SENSORY MAPPING FOR COMMON SPECIAL ESTERS IN CREAM PRODUCTS

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Abstract: Emollients are essential ingredients in all types of personal care products and cruial especially for skin care category. The basic building blocks of most emollients are long chain hydrocarbons, often combined with alcohols and acids in the form of esters. Esters have been increasingly used in cosmetic formulations over the past few years in a wide variety of applications for their sensorial and emollient properties. The majority of esters are either derived synthetically from petroleum or from natural triglycerides. The raw materials which are commonly used in FMCG like cyclomethicone, natural silicone, mineral oil, jojoba oil, lanolin oil, antimicrobial efficiany agent and preservative have their alternatives in the form of emollients which are special esters products. In this paper, common special emollients which have an ester form will be evaluated in terms of their end user sensory feelings as well as general informations about their production details.

Keywords: ester, emollient, sensory feeling, natural derivatives

INTRODUCTION

Esters are one of the most widely used types of chemical compound in the world today for cosmetics and the personal care industry because of their versatile chemistry. The majority of esters are either derived synthetically from petroleum or from natural triglycerides (Transparency Market Research, 2020).

The basic synthesis of esters are shown in Figure 1. It is a condensation product of carboxylic acid and alcohol heated in the presence of a mineral acid catalyst to form an ester and water.

$$RCOOH + R^1OH \overset{H^{\oplus}}{\rightleftharpoons} RCOOR^1 + H_2O$$

Fig. 1: Synthesis of esters (Esterleşme reaksiyonu, 2020)

Due to the variability of crude oil prices, Petroleum-derived esters are become more expensive so that their usage decrease day by day. Besides this, trends in cosmetics goes to green, organic, natural, natural derived and sustainable formulations. That situation lead to the need of natural alternatives of petroleum-derivatives in personal care, which could be met by increased use of naturally derived esters (Transparency Market Research, 2020).
The raw materials which are commonly used in FMCG like cyclomethicone, natural silicone, mineral oil, jojoba oil, lanolin oil, antimicrobial efficiany agent and preservative have their alternatives in the form of emollients which are special esters products as shown in **Table 1.**

Table 1: Special esters and their properties & replacements

Special Esters	**Properties**
Coco-Caprylate/Caprate	Alternative to Cyclomethicone, Natural Silicone and Mineral Oil
Oleyl Erucate	Alternative to Jojoba Oil (cost effective)
Decyl Oleate	Similar Sensory Mapping to MCT
Bis-Diglyceryl Polyacyladipate-1	Alternative to Lanolin Oil
Propylene Glycol Dicaprylate / Dicaprate	Alternative to Low Molecular Weight Silicone Oil
Glyceryl Caprylate	Antimicrobial efficacy against microorganisms & the most widely used natural preservative booster in the world

Coco-Caprylate/Caprate

Coco-Caprylate/Caprate is primarily used in cosmetics as an emollient and emulsifier for formulations. It is an ester of coconut fatty alcohol, capric acid and caprylic acid. Straight, unbranced wax ester made of C12 – C18 vegetable fatty alcohol and a defined blend of fractionated fatty C8/C10 acids of vegetable origin. It leaves a non-greasy, soft after touch on the skin. It is a successful sensory alternative to cyclomethicone, natural silicone and mineral oil and provides such kinds of claims like vegan, 100% natural vegetable source to the final products (IOI Oleochemical, 2019).

Oleyl Erucate

Oleyl erucate is a natural based highly pure cosmetic oil with properties similar to natural jojoba oil. It is produced by enzymatic catalysis.

Oleyl erucate is a wax ester of vegetable fatty alcohol and fatty acids. It is manufactured by esterification of vegetable C16/C18 and C18 unsaturated fatty alcohol and C16-C22 unsaturated fatty acid from Palm and Rapaseed. It is used as cost effective alternative of natural jojoba oil and provides such kinds of claims like vegan, palm based, 100% natural, 100% vegetable renewable source to the final products. (IOI Oleochemical, 2019).

Decyl Oleate

Decyl oleate is a wax ester made of straight chained decyl alcohol and oleic acid. It is used in variety of cosmetics and personal care products, including make up, and skin and hair products. The sensory performance is often compared to popular MCT oil. It is palm based, obtained from 100% vegetable renewable source. As antioxidants, mixed vegetable tocopherols and citric acid esters (Glyceryl Citrate/Lactate/Linoleate/Oleate) are used in the process (IOI Oleochemical, 2019).

Bis-Diglyceryl Polyacyladipate-1

It is a partial ester of natural diglycerin with medium chain fatty acids, isostearic acid, 12-hydroxystearic acid and adipic acid. It is promoted as vegan alternative to lanolin oil or without the potential skin irritation problems of lanolin. It provides high water absorption capacity, conditioning and film forming effect, stable against air oxidation and is produced with 85% vegetable renewable source that is palm based (IOI Oleochemical, 2019).

Propylene Glycol Dicaprylate/Dicaprate

Propylene Glycol Dicaprylate/Dicaprate is a mixture of the propylene glycol diesters of caprylic and capric acids (Wenninger and McEwen 1997). Propylene Glycol Dicaprylate/Dicaprate is also defined as the propylene glycol diester of short chain, predominantly naturally derived C8-Cl0 fatty acids (Nikitakis and McEwen 1990). It is soluble in alcohol containing up to 20% water and its viscosity is usually low (Stepan Company 1996).

Propylene Glycol Dicaprylate/Dicaprate has been defined as the propylene glycol diester of saturated vegetable acids (C8-ClO chain length) that contains 65 to 80% caprylic acid and 15 to 30% capric acid (Mahjour et al. 1993).

Propylene Glycol Dicaprylate/Dicaprate is produced via the combination of Propylene Glycol with capric and caprylic acids. The mixture is heated to temperatures high enough to cause esterification. Water of reaction is removed to drive the reaction to completion and to obtain the low hydroxyl specification. The product is then fully refined and deodorized (Stepan Company 1996).

It is promoted as excellent dispersing and dissolving properties for pigments and sunscreens. It is light emollient for many formulations such as sun care and BB creams, high polarity with high % vegetable source palm based product.

Glyceryl Caprylate

Glyceryl Caprylate is obtained by esterification of glycerol and caprylic acid. It is promoted as palm based, 100% natural and vegetable renewable source which exhibits excellent antimicrobial efficacy against microorganisms, voluable support for anti-acne poducts. It is the most widely used natural preservative booster in the world. 88% min. content of monocaprylate used for alternative preservation, refatting and wetting (Thiemann et. al, 2017)

Sensorial properties of ester emollients

The performance of emollients in the form of esters can have a significant effect on the final personal care product formulation depending on the chemical structure of the ester and the base formula of the final product as well. It seems difficut in the beginning to select the best ester for a particular formulation. However, formulators who understand how the structure of an ester affects its characteristics can select the optimum ester for their application quickly and reliably. The most important parameters given in the literature are as follows:

1. London dispersion forces

The attraction between molecules due to instantaneous areas of charge as a result of localised electron movement is called London dispersion forces. These forces are weaker than hydrogen bonds or covalent bonds. As molecules start to get bigger, the degree of interaction increases and the sum of the forces starts to become significant. This effect causes the increase in boiling points of esters as their molecular weights increase and so does the boiling point consequently. This is because of the increased attraction between molecules as a result of London dispersion forces. This increase of intermolecular attraction is also felt in the sensory properties of the material. As the attraction between the molecules increases, more force has to be applied in order for the layers of molecules to slide against each other, leading to lower spreadability and a heavier feel (Alander, 2012).

2. The effect of branching

For higher molecular weight, London dispersion interaction increase and heavy skinfeel occures for linear molecule but vise versa for branched ones. Branched molecules are less 'stack' in layers. Branching reduces the amount of interaction between the molecules and results in a lower boiling point and a lighter skin-feel.

3. The effect of unsaturation

In a saturated compound, each bond has 360° free rotation, allowing the material to be extremely flexible and conform to the most energetically favourable state so that high London dispersion interactions occur. Double bonds do not have this free rotation and fix the molecule in a certain conformation. This makes them less flexible and leads to a reduction in the strength of London dispersion forces and provides a lighter skinfeel. (Williams et. al, 2012).
Cis and trans conformations also have an impact on sensorial parameter. The cis conformation disrupts the structure far more and results in a lower melting point and therefore provides a lighter skin-feel (Williams 2012, Wu 2014).

4. Polyol derived esters

A polyol molecule has a multiple alcohol functional groups. Esters derived from polyols are inherently more branched than ones derived from mono alcohols, and so even though they can be quite large molecules, they feel quite light on the skin. The complex structures of polyols give a unique skin-feel (Barel et. al, 2009)

5. Hydrogen bonding and hydroxyl groups

Hydroxyl groups are common functional group in ester compounds and are easily identifiable from the INCI name, such as Ethylhexyl Hydroxystearate. These groups tend to make the material feel heavier and more moisturising (Iwata et. al, 2013).

Although the data in the literature provide significant information about sensory performance, panel tests are more common in FMCG, where the opinion of the end user is taken. In this study, the common emollients in ester form were used. For this purpose, a basic cream base was used and the amount of ester kept same in order to get comparable results. The results of the sensory map obtained were compared.

MATERIALS AND METHODS

In this study, 6 special ester given in Table 1 used to make cream samples. Basic cream formulation was used given in Table 2 for each esters.

Table 2: Basic cream formula

Phase A	**Water Phase**
Ethylhexylglycerin	0,25 %
Phenoxyethanol	0,65 %
Methylpropanediol	2 %
Carbomer	0,35 %
Water	up to 100
Phase B	**Oil Phase**
Stearic Acid	2 %
Cetyl Alcohol	1 %
Sodium polyacrylate	0,2 %
Potassium Cetyl Phopsphate	0,21 %
Ester	**5 %**

6 esters were evaluated with 5% usage ratio in cream base. In order to see a significant emollient effect in the cream formula, 5% usage ratio was selected. Sensory test was performed with 7 people and applied on forearm area in a conditioned laboratory. All the sensory evaluation results were noted after 15 minutes of the application time for each sample of creams. The parameters of dry time, softness, stickiness, velvetiness, dryness, shining were marked by the panellists and evaluation scores were noted between 1 to 10.

The following list explains how to perform sensory criteria:

Dry time: The time that emollients appears on skin that indicates absorption of emollients into skin. If the dry time is long, it means bad absorption, so the longer dry time gets lower mark.

Softness: The first feeling of the emollient on skin that shows the quality of sensory feeling of raw material. Best performance:10 points

Stickiness: It is an undesired feature for a cosmetic product to have. Non-sticky performance was marked with 10 points.

Dryness: It is an indication of moisturization on skin. Therefore, dry skin is marked with lower point. For the least dryness: 1 point, maximum dryness: 10 point.

Shining: 1 point is marked as less shining and 10 point is marked as more shining.

Velvetiness: The first velvety feeling of the emollient on skin that shows the quality of sensory feeling of raw material. Best performance:10 points

RESULTS AND DISCUSSION

By using the same cream base formula, 6 esters were successfuly evaluated for sensory mapping and spider graph introduced in Figure 2. Sensory test was performed with 7 people for applied on forearm area in a conditioned laboratory. 252 sensorial evaluation conducted in total, summarized in Table 3. The parameters of dry time, softness, stickiness, velvetiness, dryness, shining were marked by the panellists and evaluation scores were noted between 1 to 10.

Table 3: Summary of trial list

Sensorial Evaluation Criteria	**5% emollient in cream**	
Dry Time	6 EMOLLIENTS APPLIED	**252 Sensorial Evaluation in Total for 7 Panellists**
Softness		
Stickiness		
Velvetiness		
Dryness		
Shining		

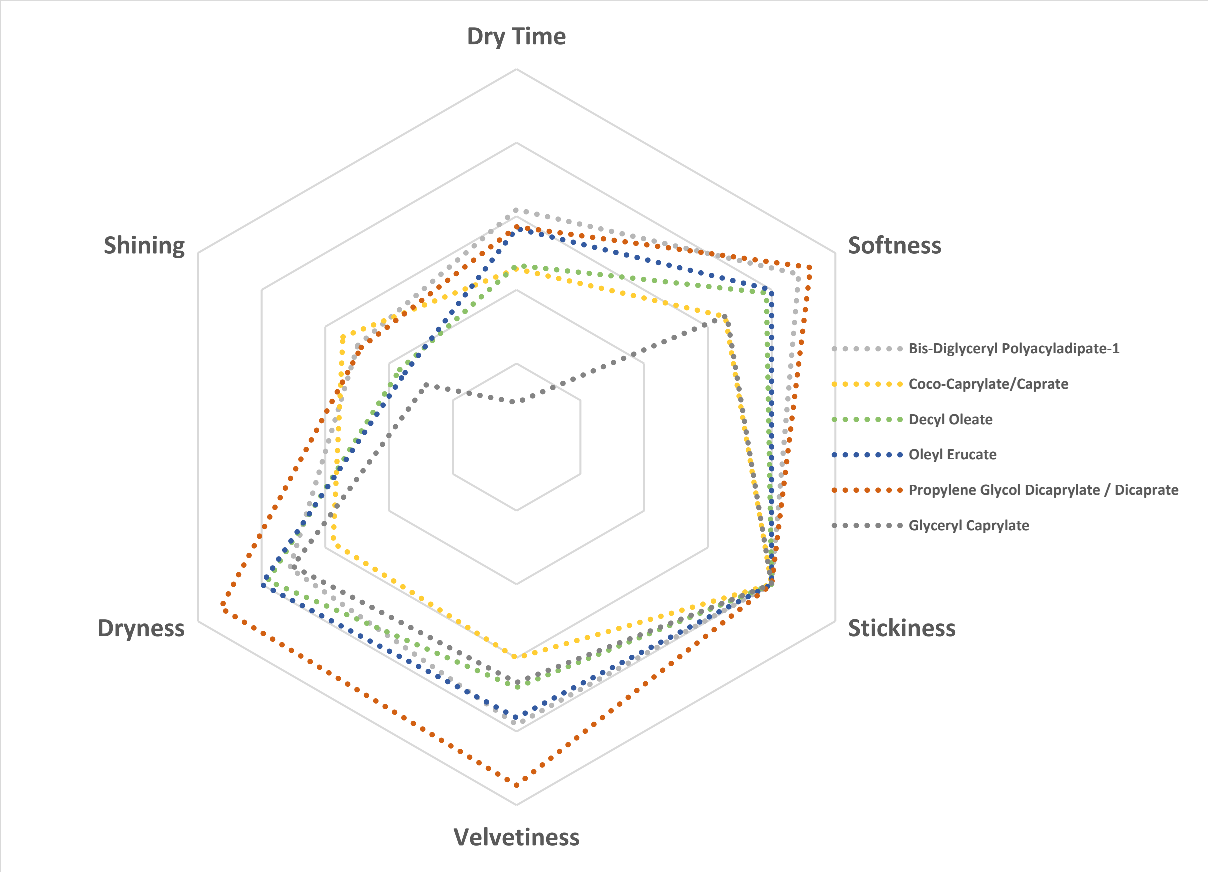

Fig. 2: Sensory mapping spider graph of common special esters

All the esters have similer stickiness performance. The best velvetiness, softness and dryness performance obtained with propylene glycol dicaprylate/dicaprate which is an alternative to low molecular weight silicone oil. Decyl oleate and oleyl erucate has similar shining, dryness, softness and stickiness performances. Oleyl erucate is cost effective alternative of jojoba oil and decyl oleate is alternative to middle chain triglycerides which has a high cost either. The worst performance belongs to glyceryl caprylate with poor dry time performance.

CONCLUSION

Esters provide a drier feel than traditional oils, reducing the greasy feel of formulations. With natural cosmetics becoming more important, having functional natural alternatives instead of synthetic ingredients becomes crucial. Esters can provide formulators with effective and natural replacements for potentially unwanted materials such as mineral oils and silicones. In the future, the selection of an emollient mixture for a formulation consider parameters such as purity, biodegradability, and sustainability, leading to the development of new processes and types of emollients.

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