Innovative bio-based carrier for Personal Care applications

Le Meur, Morgane[1*]; Van Reeth, Isabelle[1]; Vincent, Anne-Marie[1],Collins, Donna[2]
[1] Home & Personal Care, DOW Silicones Belgium sprl, Seneffe, Belgium
[2] Home & Personal Care, DOW Silicones UK Ltd, Barry, UK

* Morgane Le Meur, Rue Jules Bordet – Parc Industriel zone C, +32 64 88 9333, morgane.lemeur@Dow.com

Abstract

With upcoming European regulations limiting the use of volatile cyclomethicones in leave-on applications combined with the strong demand from customers and consumers to use bio-based and biodegradable materials, there is a need for new biodegradable carriers using sustainable and up-cycled feedstocks. Levulinic acid ketal derivatives, with the INCI name of Ethyl PG-Acetal Levulinate (EPAL), can be used as a medium-to-low volatility carrier in leave-on skin care formulations, providing an additional unique feature, a broad compatibility profile due to a higher polarity.

This innovative fluid produced by the conversion of biomass such as by-products from sugar and corn production, is ultimately biodegradable and has a naturality index of 0.7.

The purpose of this paper is to share how a novel levulinic ketal derivative can be used in leave-on applications as an alternative to cyclomethicones, fossil-based hydrocarbons and other oils as well as bring additional properties and provide new formulation possibilities.

The following evaluations were performed:

- Volatility profiles at room and skin (32°C) temperatures;
- Sensory comparisons with cyclomethicones and organic fluids using an experienced Dow internal panel, showing that EPAL provides a soft skin feel with a non-tacky and non-greasy feel combined with a good spreadability allowing to be used as a good bio-based emollient;
- Comprehensive compatibility study with a broad range of cosmetic materials at several ratios, demonstrating that EPAL, with an excellent compatibility profile, is an ingredient of choice to prepare high naturality content cosmetic formulations;
- Cleansing properties for waterproof color cosmetics, indicating that EPAL is effective as a make-up remover which opens a wider type of applications within skin care.

Several cosmetic formulations have been also developed, demonstrating the feasibility of using this new fluid in AP/Deo, skin care and colour cosmetics.

Keywords: Levulinate Ketals, natural feedstock, sensory benefits, sustainable, green carriers

Introduction.

With upcoming European regulations limiting the use of volatile cyclomethicones in leave-on applications combined with the strong demand from customers and consumers to use bio-based and biodegradable materials, there is a need for new biodegradable carriers using sustainable and up-cycled feedstocks. Levulinic acid ketal derivatives, with the INCI name of Ethyl PG-Acetal Levulinate (EPAL), can be used as a medium-to-low volatility carrier in leave-on skin care formulations, providing an additional unique feature, a broad compatibility profile due to a higher polarity.

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The following evaluations were performed:

- Volatility profiles at room and skin (32°C) temperatures;
- Sensory comparisons with cyclomethicones and organic fluids using an experienced Dow internal panel;
- Comprehensive compatibility study with a broad range of cosmetic materials at several ratios;
- Cleansing properties for waterproof color cosmetics;
- Preparation of applicative cosmetic formulations.

Materials

- Ethyl-PG Acetal Levulinate (EPAL)
- Cyclopentasiloxane (D5)
- Undecane (and) Tridecane (UT)
- Dimethicone 2 cSt
- Dimethicone 6 cSt
- C13-15 Alkane (AK)

- Caprylyl Methicone (FZ)

Methods.

1. Spreadability

To measure the spreadility of ingredients on a substrate, a droplet of 20 µL of each tested product is deposited on the black section of a Leneta chart. Diameters of droplets were measured after 1 min of spreading. The test was conducted in triplicate and the average value of the diameter of spreadability was reported.

2. Refractive index

The shine property of a cosmetic ingredient was evaluated by the refractive index of the ingredient. Refractive indexes of each tested materials were measured using the Refracto 30 GS equipment (from Mettler Toledo).

3. Volatility profiles

Volatily is a physical parameter that will impact the sensory profile of a cosmetic product, low or high volatility is needed depending on the application and seeked benefits. Usually, a high volatility is critical to achieve a perception of fast absorption of a product on skin. The volatility profile of a substance is measured *in-vitro* by monitoring the weight loss over a fixed period of time at a standardized temperature and relative humidity conditions.

1 g of each product was poured in aluminum cups (diameter 57 mm) and products were tested in triplicate. Water was used as control. Two sets of cups were prepared: one was left at room temperature (climate room with temperature between 20 °C +/- 2 ºC and relative humidity between 50% ± 5% and one was placed in a ventilated oven at 32 °C (±1 °C) for a total period of 6 hours. Weights of cups were recorded at different time interval (30 min, 1h, 2h, 4h and 6h) and the quantity of remaining products (%) was finally plotted versus time.

4. Sensory comparisons

Sensory profile of neat materials is evaluated by paired-comparison. The evaluation was conducted in a climatic room (temperature of 22 ºC +/- 2 ºC and relative humidity of 50 % +/- 5 %) by 18 experienced panelists. 20 mg of each tested product were applied on a dedicated sites on panelists forearms. Each panelist rubbed the two products with a separate finger and rated the different sensorial parameters before and after absorption of the product onto the skin. Results were recorded directly by each panelist. Results were then statistically analyzed using the student test and displayed in spider graphs.

5. Compatibility study

The compatibility test is a method used to determine the affinity of a specific ingredient with commonly used cosmetic ingredients of various polarities. The tested product was mixed at three different ratios in a 15 mL glass vial: ratio 1:9, ratio 5:5 and ratio 9:1. All solutions were mixed for 20 s with a high shear equipment (top bench mixer) at room temperature. The clarity of the solution was recorded the day of the testing and the day after. If the solution was one phase and transparent, the trial was recorded as C (compatible), if the solution was one phase and hazy, the trial was recorded as H (compatible and Hazy), if the solution was two phases, the trial was recorded NC (not compatible). NT record means that the specific ratio was not tested.

6. Cleansing properties

The evaluation of removability of color cosmetic products is designed to provide information on the efficiency of an ingredient to act as a make-up remover. A commercial mascara and a commercial liquid lipstick, both positioned as waterproof, were applied on a panelist forearm and left to dry for 1 h. Then both mascara and lipstick were removed using a cotton pad impregnated with a standardized amount of each tested products. Caprylyl Methicone (FZ) was used as a positive control since it is very well-known for its excellent cleansing properties. Test was conducted using only one panelist and pictures of the results were taken.

Results & Discussion.

1. Spreadability

Spread diameters of droplets of the evaluated materials are illustrated in Table 1. First, it is noticeable that PolyDimethylSiloxane fluids, both D5 and 2cSt, have a higher spreadability with respective values of 19.0mm and 23.3 mm, confirming their ability to facilitate the spreading of formulations. Although EPAL, UT, FZ and AK have lower values ranging from 14.0 mm to 16.7 mm, they still demonstrate a good spreadability.

2. Refractive index

Values of the ingredients' refractive indexes (RI) are reported in the Table 1: Comparison of ingredients' spreadability and refractive indexes. EPAL has a RI of 1.430, significantly higher than the silicone fluids evaluated in this study and therefore having the potential to bring more shine.

Products	Average spreadability (mm)	Diameter 1 (mm)	Diameter 2 (mm)	Diameter 3 (mm)	Std (mm)	Refractive index
Ethyl PG-Acetal Levulinate	14.3	14	15	14	0.58	1.430
Dimethicone 2 cSt	23.3	23	23	24	0.58	1.390
Cyclopentasiloxane	19.0	19	19	19	0.00	1.402
Undecane (and) Tridecane	16.7	17	17	16	0.58	1.418
Caprylyl Methicone	15.0	15	15	15	0.00	1.413
C13-15 Alkane	14.0	14	14	14	0.00	1.430

Table 1: Comparison of ingredients' spreadability and refractive indexes

3. Volatility profiles

As expected the difference in volatility profile is a lot more visible at 32 °C than at room temperature, see Figure 1, where 3 groups can be identified: high volatility ingredients, water, UT and D5; medium to low volatility levels ingredients, EPAL and AK; and the Dimethicone 6cSt as non-volatile.

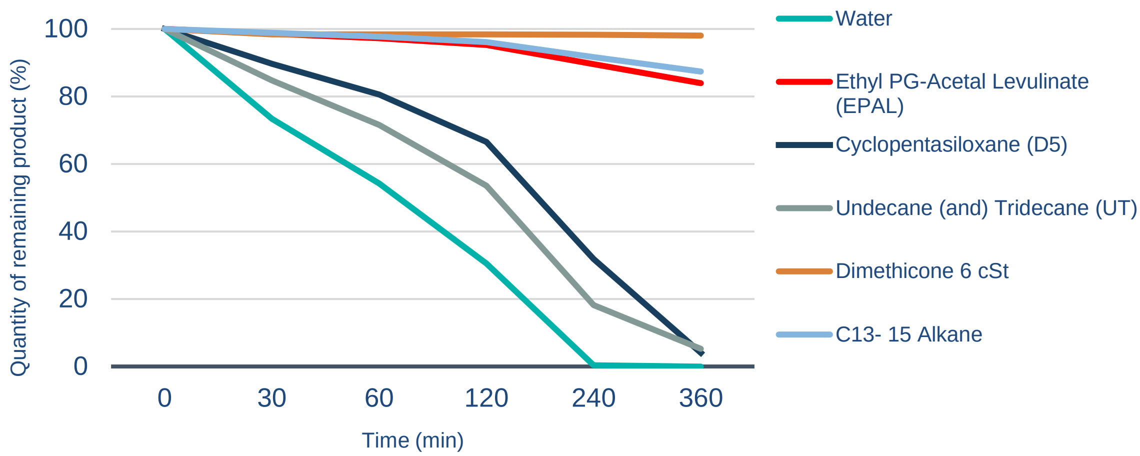

Figure 1: Comparison of volatility profiles at skin temperature (32 °C)

4. Sensory comparisons

When comparing the sensory profiles of Ethyl PG-Acetal Levulinate (EPAL) and Cyclopentasiloxane (D5), see Figure 2, EPAL provides similar wetness, spreadability and tackiness than D5 before products absorption and a similar slipperiness, gloss, tackiness, smoothness, greasiness and film residue than D5 after products absorption, demonstrating that EPAL could be a good alternative to D5 from a skin sensorial perspective.

Likewise when comparing sensory profiles of EPAL versus C13-15 Alkane (AK), see Figure 3, no significant differences are found before and after products absorption, making EPAL an acceptable bio-based emollient.

Finally, more differences can be observed when comparing sensory profiles of EPAL and Undecane (and) Tridecane (UT), see Figure 4. If before products absorption, EPAL and UT exhibit similar profiles, after products absorption, EPAL provides more smoothness, slightly more greasiness and higher film residue on panelists' skin. This indicates that EPAL is a very effective bio-based emollient in providing skin smoothness.

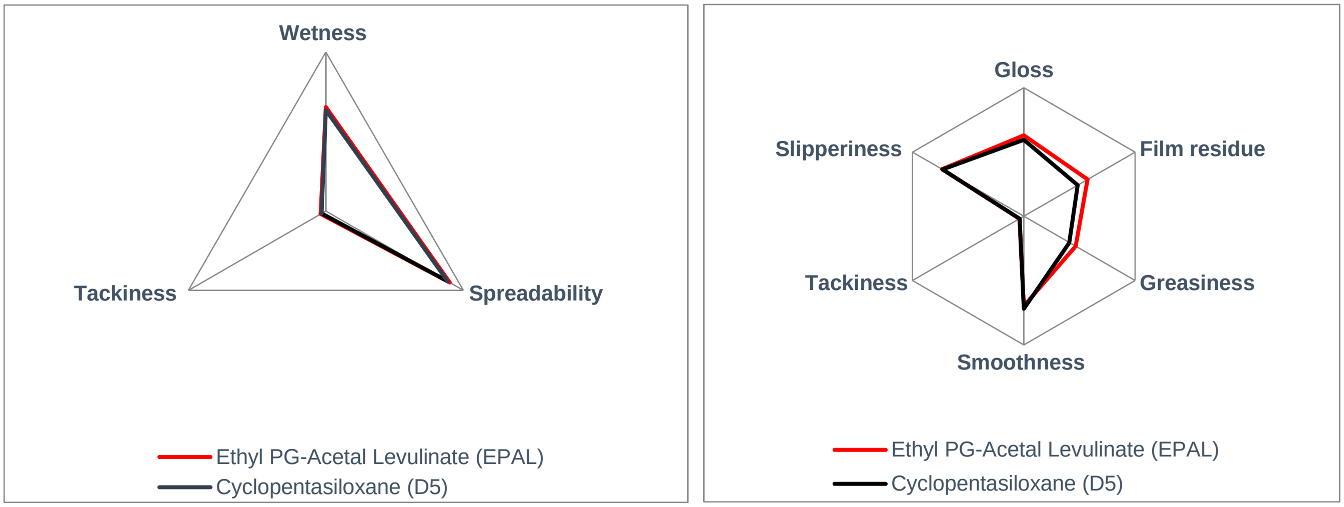

Figure 2: Sensory profile comparison vs. Cyclopentasiloxane (D5),

Before (left) and after (right) product absorption on skin

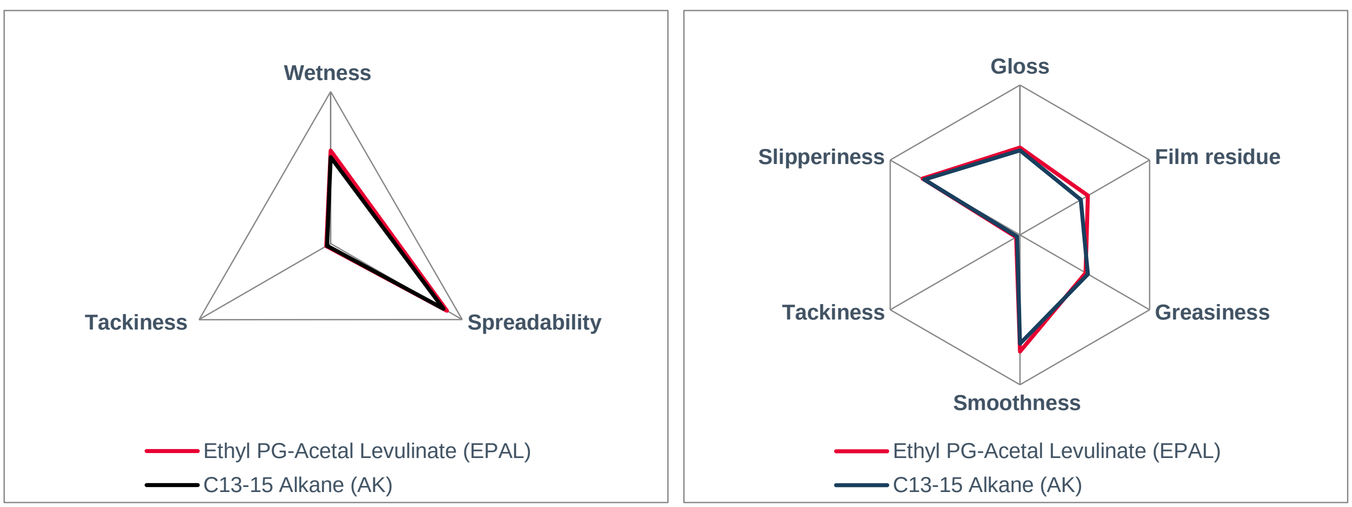

Figure 3: Sensory profile comparison vs. C13-15 Alkane (AK),

Before (left) and after (right) product absorption on skin

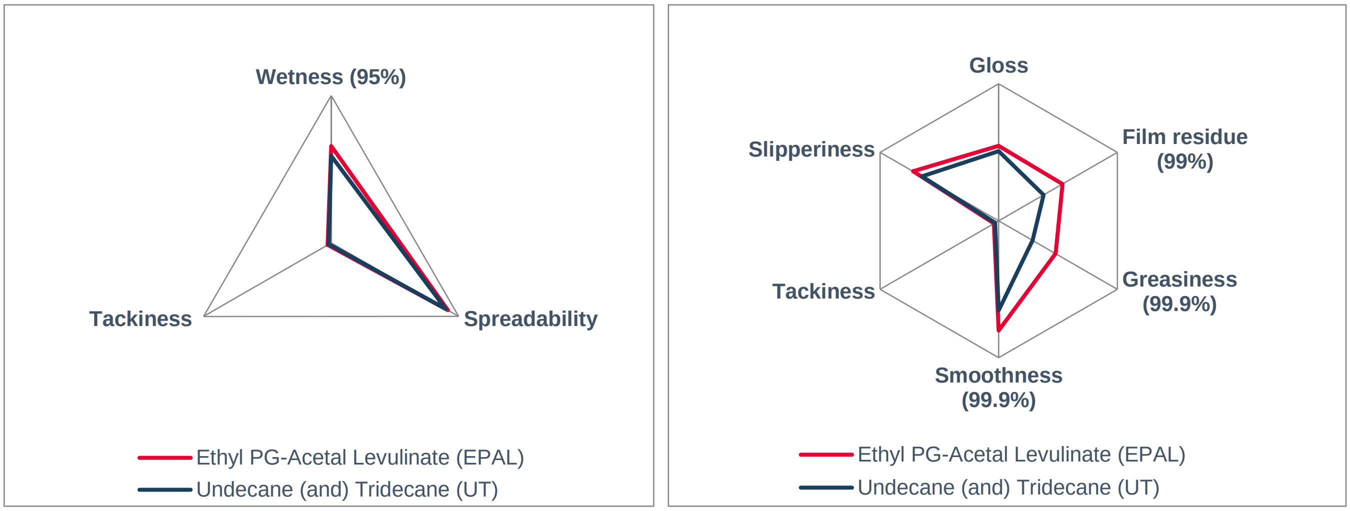

Figure 4: Sensory profile comparison vs. Undecane (and) Tridecane (UT),

Before (left) and after (right) product absorption on skin

5. Compatibility study

Results of the compatibility study, see Table 2, shows a very good compatibility with common cosmetic ingredients: alcohol, glycols, hydrocarbons, vegetable oils and butters, esters and ethers. This clearly demonstrates that EPAL is a good cosmetic ingredient for the preparation of high naturality index formulations.

Noticeably, it is not compatible with water nor glycerin meaning that EPAL needs to be added into the oil phase of an emulsion or to be used in an anhydrous formulation.

Compatibility with silicone ingredients is more differentiated: there is a good compatibility between EPAL and silicone fluids like D5, low viscosity Dimethicone or short chain silicone polymer with an organic functionality (Caprylyl Methicone, PenylTrimethicone). However when the molecular weight of the silicone polymer increases the compatibility is getting more challenging: either there is a compatibility at certain ratio only (Dimethiconol) or the compatibility is fully lost (Dimethicone Crosspolymer).

EPAL can be used as a bio-based alternative to D5 or as a bio-based emollient in the preparation of high naturality index formulations.

Ratio EPAL / ingredient	1:09	5:05	9:01
Polar ingredients			
Water	NC	NC	NC
Ethanol	C	C	C
Glycerin	NC	NC	NC
Propylene Glycol	C	C	C
Silicones			
Cyclopentasiloxane	C	C	C
Dimethicone 2 cSt	C	C	C
Dimethicone 6 cSt	C	C	C
Caprylyl Methicone	C	C	C
Phenyltrimethicone	C	C	C
Dimethicone (and) Dimethiconol	C	NC	NC
C13-15 Alkane (and) Dimethiconol	C	NC	NC
Dimethicone (and) Dimethicone/ Vinyl Dimethicone Crosspolymer	NC	NC	NC
Dimethicone (and) Dimethicone Crosspolymer	NT	NC	NC
Caprylyl Methicone (and) PEG-12 Dimethicone/PPG-20 Crosspolymer	NT	NC	NC
C13-15 Alkane (and) Dimethicone/ Vinyl Dimethicone Crosspolymer	NT	NC	NC
Hydrocarbons			
Isododecane	C	C	C
Isohexadecane	C	C	C
Mineral Oil	C	C	C
C13- 15 Alkane	C	C	C
Undecane (and) Tridecane	C	C	C
Vegetable oils & butter			
Sunflower Oil	C	C	C
Jojoba Oil	C	C	C
Apricot Kernel Oil	C	C	C
Sweet Almond Oil	C	C	C
Butyrospermum Parkii (Shea) Butter	C	H	H
Castor Oil	C	C	C
Esters			
Isopropyl Myristate	C	C	C
Cetyl Ethylhexanoate	C	C	C
Isononanoate Isononyle	C	C	C

Caprylic/Capric Triglyceride	C	C	C
Ethers			
Dicaprylyl Ether	C	C	C
Dicaprylyl Carbonate	C	C	C

Table 2: Compatibility study of Ethyl PG-Acetal Levulinate (EPAL)

6. Cleansing properties

Results of the colour cosmetics removability test, see Figure 5, clearly demonstrates that EPAL (Product 2) has excellent cleansing properties for both li[illegible]ara. Those cleansing properties are similar to the one of Caprylyl Methicone (FZ- Product 1).

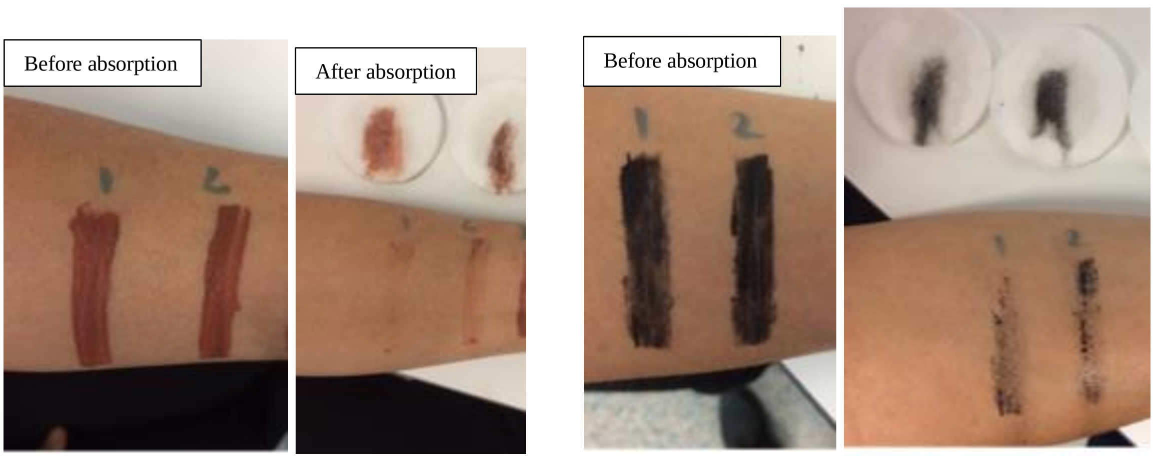

Figure 5: Colour cosmetics removeability _ Lipstick (left) and mascara (right)

Product 1: Caprylyl Methicone (FZ) _ Product 2: Ethyl PG-Acetal Levulinate (EPAL)

7. Cosmetic formulation development

Several cosmetic formulations have been developed with EPAL in order to demonstrate the ease of preparation of high naturality content cosmetic formulations. Four formulation types are presented below: AP/Deo, skin care and colour cosmetics.

a) AP/Deo Roll-On – Water-in-Oil emulsion

Phase A ingredients were mixed together until getting homogeneous; and phase B ingredients were mixed together until getting homogeneous.

Phase B was then slowly added to phase A under mixing (~700 RPM). The speed had been increased up to 1000 RPM as needed.

After addition of the phase C ingredient under mixing, the resulting emulsion is mixed for an additional 5 min at 2000 RPM.

The emulsion is finally subjected to a high shear mixing for 30s.

Phase	INCI name	Wt%
A	Lauryl PEG-10 Tris(Trimethylsiloxy)silylethyl Dimethicone	3
	Ethyl PG-Acetal Levulinate	**10**
	Dicaprylyl ether	9.6
	Isohexadecane	4
B	Water	41
	Sodium Chloride	1
	Glycerin	5
	Aluminum Chlorohydrate	25
C	Phenoxyethanol (and) Ethylhexylglycerin	0.9
	Perfume	0.5

Table 3: Composition example of an AP/Deo roll-on containing EPAL

b) AP/Deo Stick

Phase A ingredients were heated together to 82 °C using a water bath and mixed under a gentle stirring (100 RPM) until getting homogeneous.

Phase B ingredient was added to phase A under a slightly higher mixing (~450 RPM).

Phase C ingredient was then added under mixing. Mixing and heat were maintained until getting a homogeneous dispersion.

The formulation was finally allowed to cool down under gentle mixing (~450 RPM) and was poured into final container around 55 °C.

Phase	INCI name	Wt%
A	**Ethyl PG-Acetal Levulinate**	**41**
	PPG-15 Stearyl Ether	7.5
	PPG-14 Butyl Ether	7.5
	Strearyl Alcohol	18
	Hydrogenated Castor Oil	4
	PEG-8 Distearate	1
B	Aluminum Zirconium Tetrachlorohydrex GLY	20
C	Talc	1

Table 4: Composition example o fan AP/Deo stick containing EPAL

c) Body Cream _ Oil-in-Water emulsion

Hydroxyethyl Cellulose was dispersed into water under low agitation and heat (75 °C).

Phase B ingredients were heated together to 75°C under mixing until making a homogeneous phase. Phase C ingredients were added to phase B under mixing and heat was maintained until getting all homogeneous.

Phase BC was added to phase A under mixing and heat was maintained until getting all homogeneous.

Emulsion was then allowed to cool down to 40°C before pH was adjusted to 6.5-7 with Tromethamine. Finally phase E ingredients were added to phase ABCD under mixing.

Phase	INCI name	Wt%
A	Water	73.6
	Hydroxyethyl Cellulose	1.3
B	**Ethyl PG-Acetal Levulinate**	**6**
	Cetearyl Olivate (and) Sorbitan Olivate	4
	Cetearyl Alcohol	1
C	Sesamum Indicum (Sesame) Seed Oil	2
	Prunus Amygdalus Dulcis (Sweet Almond) Oil	2
	Butyrospernum Parkii (Shea) Butter	4
	Cocos Nucifera (Coconut) Oil (and) Aloe Barbadensis Leaf Extract	4
	Stearic Acid	0.5
D	Tromethamine	Q.S.
E	Tocopheryl Acetate	0.4
	Perfume	0.3
	Phenoxyethanol	0.9

Table 5: Composition example of a body cream containing EPAL

d) Foundation _ Water-in-Oil emulsion

Phase A ingredients were mixed in the order listed until making a homogeneous phase.

Phase C ingredients (pigment dispersion blend) were mixed together using a shear device (Ultra-Turrax). Then phase C was added to phase A while maintaining mixing until getting a homogeneous pigmented oil phase.

Phase B ingredients (water phase) were as well mixed together and slowly added to blend AC under mixing until getting a homogeneous emulsion. Finally, phase D and E ingredients were added under mixing which was maintained for an additional 5 min at 2000 RPM.

It is noticeable that in this formulation, EPAL was used as both an emollient in the oil phase but also as a dispersion aid for the preparation of the pigment blend.

Phase	INCI name	Wt%
A	Tri(Polyglyceryl-3/Lauryl) Hydrogenated Trilinoleate	3
	C13-15 Alkane (and) Dimethiconol	8
	Ethyl PG-Acetal Levulinate	**6.5**
	Undecane (and) Tridecane (and) Acrylates/Polytrimethylsiloxymethacrylate	6
	Ethanol	3
B	Water	56
	Sodium Chloride	1
	Glycerin	5
C	CI 77499 (and) Persea Gratissima (Avocado) Oil (and) Hydrogenated Vegetable Oil (and) Tocopherol	0.07
	CI 77491 (and) CI 77499 (and) Persea Gratissima (Avocado) Oil (and) Hydrogenated Vegetable Oil (and) Tocopherol	0.25
	CI 77891 (and) Persea Gratissima (Avocado) Oil (and) Hydrogenated Vegetable Oil (and) Tocopherol	5.81
	CI 77492 (and) Persea Gratissima (Avocado) Oil (and) Hydrogenated Vegetable Oil (and) Tocopherol	1.09
	Ethyl PG-Acetal Levulinate	**3.28**
D	DMDM Hydantoin	0.5
E	Perfume	0.5

Table 6: Composition example of a foundation containing EPAL

Conclusion.

Benefits and performances of Ethyl PG-Acetal Levulinate have been demonstrated throughout the present study. This innovative fluid is an excellent solution for formulators looking at using more sustainable ingredients in their formulation development.

It has a similar sensory profile to Cyclopentasiloxane after product absorption on the skin providing a soft skin feel with a non-tacky and non-greasy feel combined with a good spreadability. Although being less volatile than D5, EPAL can be considered as a suitable alternative to D5 knowing that the final volatility level of a cosmetic formulation can be increased by adding more volatile ingredients.

Its excellent compatibility profile with cosmetic ingredients makes it an ingredient of choice to prepare high naturality content cosmetic formulations.

Several cosmetic formulations have been also developed, demonstrating the feasibility of using this new fluid in AP/Deo, skin care and colour cosmetics. And its ability to cleanse and remove colour cosmetics opens a wider type of applications within skin care.

Acknowledgments.

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Conflict of Interest Statement.

NONE.