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▶ **To cite this version:**

Daria Terescenco, Nicolas Hucher, Celine Picard, Géraldine Savary. Sensory perception of textural properties of cosmetic Pickering emulsions. International Journal of Cosmetic Science, 2020, 42 (2), pp.198-207. 10.1111/ics.12604 . hal-02612551

HAL Id: hal-02612551

https://normandie-univ.hal.science/hal-02612551

Submitted on 19 May 2020

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SENSORY PERCEPTION OF TEXTURAL PROPERTIES OF COSMETIC PICKERING EMULSIONS

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KEYWORDS

Emulsion
Formulation/stability
Delivery/vectorisation/penetration
Pickering
Particle stabilization
Sensory analysis

ABSTRACT

OBJECTIVE: The increasing interest for the Pickering emulsions is based on the possibility to replace classical emulsifiers by the solid particles. This approach is extremely attractive for the cosmetic field. But, the main difficulty is to obtain stable emulsions with appreciable skin feel. However, there is no information about the texture of such systems. The aim of this study is to formulate and describe the textural properties of cosmetic Pickering emulsions compared to conventional systems.

METHODS: Three metal oxides were selected: titanium dioxide, zinc oxide and silicon dioxide, able to form stable and totally emulsified systems. A conventional emulsifier was used to formulate the emulsion of reference. Finally, the mixture of two emulsifying systems, combining both, surfactant and particles, was also studied. Then, a sensory panel was asked to quantify the intensities of the perception of the seven discriminating attributes.

RESULTS: Each particle brought its properties to the textural perception of the emulsion. TiO_2 particles ensured the *whitening effect* of the emulsions, SiO_2 provided the *screech* residue, while ZnO gave intermediate results. The conventional surfactant was perceived as *glossy*, *greasy* and more *difficult to spread*. The particle/surfactant mixtures gave mostly in-between results.

CONCLUSIONS: The study shows that the sensory profile of Pickering emulsions is indirectly and directly governed by the particle properties used for the emulsion stabilisation: indirectly, through affecting the

emulsion orientation (oil in water or water in oil), the droplet organisation and viscosity, and directly, through the particle perception on the skin surface.

INTRODUCTION

The main interest of Pickering emulsions is the possibility to replace conventional emulsifiers with solid particles [1,2]. An important number of solid particles, of different characteristics, were studied in the literature able to stabilise the interface of two non-miscible liquids: clay, chitosan, cyclodextrin [3], starch [4], iron oxides [5], titanium dioxide [6], silica [7–10], etc.

Pickering emulsions are considered as stable when droplets are completely stable to coalescence and their size does not evolve over time [11]. Although all these emulsions are completely stable to coalescence, oil external (W/O) Pickering emulsions can sediment and water external (O/W) ones can cream under gravity [12]. This two processes, considered as destabilisation mechanisms for classical emulsions [13], are accepted by the authors in case of Pickering emulsions. In fact, they do not induce the droplet evolution, but only the macroscopic droplet reorganisation. For example, Binks and Lumsdon [14] made the difference between the creaming of an O/W emulsion and the coalescence: "The stability of o/w emulsions to creaming was assessed by monitoring the increase with time of the position of the clear water (serum)-emulsion interface, whereas the coalescence extent was estimated from the movement of the oil-emulsion boundary." In this case, the final system, considered stable over time, is finally not homogenous, due to the gradual distribution of the droplets in the continuous phase. Consequently, the macroscopic study of such a system becomes difficult, the separated phase should be avoided when the sample is collected [15]. Consequently, in order to use this type of emulsions in food, pharmaceutical and cosmetic fields, one should also guarantee the emulsions total emulsification.

Pickering emulsions, due to their physical stability [16], can be potentially used as delivery systems of actives in biomedical [17] and food applications [18,19], or pharmaceutics and cosmetics [20,21], namely for all-*trans*-retinol [9,22] or caffeine [23] skin delivery.

The sensory analysis is essential when developing products with further applicative interest. It was largely described for cosmetic raw materials and emulsions [24–29], but only a few results were given for Pickering emulsions. Marto *et al*. [4] evaluated the textural properties of the Starch-based emulsions using a simple sensory questionnaire in which the basic characteristics, i.e. texture and skin feel, were evaluated by the volunteers. In their work, the authors were mostly focused on the oil phase-type in starch-stabilised emulsions and their results did not discriminate the products according to the analysed parameters. Marku *et al.* [21] developed Pickering emulsions stabilised by octenyl succinic anhydride-modified quinoa starch containing three different oil phases. A small panel of volunteers was recruited to scale the intensities of the visual appearance of the formulation, the feel of the cream (thick, sticky, slippery, watery), the skin feel during and after absorption. The results of this study gave an interesting perspective of the oil phase impact on the sensory perception but did not explain the impact of the particle on the studied parameters. Besides, only usual attributes for the cosmetic emulsions were selected, without analysing the perception brought by the starch particles.

Considering Pickering emulsions stabilised with inorganic particles, there is until recently no information in the literature about their textural properties [30].

The authors developing such systems with silica particles are more focused on the emulsions capacity to play the role of the vehicles for the active ingredients and their diffusion in the *Stratum Corneum* [9,23,31] with no information about the sensory profile of the formulations. Other inorganic particles of the great interest for

the formulation of the Pickering emulsions are titanium dioxide and zinc oxide. Usually, TiO_2 and ZnO are used in sunscreens for the sensitive skin and for the sunscreens with high sun protection factor [32], but they can also play the role of both, emulsion stabiliser and photo protector, by using an important quantity of physical filters (35%) of titanium dioxide and/or zinc oxide type combined with melatonin [33] or green coffee oil [34,35]. In our recent study, we described the microscopic, macroscopic and applicative proprieties of the TiO_2 stabilised system from an instrumental point of view [30].

Taking into account the applicative interest of the Pickering sunscreen emulsions, the sensory description of such systems is awaited, but there is still a lack in the literature on this point [36].

The novelty of our study lies in the development of an original methodology to characterise the sensory properties of the Pickering emulsions. First, three inorganic solid particles, able to stabilise the interface and to form totally emulsified systems, were selected: silicon dioxide (SiO_2), zinc oxide (ZnO) and titanium dioxide (TiO_2). Due to their physicochemical properties, the particles were able to form emulsions, which will be described further. To bring new elements of comprehension of how the Pickering emulsions are perceived on the human skin, we completed the studied systems with two new formulations: reference emulsions, which were formulated with a conventional Steareth-2/21 surfactant and, finally, emulsions combining both emulsifying systems were also developed and investigated.

MATERIALS AND METHODS

MATERIALS

The raw materials used in this study were kindly provided by the suppliers listed in **Table I**. The selected raw materials were of cosmetic grade considering the further interest of emulsions topical application.

The surfactant chosen for this study is a combination of two ethoxylated ethers: Steareth-2 is a polyoxyethylene (2) stearyl ether and the Steareth-21 a polyoxyethylene (21) stearyl ether [37].

Table I. INCI, CAS, trade name and the supplier of raw materials

INCI	CAS	Trade name	Supplier
Titanium Dioxide, Silica, Cetyl phosphate	13463-67-7; 7631-86-9; 3539-43-3	Eusolex® T-Easy	Merck
Zinc Oxide, Jojoba Esters	1314-13-2; 61789-91-1	ZnO-750-NJE7	Kobo
Silica cetyl silylate	199876-45-4	Aerosil®	
Steareth-2	9005-00-9	Massocare® S2	Massó
Steareth-21	9005-00-9	Massocare® S21	Massó
Caprylic capric triglycerides (CCT)	73398-61-5	Triglycerides C8C10 55/45	Stéarinerie Dubois
Deionized Water			
Phenoxyethanol and Methylparaben and Ethylparaben and Propylparaben and Butylparaben	122-99-6; 99-76-3; 120-47-8; 94-13-3; 94-26-8;	Sepicide HB	Seppic

SYSTEMS AND CHARACTERISATION

Three solid particles were selected for the emulsion stabilisation: titanium dioxide **TiO_2** (at **4%** and **10%**), zinc oxide **ZnO** (at **10%**) and silica **SiO_2** (at **4%**). Then, a conventional surfactant, solid at ambient temperature, was used for the formulation of the reference emulsion (at **4%** and **10%**). Classical emulsifier mixture of non-ionic surfactants Steareth-2/Steareth-21, often used for topical applications, is well known for

its stabilizing property [38] and was already used for previous studies of the nanoparticle-based emulsions [39,40].

To explore the effect of the solid stabiliser versus a classic emulsifier, several emulsions were formulated as a mixture of both stabilising systems (at **2%+2%** and **5%+5%** of the mixture). The composition of the nine emulsions formulated for this study is presented in **Table II**. The oil/water for each system ratio was fixed at 40/60 and a preservative was introduced to avoid bacterial proliferation.

Table II. Emulsion code and composition of the stabilizing system/oil phase/water phase for each of the nine studied emulsions.

Emulsion code	Stabilizing system				Oil phase	Water phase	
	ZnO (%)	TiO_2 (%)	SiO_2 (%)	Steareth-2/21 (%)	Caprylic capric Triglycerides (%)	Water (%)	Preservative (%)
ZnO10	**10**	-	-	-	35.6	53.4	1
ZnO5St5	**5**	-	-	**5**	35.6	53.4	1
$TiO_2$4	-	**4**	-	-	38	57	1
$TiO_2$10	-	**10**	-	-	35.6	53.4	1
$TiO_2$5St5	-	**5**	-	**5**	35.6	53.4	1
$SiO_2$4	-	-	**4**	-	38	57	1
$SiO_2$2St2	-	-	**2**	**2**	38	57	1
St4	-	-	-	**4**	38	57	1
St10	-	-	-	**10**	35.6	53.4	1

EMULSIONS FORMULATION

The formulation process of the nine emulsions is strongly dependent on the emulsifying system type. In the case of the conventional emulsifier, the heating step is necessary before the emulsifying step. The physicochemical properties of the solid particles should also be taken into account to choose an adapted method of the pre-dispersion step in the suitable oil or water phase. All the systems were formulated at 200 mL to ensure the instrumental and the sensory analysis.

$TiO_2$10 / $SiO_2$4/ ZnO10 emulsion – the particles were first pre-dispersed in the water phase for TiO_2 and SiO_2, and in the oil phase for ZnO. Next, the internal phase is added to the continuous phase during 30 seconds under vigorous stirring (11000 rpm) using a rotor-stator T25 digital ultra-turrax (IKA, Freiburg, Germany) equipped with the dispersing head S25N-25F. Then, the homogenization is continued for 1.30 minutes to form an emulsion. Finally, after adding the preservative, the mixture was put under stirring (Turbotest, radial flow turbine of 55 mm diameter, VMI Raynerie) at 500 rpm for 15 minutes. All the emulsion formulation process was carried out at the ambient temperature.

St10 / St4 emulsion– the oil phase containing the emulsifier was heated up to 80°C under mechanical stirring (400 rpm), as well as the water phase. Then, as for the previous system, the oil phase was added to the water for 30 seconds and the homogenisation was continued for 1.30 minutes at 11000 rpm. The formulation was left cooling down to 30°C under stirring (Turbotest, radial flow turbine of 55 mm diameter, VMI Raynerie) at 400 rpm. Next, the preservative was added and the emulsion was left under the same stirring for more 15 minutes.

$TiO_2$5St5 / $SiO_2$2St2 / ZnO5St5 emulsion was prepared using both protocols – particles were pre-dispersed in the water phase for TiO_2 and SiO_2, and in the oil phase for ZnO and then heated up to 80°C, the surfactant is mixed with the oil phase and also heated up to 80°C. Next steps are identic to the previous emulsions.

Once prepared, the mixtures were split into three samples, stored at 4°C, 40°C and ambient temperature, respectively, for stability monitoring. Before any sensory analysis, the stability of the systems over time (D+7, D+15, D+30) was checked by classical techniques: microscopy, particle size analysis, rheological studies. This approach was necessary to ensure that the properties of the system will not evolve during the sensory study.

EMULSIONS ASPECT

Microscopy

The emulsions microstructure was observed using an optical microscope (Leica DMLP microscope) equipped with a digital camera at a magnification of x100 under the bright field at the ambient temperature of storage at D30. Leica IM 1000 software was used to analyse the micrographs.

Droplet size distribution

The emulsion droplets size were measured by static light scattering (SLS) using a laser diffraction particle size analyser SALD-7500 nano (Shimadzu Co., Ltd, Japan) equipped with a violet semiconductor laser (405 nm). The emulsions, except the ZnO containing emulsions, were diluted with deionized water to achieve the absorption parameter equal to 0.2. For the ZnO containing, inverse water in oil emulsions, the dilution was done with the oil phase. Considering the important chemical inhomogeneity of the medium (presence of the particles and their agglomerations besides to the oil phase droplets), and to get rid of the optical properties of all of them, the Fraunhofer theory was used. The droplets median values D[4,3] were acquired, representing the size in microns that splits the distribution with half above and half below this diameter.

Rheology

Rheological tests were performed using a controlled stress rheometer (HR2, TA instruments). All the measurements were carried out in duplicate at 25°C. The solvent trap was used to prevent sample drying. Once loaded, the samples were left at rest for two minutes prior to any measurement. Samples were analysed once and then changed prior to further analysis. *Flow curves* were obtained by recording shear stress and viscosity values at increasing shear rates ranging from 0,001 to final 5000 1/s (continuous ramp, logarithmic mode) for 300s. 60 mm aluminium parallel-plate device was used for the test and the gap was fixed at 200μm.

SENSORY ANALYSIS

The recruited panel was composed of 23 volunteers aged from 22 to 45 years old and selected among Le Havre University. Subjects were voluntary and gave all their written consent to participate in the study. The study and all protocols were approved by the Ethics Committee from Le Havre University. Prior to any sensory analysis, a microbiological test was performed (ACM,Bellegarde, France) to make sure that each product was in accordance with the cosmetic criteria for bacterial contamination (< 100 UFC/g or/ml) for both the search of aerophilic mesophilic bacteria [41] and the enumeration of yeasts and molds [42]. All the samples presented <10 UFC/ml, so suitable for the sensory analysis. First, two training sessions were organized to acquire the definition of each attribute, the evaluation procedure, the rating scale (from 0 to 9) and the commercial references (**Table III**). The used references: A - deionized water, B - Vichy "Ideal soleil" Gentle milk for children SPF 50; C – URIAGE "Bariesun" Mineral cream, SPF30. Then, each of the nine products was evaluated twice in the same conditions in individual booths.

Table III. Application phase, studied attributes, their definitions and the reference scales used for the sensory analysis

Phase	Attribute	Definition	A	B	C
Rub-out	Non-aqueous	Quantity of water perceived during application	0	5	8
Rub-out	Difficulty of Spreading	Force required to move product over skin	0	5	8

Rub-out	Whitening effect	Quantity and intensity of white colour covering the skin	0	5	8
After feel	Film whiteness	Quantity and intensity of white colour covering the skin	0	5	8
After feel	Film glossiness	Amount of reflected light from the film	0	4	6
After feel	Greasiness	Quantity of thick, rich, unctuous residue on the skin	0	6	8
After feel	Screech residue	Friction sound, the stick-slip character of the residue	0	1	3

Each assessor respected a precise protocol: "Wash your hands and your forearms with a hydroalcoholic gel. Place 40µL of the product in the middle of the circle (Ø = 5cm) drawn on the inner surface of the forearm. Spread the product within the circle using forefinger, by making one circular motion per the sound signal of the metronome (corresponding to 90 beeps/minute). Evaluate the **Non-aqueous** property between the 1st and the 5th circle. Continue the circular motions and evaluate the **Difficulty of spreading** between the 10th and the 20th circle. Evaluate the **Whitening effect** of the product on the skin between the 20th and the 30th circle outside a direct source of light and continue the application towards 50 circles. At 1min and 1min30 after application, visually assess the **Whiteness** and the **Glossiness of the residual film,** respectively. At the end of 2min, evaluate the **Greasiness** of the residue by pinching 5 times the area where the product was applied. After each pinch, evaluate the **Screech**, by compressing the rest of the product between the index finger and the thumb."

The evaluation was performed in a sensory laboratory composed of individual booths, according to the NF EN ISO 8589. Each product sample was presented in a 5 ml jar and identified with a randomly assigned three-digit code. Presentation order was randomly defined and changed for each session to reduce bias in evaluation.

The sensory methodology developed for the study of the nine emulsions was based on the perception of the product during and after application. It is an original methodology, never discussed for the Pickering emulsions before. The choice of the attributes for the evaluation was based on the differences between the products.

Seven discriminant attributes were evaluated consequently: three during (non-aqueous, difficulty of spreading, whitening effect) and four after the application of the product (film whiteness, glossiness, greasiness and the screech effect of the residue). *Non-aqueous* and *difficulty of spreading* are two key attributes particularly influenced by the composition of cosmetic emulsions [43–45]. Other attributes were selected according to the properties of the stabilising systems: *whitening effect*, *film whiteness* and *screech residue* related to the particle stabilised emulsions; *film glossiness* and *greasiness* related to the Steareth-2/21 containing emulsions.

DATA ANALYSIS

Results were presented as the mean value ± standard deviation (SD).

XLSTAT software (Addinsoft, Paris, France) was used to perform the statistical analyses of the collected data. The ANOVA test (two-way analysis of variance) was applied to the results to spot the significant differences between the emulsions ($P<0.05$). Mean intensities were compared using the Tukey multiple comparison tests to distinguish different groups of products. Principal component analysis (PCA) was also performed on centred and autoscaled mean data to study the relationships between products and attributes.

RESULTS

All the formulated systems were first analysed from the microscopic and macroscopic point of view to understand the mechanism of their formation, depending on the emulsifying system. Then, the textural properties of the nine emulsions were described by a panel of assessors during the sensory analysis. The obtained results will now be discussed.

INDIVIDUAL PROPERTIES OF FORMULATED SYSTEMS

First of all, the behaviour of the formulated samples was monitored over time for three temperatures of storage: 4°C, ambient temperature and 40°C. The samples were checked at D7, D15 and D30 by the microscopy, the particle size analysis and the rheology for the tree temperatures of the storage. No phenomena of destabilisation were observed over this time. The instrumental results that will be further presented were taken at the same time (D30) and at the same storage temperature (ambient temperature), as for the sensory analysis.

Considering the mechanism of the emulsion formation, it is interesting to notice that the ZnO containing emulsions are both of water in oil type (W/O), while the rest of the systems did orient the emulsion towards oil in water (O/W) organisation. Also, the microscopic organisation of the systems is remarkably different: the particle-stabilized emulsions form bigger oil droplets, while the Steareth-2/21 presence favours the formation of smaller oil droplets (**Figure 1**) as it could be expected according to the literature [46]. The complementary information about the physicochemical properties of TiO_2 and/or Steareth-2/21 stabilised emulsions were given in our previous work [30].

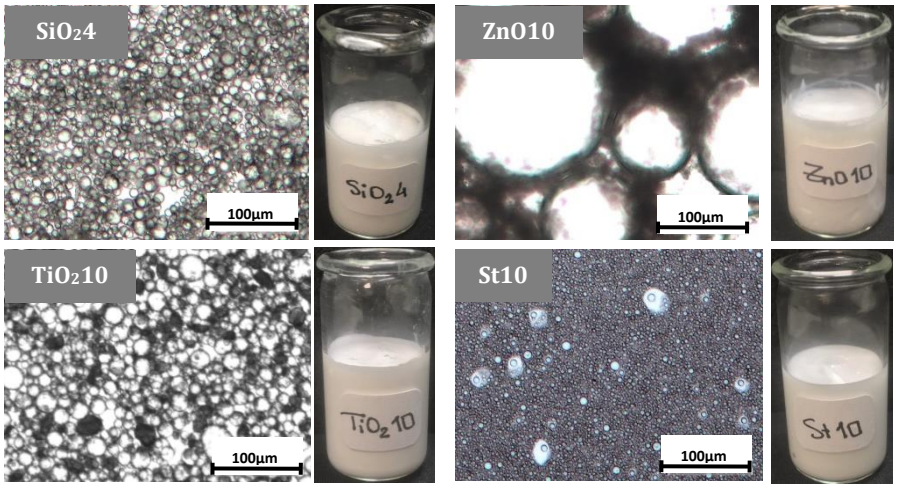


Figure 1. Microscopic organization of four studied emulsions: $SiO_2$4, ZnO10, $TiO_2$10, St10 stored at the ambient temperature (D30) at x100 magnification, as well as a photography of homogenous and totally emulsified emulsions.

It is important to mention the specific properties of the ZnO containing emulsions. As it could be seen from Fig. 1, the droplet size of the ZnO10 emulsion is extremely big, compared to the other systems. Moreover, the inverse water in oil emulsions stabilised by the ZnO are very fragile and the large droplets are immediately destroyed after even a weak solicitation. For this reason, the ZnO samples were the only ones not covered with the cover glass during the microscopic analysis due to immediate droplet destruction by this act. Consequently, one can expect a specific behaviour during the rheological investigation and the sensory application of these systems.

Table IV. Emulsions type (water in oil for W/O or oil in water for O/W) and D[4,3], the volume mean diameter, obtained by static light scattering measurements.

Emulsion	ZnO10 (W/O)	ZnO5St5 (W/O)	$TiO_2$10 (O/W)	$TiO_2$4 (O/W)	$TiO_2$5St5 (O/W)	$SiO_2$4 (O/W)	$SiO_2$2St2 (O/W)	St4 (O/W)	St10 (O/W)
D[4,3] µm	1,11±0,02	29,78±3,06	12,92±0,33	27,07±1,44	3,28±0,38	9,53±0,76	5,68±0,18	2,01±0,03	1,74±0,03

The D[4,3] values also show the fragility of the ZnO10 system (Table IV). The obtained values equal to 1µm demonstrates that the droplets seen on the micrographs are destroyed even by the dilution of the sample.

The dynamic viscosity values at the $1s^{-1}$ shear rate for each emulsion are given in **Table V**. The important differences between the registered values are pointing at the fact that the stabilising system also affects the macroscopic organisation of the emulsion. For example, at the same particle concentration, $SiO_2$4 emulsion is thirty times more viscous than $TiO_2$4 and it may be due to the system's gelation by silica particles [7].

Table V. Dynamic viscosities values at $1s^{-1}$ shear rate for the samples stored at the ambient temperature at D30.

Emulsion	ZnO10	ZnO5St5	$TiO_2$10	$TiO_2$4	$TiO_2$5St5	$SiO_2$4	$SiO_2$2St2	St4	St10
Viscosity at $1s^{-1}$ (Pa.s)	30,90±1,22	21,09±2,04	26,62±0,04	9,46±0,31	15,35±0,52	276,11±8,47	6,94±0,21	4,79±0,05	35,29±1,04

Microscopic and macroscopic variations between the obtained emulsions suggest that the texture of the systems will be differently perceived by the assessors.

SENSORY PROPERTIES OF PICKERING EMULSIONS COMPARED TO CONVENTIONAL SYSTEMS

The main purpose of the sensory analysis was to draw the sensory profile of Pickering emulsions. A conventional surfactant Steareth-2/Steareth-21 was used at 4% and 10% for the formulation of the references at the same concentration in stabilizer as for the Pickering emulsions. Two groups will be discussed hereafter: containing 4% of emulsifier ($SiO_2$4, $TiO_2$4 and the St4 reference) and containing 10% of emulsifier (ZnO10, $TiO_2$10, St10).

COMPARISON OF THREE SYSTEMS CONTAINING 4 % OF THE EMULSIFIER

Two Pickering and one conventional emulsion were compared on the scale between 0 and 9 (Figure 2). The important SD for the obtained results are usual for the sensory analysis inherent to differences in assessors evaluation [26–29]. Despite the identic water quantity in all the samples, the panel could statistically discriminate the products. $TiO_2$4 emulsion was perceived as the most *aqueous (0.8)*, approaching the pure water value. Moreover, it was also scored as easy to *spread (1.6)*, with an important *whitening effect (4.1)* and *film whiteness (3.0)* when compared to two other systems. It is interesting to notice that for these three attributes (*difficulty of spreading, whitening effect and film whiteness)*, the panel could not notice any important difference between $SiO_2$4 and St4, stabilised by extremely different emulsifiers. The differences between both systems are more significant for the final properties of the film: the silica particles could reduce the *film glossiness (2.6)* and *greasiness (2.1)*, compared to Steareth-2/21 emulsion. Finally, the panel could specifically designate the particle-containing emulsions through their low *greasiness* and their *screech residue* properties.

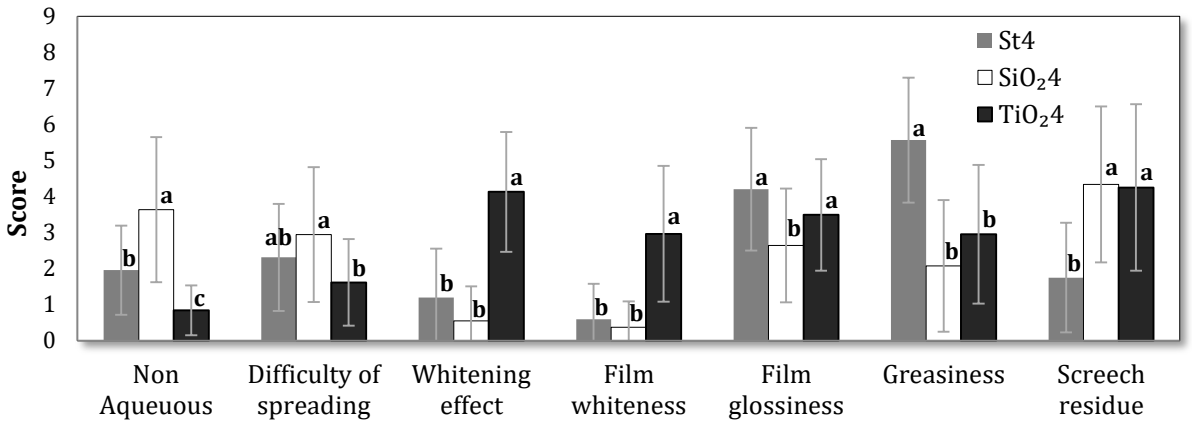


Figure 2. The average score and the standard deviation obtained by St4, $SiO_2$4 and $TiO_2$4 emulsions for each of the seven studied attributes. a-c Values with a different letter for each attribute indicate that corresponding products are significantly different (P<0.05).

COMPARISON OF THREE SYSTEMS CONTAINING 10 % OF THE EMULSIFIER

The perception of the systems containing 10% of the emulsifying system is more pronounced than for 4%. In Figure 3, two Pickering emulsions stabilised by 10% of TiO_2 (O/W) and ZnO are compared with a conventional emulsion containing 10% of Steareth2/21 emulsifier.

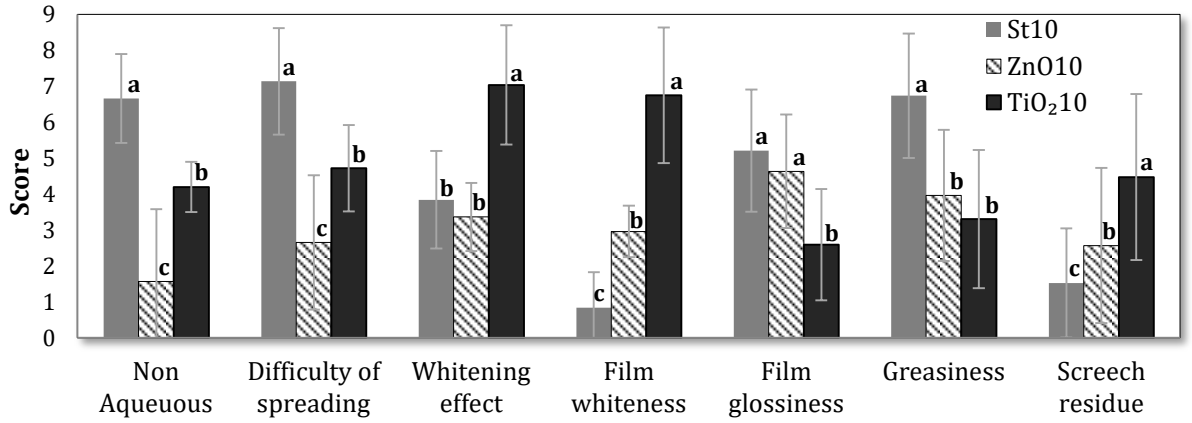


Figure 3. The average score and the standard deviation obtained by St10, ZnO10 and $TiO_2$10 emulsions for each of the seven studied attributes. a-c Values with a different letter for each attribute indicate that corresponding products are significantly different (P<0.05).

The St10 emulsion was considered as the least *aqueous* and the most *difficult to spread*, followed by $TiO_2$10 and, finally, by the ZnO10 emulsions. One can notice that the judges could not differentiate St10 from ZnO10 for the *whitening effect* attribute during the application, due to the "soap" effect of the Steareth-2/21 surfactant at a high amount. During the penetration, this effect disappears for the St10 emulsion, while the ZnO particles on the surface of the skin increase the score for the *film whiteness*. The TiO_2 particles at 10%, with an important whitening effect, mitigate the film glossiness and greasiness. Even though two Pickering emulsions contain the same quantity of particles, the *screech* of the residue is more pronounced for the titanium dioxide particles.

THE PARTICLE EFFECT

Since conventional surfactants and particles are able to stabilise the oil/water interface and to totally emulsify both phases, it is interesting to observe the role of each type of stabilising system in a mixture of both. For this purpose, the silicon dioxide/titanium dioxide/zinc oxide particles were formulated together with the Steareth-2/21 surfactant. Three systems are here compared containing 0%/100%, 50%/50%, 100%/0% of surfactant/particles mixture.

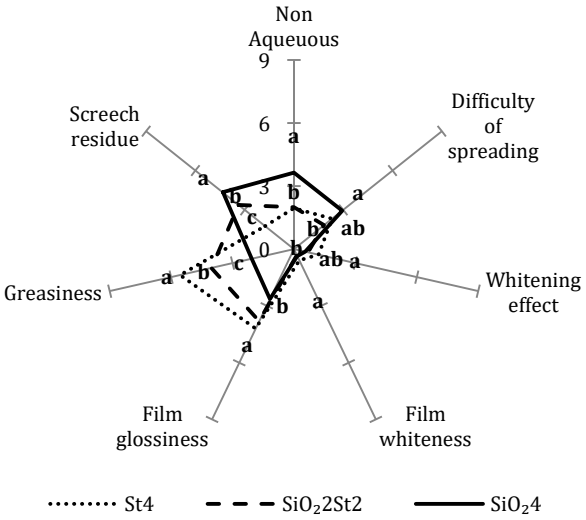


Figure 4. Comparison of St4, $SiO_2$2St2, $SiO_2$4 emulsions over seven studied attributes. a-c Values with a different letter for each attribute indicate that corresponding products are significantly different (P<0.05).

Steareth-2/21 4% emulsion is compared with the emulsion stabilised by the mixture Steareth-2/21 2%$SiO_2$2% and with $SiO_2$4 (Figure 4). For the *difficulty of spreading*, the *whitening effect* and the *film whiteness*, the three emulsions are statistically similar. However, it is interesting to notice that adding the silicon dioxide particles to the conventional surfactant reduces the *greasiness (4.0)* of the residue and slightly the *film glossiness (3.8)*, while the $SiO_2$4 emulsion shows the lowest values for these attributes (*greasiness - 2.1*, *film glossiness - 2.6),* pointing at its capacity to reduce the "fatty" perception.

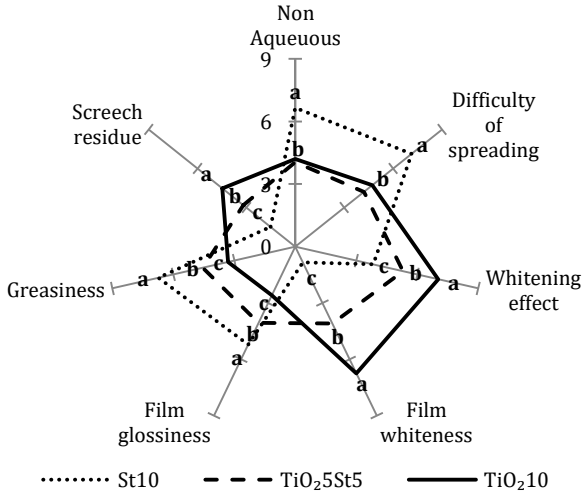


Figure 5. Comparison of St10, $TiO_2$5St5, $TiO_2$10 emulsions over seven studied attributes. a-c Values with a different letter for each attribute indicate that corresponding products are significantly different (P<0.05).

Graphical representation of St10, $TiO_2$5St5, $TiO_2$10 emulsions in Figure 5 illustrates an important divergence of the scores between the products. The use of the titanium dioxide particles alone or together with the Steareth-2/21 surfactant induces the formation of the emulsions perceived as *less aqueous* and less *difficult to spread*. As expected, *the whitening effect* and the *film whiteness*, as well as the *screech of the residue* are gradually intensified when the particle quantity increase in the emulsion, while the *gloss* and the *grease* effect of the residue are reduced. The use of the TiO_2 at 5% and of Steareth-2/21 at 5% as the emulsifying system permits to obtain intermediate scores for the studied attributes.

Meanwhile, the situation is quite different for zinc oxide. As it could be seen from Figure 6, both emulsions containing ZnO are aqueous and easy to spread, contrary to the conventional emulsion. ZnO10 can be only discriminated from the other systems for *the film whiteness (3.0)* and the *screech residue (2.6)* attributes, due to the important quantity of solid particles. The *film glossiness* is not impacted by the emulsion composition, only the *greasiness* of the Steareth-2/21 is constantly more important due to the intrinsic surfactant properties.

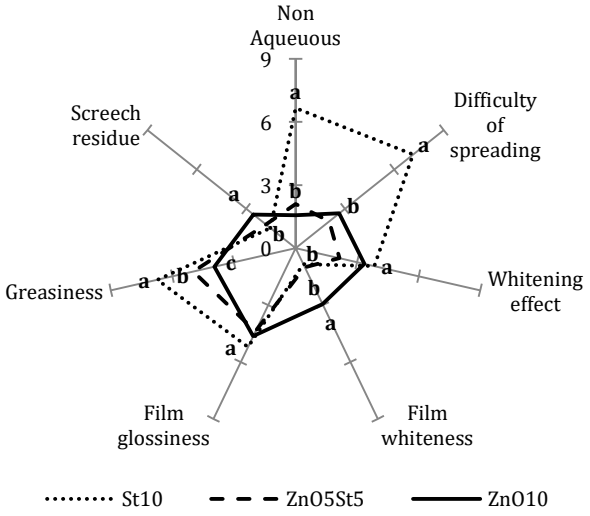


Figure 6. Comparison of St10, ZnO5St5, ZnO10 emulsions over seven studied attributes. a-c Values with a different letter for each attribute indicate that corresponding products are significantly different (P<0.05).

DISCUSSION

The aim of this study was to describe the textural properties of Pickering emulsions compared to the properties of conventional formulations.

It is known that the surfactant is an amphiphilic molecule able to reduce the oil/water interfacial tension and it forms an electrostatic and steric barrier at the interface between two liquids [47]. Meanwhile, due to the partial wetting of the surface of the solid particles by water and oil [12,48], particle stabilisation is an anchoring of solid particles at the oil-water interface, creating a barrier against coalescence [49,50]. One should consider the differences in the formation mechanism of surfactant-stabilised and particle-stabilised emulsions, which clearly impact the sensory perception of the formulas.

The first purpose of the study was to obtain stable, totally emulsified systems. Three different particles were selected: Titanium Dioxide coated with Silica and Cetyl Phosphate (at 4% and 10%); Zinc oxide coated with

Jojoba Esters (at 10%) and finally Silica Cetyl Silylate (at 4%). Each particle could efficiently stabilise the interface and integrally emulsify both phases, with no creaming or drainage destabilisation over time. The retained quantities of solid particles were optimal for the formation of the stable system: TiO_2 can stabilise at 4% and 10% in the emulsion, ZnO is efficient only at 10%, while SiO_2 at more than 4% is forming too consistent emulsions.

The micro and macrostructure of the emulsions are strongly affected by the emulsifying system (Figure 1 and Table V), and, as a consequence, the sensory perception is also influenced. According to diverse studies, the *difficulty of spreading* attribute is related to the emulsion consistency: less consistent emulsion is easier to be spread [51–53]. These results are coherent with the Steareth-2/21 emulsions. But, unlike the literature examples, the emulsions stabilised by solid particles do not demonstrate this behaviour. Each particle showed the individual effect on this attribute: TiO_2 containing emulsions, being less viscous than St10, are still difficult to spread, followed by ZnO (Figure 3). Meanwhile, the $SiO_2$4% emulsion, clearly shows high viscosity value for the rheology test (Table V), due to the silica gel formation in the continuous phase, but is considered as easy to spread by the sensory panel (Figure 2). For this reason, the emulsions containing or stabilised by the solid particles are different from conventional emulsions, as proved by previous results.

The sensory analysis allowed the classification of the studied emulsions as a function of the seven attributes, which is graphically represented, thought a PCA (Principal Component Analysis) in Figure 7.

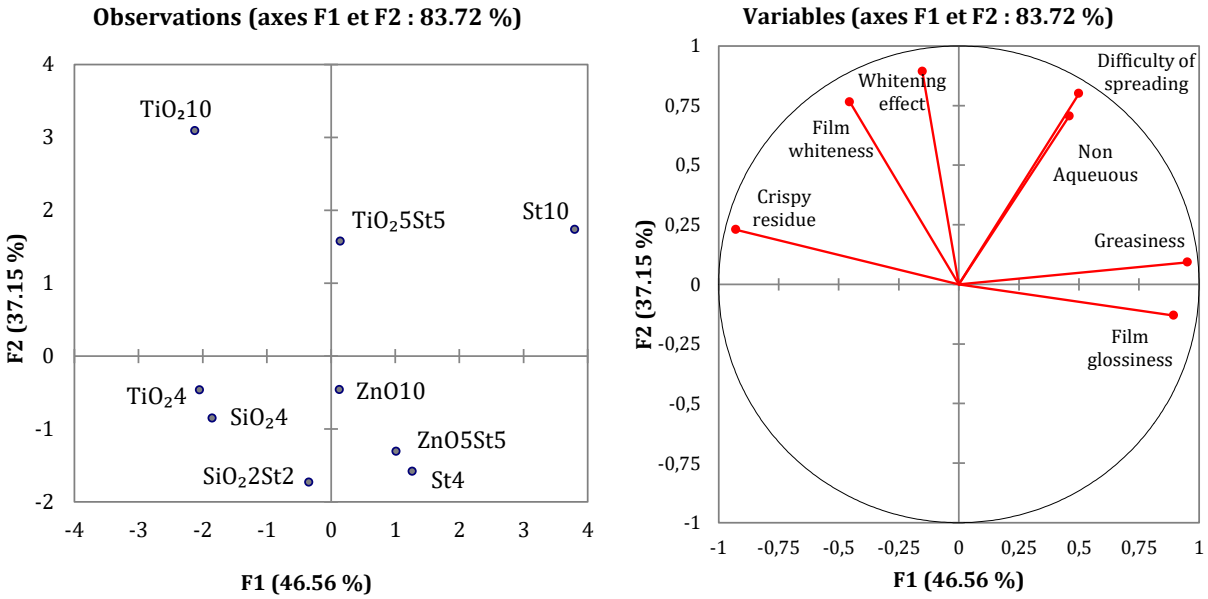


Figure 7. Graphic representation of Principal Component Analysis (PCA) of the products (on the left) and the correlation circle of the attributes (on the right).

The titanium dioxide containing emulsions are highly governed by the particle presence: the whitening effect during and after application (due to an important refractive index of the TiO_2≤4 [54]), as well as the screech residue, prevail for the $TiO_2$10 emulsion, followed by $TiO_2$5St5 and $TiO_2$4. It is obvious that the particle quantity, more than the emulsion organisation, will affect these three attributes. However, the presence of Steareth-2/21 in $TiO_2$5St5 inclines its properties towards more "fatty" perception.

It is interesting to notice that the Silica Cetyl Silylate containing emulsions are nearly identic over the F2 axe. $SiO_2$4, $SiO_2$2St2 and St4 emulsions were more distinguished over F1 axe: screech residue, highly pronounced

for the silica at 4%, is reduced with silica decrease and the Steareth-2/21 addition to the system, while the residue becomes glossy and greasy.

For the common oil in water emulsions, the aqueous perception is related to the water quantity of the system and the ability of the surfactant to organise itself in different liquid crystal shapes, affecting the water retention and perception. Considering the water in oil, ZnO containing emulsions, the results were quite unexpected. Despite the high concentration (10%) of metal oxides in ZnO10 emulsion, its whitening effect and the screech of the residue is surprisingly lower than for $TiO_2$10 emulsion. Moreover, the water liberation during the spreading of the product so-called "quick breaking" effect [55], made the panel perceive the ZnO emulsions as aqueous, even at 10% of the emulsifying system.

For the particles/Steareth-2/21 mixture, the behaviour is intermediate. From the sensory perception, no matter which system plays the main role in the stabilisation process, the applicative properties and the final residue evolve gradually, depending on the emulsion composition: for the particle stabilised systems, the metal oxide governs the final perception. The addition of Steareth-2/21 with long carbon chains contributes to the increase of the "fatty" after-feeling of the emulsions.

CONCLUSION

The present work focused on the sensory analysis of Pickering emulsions, stabilised by three types of solid particles: titanium dioxide, (coated with Silica and Cetyl Phosphate), Zinc oxide (coated with Jojoba esters) and Silica Cetyl Silylate. The same particles were used to formulate 50/50 particle/Steareth-2/21 emulsions. Finally, two emulsifier-stabilised emulsions served as references in this study.

The sensory perception is strongly affected by the type of the metal oxide: the SiO_2 particles form emulsion sufficiently similar to one stabilised by a conventional surfactant used for the study. Undoubtedly, the presence of the particles at 4% increased the *screech* of the residue, while the Steareth-2/21 emulsion at 4% was perceived as more *greasy* and *glossy.* But the differences are less pronounces that in case of other metal oxides. For TiO_2, the sensory profile is quite different from the emulsion stabilised by the Steareth-2/21 surfactant, the mixture of them assuring the intermediate properties. The presence of this metal oxide amplifies the *whitening effect* and the *screech of the residue.* Finally, the ZnO containing emulsion, alone or in combination with the surfactant, is quite different from the classic one. The ZnO particles oriented the emulsion towards the water in oil organisation. In other words, the ZnO Pickering emulsion and the ZnO/Steareth-2/21 mixture will be similarly perceived, the small difference is only observed for the *film whiteness* and the *screech of the residue,* which is directly linked to the particle quantity in the emulsion.

Considering the emulsions stabilised by both systems, particles and surfactant, it was demonstrated that from the sensory point of view, there is no concurrence between the stabilising systems. The sensory attributes are more affected by the number of initial ingredients, metal oxides or emulsifier. The present study also showed that the metal oxides regulate the emulsions orientation (O/W or W/O), which will change the emulsion perception, depending on which phase will interact first with the skin. Meanwhile, the particles used for the emulsion formulation will directly affect the properties of the residual film, after the emulsion's penetration.

This research brings novelty in the non-studied field of the sensory profile of Pickering emulsions. It gives detailed information about the impact of solid particles on the textural properties of cosmetic emulsions. A good perspective of this work will be the demonstration of the fact that the sensory profile is not only directly governed by the properties of the particles, but also indirectly. Through a combination of microscopic and macroscopic techniques, it will be interesting to show that the particles possess a capacity to form a droplet network and also to organise the external phase. These parameters will impact the spreading properties and the aqueous feeling of the formulations.

DECLARATIONS OF INTEREST

None.

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