease of the skin shine. Their efficiency is higher than the efficiency of the technical reference.

After 2 hours of hammam, the investigated products A and B limit significantly the shine when compared to the bare skin and to the reference C (Figure 7).

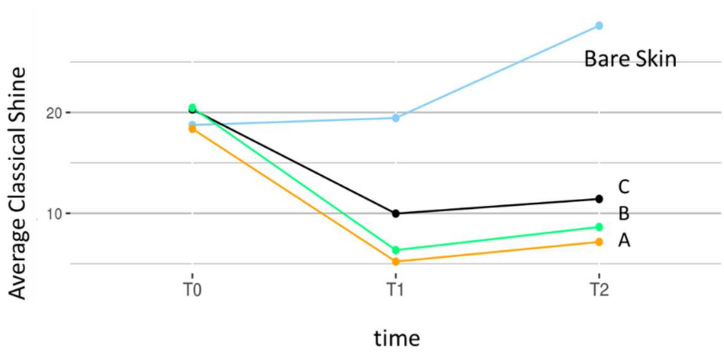
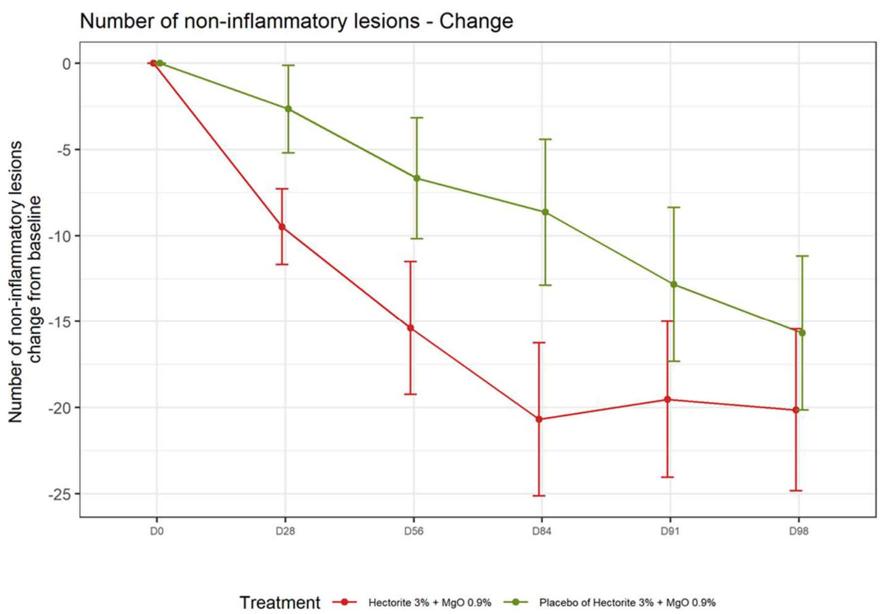


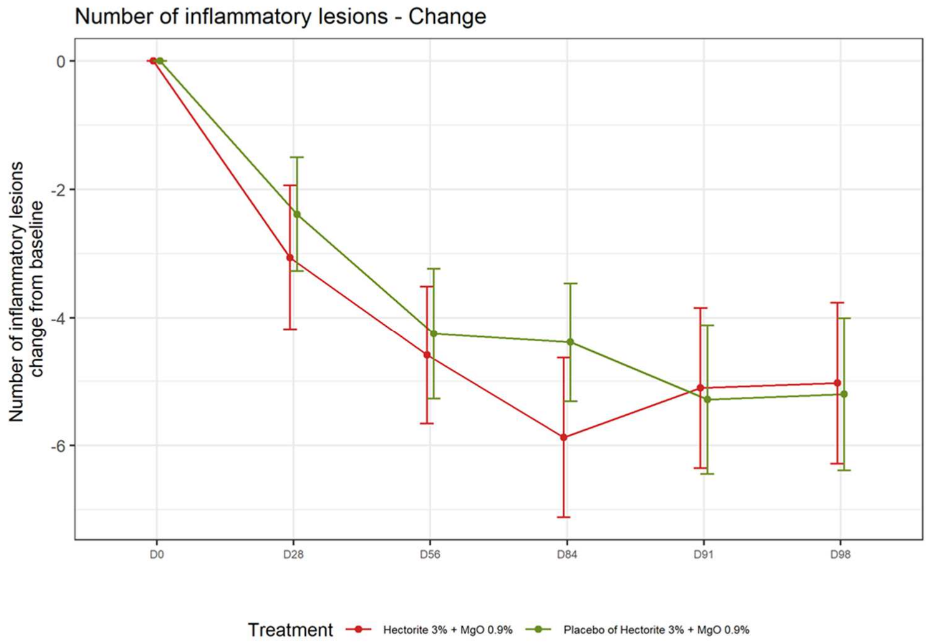
Figure 7. Skin shine evolution under hammam conditions

Clinical study

Comparison of Non-inflammatory lesions between Treatments and Placebo adjusted to baseline (D0): During the treatment phase, the association showed a statistically significant and regular efficacy on the lesions decrease vs placebo: 7.21 at D28 (very weak effect size), 9.07 at D56 (weak effect size) and 12.43 at D84 (moderate effect size) where it reaches a strong clinical efficacy. The effect is still present at the end of the relapse phase (D98) even if not statiscally significant (4.85 lesion reduction) (Figure 8).



Comparison of Inflammatory lesions between 3% of hectorite + 0.9% of MgO and Placebo adjusted for baseline at D0 (Figure 9)



On the inflammatory lesions, the association has a weak efficacy vs placebo with a statistical tendency (0.74 at D28, 0.4 at D56, 1.6 at D84 during the treatment phase and 0.1 in favor of the placebo in D98, end of the relapse phase).

Consumer study

The product containing 3% of hectorite + 0.9% of MgO + 3.7% of crystallized fatty compounds + 0.1% of polymer in water delivers on key benefits mixed and oily skins expect and long for when using a product meant to tackle oily skin.

Members love the long-lasting matte finish and the blurring effect that the formula leaves: they are impressed by the oil control provided by the product as well as its duration and find their pores to be less visible, making for an even complexion which lasts throughout the day.

Over time, our members' excitement for the product grows as they notice that the formula also tackles other deeper skin imperfections such as blemishes, spots, pores, and skin redness on top of superficial shine and oiliness.
Although apprehensive of the thick texture upon first discovery, oily skins find the product surprisingly easy to apply, gliding smoothly on their skin, and melting into their skin for a full absorption within a couple of minutes. This quick absorption means their makeup is then easy to apply.

Deo products

Sniff Test Method (Anti-odor efficacy)

<u>1st study</u>: The tested product contains 5% of hectorite + 2% of MgO + 20% propylene glycol. Syntheses of the results, given in mean (n=21) and standard deviation of the scores of the jury (n=5) obtained for each subject under both armpits, are presented in the tables below.

The table below summarizes the **score for perspiration smell intensity at T24h and T48h.**

	T24H		T48H	
	Treated armpit*	Non treated armpit	Treated armpit*	Non treated armpit
N (subjects)	21	21	21	21
Mean	4,7	5,7	5,1	6,1
SD	1,2	1	1,3	1,1
Interprétation	*"midly intense" to "noticeably intense"*	*"noticeably intense" to "rather intense"*	*"noticeably intense"*	*"rather intense"*

	T24H	T48H
% of variation	**-18%**	**-16%**
p value (Student)	**0,0007**	**0,001**

** : Product with 5% of hectorite + 2% of MgO + 20% propylene glycol.*

The collected data show a statistically significant difference in the perspiration smell intensity in favor of the armpit treated with studied product compared to the non-treated armpit at T24h (p=0.0007) and at T48h (p=0.0010).
We observed a significant decrease of odor intensity: -18% (at T24h) and -16% (at T48h) versus the non-treated armpit.

2nd study: The tested product contains 3% of hectorite + 2% of MgO + 3.5% crystallized fatty compounds + 20% propylene glycol.
It was compared to the market reference containing capryloyl salicylic acid, propylene glycol and silica silylate in aqueous polymeric gel.

Syntheses of the results, given in mean (n=21) and standard deviation of the scores of the jury (n=5) obtained for each subject under both armpits, are presented in the tables below.

The table below summarizes the **score for perspiration smell intensity at T8h and T24h**

	T8H		**T24H**	
	Treated armpit*	Bench	Treated armpit*	Bench
N (subjects)	21	21	21	21
Mean	4,7	4,9	4,6	4,6
SD	1,5	1,4	1,3	1,4
Interprétation	*"midly to noticeable intense"*	*"midly to noticeable intense"*	*"midly to noticeable intense"*	*"midly to noticeable intense"*
p value (Student)	**0,1491 (NS)**		**0,5587 (NS)**	

** : Product with 5% of hectorite + 2% of MgO + 3% fatty coumpound*

The data show a statistically no significant difference in the perspiration smell intensity between armpit treated with studied product compared to the bench at T8h (p=0.1491) and at T24h (p=0.5587).
The intensity of the perspiration is the same between 2 products, equivalent to the bench.

LUD Test

The following formulation was investigated:

A: aqueous gel containing 5% of hectorite + 2% of MgO + 20% propylene glycol in jar

B: aqueous gel containing 3% of hectorite + 2% of MgO + 20% propylene glycol + 3.5% crystallized fatty compounds in tube.

They were tested in comparison to a market deodorant reference containing capryloyl salicylic acid, propylene glycol and silica silylate in aqueous polymeric gel in roll-on.

For both tested product versus Market Reference, we are

- **at parity** on *Global satisfaction & liking*,

"Effect against the odors" *36 vs 32%*

"Efficacy against odor all day long" *21 vs 17%*

- **in superiority** on *Deodorant & Humidity dimensions*

"Protect against odor & perspiration" 71 vs 60%

"Anti-perspirant efficacy" 46 vs 33%

"Avoids feelings of underarm wetness during the day" 95 vs 87%

"Effective against underarm wetness" 93 vs 89%

- **in superiority** on *Care dimension*

"Makes the skin under my arms softer to the touch" 77 vs 66%

"Takes care of the skin under your arms" (tendency)

"Gradually improves the quality of the skin under your arms with usage" (tendency)

However, consumers needed to adapt or modify their gesture / routine to optimize the performance & usage of this technology.

Conclusion

Thanks to formulation understanding, *in vivo* efficacy of formulations based on hectorite/MgO association has been evidenced through different tests. The obtained results make us confident that the hectorite/MgO association has high potential for cosmetic applications.

Indeed, within hammam test conditions, the association was found to limit significantly the skin shine when compared to the bare skin and to the technical reference. It showed a statistically significant and regular efficacy on the non-inflammatory lesions decrease in the frame of a large clinical study.

The efficacy of cosmetic product based on hectorite/MgO association and designed for oily skins with imperfection was also perceived by the consumers. They highlighted the long-lasting matte finish and the blurring effect that the formula leaves. They were impressed by the oil control provided by the product as well as its duration and find their pores to be less visible, making for an even complexion which lasts throughout the day.

The data collected in the frame of Olfactive Sensory Experts tests show a statistically significant difference in the perspiration smell intensity in favor of the armpit treated with the studied hectorite/MgO association formulation compared to the non-treated armpit.

The consumers found the deo based on hectorite/MgO association to be superior on deodorant & humidity dimensions as well as on care dimension and, at parity on global satisfaction & liking versus a market reference in the frame of a large home use test.

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Conflict of Interest Statement. NONE.

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