Fats and oils in cosmetics – Mother Nature versus petrochemicals? (long version)

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Summary: Fats and oils are important ingredients of skin care. The properties of hydrocarbons and silicones are compared with vegetable and synthetic triglycerides. The influences on skin recovery and long term effects are described. The present literature is reviewed from the physiological point of view.
Key words: hydrocarbons, mineral oils, triglycerides, essential fatty acids, silicones, skin homoeostasis, skin recovery, skin barrier, TEWL, barrier creams, barrier repair, corneotherapy.

A subject that has launched controversial discussions over and over again is the use of mineral oil based hydrocarbons in cosmetic products. Where is the difference between oils and waxes of petrochemical origin and natural fats and oils? Based on the available literature the following article attempts to weigh up advantages and disadvantages.

Taking the skin as model

The human skin mainly protects itself with both, the barrier layers in the stratum corneum, which contain ceramides, fatty acids and cholesterol, and with the sebum of the sebum glands. Sebum consists of triglycerides (41%), fatty acids (16%), waxes (25 %), squalene (12 %) cholesterol (1,4 %) and cholesterol esters (2 %)[1)], whereas the data may slightly differ depending on the source of information. Sebum characterizes the lipid cover of the skin.
It can be assumed that cosmetic products formulated like the barrier layers and sebum of the skin provide the best possible care system for the skin. As a matter of fact, studies with barrier components that were applied on the skin show optimal skin regeneration results if the natural mixing ratio i.e. a molar ratio of ceramides (50 weight %), fatty acids (15 weight %) cholesterol (25 weight %) = 1:1:1 is obeyed[2-5)]. The influence of the sebum lipids still is entirely ambiguous. In case of doubt however it may be advantageous to consider the individual physiological conditions.

Sebum triglycerides and hydrocarbons

Sebum triglycerides resemble the fatty vegetable oils. The triglycerides of vegetable oils however contain more unsaturated acids like oleic acid, linoleic acid, alpha and gamma linolenic acid in bonded form. Yet unlike triglycerides squalene is a pure liquid hydrocarbon i.e. it only contains carbon and hydrogen ($C_{30}H_{50}$). Squalene[6)] belongs to the group of triterpenes and in biological respect it is the precursor of cholesterol which comes very close to the hydrocarbons with its chemical formula $C_{27}H_{46}O$. For cosmetic purposes, the unsaturated squalene, i.e. containing double bonds, is generally replaced by squalane ($C_{30}H_{62}$) which is less sensitive to oxygen and gained of vegetable squalene through a hydrogenation process.
Lanolin is gained from the sebum glands of sheep and also contains hydrocarbon, unlike the human sebum however only traces of it (< 1%)[7)].

Hydrocarbons - vegetable

Squalene and low molecular, partly even gaseous hydrocarbons are widespread in the vegetable kingdom. Some of them can be found in fruits as flavourings with a balmy, spicy and pine-like note[8)]. Carotene ($C_{40}H_{56}$) for instance also is an unsaturated hydrocarbon. Many of the vegetable waxes contain hydrocarbons of different composition as e.g. beeswax 15 % (among others linear and branched paraffins[9)]), candellila wax 45 %, carnauba wax 2%[11)]. Besides paraffins these hydrocarbons frequently consist of terpenes or their derivated components. Other hydrocarbons and above all saturated and thus inert hydrocarbons rather are an exception. In addition to wax esters, wax alcohols and free fatty acids the waxes on fruit peels also contain hydrocarbons[12)].

Hydrocarbons - mineral

Saturated and rather inert too are mineral hy-

drocarbons like paraffin (Paraffinum solidum, solid), paraffin oils (Paraffinum subliquidum, viscous; Paraffinum perliquidum, fluid) and vaseline (petrolatum) made from crude oil and mineral waxes[13,14]. They are characterized by a broad spectrum of singular components and are separated from crude oil by processes like fractional distillation or extraction and then purified from undesired, partly cancerogenic or mutagenous components by specific processes like e.g. chemical hydrogenation, removal of aromatic hydrocarbons and desulphurization etc. Highly purified fractions have found their entry into the pharmacopoeia as bases for ointments and suppositories[13]. They generally show an excellent tolerance whereas white vaseline in its pure form has a considerably increased acanthosis factor[14]. In other words, after a treatment of ten days a thickened epidermis with simultaneously increased stratum spinosum may be observed. It has not yet been proven whether this reaction is due to occlusivity and a subsequent swelling of the skin. Increased acanthosis factors may also be observed with singular vegetable triglycerides as e.g. castor oil applied on the skin in pure form[15]. As oils and fats only rarely are used in a 100 per cent pure from, these findings presumably are less relevant for their practical use in cosmetic creams. In the past however the contents of polycyclic aromatic hydrocarbons have played a significant role regarding the tolerance of paraffin oils since they involve a high cancerogenic potential among others. By means of today's crude oil processing techniques however these harmful side effects only are of historic importance and accordingly are mentioned in the older literature.

Hydrocarbons versus triglycerides

What is to be said against the use of inexpensive mineral hydrocarbons in cosmetic products instead of sensitive vegetable oils as even the human body produces hydrocarbons? To approach this issue, the features of triglycerides gained from vegetable oils and used as skin care components have been listed below:

- Vegetable oils are familiar substances for the skin. They integrate into the triglyceride balance of the skin and consequently can also be metabolized.
- Vegetable oils contain physiological acids like palmitic acid which is found in the skin barrier, and (unsaturated) essential omega-6- and possibly also omega-3 acids with rather powerful active agent features. Linoleic acid indirectly reinforces the skin barrier as it is integrated into ceramide I[16]. Linoleic acid, alpha linolenic acid and gamma linolenic acid produce strong anti-inflammatory degradation products[17] in the skin. These metabolites only become effective via cutaneous application of the oils, while the acids orally are metabolized into arachidonic acid respectively eicosapentaenoic acid and their reaction products.
- Many of the vegetable oils contain phytosterols as side components which are structurally related to the natural cholesterol in the skin and can substitute it if necessary. There may be further valuable natural additives like vitamin E among others.
- Due to their lipid character vegetable triglycerides have smoothing effects on the skin. The lipids cause a moderate reduction of the transepidermal water loss (TEWL) which is a welcome effect in winter with low humidity levels in rooms with windows and doors closed. An extensive reduction of the TEWL however is not desired as it is still necessary for the skin to "breathe" in order to maintain its natural functions (see below).

Hence, besides their refattening purposes vegetable triglycerides show manifold effects which of course depend on the specific kind of oil. A disadvantage of unsaturated vegetable oils however is their sensitivity to atmospheric oxygen and that is the reason why they are stabilized with anti-oxidative vitamins or their derivatives. Water-containing formulations with vegetable triglycerides only have a limited shelf life due to the fact that the triglycerides will hydrolyze although in a rather slow process which may be accompanied by a change of their olfactory features. A minimum shelf life of at least 30 months may be a handicap for the cosmetic trade though.
In comparison, paraffin oil and its related substances show a high stability against atmospheric oxygen, water and microbial degradation. Mineral hydrocarbons however do not provide any active agent features which means that mineral hydrocarbons are appropriate substances for long term and inexpensively produced formulations primarily focusing on skin smoothing effects.

Skin recovery - a question of defining...

Mineral oils will not help to repair a disordered skin barrier whereas the idea of repair should be clearly defined in this connection. In cosmetics it means the natural (endogenic) repair of the skin. Hydrocarbons undoubtedly cause

an exogenic regeneration of the skin barrier to such an extent that mineral oils and vaseline may be integrated as droplets into the surface barrier layers[18,19] above all if the barrier layers are disturbed as e.g. in case of dry skin which means that the different barrier layers (bilayers) are interrupted. Emulsifiers support this process by dispersion of the droplets. Although this kind of superficial repair of the barrier layer does not correspond with the physiological natural model, it reduces the transepidermal water loss (TEWL) as desired and preserves the skin hydration. In how far stronger occlusive effects are caused which is indicated by a further reduced TEWL depends on the dosage of the mineral oil products. Vaseline shows the strongest occlusive effect and thus a radical reduction of the TEWL.

An application of impermeable films on the skin after barrier disorders impedes an increase of the fatty acid synthesis in the epidermis[20,21] and inhibits the natural stimulation of the DNA-[22,23] and the mRNA activities[24] of the skin. Accordingly, it can be assumed that substances which cause an intense reduction of the TEWL like vaseline for instance have similar effects. This corresponds to practical experiences in cosmetic practices where reports on very dry skin of consumers using mineral oil containing creams are above-average.

Even if mineral oils may fill in droplike gaps in the barrier layers they cannot be absorbed like vegetable oils. The relatively fast absorption of vegetable triglycerides is favored by the enzymatic hydrolization into their different components (glycerin and fatty acids). This leads to the fact that hydrocarbons of mineral oil-triglyceride-compounds accumulate in the superficial skin layers where they can remain for a longer time than vegetable triglyerides. The smoothing sensation therefore will last longer which is an advantage with respect to the application and to sensory characteristics. However, this affects the natural balance and regenerative capacity of the skin[25]. Due to the marked TEWL decrease in case of an occlusive layer on the skin the epidermal cell maturation is slowed down and the skin pH value impaired. As only a few of the cosmetic products contain such critical amounts, these effects should be seen in perspective to the hydrocarbon content[26].

Natural lipid substances and mineral oils pursue different purposes though. If skin protection is required mineral oils are a favourable solution considering the price differences and sensorial features although the price to pay in the long run is that the skin becomes less active. In recent years however there has been observed the tendency to maintain a high regenerative activity of the skin as long as possible which should have priority over plain skin protection[27]. Among other things this idea lead to the development of new barrier creams with vegetable triglycerides without emulsifiers and with a physical structure similar to the barrier layers[28]. Since that time it has been observed that not only disordered barrier layers but also skin which is susceptible to cornification disorders as e.g. acne skin will benefit in the long run and above all, if linoleic acid containing triglycerides are used as additives which serve as a substrate for the ceramide I content of the barrier layers[16].

Only recently K. R. Feingold has published a review on homeostasis and skin recovery[29].

Related hydrocarbons and silicones

Microcrystalline wax and mineral solid paraffins like ozocerite[30] and ceresine[31] (refined ozocerite) are related to the paraffin products. Their fields of application are quite similar to those of petrolatum.

An interesting substance group with comparable features are the poly-alphaolefins (PAO). They are synthetic hydrocarbons as e.g. polypropylene, polybutene or polydecene. By a specific polymerization process it is possible to achieve practically any type of viscosity desired, ranging from very light over viscous to semisolid[32,33]. Certainly, the base substance here also is crude oil (via cracking process), however the finished products are not substance mixtures but uniform hydrocarbons with a precisely defined chain length and without irritating impurities. Nowadays PAO's are more and more used for the lubrication of ball and slide bearings of food industry equipment where they replace medical paraffin oils in applications with potential food contact. By way of comparison, the ADI values (acceptible daily intake) of PAO's are more favorable. That is the reason why they are also used in lipsticks (see below).

If it is about emollients in cosmetics, silicones are generally mentioned in the same breath with mineral products. Silicones - as a matter of fact we are dealing here with so called polysiloxanes with silicone-oxygen chains and hydrocarbon residues attached to the silicone atoms - are a large group of synthetic substances with various applications[34,35]. There are volatile and liquid silicones which allow easy spreading of the cosmetic products and high molecular silicones which leave an excellent feeling on the skin on the one hand and stay on the skin surface like a film similar to the mineral oils on the other hand. This is the reason why they are more and more used as refattening substances in cleansing products. While there have repeatedly been problems

with injected silicones (wrinkle reduction, cosmetic surgery), silicones in topically applied products are indifferent, very well tolerated and rated as safe. Since they are highly efficient already small dosages are enough to achieve the desired effects. The consumer above all appreciates the hydrophobic effect with the simultaneous velvety sensation. Just like mineral oils also silicones are not physiological. They do not contribute to the natural substance balance in the skin which means that the agreeable sensation does not correlate with a real endogenic regeneration of the skin.
Silicones practically have unlimited shelf life as they will neither degrade through the influence of atmospheric oxygen nor water nor can any significant microbial degradation be observed during their application.

Oral consumption and aspiration of hydrocarbons

While vegetable oils are part of the every day nutrition, the question regarding the consequences of an involuntary intake of the non-physiological hydrocarbons and silicones arises again and again. Depending on the respective country and institution there are different recommendations regarding the ADI values of the particular hydrocarbons and silicones.
Due to the steady intake of minor amounts over an extended period of time which happens e.g. with the use of lipsticks with the effect that women easily may "consume" several of them per year, above all the long term tolerance is of importance. During the long term use of paraffin oil containing laxatives for instance granuloma-like changes in the intestinal tract have been described[13)]. However, as quality standards have been increased and since the exact oil formulations applied under test conditions are unknown, the literature in this context is not representative.
Among others, an isolated case of aspiration (spray) with subsequent pneumonia has been reported[13)]. Regarding this specific observation however it should be mentioned that all non-degradable substances with a certain particle size may lead to comparable reactions. In other words: these are not necessarily hydrocarbon-specific reactions. Sprays with components which cannot be degraded by the human body however are inacceptable in cosmetics.
So called "other complex hydrocarbon containing compounds", a subdivision to which form oils in the cosmetic and food industry belong to among others, play a significant part in our daily life. This is the reason why professional associations have been dealing for quite some time with the risk assessment of hydrocarbon exposure[36)]. The problem with these oils lies in the fact that their composition may vary depending on their provenance and their processing as well as in the fact that a complete and 100 per cent analysis practically is impossible for cost reasons.
Traces of paraffin-based hydrocarbons and silicones are absorbed either orally or through the skin[13,35)]. As they are not metabolized, they are either stored in the fatty tissue or they leave the body unchanged. Due to the rather inaccurate framework conditions the available literature does not allow any valid conclusions. This is the reason why there are still no regulations to these for the manufacturers of cosmetic products. Similar to other substance groups the minor absorption of low molecular components may be more significant than that of high molecular components.

Skin ph value

The natural skin is the substrate for a natural skin flora which is severely changed by occlusive conditions[37,38)]. With the help of their own lipases and esterases the natural flora gains free acids from triglycerides and hence creates a low pH value which protects the body against external infections caused by pathogenic germs. It is an interesting fact that phospholipids which release the acids during the cornification process are a significant source of free acids[38)].
Hence it has a positive effect to favour a physiological skin care strategy and to prefer triglycerides to hydrocarbons for the re-fattening of the skin in order to support the symbiosis with the skin flora. Emulsifier-free concepts[28)] frequently use phosphatidylcholine which belongs to the group of phospholipids to create skin-barrier-like structures.

Conclusion

Seen from the perspective of a modern corneotherapy[39)] and above all its extended form[17)] it is recommended to use natural oils and lipids in cosmetic products even if sensory characteristics like long term skin smoothing may sometimes not really equal the features of (petro)chemicals.
The use of vegetable oils requires a careful adaptation of the oils to the results of the skin analysis. Not every oil is suitable for every individual case. Also potential sensitivities to certain components have to be considered. Depending on the refining processes and the provenance, oils with identical declaration may nevertheless have different characteristics[40)]. A well-funded and product-related consultation is very important for an adequate skin care result.

Mineral oil free product concepts sometimes ask for compromises due to specific technical requirements. Hence long chained hydrocarbons or silicones still today are essential carriers for pigments in smear and water proof elastic camouflage products. Pigment containing breathing foundations (make up) however may alternatively be formulated with triglycerides without any problems[41].

During the cold season the skin requires lipid-containing products. Besides water-containing creams also water-free products are recommended for extreme conditions whereas the latter-mentioned are of advantage as they are free of emulsifiers which cause the wash-out of both, cream and skin components during skin cleansing. As to that, there are now alternatives to vaseline products on the market which are based on triglycerides and have far higher lipid contents compared to barrier creams. The focus here is on oleogels which contain phosphatidylcholine (see above) that supports a quick penetration into the skin[42] due to its specific permeating properties.

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