Flexible wax derivatives via polyglycerolysis

Natural waxes are sustainable materials that remain under-exploited today in cosmetics while they represent a unique starting block for many green chemistry reactions.

Moisturisation is one of the main objectives in skin care cosmetics. Moisturising properties are generally brought by glycols, mainly glycerin, and emollients such as mineral oil which are used to decrease the transepidermal water loss (TEWL). Whereas it is acceptable in temperate conditions, these solutions lead to overloaded skin and discomfort in tropical conditions.

Functionalised waxes, prepared through transesterification and polyglycerolysis of specific wax blends are efficient moisturisers and usable in a wide variety of usage conditions. These products named Acticire® (active texturising agent) and Emulium® Mellifera (PEG-free sensorial emulsifier) contain a variety of modified waxes and bring true benefits to the skin (see Table 1).

Natural waxes
These natural waxes have been selected mainly due to their availability and composition:

- Beeswax is principally composed of linear monoesters and hydroxymonoesters with chain length C40-C52, complex wax esters, natural odd-numbered hydrocarbons and free fatty acids.
- Jojoba wax, the only existing liquid wax at room temperature, consists essentially of long chain monoesters of unsaturated fatty acids and alcohols. In addition to being stable against oxidation, jojoba wax is often used in natural cosmetics to bring spreadability and softness.
- Mimosa wax (Acacia decurrens) contains an association of free fatty alcohols, saturated mono-esters and a large amount of odd-numbered hydrocarbon chains.
- Sunflower seed wax, a hard and high melting point wax, is principally constituted by mono-esters of long chain saturated fatty acids and alcohols.

The composition and melting point of the different waxes used are presented in Table 2. These waxes present value benefits for personal care products. They can act as a barrier against water loss thanks to their lipophilic nature and non occlusive properties. They also offer excellent skin

Table 1: Description of the texturising agent and the wax-based emulsifier.

<table>
<thead>
<tr>
<th>Product name</th>
<th>Wax used</th>
<th>INCI name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acticire®</td>
<td>Jojoba, Mimosa (Acacia decurrens)</td>
<td>Jojoba Esters, Helianthus Annuus</td>
</tr>
<tr>
<td></td>
<td>Sunflower (Helianthus annuus)</td>
<td>(Sunflower) Seed Wax, Acacia Decurrens Flower Wax, Polyglycerin-3</td>
</tr>
<tr>
<td>Emulium Mellifera®</td>
<td>Jojoba, Beeswax</td>
<td>Polyglyceryl-6 Distearate, Jojoba Esters, Polyglyceryl-3 Beeswax, Cetyl Alcohol</td>
</tr>
</tbody>
</table>

Table 2: Waxes composition and melting point.

<table>
<thead>
<tr>
<th></th>
<th>Beeswax</th>
<th>Jojoba wax</th>
<th>Mimosa wax</th>
<th>Sunflower seed wax</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbons</td>
<td>10-17% (C21-C33)</td>
<td>–</td>
<td>27% (C27-C33)</td>
<td>–</td>
</tr>
<tr>
<td>Esters</td>
<td>68-80% (saturated and unsaturated C40-C52)</td>
<td>&gt;98% (only unsaturated C38-C44)</td>
<td>22% (saturated C40-C56)</td>
<td>96% (saturated C38-C54)</td>
</tr>
<tr>
<td>Free fatty acids</td>
<td>8-16% (C24-C32)</td>
<td>–</td>
<td>1% (C16-C22)</td>
<td>3% (C16-C30)</td>
</tr>
<tr>
<td>Free fatty alcohols</td>
<td>0-2% (C24-C32)</td>
<td>–</td>
<td>7% (C24-C32)</td>
<td>0-1% (C18-C32)</td>
</tr>
<tr>
<td>Others</td>
<td>–</td>
<td>–</td>
<td>34% (sterols, triterpenoid compounds)</td>
<td>–</td>
</tr>
<tr>
<td>Melting point</td>
<td>61-65°C</td>
<td>7-10°C</td>
<td>60-65°C</td>
<td>77°C</td>
</tr>
</tbody>
</table>
tolerance and show sensorial and functional characteristics very different from plant oils and butters.

However, they also have some disadvantages in cosmetic use. For solid waxes, it is indeed necessary to work at high temperature, and their low solubility in oils leads to some recrystallisation phenomena and destabilisation, particularly in emulsion. Their solid state can also give a poor sensory profile to formulations.

The objective of the chemical functionalisation is to counter these disadvantages while keeping the benefits of the raw waxes.

**Oleochemistry reaction**

Except for hydrocarbons, these natural waxes contain fatty acids and esters which have reactive groups. Adding polyglycerol-3 brings mobility and provides hydrophilicity to the derivatives, giving them new and interesting properties in formulation. The process of functionalisation involves two types of reactions that occur simultaneously (see Fig. 1):

- Polyglycerolysis (alcoholysis with polyglycerol) creates polyglycerol-3 wax esters with amphiphilic properties.
- Transesterification between the different waxes (at least one liquid = jojoba wax, and one solid/hard wax) creates new esters that combine the rigidity of the saturated chain with the flexibility of the unsaturated carbon chain (unsaturated ones come from jojoba wax essentially). These esters show intermediate physicochemical properties between solid and liquid waxes.

**Properties of wax derivatives**

Transforming the waxes improves their behaviour and functionalities. Among these new properties can be observed a better solubilisation in the lipid phase, an amphiphilic behaviour, good moisturising properties and enhanced sensory profile.

**Improved solubility**

Polyglycerol esters allow a better solubilisation of waxes in the oil phase of emulsions. If we compare an O/W emulsion containing non modified waxes with the same O/W emulsion containing polyglycerised waxes, a clear difference is seen under a microscope (Fig. 2). In the first case, large crystals formed by the non-solubilised waxes are observed, generating instability and sensory issues. In the second case, it results in a good solubilisation into the emulsion.

**Amphiphilic behaviour**

The reaction product is a homogeneous soft butter of drop point around 60°C that can absorb up to four times its weight in water. This capacity to absorb water is specific to polyglycerol modified waxes as the blend of non modified waxes is unable to hold water and shows an immediate leakage.

For example, a test has been done in a standard lipstick formulation, with no pigments but containing a water phase including a red hydrophilic colorant, with the aim of seeing where the water is
distributed throughout the stick. In the case of the placebo formula, we get red droplets appearing where the water is grossly dispersed. When we use the wax derivatives in the formulation, the water phase is homogeneously dispersed as we can see by this even colour, with no visible droplets (Fig. 3).

Polyglycerol esters also possess some co-emulsifying properties, low HLB. The texturising agent can be used as a co-emulsifier in W/O and O/W emulsions when combined with another emulsifier, low or high HLB.

The wax-based emulsifier (Emulium Mellifera) combines a wax derivative with a primary emulsifier, polyglyceryl-6 distearate, to create a ready to use PEG-free emulsifying base for O/W emulsions.

**Moisturising benefits**
Different studies have been done on both the texturising agent and the wax-based emulsifier. In wide conditions of use, these wax derivatives help to improve the moisturisation of the skin and even more:

- **Substantiation – texturising agent**

  A clinical study was carried out during four weeks on 25 volunteers with dry skin, aged 28 to 68. Applied twice daily, two formulations were compared, one containing 5% texturising agent, the other 5% lanolin (as reference product). Each formula also contains 3% of glycerin. A triplet of measures was performed to evaluate the moisturising power of the formulations: corneometry, trans epidermal water loss (TEWL) and evaluation of skin microrelief by microscopy followed by visual evaluation by a dermatologist. A self-assessment was also conducted by the panellists.

  **Trans epidermal water loss (TEWL)**
  TEWL represents the passive diffusion of water through the horny layer. This parameter is directly correlated to the skin barrier function. In this study, the measurement of the TEWL was carried out using a Tewameter. A decrease of TEWL indicates a good protective effect of a formulation.

  The results presented in Figure 4 demonstrate that the formulation containing the texturising agent offers a 2-fold improvement of the water retention ability of the skin, compared with the non-treated control area.

  **Corneometry**
  Corneometric measurements are genuine values of the skin’s free water content.

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On the test area, the higher the electrical capacitance, the more moisturised the stratum corneum.

The results of the corneometry measurements are given in Figure 5. The entire panel showed a very high moisturising efficacy after treatment with the formulation containing the texturising agent with an average increase of the level of moisturisation by 23%. This improvement is similar to that obtained using 5% lanolin.

The moisturising effects shown by both corneometry and TEWL are most likely due to a semi-occlusive film-forming effect of the polyglyceryl-3 wax esters. This film, while letting the skin breathe, acts to prevent excessive water loss and appears to have a durable effect. The sensorially pleasing skin-feel of the ingredient suggests that it could have an advantage in formulations over lanolin, which is sticky and non soft, for treating dry and dehydrated skins.

Skin microrelief

The observation under microscope of the skin’s surface network (called microtopography) shows the presence of visible furrows. This surface, also known as ‘skin microrelief’, is a direct representation of the level of skin’s moisturisation. With age, or in dry skins, the microrelief becomes uneven and disorganised. An improvement of the skin microrelief does reflect an even, organised network, and brings about improved skin stretching and firmness.

As depicted in Figure 6, the quality of the skin surface of the 25 volunteers is much better after application of the formula containing 5% texturising agent.

Microscopy pictures also show the efficacy on the surface aspect of the skin. In comparison with a non treated control area and one treated with a lanolin formulation, the area treated with the texturising agent formulation showed a better organisation after 28 days (Fig. 7). All the furrows of the area treated with formulation containing the texturising agent are very well orientated; their uniformity is visible without appearance of any scales.

Substantiation – wax-based emulsifier

Corneometry measurements show that a unique application of a formulation containing 4% wax-based emulsifier induces an increase of 42.8% of skin moisture after 30 minutes. This efficacy is maintained throughout the day as, measured after 8 hours, the improvement in moisturisation remains at 39.9%.

A clinical test on a simple emulsion containing 4% wax-based emulsifier but no active ingredients was carried out on a panel of women in Guangzhou, China, over 21 days. The panel was composed of 21 Asian subjects (phototypes II & III) with

![Figure 7: Microscopy photographs of the skin microrelief after treatment with a formulation containing either lanolin or Acticire. Volunteer #28.](image)

![Figure 8: Results obtained by dermatological scoring on an emulsion containing 4% Emulium Mellifera and no active ingredients. ***p< 0.001 statistically significant variation.](image)
varied skin types (from very dry to oily), between 22 and 50 years old (average: 36.9). The emulsion was applied on the face twice a day (morning & evening) for 21 days, under normal conditions of use. Appraisal was made at D0 and D21 by acceptability/use test and clinical scoring – dermatological and self assessment. Dermatological scoring confirms that the wax-based emulsifier used at 4% in a simple oil in water emulsion brings significant visible improvement to the quality of the skin. The skin is visibly better moisturised and shows improvement in radiance, skin texture, smoothness and tonicity (Fig. 8).

Self-assessment by panellists confirms the visible efficacy brought by the wax based emulsifier. In the use test, despite the wide range of different skin types in the panel, 100% of testers found that the emulsion perfectly suited their skin type.

**Good tolerance**

Waxes are known to be well tolerated by the skin, and this is also the case for wax derivatives.

A clinical study was performed on sensitive and hypersensitive skins, with a formula containing 4% of wax-based emulsifier applied on the face twice a day (morning and evening) for 28 days, under normal conditions of use. Dermatological scoring confirmed that the formulation brings significant visible improvement to the quality of the sensitive skin. Not only is the skin well moisturised, it shows improvement in vitality, skin softness, and decrease of skin redness.

The panellists confirmed with self-assessment the efficacy noted by the dermatologists. They also highlighted the fact that their skin was more comfortable.

In the same study, using a stinging test, it was demonstrated that the wax-based emulsifier brings an immediate soothing effect of 29%, and a long-term soothing effect of 45% after 28 days of application.

**Sensory characteristics**

Wax derivatives show improved sensory profile compare to original waxes used. They help to create thin/light textures and to decrease heaviness and tackiness that may be brought by some other ingredients of the formula such as UV filters or glycols.

Moreover, wax derivatives are interesting for the development of formulas that could be adapted to all climates. We have indeed seen that they are able to bring moisturising properties in different conditions, but they also help to stabilise the sensory properties in these different conditions, for example from temperate/dry environment to tropical/humid environment.

Sensory properties were evaluated by expert sensory analysis. The sensory analysis was carried out in a quiet room with controlled temperature and humidity. The panel have evaluated criteria related to the appearance of the product, to the direct contact with the product, then the sensory characteristics during application and finally perception after application. Seven criteria were studied in depth: thickness, spreadability, softness upon application, greasiness, film residue, soft after-feel and greasy after-feel.

The sensory properties were measured by the expert panel in temperate and in tropical conditions (temperate conditions 21°C +/-1°C and relative humidity 40 +/-2 %, temperate conditions 21°C +/-1°C and relative humidity 40 +/-2 %). Results showed that wax derivatives used at 1% in emulsion and applied on the skin prevents from negative sensory effect of high heat and humidity. The increase in greasiness, film residue and greasy after-feel resulting from high heat and humidity are significantly reduced when functionalised waxes are added to the formulation, increasing comfort and pleasure for the user. The emulsions obtained are very white and glossy and present no pilling effect or stickiness on the skin. The evaluation – in a climate chamber – of the sensory properties of different formulations, from rich to light, all containing 4% of the wax-based emulsifier, confirm the stabilisation of skin-feel whatever the external heat or humidity (Fig. 9).

**Conclusion**

Using green chemistry, natural waxes were transformed using polyglycerolysis and transesterification, resulting in a sustainable texturising agent (Acticire) and a wax-based PEG-free emulsifier (Emulium Mellifera). Both are highly flexible in formulation and bring clinically visible efficacy, combined with improved sensory characteristics: better solubilisation, amphiphilic behaviour and moisturising properties.

**References**


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Figure 9: Sensory analysis in temperate/dry conditions vs. tropical/humid conditions of a) one rich cream, and b) one light serum, formulated with Emulium Mellifera.

<table>
<thead>
<tr>
<th>Sensory Property</th>
<th>Temperate Conditions</th>
<th>Tropical Conditions</th>
</tr>
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<tbody>
<tr>
<td>Thickness</td>
<td></td>
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<td>Greasiness</td>
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<td>Speadability</td>
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<tr>
<td>Softness on application</td>
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<tr>
<td>Greasy after-feel</td>
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Table showing sensory properties comparison between temperate and tropical conditions.