CANDELILLA WAX.

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Waxes are often considered as old-fashioned materials. Indeed, beeswax and carnauba wax have been used since time memorial, and the same can be said for many other waxes. Candelilla wax is different. The use of this wax goes back to the beginning of this century when it was announced in the Journal of the Royal Society of Arts that "the wild plant known as candelilla contains a wax of excellent quality and available in sufficient amount to make it extremely valuable". We were not yet around at the time of commercial introduction of candelilla wax in cosmetic and personal care products, but we can assure you that life would not have been the same for us if we would not have been able to use it. Recently we had the pleasure to travel through the north of Mexico, and to take a look how the wax is obtained. And we can tell you: we were amazed !

According to the official COLIPA list candelilla wax comes from *Euphorbia cerifera* or *Euphorbia antisyphilitica*, named the candelilla plant. These are succulents that are harvested in wild nature. The wax is deposited on the surface of the plants, and forms a protection for the plants for excessive water loss. In the wet season the wax deposits on the surface are minimal as there is no need for the plant to protect itself for that. Than again, candelilla plants do not like wet grounds and for that reason it prefers to live on the slopes of the hills rather than in the plains: drainage of water in the rainy season is indeed so much better on a slope.

The Euphorbia species that produce candelilla wax are indigenous to Mexico, especially in the northern states of Chihuahua, Nuevo Leon and Zacatecas. They also occur in the southern states of the USA, Texas, California and Arizona. Other Euphorbia species occur in Central and South America (e.g. Peru, Bolivia and Colombia), but these do not deliver suitable waxes. To yield economical amounts of waxes a desert-like climate is a boundary condition. Some like it hot.

One could easily accuse the candelilla plant from anarchism. Efforts to cultivate the candelilla plant all failed. It indeed does not like it at all to live in captivity. The local inhabitants harvest the candelilla plants in the hills, they are than approximately 40-50 cm high, load them on their donkeys and bring them to the processing site. Donkeys are still indispensable for this job as there is hardly any infra-structure in the desert. Not a job without risks as rattlesnakes and scorpions are everywhere around and if you've managed to avoid these creatures there are always the thorns of the notorious (but beautiful) desert hedgehogs. Some cactuses are highly appreciated, for obvious reasons, such as Lophophera williamsii (Peyote) and Trichocereus bridgesii. Hemingway wrote about Peyote:

"Speak to Peyote with your heart, with your mind,
and Peyote will see your heart, and if the Gods want
you will see and hear things".

These cactuses produce a wide variety of alkaloids such as mescaline (3,4,5-trimethoxyphenetylamine), hordenine (N,N-dimethyl-4-hydroxyphenetyl-amine) and tyramine (4-hydroxyphenetylamine). Lophophera williamsii is on the list of products that are not allowed to be present in cosmetic products, although dried Trichocereus bridgesii contains even larger amounts of mescaline (up to 2%), next to other physiologically active substances. These, and other, cactuses were and are important in local ceremonies but nowadays it is much easier to make them chemically.

On the processing site the plants are boiled together with diluted sulphuric acid in iron pans that are heated by burning sun-dried, already processed candelilla plants. Sulphuric acid is needed to destabilise the aqueous emulsion of the candelilla wax that is formed during extraction. The iron pans may contain up to 100 kg fresh blue-green candelilla plants producing some 3-5 kg of crude candelilla wax. After completion of the extraction the brownish remains of the candelilla plants are sun-dried. If the donkeys are lucky some of it is made available to them for food (and they seemed to like it).

During the extraction the wax floats to the surface of the water. It is skimmed off and a brittle, light brownish opaque waxy material is obtained: cerote. The colour can best be described as “café-au-lait”. After solidification the crude molten wax already gives the nice and glossy appeal on the surface, so characteristic for candelilla wax in its applications.
The yield of wax during extraction is low. Small scale operation will yield 3-5%, while larger scale operation will only give 1,5-2% wax as the efficacy is lower. The cerote still contains a significant quantity of water and small amounts of other, innocent, impurities. These need to be removed before the wax can be further processed and used.

When visiting Mexico it became apparent to us that no crop control agents or pesticides are used during the cultivation of the Euphorbia species; it would make no sense at all, in the middle of the desert. What a different situation with other botanical extracts ! It cannot be denied that a pesticide specification should be on any product data sheet of our chamomile, calendula or elder extracts, and even on our vegetable oils, but in the case of candelilla wax such a specification is totally superfluous. A similar situation occurs with polycyclic aromatic hydrocarbons. The extraction process is not at all giving any reason for their formation.

No matter what type of candelilla wax you’re using, if the wax is pure you can be sure that these nasty contaminants are per definition absent. If the analysis is positive you can be sure about something else: you must immediately change your supplier as he’s fooling around to earn a quick buck while adulterating the wax.

REFINING CRUDE CANDELILLA WAX.

The refining of the wax is not done in the desert but in specially designed plants. This industry started in 1913 in the area around Monterrey/Mexico, where also now the major candelilla wax processing unit is located. In the old days there were a number of these refineries, that were producing sun-bleached candelilla wax. That is economically not feasible anymore, and processing is done in different ways.

The wax is molten with water and washed with phosphoric acid. Solid impurities such as vegetable fibres are separated and mineral impurities (Ca^{2+}, Mg^{2+}, $Fe^{2+/3+}$ salts) or hydro-soluble substances (hydrocolloids, latex-like materials) are washed out. This process usually takes a number of hours. The wax is decanted and than heated to 130º C to remove the remaining water. The next step is a filtration with clay and carbon black to decolourise the wax without further chemical processing. This grade of candelilla wax, a nice glossy wax with a red-brownish colour, is known in the industry as "filtered candelilla wax". It is most suitable indeed for the production of many cosmetic and personal care products such as lipsticks, but it is also applied for the production of chemical-technical products such as polishes and highly specialised applications such as toners for photocopiers and printers.

Additional purification of candelilla wax can be done by filtrating a second time with clay and carbon black to further improve the colour: "double refined candelilla wax". This refining step, however, does not contribute to the overall performance of the wax. Much more effective is chemical bleaching of the wax. This can be done using hydrogen peroxide or potassium permanganate/phosphoric acid. In the past bleaching of candelilla wax was also carried out with chromic acid or benzoyl peroxide. For reasons of toxicity these routes have been left already for a long time. Sun-bleached candelilla wax is not produced anymore these days.

Bleaching of candelilla wax is preferably done with 30% hydrogen peroxide. However, hydrogen peroxide might not only attack the coloured species present in the wax but also the functional ingredients. This type of bleaching is therefore an art indeed, to bleach the wax without jeopardising the properties of the wax. Bleaching with aqueous potassium permanganate/phosphoric acid is less preferred because candelilla wax easily goes into emulsion and hydrolysis of the esters may occur.
Hydrogen peroxide is converted into water which needs to be removed from the wax before solid finishing. The preferred solid finishing form is in pastilles rather than as flakes to avoid dusting of the wax during handling.

CHEMICAL COMPOSITION OF CANDELILLA WAX.

It is quite common in the wax industry to define a wax on a number of chemical and physical parameters. Candelilla wax is no exception to that.

Melting point, º C	66 - 71
Specific gravity @25º C	0,982 - 0,983
Acid value, mgKOH/g	11 - 19
Ester value, mgKOH/g	40 - 47
Unsaponifiables, %	47 - 62
Iodine number, gI/100g	19 - 44

The unsaponifiable fraction of candelilla wax is quite high indeed, and consists largely of n-alkanes. In actual fact a level of 50-53% is more in line with practice rather than the wide span of 47-62% as mentioned in the table.

Nonacosane ($C_{29}H_{60}$), hentriacontane ($C_{31}H_{64}$) and tritriacontane ($C_{33}H_{68}$) are the most abundant hydrocarbons, hentriacontane being the absolute winner with ≈35-45%. With increasing molecular weight the degree of unsaturation of the hydrocarbons will also increase. A similar observation is made for beeswax, whereby the lower molecular weight hydrocarbons (heptacosane being the predominant n-alkane in beeswax) are saturated while the higher hydrocarbons tend to unsaturation. It is most conspicuous indeed that both beeswax and candelilla wax do hardly contain hydrocarbons with an even number of carbon atoms in the main chain. This is a very useful tool to identify adulterations of candelilla wax with mineral hydrocarbons such as paraffin wax, ozokerite and/or ceresin, but to find that out a gas chromatograph will be needed.

Next to the hydrocarbons also sterols and fatty alcohols are part of the unsaponifiable fraction of candelilla wax. The presence of sterols, mostly ß-sitosterol and small amounts of other steroids such as campesterol, is easily explained as these sterols play an important role in plant physiology, in a similar fashion as cholesterol does in the animal kingdom. Also free long-chain fatty alcohols are present in commercial candelilla wax, but it is doubtful whether these substances are present in candelilla wax on the surface of the succulents. It is more likely that they are formed during processing of the wax, which is further supported by the fact that filtered candelilla wax usually contains less fatty alcohols than candelilla wax that has been bleached with potassium permanganate/phosphoric acid. The fatty alcohols are likely to originate from hydrolysis of monoesters that are present in candelilla wax.

Carboxylic acids and esters present in the wax are responsible for the acid and ester value. Part of the esters are monoesters (20-25%), i.e. esters derived from straight-chain fatty acids (saturated or unsaturated) and straight-chain fatty alcohols (saturated or unsaturated). The longer the chain length of the esters, the higher the degree of unsaturation. The chain length of the carboxylic acids is much longer as what is found in vegetable triglycerides (maximum 24 carbon atoms), while the acids in candelilla wax may go up to 36 carbon atoms.

Also esters derived from hydroxy fatty acids are present, although little is known about their chemical identity. It has been suggested that a major part of this group (8-10%) consists of the sitosteryl ester of dihydroxytriacontanoic acid ($C_{30}H_{62}O_4$). Until present the position of the two hydroxy groups is unsure and it is unknown what the function of this ester for the candelilla plant is. This may be comparable to esters of ω-hydroxytriacontanoic acid as found in beeswax. The hydroxy esters are probably responsible for several of the particular properties of candelilla wax, and also here there are similarities with beeswax.

PROPERTIES AND APPLICATIONS OF CANDELILLA WAX.

The traditional application of candelilla wax in personal care and cosmetic products is in decorative cosmetics: lipsticks, pressed powders. It is also frequently found in mascara's and eye liners. It gives lustre and gloss, it is an excellent film forming agent and it enables to generate water-repellence. Next to the applications in cosmetic and personal care products should be mentioned the use in polishes for wood, leather, coated surfaces, polymer processing, textile impregnation, inks, toners for photocopiers and printers, paper sizing and dental products. For food application, candelilla wax has a GRAS status, it is used as a protective coating for chocolates, wine gums, and other sweets to avoid that the surface because dull and mat. In such an applications the candelilla wax can be applied as a low viscous emulsion that is sprayed on the candies.

In lipsticks candelilla wax usually goes together with carnauba wax, beeswax, ceresin, ozokerite and castor oil. The combination beeswax & castor oil forms a gel, in which the pigments are suspended. However, the viscosity and the gel strength are low, and need to be reinforced. For that reason ozokerite and ceresin are used, while carnauba wax gives hardness to the gel structure and improves the stability of the lipstick. The function of candelilla wax is to give gloss and good pay-off properties to the lipstick, not to be forgotten to improve the water resistance of the lipstick.
In many cases the stability of the pigment suspension at high temperature is insufficient and for that reason additional ingredients are used that support the matrix of waxes: lanolin, acetylated lanolin, lanolin alcohols, petrolatum, opal wax (hydrogenated castor oil), and fatty acid/fatty alcohol esters of 12-hydroxystearic acid (e.g. octyldodecyl 12-stearoyl stearate). Instability of the pigment dispersion may result in segregation of the pigments, particularly if the density of the different pigments varies and therefore (in the best case) a colour gradient over the lipstick will be observed. The demands are high as lipsticks are poured at 80-90°C and than rapidly cooled to 30°. This puts enormous constraints to the stability of the gel structure as well as to the ability to form the gel network structure.

One particularly significant parameter to be satisfied in lipstick production is proper mould release during confectioning of the lipsticks in an industrial environment given the fact that in most cases the production is fully automated. If one of the lipsticks is not properly released the consequences can be quite disastrous indeed. This phenomenon is not limited to lipstick making only, but is also encountered with e.g. automated bread making. In earlier times silicones (mostly phenyltrimethicones) were used, but it has clearly been demonstrated that the composition of the wax matrix is determining, especially relative to the proper functioning of candelilla and carnauba wax.

It does not require to much thinking to identify the above described parameters as rheological parameters. The formation of a gel network structure and the film-forming properties can best be described using rheology and rheometrics, while the suspending power of the waxy matrix is best studied in terms of the yield stress value. However, complete studies have so far not been reported in the literature.

From our own experimental work it was observed that the yield stress value of lipsticks is largely determined by polyesters as present in candelilla wax (and beeswax). Chemically they are esters of hydroxycarboxylic acids, long-chain 1,2-diols and dicarboxylic acids. The mechanical strength of the gel network structure determines the pay-off of the lipstick: the lipstick must “melt” around 32°C, lip temperature, while applying shear (i.e. application of the lipstick on the lips). However, the liquid shall not release oil in absence of shear (sweating of the lipstick) until at least 40-45°C. Sweating is a frequently encountered problem with lipsticks, and usually this phenomenon can be deduced to improper formulations or the use of adulterated waxes. When candelilla wax and/or beeswax are adulterated the concentration of the polyesters *nolens volens* is reduced and the gel network cannot be formed properly. Sweating and corruption of the surface of the lipsticks is the result. In extreme cases even pigment segregation is observed, seen as a colour gradient over the lipstick.

The amount of candelilla wax, carnauba wax and beeswax is important, as with increased wax concentration the sticks may become to hard. If the suspending power for the pigments is to low, particularly for high density pigments, it is more and more practice to add additional polyesters such as esters of 12-hydroxysteraric acid.

The use of candelilla wax in skin care products received little attention, despite the fact that it is an excellent rheological additive. In the daily practice of the cosmetic chemist rheology control is done on the basis of natural gums, cellulosics, carbomers and other waterborne rheological additives, despite the fact that these (mostly polymeric) products are shear sensitive and highly sensitive to electrolytes. When applied on the skin the hydrocolloids denature and the emulsion breaks almost instantaneously. Fatty alcohols and partial esters of propylene glycol and glycerol are lipophilic alternatives to these systems and enable to protect the emulsion from quickly breaking on the skin. On the other hand, they are also responsible for the high viscosity of the final emulsions, to such an extent that lotions are difficult to make. Candelilla wax offers the possibility to apply for rheology control while keeping the viscosity low, enabling to simultaneously adjusting the thixotropy and the elastic behaviour of low viscous emulsions.

The fact that the final emulsions are superior in stability compared to e.g. carbomer stabilised emulsions is an important tool to achieve controlled release of active substances from a liquid crystalline matrix in lotion type of products. Well-chosen combinations of emulsifiers and emollients, in conjunction with candelilla wax as rheological additive, enable to achieve controlled release from the liquid crystalline matrix while being able to adjust the skin feel of the final emulsion in such a manner that the treated skin is not subject to a fatty feel or staining to clothing. This is an angle of incidence that offers quite some additional scope to controlled release, also because the porosity of the liquid crystalline matrix can be adjusted using cholesterol.

The film-forming properties of candelilla wax offer the possibility to use it as a fixative for UV filters in sun care products. As the constituents of candelilla wax are only slowly absorbed by the skin fixation of the UV filters on the skin can be assured for a prolonged period of time. In this respect candelilla wax is competitive to water-soluble resins such as PVP/VA copolymers, acrylates, and dimethicone-based film-forming agents.

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Looking at the efforts that are required to obtain a good quality candelilla wax and the application potential it must be concluded that the performance/price ratio is highly favourable for candelilla wax. In other words: candelilla wax is good value for money. In many products candelilla wax is already an indispensable ingredient, and we predict that candelilla wax will be also indispensable in formulations that are yet to come, particularly when controlled release is desired.