Nascent Technologies Corp.

Emerging Technology

Esters

A Compilation of Articles

Tony O'Lenick
Nascent Technologies Corporation
Lawrenceville, Ga 30043
tolenick@mindspring.com

January 2021

Nascent Technologies Corp.

Emerging Technology

Introduction

This compilation contains articles written between 2019 and 2021, on esters and their application in personal care formulations. The takeaway message is that formulations are complex, having many ingredients many of which often interact with each other, sometimes unpredictably. The intent of this compilation is to provide information on the types of esters available and an approach to choice the best one for your formulation.

Happy Formulating!

Tony O'Lenick
January 2021
Nascent Technology Corporation
tolenick@mindspring.com

Nascent Technologies Corp.

Emerging Technology

Tony O'Lenick

Tony O'Lenick is President of Nascent Technologies Corporation, a product development and intellectual property and consulting company he founded in 1999, to develop raw materials and formulations that have an improved environmental footprint. Prior to Nascent, Tony was President and Co-founder of Siltech LLC, a specialty silicone company for 31 years. He also held technical and marketing positions at Alkaril, Henkel Corporation and Mona Industries.

Tony has written seven books, 100 technical articles, and has over 300 patents. He teaches courses in silicone and organic chemistry and has received industry awards including the Samuel Rosen Award (American Oil Chemists' Society), the Innovative Use of Fatty Acids Award (Soap and Detergents Association), and the Partnership to The Personal Care Award (Advanced Technology Group). Tony was Education Committee Chair of the International Federation of the Societies of Cosmetic Chemists (IFSCC) from 2016 -2020. He received the Maison G. de Navarre Medal Award in 2018 and the Merit Award in 2019 from the Society of Cosmetic Chemists, the Society's highest accolade. He also is serving as a Board Member of the American Oil Chemists Society from 2017- 2021.

Tony O'Lenick
January 2021
Nascent Technology Corporation
tolenick@mindspring.com

Polyol esters in personal care formulations part 1 - Chemistry

TONY O'LENICK
Siltech LLC, Lawrenceville, USA

Tony O'Lenick *is President of Siltech LLC. Tony has published six books, numerous articles and has over 300 patents. He received the 1996 Samuel Rosen Award, the 1997 Innovative Use of Fatty Acids Award and the 1996 Partnership to The Personal Care. Tony was President of the U.S. SCC in 2015 and is currently Education Chair of IFSCC.*

KEYWORDS: Esters, simple esters, polyol esters, pentaerythritol, neopentyl glycol, trimethylol propane, guerbet alcohol, skin feel, cushion, play time, slip, drag, soaping and dehydration, science for formulators.

ABSTRACT

As the quest for natural, renewable, biodegradable and green products continue there has been increased interest in working with a variety of esters and triglycerides. Esters when applied to the skin, not only act as emollients but also provide an aesthetic effect which can be varied by structure. This article is the first of two that deal with polyol esters themselves, synthesis and properties of the polyol esters. This particular class of polyol esters are based upon specific highly branched polyols namely. neopentyl glycol (2 OH groups), trimethylol propane (3 OH groups) and pentaerythritol (4 OH groups). These esters find their main use in industrial lubrication because not only are they effective lubricants, they are oxidatively stable and have a relatively low viscosity when one considers their molecular weight.

CHEMISTRY

Esters are a class of compounds that have been used as polar oils in many formulations. Esters consist of a carbonyl group (C=O) covalently bonded to –OR, where R is an alkyl group. Esters cover a wide range of products and are classified by the groups connected on either side of the -C(O) O- bond. The majority of esters used in the cosmetic field are produced by the so called "direct Esterification" process". Direct esterification is a process by which organic acid and an alcohol are directly reacted. This distinguishes them form "trans-esterification esters", which as the name suggests are made by trans-esterification. Trans-esterification is a process of reacting alcohol with an ester, rather than an acid. A simple example is reacting methyl stearate with decanol, making decyl stearate and methanol. Instead of getting water as a byproduct like direct esterification, the byproduct of a trans-esterification reaction is an alcohol. Figure 1 shows the reaction sequence.

R'OH	+	R-C(O)OH	→	R-C(O)OR'	+	H_2O
Alcohol		Organic Acid		Ester		Water (distilled off)

Figure 1. Direct Esterification Reaction

The progress of the reaction can be followed by (1) the change in acid value (which decreases as the acid reacts); (2) the hydroxyl value (which drops as the reaction proceeds); (3) the saponification value (which increases as the reaction proceeds) and (4) the amount of water generated (which increases as the reaction proceeds. Figure 2 shows the observed changes.

Reactants			Products
Acid value	HIGH	Acid value	LOW
Saponification value	LOW	Saponification value	Increase
Hydroxyl value	HIGH	Hydroxyl value	LOW

Table 1. Esterification Reaction.

Figure 2 (1) the reaction in a graphic form.

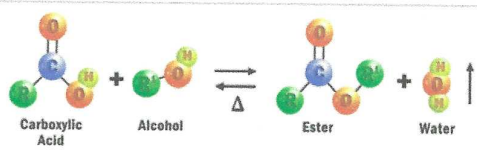


Figure 2. Graphic Image of the Esterification Reaction (1).

This particular paper deals with the reaction of a polyol, a compound with more than one hydroxyl group that is reacted with the proper number of carboxylic acid groups. These esters are so-called "polyol esters" and are an important class of compounds in the personal care market. These specific classes of esters find use as skin emollients and in addition provide a pleasant aesthetics to skin. This class of compounds finds the primary use in high temperature industrial lubrication applications, and some usage in

The esters of this class are different from many other esters in that they have no beta hydrogen on carbon atom. This results not only in better oxidative stability at

high temperatures, but better oxidative stability at lower temperatures in formulations. Figure 3 shows a cartoon of the structure.

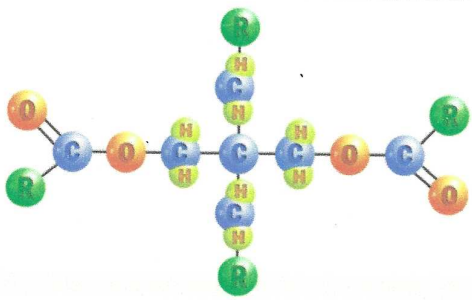


Figure 3. Ester without a Beta Hydrogen.

These materials are made from mono-substituted fatty acids and di-, tri- or tetra-functional hydroxyl compounds (neopentyl glycol (NPG), trimethylol propane 1(TMP) and pentaerythritol (PE). One of the major uses of polyol esters is for low viscosity, cosmetically elegant oil phases. The PE esters have the most cushion and playtime while the NPG has the least cushion and is a dry oil. The polyols were reacted with a molar equivalent amount of fatty acids that include oleic acid and erucic (mono-unsaturated), isostearic acid and octyldodecanoic acid (two branched materials). Figure 4 shows the esterification reaction of pentaerythritol and oleic acid, making a primarily a tetra substituted ester.

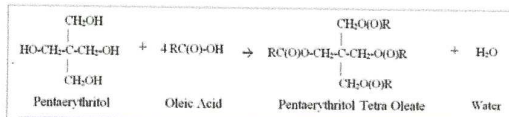


Figure 4. Polyol Ester Synthesis.

The ester is highly branched because of the structure of the polyol and highly unsaturated due to the structure of the acid, it also lacks the reactive hydrogen on the beta carbon atom. Figure 5 shows a cartoon of the structure.

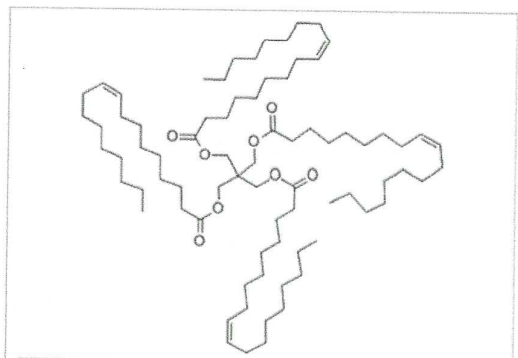


Figure 5. Structure of Pentaerythritol Tetra Oleate (3).

The material balance for the reaction of pentaerythritol with oleic acid to make pentaerythritol ester and water is shown in Table 2.

Material	Molecular Weight	Mole Ratio	Weight (%)
Oleic Acid	282.5	4.0	89.24
Pentaerythritol	136.2	1.0	10.76
		Total	**100.00**

Products	Weight (%)
Pentaerythritol Tetraoleate	94.13
Water	5.87

Table 2. Synthesis pf Pentaerythritol Tetra Oleate (PTO).

There are three different polyols used to make polyol esters. Table 3 shows the structure and melt point of the polyols.

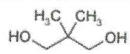
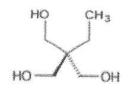
Name	Structure	Melt Point (°C)
Neopentyl Glycol[4]		129.1
Trimethylol Propane[5]		58.0
Pentaerythritol[6]		58.0

Table 3. Raw Materials – Polyols.

Fatty Acids are reacted with the polyols to make polyol esters. The properties of the fatty acids useful in synthesis of polyol esters are shown in Table 4.

Name	Structure	CAS	IUPAC	Melt Point (°C)
Oleic Acid[7]	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	112-80-1	(9Z)-Octadec-9-enoic acid	13.0
Erucic Acid[8]	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$	112-86-7	(Z)-Docos-13-enoic acid	34.0
Guerbet C20 Acid[9]		619-39-6	2-Octyl Dodecanoic acid	37.0
Isostearic Acid[10]		30399-84-9	Isooctadecanoic Acid	< 10.0
Stearic Acid	$CH_3(CH_2)_{16}COOH$	57-11-4	Stearic acid	70.0

Table 4. Raw Materials – Fatty Acids.

PROCESS FOR THE ESTERIFICATION REACTION

Reactions were run in a two-liter, 4-neck flask fitted with an overhead stirrer, Dean-Stark trap, thermometer, N_2 sparge and Thermowatch controlled heating mantle. Stochiometric amounts of acid and polyol were placed in a flask and heated to 110 °C. The reaction flask was evacuated to degas and after about 30 minutes the vacuum was broken with nitrogen. The reaction was then heated to 190 – 200 °C.

The reaction was then held for about 6 hours at the temperature where water was distilling off and then slowly raised to 230 °C (over about 4 hours) to maintain the rate of distillation. The reaction was monitored for acid value. The temperature of the reaction was raised above 230 °C if needed until the AV was below 5.

The following polyol esters were prepared and evaluated. The analysis is summarized in Table 5-7.

Property	1	2	3	4
Appearance @ 25 °C	Cl. Liquid	Cl. Liquid	Cl. Liquid	Cl. Liquid
Odor	Bland	Bland	Mild	Mild
Color, Gardner	4	3	4	2
Specific Gravity @ 25 °C	0.90	0.90	0.88	0.91
Saponification Value, mg KOH/gram	178	163	162	176
Acid Value, mg KOH/gram	2	1	7.4	3.3
Iodine Value, cg Iodine/gram	80	93	0.5	0.9
Hydroxyl Value, mg KOH/gram	9	6	11	
Viscosity @ 40 °C, cSt	24	32	36	45
Pour Point, C	-35	-25	-40	-35
MW (From Saponification)	630 g/mol	688 g/mol	692 g/mol	637 g/mol

Table - Neopentyl glycol esters
(1) Neopentyl glycol di-oleate.
(2) Neopentyl glycol di-erucate.
(3) Neopentyl glycol di-2-Octyl Decanate
(4) Neopentyl glycol di-isostearate

Table 5. Neopentyl Glycol Esters.

Property	5	6	7	8
Appearance @ 25 °C	Cl. Liquid	Cl. Liquid	Cl. Liquid	Cl. Liquid
Odor	Bland	Bland	Mild	Mild
Color, Gardner	4	3	4	3
Specific Gravity @ 25 °C	0.91	0.90	0.89	0.91
Saponification Value, mg KOH/gram	181	164	166	178
Acid Value, mg KOH/gram	0.8	0.1	2.5	3.8
Iodine Value, cg Iodine/gram	85	90	0.3	0.6
Hydroxyl Value, mg KOH/gram	10	11	14	12
Viscosity @ 40 °C, cSt	48	71	73	105
Pour Point, C	- 20	- 25	- 50	- 26
MW (From Saponification)	930 g/mol	1026 g/mol	1014 g/mol	945 g/mol

Table - (5) Neopentyl glycol di-isostearate
(6)Trimethylol Propane esters
(7) Trimethylol Propane tri-oleate.
(8) Trimethylol Propane tri-erucate.

Table 6. NPG and TMP Esters.

Property	9	10	11	12
Appearance @ 25 °C	Cl. Liquid	Cl. Liquid	Cl. Liquid	Cl. Liquid
Odor	Bland	Bland	Mild	Mild
Color, Gardner	4	3	5	2
Specific Gravity @ 25 °C	0.91	0.91	0.89	0.91
Saponification Value, mg KOH/gram	188	167	171	181
Acid Value, mg KOH/gram	3.7	1	3.1	3.2
Iodine Value, cg Iodine/gram	87	89	0.5	0.8
Hydroxyl Value, mg KOH/gram	7.0	1.6	13.6	6.0
Viscosity @ 40 °C, cSt	64	90	90	167
Pour Point, C	-25	-9	-45	-18
MW (From Saponification)	1193 g/mol	1343 g/mol	1312 g/mol	1240 g/mol

Table - Pentaerythritol esters
(9) Pentaerythritol tetraoleate.
(10) Pentaerythritol tetraerucate.
(11) Pentaerythritol tetra-2-Octyl Decanate
(12) Pentaerythritol tetraisostearate

Table 7. Pentaerythritol esters.

POLYOL ESTER EVALUATIONS

Viscosity

The products produced in this study vary in molecular weight. While it is difficult to compare all of the esters prepared, there are some interesting observations. The pentaerythritol products have the highest molecular weight since they are tetra substituted, trimethyol propane products the next highest and the neopentyl glycol products the lowest molecular weight for a given fatty acid. When comparing the effect of the fatty group, we decided to look at the viscosity difference of the esters produced as shown in Figure 6.

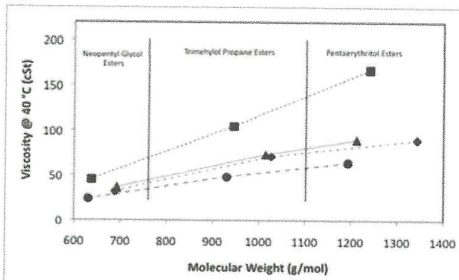


Figure 6. Viscosity vs. Molecular weight for (■) isostearate, (▲) guerbet, (◆) eurcate, and (●) oleates.

Figure 6. Viscosity v. MW of Polyol Esters.

Figure 6 shows a unique property of polyol esters, there is relatively little change in viscosity over a wide difference in molecular weight. The different types of fatty group studied include (■) isostearate, (▲) guerbet, (◆) eurcate, and (●) oleates. Viscosity was tested for viscosity at 40 °C. The oleates and eurcates, which are cis/trans tautomer are very different in terms of viscosity. The trans configuration (eurcrate), had a higher viscosity in each case NPG, TMP, PE. For example, the pentaerythritol esters of eurcic acid had the viscosity of 90 cSt while the oleate had a viscosity of 64 cSt. The *trans* configuration allows for more overlap of the alkyl groups, thus increasing the van dar Waals forces, leading to a high viscosity. The cis conformation (oleate) of the alkyl group restricts rotation, causing less packing and van dar Waals forces, resulting in a lower viscosity.

It is interesting to note that the Guerbet and Eurcate groups have essentially the same effect on viscosity, the greatest difference was in the NPG esters which had the viscosities of 36 and 32 cSt respectfully. The largest increase of viscosity shown was seen in the isostearates. Specially, Pentaerythritol tetraisostearate which had the viscosity of 167 cSt.

Structural effects on the viscosity of the esters

Viscosity is a physical property, not chemical. Viscosity is very similar to melt point, boiling point, and freezing point. These physical properties are controlled by the structure of the material. More specifically, the amount of intermolecular forces the molecule has, the higher the viscosity and melt point. Molecular weight is a large component of this as well. The higher the molecular weight, the higher the viscosity. This rings true all the way up to the molecular weight of entanglements. After that critical point is reached the viscosity vs. molecular weight has to be studied using Flory Huggins theory and polymer chemistry begins. In small molecular weight molecules (i.e. under the molecular weight of entanglement) several factors can have a drastic effect on viscosity. The more branching, the lower the viscosity, melt point, and boiling point. When studying these esters, a connection between the melt point of the acid from which they are derived vs. viscosity can

be studied. By holding the alcohol consistent, the differences in viscosity can be easily explained by using the melt point differences of the starting acids. The melt point of the raw material fatty acids are shown in Table 8.

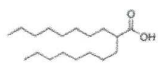
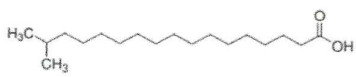
Name	Structure	Melt Point (°C)
Oleic Acid[7]	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	13.0
Erucic Acid[8]	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$	34.0
Guerbet C20 Acid[9]		38.5
Isostearic Acid[10]		

Table 8. Fatty Acid Properties.

As observed in Table 8 isostearic acid has the lowest melt point. This comes as a direct result in the isopropyl group at the end of the alkyl chain. This small branch weakens the van dar Waals forces and lowers the melt point. When comparing all of the esters,
The highest melt point in the series is the fully saturated compound. For purposes of illustration, stearic acid. Introduction of double bonds into the molecule results in a marked drop in melt point. This can be seen with oleic acid. An additional point is that the increasing molecular weight by addition of methylene groups increases the melt point. Erucic acid has a higher melt point than oleic, but lower than stearic acid.

When unsaturation exists in the molecule, the cis- isomer has the lower melting point than the trans isomer. Elaidic acid (*trans* "oleic acid") has a 34 °C higher melt point than oleic acid (the *cis* version).
The introduction of branching will also lower the melting point of the acid. One example is isostearic acid. Isostearic acid has a melting point 57 °C 23 °C lower than oleic acid.

D. Guerbet Branched Fatty Acids

An example of obtaining a very low melt point is to introduce beta branching (Guerbet branching) and lower number of carbon atoms, resulting in a very low melting point.

Color

The color of these esters was studied and compared. It was observed that the reaction time controlled color. The longer the reaction time, the darker the color. The reaction of the guerbet 20 fatty acid required a longer period of time to obtain a low acid value. This in turn led to a somewhat darker color. We attribute this to steric hindrance. The branching on the isostearic acid is much farther from the carboxyl group and has much less bulk. Consequently, the longer reaction time lead to a darker color.

REFERENCES

1. https://www.machinerylubrication.com
2. https://cosmetics.specialchem.com/product/i-phoenix-chemical-pelemol-ptis
3. http://www.chemicalbook.com/ProductChemicalPropertiesCB3918430_EN.htm
4. http://en.wikipedia.org/wiki/Neopentyl_glycol
5. http://en.wikipedia.org/wiki/Trimethylolpropane
6. http://en.wikipedia.org/wiki/Pentaerythritol
7. http://en.wikipedia.org/wiki/Oleic_acid
8. http://en.wikipedia.org/wiki/Erucic_acid
9. http://pubchem.ncbi.nlm.nih.gov//compound/21859 ■

Polyol esters in personal care formulations part 2*

TONY O'LENICK
Siltech LLC, Lawrenceville, USA

***Tony O'Lenick** is President of Siltech LLC. Tony has published six books, numerous articles and has over 300 patents. He received the 1996 Samuel Rosen Award, the 1997 Innovative Use of Fatty Acids Award and the 1996 Partnership to The Personal Care. Tony was President of the U.S. SCC in 2015 and is currently Education Chair of IFSCC.*

KEYWORDS: Esters, simple esters, polyol esters, pentaerythritol, neopentyl glycol, trimethylol propane, guerbet alcohol, skin feel, cushion, play time, slip, drag, soaping and dehydration.

ABSTRACT

As the quest for natural, renewable, biodegradable and green products continue there has been increased interest in working with a variety of esters and triglycerides. Esters when applied to the skin, not only act as emollients but also provide an aesthetic effect which can be varied by structure. This article is the second of two that deal with the formulation properties of polyol esters based upon specific highly branched polyols namely; neopentyl glycol (2 OH groups), trimethylol propane (3 OH groups) and pentaerythritol (4 OH groups). These esters find their main use in industrial lubrication because not only are they effective lubricants, they are oxidatively stable and have a relatively low viscosity when one considers their molecular weight.

The proper selection of esters for personal care product development often determines if the consumer perceives a smooth spreading, less oily feeling, dry product or a greasy wet product when applied to the skin. In short, the feel of a skin care formulation is very dramatically affected by the choice of ester in the oil phase.

TERMINOLOGY (1,2)

Emollient - an emollient is an ingredient that provides a barrier to the skin. An emollient minimizes natural moisture loss, preventing the natural evaporation of water and improving the smooth feel of the skin.

Dehydration is the leading cause of dry skin and for any moisturizer to really improve the condition of the skin it must first prevent, or slow, that natural moisture loss. Oils, and derivatives, are all emollients.

Slip - when you apply a cream, or lotion, to your skin the first thing that you notice is how it feels on your skin and how well it spreads across the skin. A sticky oil drags on the skin as you try to spread it, producing 'tack' or 'drag'. The absence of that 'tack' or the ability of the cream, or lotion, to spread smoothly without dragging the skin or causing any uncomfortable stretching, is called 'slip'. If you think of how a straight oil feels on the skin that is 'slip', or 'glide'.

Soaping - when you apply a cream, or lotion, to your skin the last thing that you notice is how well it absorbs into your skin and how much does not absorb and just slides around on the top of the skin ... when it won't rub in it will start to turn white on the skin as you spread it around and it just stays on the top rather than absorbing, that is referred to as 'soaping' (because of the white effect). This is also referred to as 'rub-out'.

The way in which oil phases interact with the skin is an important part of what is called *cosmetic elegance*. Oils placed on the skin generally are rubbed into the skin. This rubbing results in the spreading out of the oil. How the oil spreads and the amount of time it takes to spread are respectively referred to as *cushion* and *playtime*.
Think of a drop of honey applied to the back of the hand. Rubbing it with a finger results in spreading out of the honey. During the rub out, a film is formed between the finger and the back of the hand. The thickness of this film is generally what is referred to as *cushion*.
Honey has a good amount of cushion but ingredients like isopropyl myristate have little cushion. Cushion is related to the viscosity of the liquid, the volatility of the liquid, the surface tension of the liquid, and the tendency of the liquid to be absorbed into the skin. Cushion is an important cosmetic property of oils.
Cushion does not last forever, and the length of time it takes for the cushion to disappear is referred to as *playtime*. Similar to cushion, playtime is dependent upon a variety of factors intrinsic to the oil and how it interacts with the skin.
Generally, the cushion and the playtime are intrinsic properties of the molecule, where manipulation of the properties require molecular changes of the oil. Recently, it was found that the inclusion of minor amounts of surface-active materials to the oil can result in a change to the cushion, the playtime or both (3).

Data on ingredient usage are provided to the Food and Drug Administration (FDA) Voluntary Cosmetic Registration (4) Program (VCRP) and a survey conducted by the Personal Care Products Council (Council) collected use concentrations for ingredients in this group (5-12). The total number of VCRP reported uses of pentaerythrityl tetraisostearate was 532 for leave-on and 9 for rinse-off products and the Council survey found that pentaerythrityl tetraisostearate was used up to 0.1% - 55% (highest concentration in lipstick) in leave-on products and up to 0.1% in paste masks (mud packs), a rinse-off product. Table 3 summarizes the VCRP and Council survey data for all ingredients in this group.

Pentaerythrityl tetracaprylate/tetracaprate was reported to be used in 26 leave-on products at 0.07% - 5%; up to 1% in hair sprays.

Pentaerythrityl tetraethylhexanoate was reported to be used in 224 leave-on products up to 0.06% - 50% and 17 rinse-off products up to 1% - 20%. This includes suntan gels, creams, and liquids up to 16 % and other suntan products up to 21%, which may or not be spray products.

(1) Pentaerythrityl tetra caprylate / tetra caprate
(2) Pentaerythrityl tetra laurate
(3) Pentaerythrityl tetra stearate
(4) Pentaerythrityl tetra behenate
(5) Pentaerythrityl tetra isostearate
(6) Pentaerythrityl tetraethylhexanoate
(7) Pentaerythrityl tetraethylhexanoate/benzoate
(8) Pentaerythrityl tetra benzoate /ethylhexanoate

Table 1. Pentaerythritol Esters Used in Cosmetic Formulations (4).

These raw materials find use in both leave on and rinse off products in concentrations ranging from 0.07 to 7% by weight.

Application areas include:

(1) Eye Area
(2) Deodorant
(3) Hair non colorinh
(4) Haur Coloring
(5) Nail

Table 2. Cosmetic Use of Pentaerythritol Esters (4).

PENTAERYTHRITYL TETRAISOSTEARATE (PTIS)

PTIS is one of the most important members of this class of information. The following information in Table 3-6 is provided by Phoenix Chemical on their Pentaerythrityl Tetraisostearate.

PTIS is a rapidly absorbed emollient. It possesses cushion and a slight amount of drag. In addition to these attributes it has an extremely bland taste, making it particularly useful to lipstick and lip treatment formulas. For applications where shine is desirable, PTIS performs well because it imparts gloss to the skin.

PTIS is supplied as a 100% active, clear, straw-colored liquid that is compatible with a variety of personal care raw materials. This medium viscosity emollient is a valuable addition to the palettes of both color cosmetic and skin care formulators.

Trade Name	PELEMOL PTIS
INCI	Pentaerythrityl Tetraisostearate
CAS #	62125-22-8
EINECS	263-423-1
Japanese Code	520782

Table 3. Pentaerythrityl Tetraisostearate.

SOLUBILITY

WATER	i
PROPYLENE GLYCOL	i
ETHANOL	i
MINERAL OIL	m
ISODODECANE	m
ISOPROPYL MYRISTATE (PELEMOL IPM)	m
CASTOR OIL	m
CYCLOMETHICONE (DC 345)	m
DIMETHICONE (DC 200-100CST)	i
ISONONYL ISONONANOATE (PELEMOL IN-2)	m
PENTAERYTHRITYL TETRAETHYLHEXANOATE (PELEMOL PTO)	m
REFRACTIVE INDEX	1.467

i = insoluble
m = miscible (all %'s)

Table 4. Pentaerythrityl Tetraisostearate.

SAFETY

*RIPT Study (50 human subjects) conclusions follow:	
SKIN IRRITATION	NON-PRIMARY IRRITANT
SKIN SENSITIZATION	NON-PRIMARY SENSITIZER

PELEMOL PTIS can be considered for use in hypoallergenic products.
* Studies conducted by AMA Labs., 216 Congers Rd. New City, NY 10956

Table 5. Pentaerythrityl Tetraisostearate.

Table 6. Pentaerythrityl Tetraisostearate.

APPLICATION OF EMULSIONS TO THE SKIN

The application of oils to the skin from emulsions are a more complicated process than might meet the eye. Assume that an oil in water emulsion is the chosen for our moisturizer. The oil phase must be chosen to give easy spread, proper shear thinning and a suitable cushion and play time and the proper final skin feel. It is clear that the properties of the oil phase after the water evaporates is one important set of attributes for the moisturizer. However, equally important is the initial feel of the emulsion with the water present. The emulsion must have many of the same desired attributes as the oil phase, easy spread, proper shear thinning and a suitable cushion and play time and the proper final skin feel when the water is present. The emulsifier must be efficient enough to keep the emulsion together, but as the water evaporates, must not inhibit the oil phase from delivering the desired effect. Figure 1 shows the application of an oil in water emulsion to the skin.

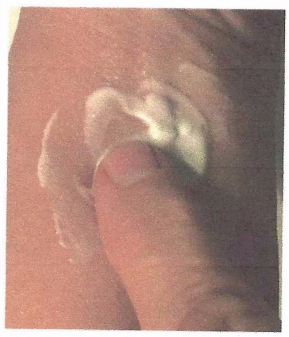


Figure 1. O/W Emulsion Application. There are clearly two different phases. In which an oil in water emulsion must deliver the desired effect, one with water present and one after the water evaporates.

In order to formulate a product that achieves the desired properties, both as applied with the water present and after the water evaporates and only the oil phase is present one must expand the type of oils used to formulate. Non-polar oils like mineral oil, polar oils like esters are commonly used. Recently, high molecular weight molecules with multiple esters present have been used to together with polar and non-polar oils to formulate highly efficient oil phases. Polyol esters provide unique aesthetic effects in personal care formulations.

Cushion

When comparing a series of products in which the polyol is kept constant and the fatty acid varied, the oleate has the lowest cushion of the series, the isostearate has more cushion than the oleate followed by the guerbet acid and the erucate having the highest amount of cushion

When comparing a series of products in which the acid is kept constant and the polyol varied, the neopentyl glycol ester has the lowest cushion of the series, the trimethylol propane ester next lowest and the pentaerythritol the highest cushion.

FORMULATION

When considering an ester for inclusion in a personal care formulation, it is appropriate to consider the interaction with all ingredients in the formulation, the area to which it will be applied, the presence or absence of fragrance and desired effect. Our conclusions are based upon the properties of the ester as is, not in formulation. The formulator is encouraged not to overlook synergies in blends. Simply put emulsions work best when the emulsifiers are paired, and cosmetic formulations work best when different types of oils are paired. One such blend is called Lorenzo's oil (13). Lorenzo's Oil is a combination of a 4:1 mix of oleic acid and erucic acid, extracted from rapeseed oil and olive oil designed to normalize the accumulation of the very long chain fatty acids in the brain thereby halting the progression of adrenoleukodystrophy (ALD).

MOLECULAR WEIGHT

Polyol esters have a high molecular weight and relatively low viscosity. This combination of properties, which also exist in silicone polymers, make them very interesting oil phases for use in personal care formulations. Variation is the number of esterified groups going form di-, tri- or tetra-functional hydroxyl compounds neopentyl glycol (2 esters), trimethylol propane (3 esters) and pentaerythritol (PE) (4 esters) provides a dramatic increase in the molecular weight of the ester, but as seen above a relatively small increase in viscosity, cushion or play time.

CONCLUSION

There are many different kinds of esters that are available to the formulator of personal care products. It is suggested that the formulator get samples of a variety of materials and become familiar with the viscosity, cushion, play time and other formulation properties. Just as there are a variety of different oily polymers that are used in personal care formulations with different properties, esters are likewise different in their contributions to formulations as oil phases. The inclusion of polyol esters in formulations offers another class of compounds that can provide different aesthetics to products.

Combination of polyol esters and simple esters in blends allow for the ability to provide products that have a very unique aesthetics, providing a great cushion with decreased play time. The dual system modifies the rheology of the product and the aesthetics.

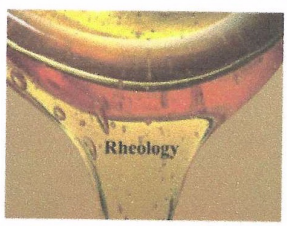


Figure 2. The ability to formulate oil phases that provide unique flow properties (rheology) and deposit uniform aesthetically appealing skin feel should be the goal of the formulator (14).

Polyol polyesters as oil phases in personal care formulations represents a new and highly effective additive for personal care applications. Unlike acrylate polymers the polyester when properly chosen in both biodegradable and not a plastic, offering a more natural approach to rheological modifiers (15-17).

REFERENCES

*T. O'Lenick, Chimica Oggi - Chemistry Today, September/October 5(14), pp 50-53, 2019

1. http://www.ingredientstodiefor.com/category/Emollients_Esters/c57/
2. https://www.cosmeticsandtoiletries.com/formulating/category/skincare/49539612.html
3. http://www.chemicalbook.com/ProductChemicalPropertiesCB3918430_EN.htm
4. https://www.cir-safety.org/sites/default/files/Pentae122011FINAL%20for%20posting.pdf
5. Personal Care Products Council. 11-7-2011. Concentration of Use Pentaerythrityl Tetraisononanoate and Pentaerythrityl Tetrapelargonate. Unpublished data submitted by Personal Care Products Council. 1 pages.
6. Personal Care Products Council. 11-16-2011. Updated Concentration of Use by FDA Product Category: Pentaerythrityl Tetraesters. Unpublished data submitted by Personal Care Products Council. 4 pages.
7. Personal Care Products Council. Updated Concentration of Use by FDA Product Category Pentaerythrityl Tetraisostearate, Pentaerythrityl Tetraabietate, Pentaerythrityl Tetraacetate, Pentaerythrityl Tetrabehenate, Pentaerythrityl TetrabehenatefBenzoate/Ethylhexanoate, Pentaery thrityl Tetrabenzoate, Pentaerythrityl Tetra C5-9 Acid Esters, Pentaerythrityl Tetra CS-b Acid Esters, Pentaerythrityl Tetracaprylate/Tetracaprate, Pentaerythrityl Tetracocoate, Pentaerythrityl Tetraethylhexanoate, Pentaerythrityl TetraethylhexanoatefBenzoate, Pentaerythrityl Tetralaurate, Pentaerythrityl Tetramyristate, Pentaerythrityl Tetraoleate, Pentaerythrityl Tetrapelargonate and Pentaerythrityl Tetrastearate. 2011. pp. 1-3. Unpublished data submitted by the Personal Care Products Council.
8. Personal Care Products Council. Concentration of use by FDA product category pentaerythrityl tetraisostearate, pentaerythrityl tetraabietate, pentaerythrityl tetraacetate, pentaerythrityl tetrabehenate, pentaerythrityl tetrabehenate/benzoate/ethylhexanoate, pentaery thrityl tetrabenzoate, pentaerythrityl tetra C5-9 acid esters, pentaerythrityl tetra C5-10 acid esters, pentaerythrityl tetracaprylate/tetracaprate, pentaerythrityl tetracocoate, pentaerythrityl tetraethylhexanoate, pentaerythrityl tetraethylhexanoate/benzoate, pentaerythrityl tetralaurate, pentaerythrityl tetramyristate, pentaerythrityl tetraoleate, pentaerythrityl tetrapelargonate and pentaerythrityl tetrastearate. 2011. pp. 1-3. Unpublished data submitted by the Personal Care Products Council.
9. Personal Care Products Council (Council). 2008. Concentration of use - Additional coconut oil-derived ingredients. Unpublished data submitted by Personal Care Products Council. 7 pages.
10. U.S.Food and Drug Administration. Defoaming agents used in the manufacture of paper and paperboard. http://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfCFR/CFRSearch.cfm?fr=176.210
11. http://www.ingredientstodiefor.com/category/Emollients_Esters/c57/
12. https://www.cosmeticsandtoiletries.com/formulating/category/skincare/49539612.html
13. http://en.wikipedia.org/wiki/Lorenzo%27s_Oil
14. http://slideplayer.com/slide/7057478
15. U.S. Patent 9,283,168, entitled Polyol Polyesters. to O'Lenick et al issued March 2016
16. U.S. Patent 7,989,648 entitled Esters to O'Lenick et al issued August 2011.
17. U.S. Patent 8,455,670 entitled Mixed Polyol Esters to O'Lenick et al issued June 2013. ■

Liquid esters

TONY O'LENICK[1], THOMAS O'LENICK[2]
1. Siltech LLC, Lawrenceville, USA
2. SurfaTech Corporation, Lawrenceville, USA

***Tony O'Lenick** is President of Siltech LLC. Tony has published six books, numerous articles and has over 300 patents. He received the 1996 Samuel Rosen Award, the 1997 Innovative Use of Fatty Acids Award and the 1996 Partnership to The Personal Care. Tony was President of the U.S. SCC in 2015 and is currently Education Chair of IFSCC.*

KEYWORDS: Liquid Esters, unsaturation, branching, guerbet alcohol, propoxylation, isostearic acid esters, 2 ethylhexyl esters, melting point, science for formulators.

ABSTRACT

Liquid esters are of interest in the formulation of personal care products for use as emollients, moisturizers, conditioners and aesthetic modifiers. The ability to control melting point is very useful in formulating skin care products. The options to make liquid products in the past were principally accomplished by (1) incorporation of unsaturation or (2) branching into the molecule. One particular branch type, the Guerbet branch is very effective for liquidity, but very expensive. Other less expensive branched materials and propoxylated linear esters were evaluated to determine their effectiveness in lowering melting point.

BACKGROUND AND INTRODUCTION

The ability to manufacture liquid, dry, cost effective esters for use in personal care products has long been a goal for manufacturers of cosmetic ingredients. This need has increased dramatically with the increased regulation on D5 in cosmetic products.
A great deal of work has been done in recent times to prepare liquid esters that provide benefit to hair and skin.
One very important benefit of such a product depending upon the exact structure is providing moisturization for the skin.
One mechanism for emolliency is to deposit of an oil on the skin that acts as a barrier to minimize transepidermal water loss. The process of transepidermal water loss is shown graphically in Figure 1. In this case liquid esters are of interest since they can easily form a thin oily film on the skin.

Esters based upon wax technology generally are neither effective nor have a desirable skin feel. There have been a number of approaches used to obtain liquid esters for use as moisturization agents.

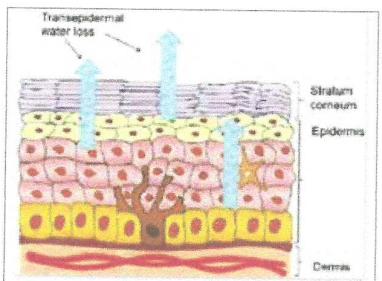


Figure 1. Transepidermal Water Loss (1).

One approach to getting functional liquid products has been the use of unsaturated hydrophobes. These materials include oleyl materials (C18 one unsaturation), linoleyl (C18 two unsaturation), eurucal products (C22 one unsaturation) and the like. This approach results in liquid products, but the products suffer from a process called rancidity. Rancidity is a process in which the double bonds present in the molecule is converted to an aldehyde, cleaving the double bond and producing an aldehyde that has half the molecular weight of the starting Unsaturated material. Unfortunately, these aldehydic compounds have a very bad smell and have been thought to be unacceptable in personal care product. The problem is likewise to occur in oils having unsaturation like soybean, rapeseed (also called HEAR oil) and olive oil. These oils have also been deemed unacceptable for personal care applications for rancidity considerations.

Materials having conjugated double bonds are much more likely to oxidize than two double bonds that are distant from each other. The conjugated double bond is an order of magnitude more reactive than the simple double bond. This makes the conjugated double bond very undesirable vis-a-vis cosmetic products. What is very important to note is that the aldehyde resulting from the rancidity process in addition to having mal odor also can react with fragrances to destroy their effectiveness. Because of malodor and generation of color using unsaturated esters, we have decided to look at other approaches.

INCI NAME (EU): Limnanthes Alba Seed Oil
INCI NAME (PCPC): Limnanthes Alba (Meadowfoam) Seed Oil
CAS NUMBERS: 153065-40-8, 169107-13-5
EC NUMBER: 604-884-4
JCLD: 552440 JSQI: 521124

Table 1. Meadowfoam seed oil.

It has been found that meadowfoam oil when added to an ester, can result in making a blend with improved oxidative stability.

A. Meadowfoam Seed Oil *(Limnanthes alba)*

Despite the fact that meadowfoam oil that is very high in unsaturation is nonetheless very stable to oxidation. This oil, and the derivatives thereof, overcomes many of the problems associated with other oils. The material is both intrinsically stable to oxidation due to the distance between the two double bonds, but also appears to possess a natural antioxidant that retards rancidity (Table 1).

Meadowfoam oil is a triglyceride derived from the herbaceous winter plant (Limnanthes Alba). It is grown in the southern portion of the State of Oregon. Since the flowers have an appearance of a canopy of white foam, the name meadowfoam was given to the plant. This material is a relatively new raw material and is unique in that it has both a high concentration of fractions at or above twenty carbons and it has a unique arrangement of double bonds. The fact that the double bonds in the doubly unsaturated product are not conjugated, as in linoleic acid, the oil is liquid to very low temperatures, and is stable to oxidation (Table 2).

Component	Typical % Weight
C20:1 (n= 5)	63
C20:2 (= 5, 13)	12
C22:1 (n= 5)	3
C22:1 (n= 13)	12
C22:2 (n= 5, 13)	10

Table 2. Carbon Distribution (2).

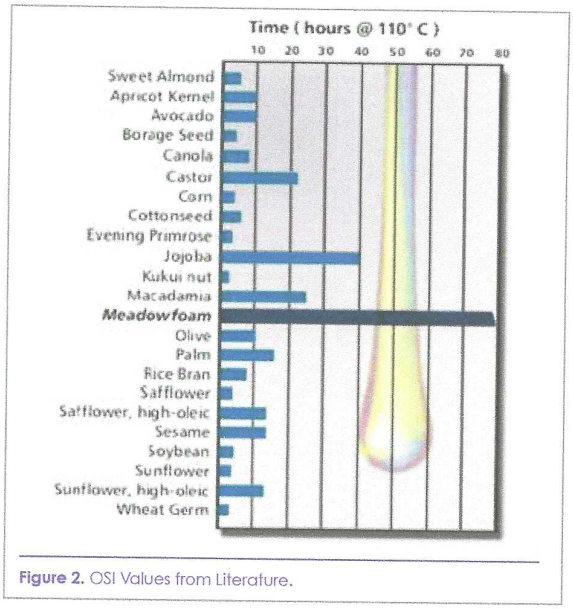


Figure 2. OSI Values from Literature.

Oil	No Blend	+20% MSO	+35% MSO
Meadowfoam Seed	80.80		
Sweet Almond	5.39	7.02	9.22
Borage	5.84	7.63	9.17
Evening Primrose	4.14	5.11*	6.14
Sunflower, high-oleic	12.90	15.20	18.20

Figure 3. OSI Values of Select Oils and Blends.

OXIDATIVE STABILITY INDEX (3)

Outstanding work has been done in evaluation Meadowfoam Seed oil by Natural Plant Products Inc, the results of which are shown below.

The Oxidative Stability Index (OSI) is becoming the most widely used method to assess stability in lipid materials. During the analysis, a sample of oil is exposed to a steady stream of air at a specified temperature. A computer measures subtle changes resulting from the degradation of the oil and creates a "portrait" of the oil resisting oxidation. The final result is reported as the number of hours required for the oil's resistance to be overcome (4).

Meadowfoam Seed Oil (MSO) is one of the most stable lipids known (Figure 2) (3). This high stability is due to the presence of naturally occurring tocopherols (antioxidants), and the absence of oxidatively susceptible polyunsaturated fatty acids common in other vegetable oils (5-8). OSI analyses were conducted on a variety of oils used in the cosmetic industry as well as on blends of those oils with Meadowfoam Seed Oil (Figure 2) (3). The results confirm Meadowfoam's superior stability, but more importantly show how Meadowfoam can be used to increase the stability of other oils (Figure 3) (3).

Effective use of oil blends incorporating Meadowfoam can result in increased stability and improved formulations showcasing the unique benefits of a range of natural oils (3).
The ability to transfer oxidative stability into blends of oils is an excellent development.

B. Guerbet Alcohols

A particularly potent branch pattern that can be introduced is the guerbet branch. Guerbet Alcohols have been known since the 1890s when Marcel Guerbet first synthesized these materials (9). The reaction sequence that bears his name is related to the Aldol Reaction and occurs at high temperatures under catalytic conditions (10).
The overall Guerbet reaction can be represented by the following equation (Table 3)

$$CH_3(CH_2)_9OH \dashrightarrow CH_3(CH_2)_9CHCH_2OH$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad CH_3(CH_2)_7$$

Table 3. Guerbet Alcohol Reaction.

Whilst a very interesting process and if properly chosen, a very effective one in making liquid products, the guerbet products suffer from high costs. This is due not only to the technical sophistication of the guerbet process, but also the high cost added to product by the various post process sequences used to refine and purify the product.

These steps include, but are not limited to, distillation (to increase purity), hydrofinishing (to lower unsaturation), washing (to remove soap), and filtration (to remove catalyst).

There is therefore a need for a cost-effective method to obtain a series of products that are liquid and have a range of melting points for cosmetic and other applications. It is interesting to note that the product is highly branched and a primary alcohol.

MELTING POINT

In order for a material to be a crystalline solid, the particles need to be arranged in a very regular, symmetrical manner so as to make up the repeating unit of the crystal. Liquid materials on the other hand are random is their order and move about freely. Melting is the change from orderly arrangement of a solid into a random liquid form. To the extent the forces that lead to an ordered system are destroyed, the melting point of a material decreases.

Stated another way, the amount of energy necessary to disrupt the organized structure of a solid making it a liquid (i.e. melting it), decreases for those molecules that have structural features that tend to prevent disrupt the crystalline structure. This is the precise reason that branching lowers melting point. The branched molecule rotates more rapidly as the temperature increases until the crystalline structure is destroyed. A particularly striking example of the effect of symmetry on melting point is seen by comparing the melt point of benzene with that of toluene. The presence of the methyl group in the toluene lowers the melting point from 5°C to –95°C (8) ! The raw materials used in the synthesis are shown in Table 4.

CH_3-$(CH_2)_{16}CH_2OH$	Stearyl Alcohol
$CH_3(CH_2)_9$-CH-CH_2-OH $(CH_2)_7$- CH_3	Guerbet Alcohol
CH_2 ----CH- CH_3 O	Propylene Oxide

Table 4. Raw Materials.

1. Propoxylation of Stearyl Alcohol

The propoxylation reaction is carried out by reaction propylene oxide with stearyl alcohol under base catalyst. The product that results is a methyl branched alcohol having three more carbon atoms, an additional oxygen atom, and a new ether linkage. As importantly, the new molecule has predominantly a secondary hydroxyl group (-CH-(CH_3)OH), rather than the primary one (-CH_2OH) that previously was present. As will hopefully become clear, the presence of the methyl group and the number of moles of propylene oxide added (the "n" value) will determine in large degree the melting point of the ester produced by reacting the propoxylated alcohol with various fatty acids. The reaction is shown in Table 5.

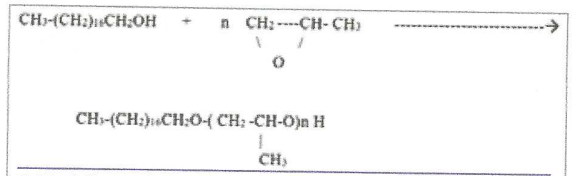


Table 5. Propoxylation of Stearyl Alcohol.

EXPERIMENTAL

Stearyl Alcohol was propoxylated to make the following compounds:

CH_3-$(CH_2)_{16}CH_2O$-(CH_2-CH-O)n H
CH_3

The number of moles of propylene oxide added (the so called "n" value) is shown in Table 6.

Designation	n value
O	0.0
A	0.7
B	1.5
C	2.2

Table 6. Products Prepared.

The analytical results are shown in Table 7.

	O	A	B	C
Color (Gardner)	1	1	1	1
Appearance 50oC	Clear	Clear	Clear	
Clear				
pH 1% Aqueous	7.0	7.0	6.9	6.8
Acid Value	0.0	0.06	0.05	0.03
Hydroxyl Value	208.7	181.2	161.2	139.3
Moisture (%)	0.1	0.1	0.1	0.1
Titer point (oC)	49	38	31	27

Table 7. Analysis Propoxylated Alcohol.

2. Stearate Esters

The resulting propoxylated alcohols were then reacted with stearic acid as shown in Table 8.

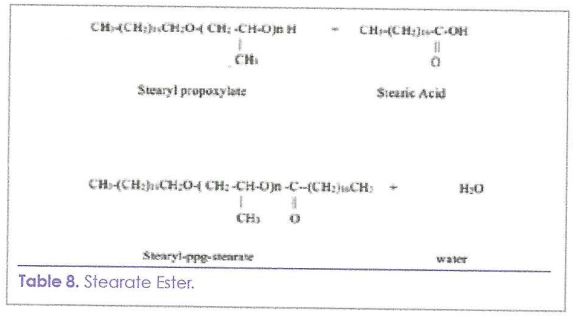


Table 8. Stearate Ester.

The analytical data is shown in Table 9.

	S-O	S-A	S-B	S-C
Color (Gardner)	5	4	3	3
Appearance 50oC	Clear	Clear	Clear	Clear
Acid Value	2.0	3.1	2.9	3.8
Hydroxyl Value	7.6	6.8	8.0	7.0
Saponification Value	104.5	97.2	89.7	84.0
Titer point (°C)	51	41	38	29

Table 9. Analysis propoxylated stearyl stearate.

3. iso-Stearate Esters

The resulting propoxylates were then reacted with stearic acid. The reaction is shown in table 10.

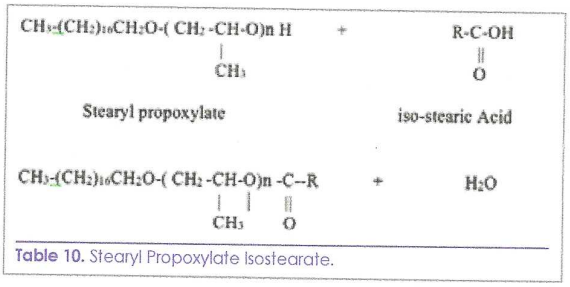


Table 10. Stearyl Propoxylate Isostearate.

The analysis is shown in Table 11.

	i-S-O	i-S-A	I-S-B	i-S-C
Color (Gardner)	4	4	3	3
Appearance 50oC	clear	clear	clear	clear
Acid Value	3.0	4.1	3.7	2.8
Hydroxyl Value	7.9	8.2	7.7	6.8
Saponification Value	104.8	98.3	89.9	85.0
Titer point (oC)	26	20	15	12

Table 11. Analysis propoxylated stearyl iso-stearate.

4. 2-Ethyl Hexanoic Esters

The resulting propoxylated products were then reacted with stearic acid as shown in Table 12.
Analysis is shown in Table 13

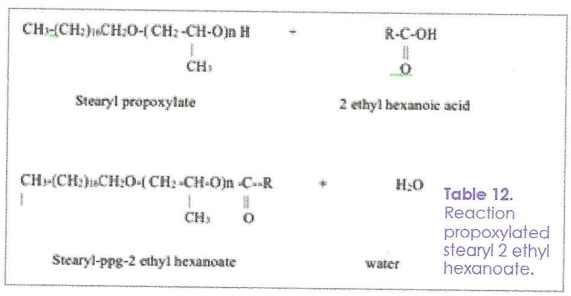
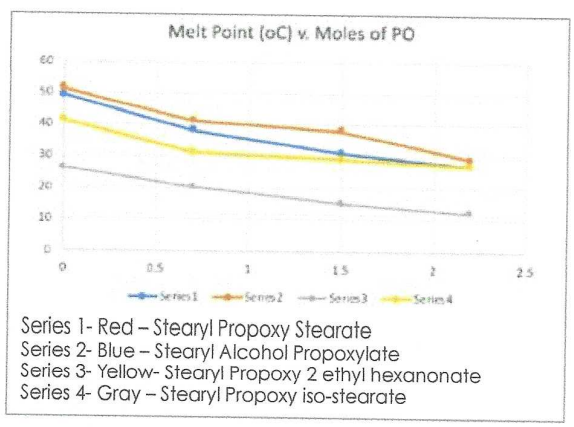


Table 12. Reaction propoxylated stearyl 2 ethyl hexanoate.

	2EH-O	2EH-A	2EH-B	2EH-C
Color (Gardner)	4	4	3	3
Appearance 50oC	clear	clear	clear	clear
Acid Value	2.6	3.2	4.1	3.8
Hydroxyl Value	7.6	7.2	6.4	7.7
Saponification Value	141.3	129.0	116.0	106.7
Titer point (oC)	41	31	29	27

Table 13. Analysis Propoxylated stearyl 2-ethyl hexonate.



Series 1- Red – Stearyl Propoxy Stearate
Series 2- Blue – Stearyl Alcohol Propoxylate
Series 3- Yellow- Stearyl Propoxy 2 ethyl hexanonate
Series 4- Gray – Stearyl Propoxy iso-stearate

DISCUSSIONS AND CONCLUSIONS

1. The propoxylation of stearyl alcohol prior to esterification results in the lowering of melting point for all the compounds studied. This confirmed the effect of branching upon melting point. Melting points of the alcohol were dropped by over 20oC by adding 2.2 moles of propylene oxide to the stearyl alcohol. Likewise, significant melting point reductions were encountered when esters were evaluated.
2. The current study added up to 2.2 moles of propylene oxide to the hydrophobe. The melting point of the propoxylate and of all derived esters were still dropping at the 2.2 mole level (relative to the lower levels). This was a surprise, since it was felt that at the 2.2 mole level the effectiveness of the oxide on liquidity would begin to drop essentially to zero. It is interesting to note that at 2.2 moles the percentage of propylene oxide added is 32.4% by weight.
3. It was likewise a surprise that the esterification of the stearyl propoxylate resulted in only a very modest increase in melting point, relative to the starting alcohol propoxylate.
4. A very significant increase in molecular weight occurred, but a marginal change in melting point was noticed.
5. The 2 ethyl hexyl esters were less efficient in lowering the melting point of the resulting esters than were the isostearate. This was a surprise, since the 2-ethyl hexanoic acid is both lower molecular weight (C8) and more branched than the C-18 branched iso-stearate. The propoxylated stearyl alcohol isostearate compounds had the lowest melting point of any of the homologous series studied.
6. We believe that the reaction of fatty alcohols with propylene oxide, then subsequent derivization will allow for the synthesis of a new class of compounds with very desirable properties on the skin.
7. The results are consistent with Carnelley's rule. It states, "of two or more isometric compounds, those whose atoms are the more symmetrically and the more compactly arranged melt higher than those in which the atomic arrangement is asymmetrical or in the form of long chains."
8. The ability to control melting point in waxes is an important part in the development of oil phases that offer cosmetically elegant properties to formulations. These can be controlled by unsaturation if a suitable antioxidant is available, or well chosen branching introduced into the molecule.

REFERENCES

1. skincareblog.squarespace.com
2. O'Lenick, Anthony, Steinberg, David , Klein, Kenneth and LaVay, Carter Oils of Nature Allured Publishing 2008, p. 76.
3. https://meadowfoam.com/wp-content/uploads/2016/09/MSO_OSI_Values_05242016.pdf.
4. AOCS Cd 12b-92 and ISO 6886
5. Abbott Thomas and Wohlman Alan U.S. 7,053,243 entitled *3-Methoxybenzyl thiourea derivatives and improved lipid compositions containing same* issued May 30, 2006.
6. Abbott Thomas and Wohlman Alan U.S. 6,653,505 entitled *3-Methoxybenzyl thiourea derivatives and improved lipid compositions containing same* issued November 25, 2003.
7. Abbott Thomas and Wohlman Alan U.S. 6,586,628 entitled *3-Methoxybenzyl thiourea derivatives and improved lipid compositions containing same* issued July 1, 2003
8. Wohlman Alan and O'Lenick Anthony U.S. entitled Methods and compositions for inhibiting free radical polymerization in skin and hair issued April 8, 2003.
9. M. Guerbet, C.R. Acad. Sci. Paris, 128, 511; 1002 (1899)
10. O'Lenick, Jr. Anthony J. and Bilbo, Raymond E., Guerbet Alcohols, Versatile Hydrophobes, SCCS, April,1987.
11. Morrison, Robert and Boyd, Robert, Organic Chemistry, 3rd Edition, (1973) p. 582.
12. Yalkowsky, S. H. (2014). Carnelley's rule and the prediction of melting point. *Journal of Pharmaceutical Sciences, 103*(9), 2629-2634. https://doi.org/10.1002/jps.24034. ■

Emollients in personal care: our songs to create your formulation playlists

ELISA ALTIERI*, PAOLO SARONNI, STEFANO FERRIGATO
Zschimmer & Schwarz Italiana S.p.A.

Abstract

Several different emollients were investigated to understand the correlation between their structure and their sensory properties. Furthermore, the emollients were also compared with synthetic mineral oils in order to have a complete overview of emollients. In this study, we will show you how to choose the proper emollients in order to achieve the desired sophisticated sensory effect in your skin care or make-up product. Let yourself be inspired by emollients and follow your own rhythm and creativity when designing your own formulation playlist.

Keywords

- Emollients
- Spreadability
- Lubricity
- Absorbency
- Esters
- Sensory cascade
- Playtime
- Science for formulators

INTRODUCTION

Looking at the ingredients used in most cosmetic products, you will always find some kind of emollient in the formulation process. Thanks to their properties and their global approval, emollients are one of the favourite ingredients of cosmetic formulators.

Emollients have the "cosmetic mission" to provide a velvety, smooth and soft feel to the final product. "Emollient" is in fact derived from the Latin term "mollis", which means soft. "Emolliency", which refers to the spreadability and lubricity the formulators aim to achieve in a product, has the same origin. Emollients also majorly influence physicochemical properties such as the consistency and spreadability of the emulsions in which they are included.

Considering their effect on the skin, emollients can be regarded as a replacement for natural lipids: they contribute to the water retention of the stratum corneum, leaving a film on the skin that can last for hours (1).

Lipophilic emollients are one of the most commonly used ingredients in cosmetic emulsions; in the past were naturally represented by oils and fats. However, they can also be obtained by chemical synthesis. Considering their chemical structure, they are classified as either "nonpolar" or "polar" substances, although this polarity parameter is hardly ever determined or given (2). However, regardless of their polarity, emollients offer a myriad of sensations and textures when applied to the skin because they play an important part in the ***sensory cascade process*** of the cosmetic product, which is also called ***cosmetic elegance*** (3).

The aim of the present study is to inspire formulators to create unique playlists, imagining emollients as songs which, properly combined, create the desired mood.

MATERIALS & METHOD

Materials

In this study 24 emollients of different nature and chemical structure were analysed, including three commonly used synthetic emollients. The materials are described in Table 1.

	Emollient	Tradename
1	C12-15 Alkyl Benzoate	ZETEMOL AB
2	Caprylic/Capric Triglyceride	ZETEMOL GTCC
3	Cetearyl Ethylhexanoate	ZETEMOL CSO
4	Decyl Oleate	ZETEMOL DO
5	Dicaprylyl Ether	ZETEMOL OE
6	Diethylhexyl Sebacate	ZETEMOL OSB
7	Ethylhexyl Cocoate	ZETEMOL OC
8	Ethylhexyl Laurate	ZETEMOL OL
9	Ethylhexyl Palmitate	ZETEMOL OP - RSPO - MB
10	Ethylhexyl Stearate	ZETEMOL OS - RSPO -MB
11	Isoamyl Laurate	ZETEMOL 512
12	Isodecyl Neopentanoate	ZETEMOL IDN
13	Isononyl Isononanoate	ZETEMOL 99
14	Isostearyl Isostearate	ZETEMOL 2IS
15	Isostearyl Neopentanoate	ZETEMOL 518
16	Isostearyl PCA	SEBUMOL SPC
17	Myristyl Lactate	ZETEMOL AL - RSPO - MB
18	Octyldodecyl PCA	SEBUMOL ODPC
19	Oleyl Oleate	ZETEMOL OLO
20	Pentaerythrityl Tetraisostearate	ZETEMOL 5418
21	PPG-15 Stearyl Ether	OXYPON SP 15
22	Cyclopentasyloxane (D5)	
23	Dimethicone (350)	
24	Paraffinum Liquidum (170)	

Table 1. Emollients.

Method

All abovementioned emollients were analysed evaluating two of their most important properties:

- Absorbency as the transfer rate of a liquid to a solid surface. The transfer can occur naturally – by gravity – or thanks to a force applied to the liquid.
- Spreadability or lubricity as a reduction of friction between two solids, one stationary and one in motion, by means of a layer of liquid placed between them. In cosmetics, the emulsions placed on the skin generally need to be rubbed into the skin. The time it takes to spread these ingredients on the skin is defined as playtime.

Absorbency

The emollient droplets were deposited on a porous support (cellulose filter paper) equipped with a millimetre grid.
All absorbency data were obtained by taking a picture every 10 minutes and calculating the area covered by the single ingredients with the help of the grid.

Spreadability

For the data on spreadability (or lubricity), we adapted a scientific instrument to our needs which is especially well-known in the hair care sector: the Dia-Stron MTT 175 (Figure 1).

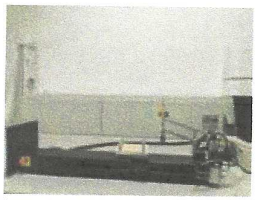


Figure 1. Picture of the "adapted" instrument, the Dia-Stron MTT 175.

The analysis of the emollients' spreading properties was performed using a kidskin substrate[a], a material as close as possible to human skin. Its surface had been pre-treated in order to mimic the porosity and roughness of the skin of the face and body.

A quantity of 0.5 g of a single emollient was placed on this support. Then, the neoprene probe was moved across the support, and the ease with which it was gliding was registered. Data related to the friction between the two parties were analysed using the installed software. The lubricity of the series of emollients was determined.

RESULTS

In the first part, results focus on the diffusion by gravity (absorbency) of 24 emollients. In the second part, their spreadability is discussed in detail.

Results in terms of absorbency

This test was performed in duplicate for each emollient, setting the ingredients on the porous substrate and monitoring the trial for 30 minutes. A series of photographs was taken at set times: after 1 minute, 10 minutes and 30 minutes, respectively. With the help of the unit area of the millimetre substrate, we could identify the areas for each product. The sum of all the unit areas wetted by the emollient at the same time (10 minutes) corresponds to the absorbency area of the analysed emollient.

Figure 2 illustrates the results of each mean absorbency value expressed in mm²/10 minutes for each emollient in increasing order.

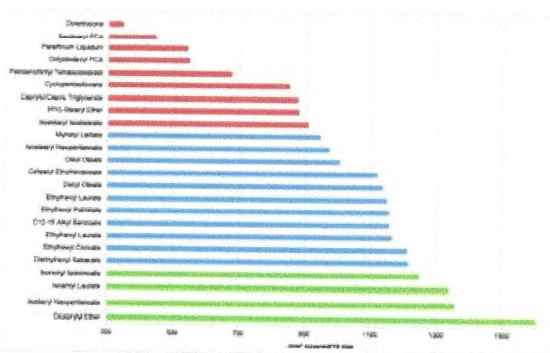


Figure 2. Absorbency areas of each emollient in increasing order.

According to the resulting data, we classified the selected emollients in three different categories: low absorption (red), medium absorption (light blue) and high absorption (green). The above results are in line with the dynamic viscosity data obtained from Brookfield DV2T (Spindle 61, 20 °C, 20 rpm) and the calculated kinematic viscosity.

As can been seen in Table 2, the measured absorbency is directly proportional to the kinematic viscosity of the emollients, with cyclopentasiloxane being the only exception: indeed, low absorbency values and with low viscosity occur. The different behaviour of this emollient lies in the chemistry of silicones: due to their low polarity, absorbency is difficult. However, it is still problematic to apply the term "polarity" to all the ingredients, particularly to mineral oil, because their precise composition is not known (4).

Product	Density	Dinamic viscosity (20°C, measured)	Dinamic viscosity (20°C)	Kinematic viscosity	Kinematic viscosity
Trade name	g/cm³	cPs	(g/cm*s) - Ps	(cm²/s) - St	cSt
Dicaprylyl Ether	0.806	3.60	0.036	0.0447	4.4665
Isodecyl Neopentanoate	0.855	4.20	0.042	0.0491	4.9123
Isoamyl Laurate	0.856	6.00	0.060	0.0701	7.0093
Isononyl Isononanoate	0.854	6.60	0.066	0.0773	7.7283
Diethylhexyl Sebacate	0.913	18.00	0.180	0.1972	19.7152
Ethylhexyl Cocoate	0.859	7.50	0.075	0.0873	8.7311
Ethylhexyl Stearate	0.857	12.60	0.126	0.1470	14.7025
C12-15 Alkyl Benzoate	0.929	12.40	0.124	0.1335	13.3477
Ethylhexyl Palmitate	0.857	12.00	0.120	0.1400	14.0023
Ethylhexyl Laurate	0.858	6.30	0.063	0.0734	7.3427
Decyl Oleate	0.872	17.10	0.171	0.1961	19.6301
Cetearyl Ethylhexanoate	0.854	12.30	0.123	0.1440	14.4028
Oleyl Oleate	0.870	23.10	0.231	0.2655	26.5517
Isostearyl Neopentanoate	0.859	15.30	0.153	0.1781	17.8114
Myristyl Lactate	0.906	15.90	0.159	0.1755	17.5497
Isostearyl Isostearate	0.867	48.30	0.483	0.5571	55.7093
PPG-15 Stearyl Ether	0.942	78.00	0.780	0.8280	82.8025
Caprylic/Capric Triglyceride	0.943	26.40	0.264	0.2800	27.9958
Cyclopentasiloxane (D5)	0.950	4.50	0.045	0.0474	4.7368
Pentaerythrityl Tetraisostearate	0.920	330.00	3.300	3.5870	358.6957
Octyldodecyl PCA	0.933	367.80	3.678	3.9421	394.2122
Isostearyl PCA	0.928	762.00	7.620	8.2112	821.1207
Dimethicone (350)	0.955	312.00	3.120	3.2670	326.7016
Paraffinum liquidum (170)	0.835	143.40	1.434	1.7174	171.7365

Table 2. Results of the density measurements, dynamic and kinematic viscosity of 24 emollients.

Results in terms of spreadability

The second part of this study was performed by precisely adapting the substrate friction test module of the Dia-Stron MTT 175 to our scope.

For each ester, two tests were carried out, depositing the same quantity of the product on a portion of substrate for 30 minutes. Under the terms of the method developed in our own lab 30 cycles were run with a speed off to 400 mm/min. The trial was also performed under the same conditions without any sample for control.

Figure 3 illustrates the graph obtained for the emollient Diethylhexyl Sebacate as well as for the control. It represents the force (in Newton) employed by the probe to slide on the surface.

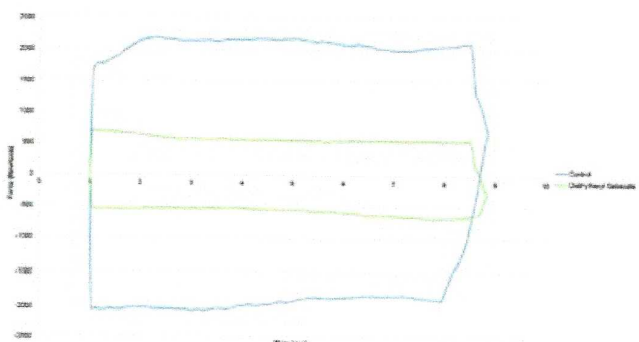


Figure 3. Force vs. time of Diethylhexyl Sebacate including control.

Conventionally, the probe's round-trip is represented as a chart, the upper part (x-axis) of which shows the forward path of the probe and the lower part (X axis) illustrating the way back. The total force applied appears as a closed cycle obtained from the average of cycles.

Figure 4 shows the charts of the 24 emollients, thus allowing a global comparison with all analysed ingredients and the control.

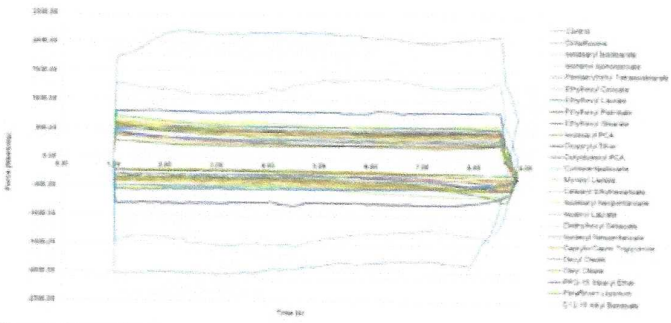


Figure 4. Force vs. time of all selected emollients including control.

Figure 5 presents the same data but expressed as total work (in Joules) of the selected emollients. These results sum up the difficulty of the probe to spread the product across the skin: they represent the area under the registered curves in Figure 4.

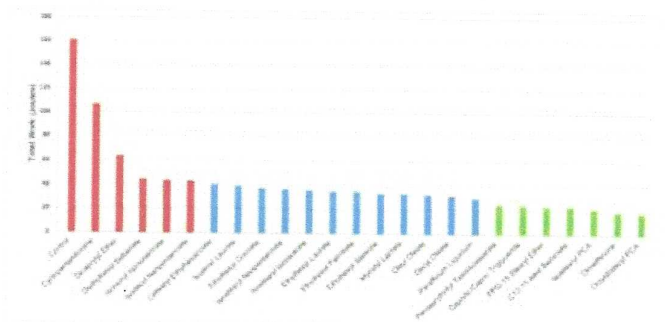


Figure 5. Total work of emollients expressed in Joules.

Based on these results, it can be observed that the 24 emollients fall in three distinct clusters: high, medium and low lubricity. A lower value of total work corresponds to a higher lubricity of the emollient. Lubricity is a relevant parameter because it is related to the perceived skin feel of the cosmetic cream when applied to the skin, which corresponds to spreadability.

In this case, the two silicones exhibited a different behaviour as well. The high viscosity of dimethicone did not result in difficulty in terms of spreading; it showed values of spreadability similar to those of other ingredients. Cyclopentasiloxane exhibited unique characteristics: its spreadability was approximately twice as high as that of the other emollients.

DISCUSSION

The previous results highlight that it is possible to discriminate between different clusters of emollients according to their absorbency and spreadability.

The obtained data could be used during the development of new cosmetic preparations: different emollients could be selected from their clusters in order to provide different sensory characteristics (5).

Thanks to this study, it is now possible to choose the emollients that provide exactly the required characteristics to create a formulation with the desired sensory cascade (6) – or, in musical terms, a playlist that fits a certain the mood. Emollients with rapid absorbency and high spreadability give smoothness and softness to the skin, but only for a very short time; emollients with both lower absorbency and spreadability provide less smoothness but create a rich texture and long-lasting nourishing effect.

When you create a playlist for a specific mood or for an occasion with specific requirements, such as your morning workout, you only want to select songs that fit it perfectly. In our example, you would only choose upbeat songs with a pumping beat to create a motivational playlist that gets you excited. Translated to cosmetics: when a body cream formulation for dry skin is required, for example, a specific emollient mixture needs to be defined. Thanks to the tools already identified and discussed, the formulator can select and pick the emollients that perfectly fit the requirements of dry skin and determine the amount required of each of them.

To obtain a rich body cream with a total oily liquid content of 19%, we chose three esters according to two important criteria: easy spreading (considering the wide area of application, that is, the whole body) and low absorbency in order for the cream to remain on the skin for as long as possible to create a deeply moisturising sensation. Looking at the charts in Figures 2 and 5, we selected a rich ester, Pentaerythrityl Tetraisostearate, for its low absorption combined with high spreadability and viscosity, and Isononyl Isononoate, a light ester to improve the gliding over the skin, at 8% and 5%, respectively, in the final formulation. To complete the "sensory cascade", Ethylhexyl Palmitate, an ester with medium absorbency, was added. The aforementioned ingredients were selected as they are protective emollients that leave an oily film on the skin that lasts several minutes.

The resulting ester blend was tested with the same methods mentioned above, obtaining the following chart (Figure 6). The absorbency of the ester blend is higher than that of the heaviest emollient, Pentaerythrityl Tetraisostearate, thanks also to the synergistic effects of the two lighter esters.

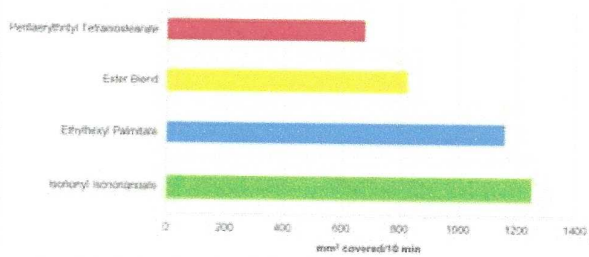


Figure 6. Absorbency of single emollients vs. blend.

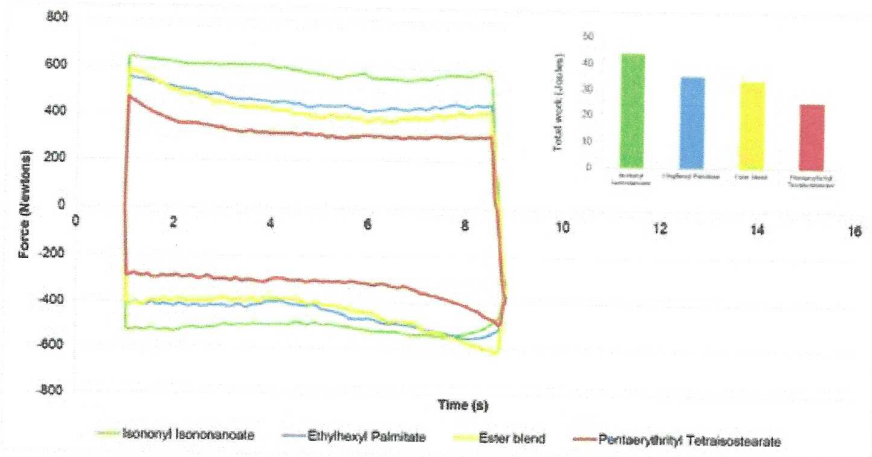


Figure 7. Spreadability of single emollients and blend.

The presence of the two lighter esters – even in smaller amounts – is essential to pull down the kinematic viscosity of the heaviest ester, thus promoting its absorbency and increasing its spreadability.

As regards spreadability, Figure 7 depicts the highly required lubricity of the ester blend, which is mainly due to Pentaerythrityl Tetraisostearate. Thanks to its high concentration, it is possible to obtain a rich emollient cream for dry skin with an easy spreadability and smoothness without any greasy and oily skin feel.

The lubricating properties of the ester blend are additive, and they are balanced by the dosage used in the formulation.
Another important aspect is that emollients are the key ingredients that influence the skin feel during the development of new cosmetic preparations. However, other ingredients like texturisers, emulsifiers and rheological modifiers help to define the desired sensory profile as well.

The emollients analysed in this study are a valid eco-friendly and cost-effective alternative to build extremely pleasant sensory textures.

CONCLUSION

The present study aims to provide a tool for the formulator to better understand the sensory contribution of the analysed emollients, thus enabling her or him to choose and combine them to obtain the desired sensory effect. The absorbency and spreadability values of emollients are particularly important during the "rub-out phase" of the cosmetic product, i.e., when it is being applied to and spread across the skin (7). Emollients also deserve to be recognised for their impact on the skin feel and appearance of personal care formulations (oily, greasy, glossy, velvety, matt, etc.).

The accurate results obtained in this study are a perfect starting point for designing a cosmetic product with the required texture as well as the desired sensorial profile and for finding effective alternatives to silicones and mineral oils. To revert to the musical imagery used earlier: Our results help you categorise all the songs on your MP3-player by certain parameters so you can create a playlist that perfectly fits your mood.

REFERENCES

a The use of this support, which is slaughter waste, does not in any way infringe animal testing legislation.

1. B. Gabard. "Testing the efficacy of moisturizers". In: Bioengineering of the Skin: Water and the Stratum Corneum (P. Elsner, E. Berardesca and H. Maibach, eds.) (1994), 147–167, CRC Press, Boca Raton, FL.
2. D. Terescenco, C. Picard, F. Clemenceau, M. Grisel, G. Savary. "Influence of the Emollient Structure on the Properties of Cosmetic Emulsion Containing Lamellar Liquid Crystals", Colloids and Surfaces A 536 (2018), 10–19.
3. O'Lenick. "Polyol Esters in Personal Care Formulations Part 2", Science for Formulators, H&PC, vol. 14 (6) November/ December 2019, 36–40.
4. D. Terescenco, C. Picard, F. Clemenceau, M. Grisel, G. Savary. "Influence of the Emollient Structure on the Properties of Cosmetic Emulsion Containing Lamellar Liquid Crystals", Colloids and Surfaces A 536 (2018), 10–19.
5. M. E. Parente, A. Gámbaro, G. Solana, "Sensory characterization of emollients", J. of Sens. Stud. 23 (2008), 149–161.
6. F. Wilson, D. Loughran, "The link between function and structure of esters", Personal Care Europe, November 2017, 57–60.
7. P. Dubuisson, C. Picard, M. Grisel, G. Savary. "How does composition influence the texture of cosmetic emulsions?" Colloids and Surfaces A 536 (2018), 38–46.

ABOUT THE AUTHOR

Elisa Altieri is Ph. D. (Doctor Europaeus) in Chemical Sciences at Messina University, finalizing her studies at Institute of Organic Chemistry (PAS) of Warsaw.
After several years as Sales and Product Manager for Personal and Home Care in different companies, she joined Zschimmer & Schwarz in July 2019 as Global Marketing Manager for the Personal care division.