Oily Components in Cosmetics from a European View[1]

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ABSTRACT

At about the turn of the century, the natural fatty acid triglycerides used as oily components in cosmetics were replaced by low-priced hydrocarbon oils of high purity. More recently the trend was reversed in Europe, and the hydrocarbon oils are being replaced by resynthesized triglycerides and liquid waxy esters derived from natural products. Apart from dermatological and toxicological safety aspects, the resynthesized triglycerides used are derived from natural fatty acids and may even be used as food additive constituents. These modern oily components are well suited for use in specialty applications and for solving problems in the formulation of cosmetics.

INTRODUCTION

For various technical reasons, liquid fatty substances are used in the formulation of many cosmetic preparations. The selection is determined by the functional requirement of the desired product under preparation and by the characteristics of these products and the possibilities afforded to the user. In general, oily components have the following functions.

In emulsions, they have a softening effect on the waxy components which give the structure; with other ingredients, they bring about the desired consistency, appearance, and temperature stability.

Furthermore, oily components are solvents for lipid-soluble ingredients. They serve as vehicles to facilitate the penetration of active ingredients into deeper layers of skin, when this property is desired. This funtion is of particular importance in preparations containing hormones, organ extracts, plant extracts, or other remedial ingredients.

Considering the different fields of application, there is such a variety of individual aspects that a full coverage is not possible within this summary. Therefore, only the effects measurable by physico-chemical methods or test setups which are close to actual use conditions will be discussed.

CHEMICAL STRUCTURE

Considering their chemical structure, there are five groups of cosmetic oily components.

Hydrocarbon oils, i.e., paraffin oils and vaseline oils, are available at different viscosities and with high standards of purity. They are considerably lower in price than ester oils. However, they are chemically unrelated to the skin as compared to ester oils. Skin surface fat (Table I) contains only small amounts of hydrocarbons, which are of a different structure than the oils obtained from mineral oils. Skin surface fat is composed mainly of free fatty acids, triglycerides, and waxes. In contrast to skin surface fat, sebum such as it is excreted from the glands, contains much higher amounts of glycerides and hardly any free fatty acids.

Much more closely related to skin surface fat are the representatives of the second group of cosmetic oily components, the fatty acid triglycerides. In the past, purified or refined vegetable triglycerides, such as peanut oil, olive oil, soybean oil, and almond oil, were used in cosmetic preparations; more recently, an increasing interest has been shown in the resynthesized triglycerides of short chain fatty acids which have significant advantages as far as oxidation stability and odor are concerned.

A third group consists of liquid waxy esters synthesized from native fatty acids and their hydrogenation products, the fatty alcohols. Within this group of substances, there is a great number of oils of varying structures and properties. These include oleic acid oleyl esters or esters from saturated fatty alcohols which must have shorter chains so that the pour points are sufficiently low, i.e., decyl oleate. There are also esters of saturated fatty acids, with lower molecular weights than oleic acid. By using these oils in cosmetic formulations, it can be shown that in waxy esters of this type the oily feeling decreases in favor of the solvent properties, if the acid component chain becomes longer and the alcohol component becomes shorter, respectively. This is the case in the isopropyl esters of myristic, palmitic, or even stearic acid (1). Dicarboxylic acid esters, such as dibutyl adipate, should also be classified with this group, which also contains waxy esters of branched fatty acids.

Fatty alcohols also are examples of oily components that have a permanent position in the European cosmetic market. The molecular weight in these substances must be sufficiently high to obtain an oily character at low temperatures, and low pour points. Therefore, the fatty alcohols are either unsaturated, i.e., especially pure and thus low odor oleyl alcohol, or saturated branched alcohols, such as 2-octyl dodecanol obtained by condensation (Guerbet reaction) from n-decanol.

Due to the great variety of synthetic possibilities, starting with fatty substances of natural origin, a great number of new developments have appeared in the course of the last years. With these substances special effects may be achieved or products with new properties may be formulated. These are water-soluble esters which are made up from fatty acids and certain polyalcohols which in spite of this property, have a distinct fatty effect on the skin, objectively as well as subjectively. The main use of these so-called water soluble oils is in superfatting water-based preparations such as bubble baths or in shaving formulations which contain only a low amount of alcohol.

Some other properties of these hydrophilic esters lead to interesting possibilities in the formulation of cosmetics: in combination with ethoxylated fatty alcohols, brilliantly clear transparent gels of a solid consistency, the so-called swinging gels, can be made.

PROPERTIES

With this relatively large selection of differently structured oily components, it is possible to select the suitable properties of the esters or mixtures in question for the product to be developed. Naturally, the oils differ in their physical properties such as pour point, viscosity, density, and refreactive index. The effectiveness on the skin is of practical importance, the oils being classified by their fatty properties.

Unsaturated esters as well as triglycerides have rather marked fatting properties. Oleic acid oleyl ester is comparable to the strong fatting vegetable oils, while isopropyl esters appear less fatting. Paraffin oil is roughly comparable with the group of caprylic/capric acid triglycerides, oleic acid decyl ester, and 2-octyl dodecanol.

Besides the fatty impression, the spreading ability of oily components is of practical interest. Here too, a sequence may be made up which allows optimum selection. As a measure for spreading, the equilibrium spreading pressure

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[1] Presented at the AOCS Meeting, New York, May 1977.

TABLE I

Composition of Skin-Surface Fat[a]

Free fatty acids	28%
Triglycerides	32%
Waxes	14%
Cholesterol and esters	4%
Squalene	5%
Other hydrocarbons	8%
Dehydrocholesterol and similar steroids	9%

[a] Frey, H., Wörterbuch der Kosmetik (1974).

(π dyne/cm) is often used. Figure 1 shows the principle for the determination of equilibrium spreading pressures. Small amounts of a drop of water-insoluble oil floating on water spread on the surface as a monomolecular layer. This process may be visualized as a two-dimensional evaporation. The substance will continue to spread until the entire surface available is covered evenly by a film of oil. When this has happened, the equilibrium spreading pressure is reached. The equilibrium spreading pressure is derived from its definition:

$$\pi = \gamma\ H_2O - \gamma\ \text{film}$$

The equilibrium spreading pressure is determined from the difference in surface tensions before and after spreading of the test substance on a pure water surface (2). The surface tensions are determined by the vertical plate method, as sketched in Figure 1. The data obtained for a series of oily components are listed in order of their equilibrium spreading pressure in Table II. Paraffin oils and esters of branched fatty acids show a very low spreading ability, while fatty alcohols and triglycerides spread best. However, branched fatty acids are also present in the preen fat of water birds. Now, if these substances spread poorly on water, this could also mean that the feathers will give off the substance only very slowly in water, thus the desired effect is maintained for a longer time. In this context oils with poor spreading characteristics on water in the formulation of suntan preparations should be used to prevent being rinsed off during bathing.

For use in cosmetic preparations the spreadability of the oily components on skin is of special importance. This was determined by Neuwald et al. (3) by the following procedure: the oils were applied to the skin surface of the forearm, which had been cleaned of fatty materials prior to the procedure. After a defined period of time, the size of the oily spot obtained was determined by taking an impression with filter paper. These investigations were taken up by Keymer (4) who found a correlation between spreading on the skin and surface tension, which he was able to describe quantitatively by a quadratic equation. The lower the surface tension, the better the spreadability on the skin. The explanation Keymer gives is that the surface of the oils becomes much larger when spreading, as the oil penetrates into the uneven and fissured top layer of the epidermis. By comparison with the surface tension, both viscosity and interfacial tension against water have a negligible influence on the spreadability. We have repeated these studies and have reached basically the same results, though it must be granted that the margin of error is considerably greater in our method of testing that indicated by Keymer.

If the oily components are aligned in the order of increasing spreadability as calculated from the surface tension, the sequence in Table II is obtained. The results confirm the poor spreadability of paraffin oil, a fact also known from practical experiences with cosmetic formulations. So-called fatty oils do not spread well, while the esters with more of a solvent character belong to the well-spreading substances. This sequence of cosmetic oily components is another important and interesting differentiation

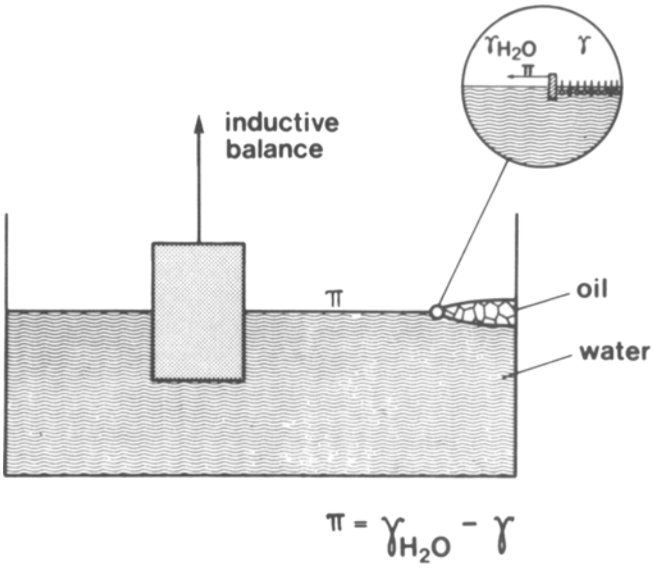

FIG. 1. Determination of the equilibrium spreading pressure.

or classification concerning this criterion of application.

However, measurements of physico-chemical data and characteristic constants calculated from these do not always strictly correlate with practical applications. We have, therefore, attempted to determine and compare the behavior of the oils, in particular the fatting properties by measurements on the skin. Two procedures are known for the determination of the amount of skin surface fat:

1. A method by Schaefer and Kuhn-Bussius using glass platelets with a frosted surface. The uptake of lipids leads to increasing transparency of the platelets, which is determined quantitatively in the photometer (5).
2. Another method using the principle of the decrease of skin surface fat has been developed by Schrader, who does not use glass platelets but a plastic strip which becomes increasingly transparent with increasing fat uptake. Numerous measurements and publications (6-8) have shown that quantitative statements on the amount of skin surface fat are possible with this method. Based on this principle, a measuring device has been developed, the so-called sebumeter. An impression is taken from the skin surface with the separate measuring head, and the transparency of the plastic strip covered with sebum is measured in the device.

First comparative measurements of paraffin oil, caprylic/capric acid triglyceride, and the above-mentioned water-soluble hydrophilic esters showed that the decrease of the oil applied to the skin is larger in the case of ester oils than it is with paraffin oil. This confirms the subjective impression of a stronger coating in the case of paraffin oil.

CONSEQUENCES AND OUTLOOK

In the formulation of cosmetics, a good deal of experience with the different oily components is necessary. On the other hand, experimental series are also necessary to achieve the desired effect, which cannot be entirely predetermined. Besides the purely practical requirements, which may be met by this large range of different oils, dermatological and toxicological aspects will have to be considered more and more in the selection of suitable oils. In the past, the testing of acute toxicity and mucous membrane irritancy potential has been sufficient, but in the future resorption will also have to be considered. In the Federal Republic of Germany, we have the following directive concerning pharmaceuticals, which was issued in

TABLE II

Equilibrium Spreading Pressure of Oily Components on Water and Their Spreading on the Skin[a]

	π (dyne/cm)	γ (cm^2) covered area of skin
Paraffinoil (ca. 120 cP)	7.6	1.5
Isononanoic acid-palmityl/stearyl ester	8.2	9.8
Oleic acid decyl ester	11.3	5.7
Lauric acid Hexyl ester	12.0	10.1
Isopropyl palmitate	15.4	11.4
Oleic acid oleyl ester	16.3	3.1
Isopropyl myristate	16.4	13.1
2-Octyl dodecanol	17.0	9.8
Caprylic/capric acid triglyceride	19.9	9.7
Oleyl alcohol	32.9	3.9

[a] Calculated from surface tension.

1971 by the Federal Ministry of Family, Youth, and Health: "In the case of drugs which are designed for topical application, it is also necessary to investigate the resorption of its vehicles. If this has been proven to be insignificant, considering the intended administration to man, the studies concerning the subacute and chronic toxicity, fetal toxicity, etc., may be omitted. If, however, a resorption is observed in clinical tests, all toxicological tests with animals are required."

At this time, the question of what is meant by insignificant resorption is open to interpretation. The formulation of cosmetics should also be guided by this directive concerning pharmaceuticals, because vehicles and additives are applied much more frequently in the case of cosmetics than in the case of drugs. Bearing this in mind, it appears obvious to select those cosmetic oils which are absolutely unobjectionable even in the case of considerable degrees of resorption. The strongly increasing use of esters, particularly triglycerides, which are basically edible fats, shows that this development is taken into account already.

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