

Supporting Information

A methodology for emulsion design based on emulsion science and expert knowledge. Part 1: conceptual approach

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S1. EXAMPLE OF ARTICLES PROPOSING METHODOLOGIES FOR FORMULATED PRODUCTS

Table S1. Example of articles proposing methodologies for formulated products

Articles	Methodological approach	Product type	Scope	Limitations	Application case
(F P Bernardo, 2016; Fernando P. Bernardo & Saraiva, 2014) ^{1,2}	Conceptual modelling and optimization approach based on 3 functions: process, property, and quality functions	It is generic. Examples are of the type liquid mixtures and emulsions	*Modelling/optimization approach *Simultaneous product/process design	*Some variables related to product's micro-structure are used in the model. But their interrelations and their effects in multiple product characteristics are not completely addressed. *Not applicable to early design stages. Because ingredients are already pre-selected.	Perfume, cosmetic emulsion, pharmaceutical Ointment
(Arrieta-Escobar et al., 2018) ³	Modelling and optimization approach using heuristics of the cosmetic sector	Cosmetic emulsion	*Heuristic based modelling/optimization approach * It enables the generation of cosmetic emulsions (ingredients and composition) using heuristics and an ingredients database	*Additional heuristics are needed to apply the methodology in other industrial sectors. *The effects of the micro-structure in product performance are not considered.	Hair conditioner
(Fung et al., 2016) ⁴	Systematic framework consisting of six models: process property, a quality, cost, pricing, and economic models.	The framework is generic. Examples are of the type polymer composites and liquid mixtures.	*It is a global approach. It enables the combination of multiple and diverse methods and tools for product design. *In the emulsion case, it considers some variables related to product's micro-structure and properties such as droplet size and emulsion viscosity and connects them to the process model.	*Some variables related to product's micro-structure are used in the model. But their interrelations and their effects in multiple product characteristics are not completely explored. *Its application depend highly on the availability of appropriated models, information and knowledge bases.	Hand lotion, die attach adhesive (polymer containing micro-particles)
(Zhang et al., 2017) ⁵	Systematic framework comprising a very complete knowledge base and models for the design of all type of formulated products	The framework is generic for formulated products (emulsions, solid and liquids)	This is a global framework for formulated product design. *This methodology does not pre-fixed the form of the product, i.e., it can be liquid, solid, emulsion in response to problem	*Its applications depend highly on the availability of appropriated models and information. *As it is global, it does not develop in detail the design of emulsified products	Electrolyte (liquid mixture) Detergent (both solid and liquid form are explored)

			specifications, giving a high range of possibilities for problem solving	and its specific problematic.	
(Conte et al., 2011), (Conte et al., 2012) ^{6, 7}	Systemic framework for liquid formulated products	Liquid formulated products	It integrates modeling and experiments for the design of formulated liquids.	*It is only applicable to homogenous liquid mixtures. It does not consider product's micro-structure	Insect repellent and sunscreen lotion
(Kontogeorgis et al., 2019) ⁸	Systematic approach specifically applicable to emulsified products	Emulsions	The design process of emulsified products is explained in detail. Process system engineering tools are systematically applied.	*Relation with micro-structure/property/process is not completely explored. *It does not include product design and manufacturing aspects.	Hand-wash detergent in emulsified form
(Hada et al., 2017) ⁹	Mixture formulation through multivariate statistical analysis	Mixture formulation	A systematic methodology is developed by integrating data-driven chemometric techniques and property based visualization and optimization tools	*Applicable to advance design stages, when product data are available	thermo-plastic
(Faust et al., 2020) ¹⁰	model-based dynamic optimization using an embedded Monte Carlo Model	Polymer synthesis	A model-based dynamic optimization of an emulsion polymerization process was done to achieve a bimodal molecular weight distribution and reduce reaction time	*Process optimization and polymer synthesis	Polymer with a bimodal distribution

S2. EXTENDED EXPLANATION OF SUB-PROBLEMS

S2.1. Appearance (A):

- **Emulsion lightness (A1)** is the emulsion's whiteness or milky appearance. It is caused by light scattering, a phenomenon whereby light is driven in multiple directions other than the incident angle when it encounters a surface (in this case, emulsion droplets) ¹¹. Raleigh theory models this phenomenon for one droplet or particle as shown in equation S1 ¹¹.

$$I = \frac{8\pi^4 r^6}{d^2 \lambda^4} \left(\frac{\left(\frac{n_1}{n_0}\right)^2 - 1}{\left(\frac{n_1}{n_0}\right)^2 + 2} \right) (1 + \cos 2\theta) \quad [S1]$$

,where I is the Raleigh scattering intensity, which depends on the angle, r is the droplet radius, λ is the wavelength of light, d is the distance from the droplet to the detector, n_0 , n_1 are the refractive indices of continuous and disperse phase, θ is the scattering angle

Equation S1 shows that lightness can be modified by varying the relative refractive indices of phases, the droplet size, and/or the incident light. Lightness increases with the difference between the refractive indices of the continuous and dispersed phases. When they are equal, emulsion turns transparent. In relation to the droplet size, the appearance of an emulsion goes from transparent to opaque and then again to transparent as droplet size is increased ¹¹, which is why nano-emulsions (20 – 100 nm) are transparent ¹² and macro emulsions (0.1 - 100µm) tend to be opaque. Additionally, light scattering increases with the dispersed phase volume fraction (ϕ), because light is multiple- scattered by a greater number of droplets.

- **Color hue (A2)** is a characteristic to be considered when colorants are added into the formulation. This characteristic is defined as spectrally pure color (red as the section of electromagnetic radiation from 740 to 625 nm) without any considerations of intensity (from light pink to bright red). It is caused by light absorption of the colorant molecule. It can be controlled by the selection of a colorant with a specific structure and by setting specific environmental emulsion conditions such as pH ¹¹.
- **Color intensity (A3)**, like color hue, is a characteristic to be considered when colorants are added. It can be described in terms of absorbance (A), which is proportional to the concentration (c) of the colorant and its absorptivity (α), as shown in equation S2 ¹¹.

$$A \propto c\alpha \text{ [S2]}$$

,where A is the absorbance, c is colorant concentration, α is colorant absorptivity

The behavior of color intensity is inverse to emulsion lightness ¹³ when lightness increases color intensity decreases).

- **Special color features (A4)** are created by selecting additives with special functions. Examples are thermo-chromic pigments and pearl pigments.

S2.2. Rheology (B):

- **Emulsion viscosity (B5)** is related to adjectives such as thick (high viscosity) and fluid (low viscosity) ¹⁴. Depending on product requirements, a more (cream) or less (lotion) viscous emulsion may be desired. Viscosity augments progressively with the dispersed phase volume fraction and with the viscosity of the continuous phase as shown in equations 3 and 4 ¹⁵.

$$\text{For low concentrations } (\phi < 0.05) \eta = \eta_0(1 + [\eta] \phi) \text{ [S3]}$$

$$\text{For intermediate and high concentrations } \eta = \eta_0 \left(1 - \frac{\phi}{\phi_c}\right)^{-[\eta]\phi_c} \text{ [S4]}$$

,where η_0 is the viscosity of the continuous phase, $[\eta]$ is the intrinsic viscosity, ϕ_c is the packing parameter

Additionally, viscosity increases when repulsive forces are augmented, with the presence of flocs, and, depending on the concentration, with smaller droplet sizes ¹¹.

- **Shear thinning (B6)** describes a behavior in which viscosity decreases as the emulsion is sheared. When shearing is stopped, the fluid recovers its original viscosity

immediately. This is a typical behavior of creams, which are frequently required to be more fluid when they are applied and more viscous in the jar to avoid spills.

Shear thinning behavior may appear at intermediate and high concentrations ($\phi > 0.2$)¹⁵, when hydrodynamic and Brownian interactions gain importance. At low shear rates, Brownian forces predominate, and concentrated emulsions show a high viscosity. At high shear rates, hydrodynamic forces predominate, particles flow in a more organized pattern and viscosity decreases¹¹. Péclet number (Pe) compares hydrodynamic and Brownian forces¹¹:

$$Pe = \frac{\dot{\gamma}}{D_R} \text{ [S5]}$$

where $\dot{\gamma}$ is the shear rate and D_R is the rotational Brownian diffusion coefficient

The main factors promoting this behavior are an increase in the volume fraction of the dispersed phase, the presence of certain rheological modifiers¹⁴, and the presence of non-spherical particles or deformable droplets¹¹.

- **Thixotropic behavior (B7)** occurs when the viscosity decreases reversibly with time under a constant shear rate. After the shearing is withdrawn, the fluid needs some time to recover its original higher viscosity¹⁶. This behavior is required when the product must have a leveling time¹⁴ to form uniform layers or films, such as in nail polish or sunscreens. The main factors enhancing this behavior are increments in the volume fraction of the dispersed phase, weak flocculation, and the presence of certain rheological modifiers.
- **Viscoelastic behavior (B8)** means that when a force is applied, part of the energy is stored and part is dissipated¹¹. Thus, the material behaves solid-like and liquid-like simultaneously. Cream-gel products are an example of this behavior. Viscoelastic behavior is characterized by a complex elastic modulus (G^*), which comprises an elastic (G') and a viscous (G'') contribution¹¹. Solid-like emulsions present a yield stress (σ), which is the onset of flow¹⁶.

$$G^* = G' + iG'' \text{ [S6]}$$

The main factors enhancing this behavior are increments in the volume fraction of the dispersed phase¹⁵, weak flocculation, relatively high effective volume fraction of the dispersed phase¹¹ and the presence of rheological modifiers¹⁴.

S2.3. Stability (C): With the exception of micro-emulsions, emulsions are not thermodynamically stable but meso-stable, i.e., their structure remains for a period, but they end up separating into phases¹⁷. The following sub-problems describe phenomena that must be controlled to delay separation at least for the duration of use of the product.

- **Gravitational separation (C9)** happens when droplets or particles move upwards or downwards within the emulsion and form a visible layer. The driving force is the difference in density between the phases¹⁸.

For dilute emulsions ($\phi < 0.01$) with no interacting particles, Stokes' equation can be implemented to calculate the velocity at which droplets cream (v)¹⁸.

$$v = v_0 = \frac{2\Delta\rho g r^2}{9 \eta_0} \text{ [S7]}$$

, where v_0 is the stokes' velocity, $\Delta\rho$ is the difference of densities of the droplets and the medium, η_0 is the viscosity of the medium and r is the droplet radio.

For moderate concentrated emulsions ($0.2 < \phi < 0.1$), hydrodynamic interactions between the droplets reduces stokes' velocity¹⁸, as shown in equation 8.

$$v = v_0(1 - k\phi) \text{ [S8]}$$

,where k is a constant equivalent to 6.55, which means a reduction of stokes velocity of 65% by increasing droplet concentration¹⁸.

Actions to avoid it include adjusting the density of the phases bringing their values closer together, reducing the volume fraction of the dispersed phase, diminishing the droplet size, increasing the viscosity of the continuous phase, augmenting the repulsive forces, avoiding flocculation, and a narrow droplet size distribution¹¹.

- **Flocculation (C10)** is the process whereby droplets associate with each other before they merge¹¹. It can be weak (reversible, sometimes desired to adjust emulsion viscosity) or strong (non-reversible, leading to coalescence).

A model for flocculation of spherical particles is shown in equation S9¹¹.

$$\frac{dn_T}{dt} = -\frac{1}{2}FE \text{ [S9]}$$

,where n_T is the total number of particles per volume (which are reduced as flocculation happens), F is the collision frequency, E is the collision efficiency

It can be controlled by decreasing the volume fraction of the dispersed phase, increasing the droplet size, and increasing the viscosity of the continuous phase¹¹. Stronger repulsive forces (steric, electrostatic) and weaker attraction forces reduce the tendency toward flocculation.

- **Coalescence (C11)** is the process where two or more droplets merge together and form a single bigger droplet¹¹. First, the droplets come into close contact for a while either in a floc, in a cream layer or in concentrated emulsions¹⁶. Then, the film between the droplets, which is composed of continuous phase and surfactants, is thinned and the droplets coagulate. Finally, the film breaks and the droplets merge together¹¹. This process is thermodynamically favorable, but the time it takes to happen can be controlled by avoiding flocculation and gravitational separation. Film rupture is controlled mainly by short range forces and the resistance of the inter-droplet-film¹¹.
- **Phase inversion (C12)** is the phenomenon in which the emulsion structure reverses, i.e., the continuous phase becomes the disperse phase and the disperse phase becomes the continuous phase¹⁹. Conditions that may produce phase inversion are an increase in the disperse phase concentration beyond a critical level and a change in the surfactant's spontaneous curvature due to a change in emulsion environment such as pH, electrolyte concentration, salts and solvents in the continuous phase²⁰. They are prevented by selecting a proper surfactant system for the use and conditions of the emulsion.
- **Ostwald ripening (C13)** consists in the diffusive transfer of the disperse phase from small to large droplets. The driving force behind the phenomenon is the difference in chemical potential of the disperse phase in the continuous phase, which is larger for material contained in small than in large droplets^{16,19}. This leads to a movement of the disperse phase, which is firstly dissolved from small droplets in the continuous phase

and, later, is re-condensed in large droplets. Ostwald ripening can be characterized according to the limiting stage: if it is controlled by the diffusion through the continuous phase (diffusion-controlled ripening) or if it is controlled by the diffusion through the interfacial layer (surface-controlled ripening)¹⁹. Depending on the limiting stage, it can be controlled by selecting a disperse phase with low solubility in the continuous phase, reducing the droplet size width distribution, modifying interfacial characteristics (for example, by increasing its Gibbs elasticity using polymeric and biopolymeric emulsifiers).

- **Lipid oxidation (C14)** is a complex sequence of chemical reactions that results from the interaction of lipids with oxygen active species²¹. Lipid oxidation in O/W emulsions can be represented by a three-step mechanism: initiation, propagation, termination²¹. It can be controlled by reducing the concentration of oxygen in the product packaging, selecting oils with a low tendency to oxidize, avoiding the presence of oxidant agents (i.e., by selecting high pure ingredients), adding antioxidants. In the Initiation, oxidative instability is originated by the interaction between lipid hydroperoxides present at the interface (and formed due to the presence of oxygen) and transitional metals present in the aqueous phase as Fe²⁺, Fe³⁺, Cu⁺, Cu²⁺²¹. Due to this interaction reactive radicals are formed. During propagation, radicals formed at the interface react with the unsaturated lipids within droplets leading to the formation of lipid radicals that propagate the reaction²¹. The reaction ends when some of the lipid radicals find other lipid radicals²¹. In an O/W emulsion pro-oxidants are normally located in the water phase, hydroperoxides are at the interface and lipids are within the droplets²¹. Therefore, the reaction is initiated at the interface and after initiation it keeps going within the droplets.
- **Biological stability (C15)** is broken when the emulsion is contaminated with biological agents (microbes and fungi). This can happen during product elaboration, storage, and use. Measures to prevent it include the use of decontaminated raw materials, good storage and sterile manufacturing conditions, products with a hostile environment. An hostile environment can be generated by changing pH, decreasing water activity, decreasing nutrient availability, using surfactants with antibiological activity, adding sequestering agents or alcohol, and adding chemical preservatives²². Chemical preservatives are of different nature. General groups are: organic acids as benzoic acid, parabens as methyl paraben, essential oils as eucalyptus oil, aldehydes as formaldehyde, phenyl compounds as phenol, and quaternary ammonium as benzethonium²³. For their selection it is necessary to consider some factors such as existing regulations, the protection they offer against different microorganism, if they are allergenic, safe, water soluble (microorganism growth in water), compatible with other ingredients, effective, among others²³.

S2.4. Transport process and phase behavior (D): For the release of an active molecule from the formulation to other medium, it is necessary to consider its diffusion and partition coefficient.

- **Release of a relative nonpolar molecule (KOW >1) to a nonpolar medium (D16).** This comprises three steps: 1) diffusion of the active molecule through the emulsion, 2) partitioning of the molecule from the emulsion into the nonpolar medium, 3) diffusion

of the active through the nonpolar medium ²⁴. Equation S10 shows a one dimension model of flux ²⁴.

$$J = \frac{KD}{L}\Delta C \text{ [13]}$$

,where K is the partition coefficient between the formulation and the stratum corneum, D is the diffusion coefficient of the stratum corneum, L corresponds to the stratum corneum thickness, and ΔC is the difference of concentration of the molecule of interest through the stratum corneum

Partition coefficient is largely influenced by the difference of polarity of the active with the emulsion and with the target medium ²⁴. When transferring a nonpolar molecule from emulsion to a nonpolar medium, if the difference of polarities between the active and the oily phase (where the active is mostly concentrated in formulation) is larger than the difference between the active and the target medium, the release is favored ²⁴. Thus, an oily phase with a polarity that favors the transport should be selected. Attention should also be paid to the solubility of the active in the formulation ²⁴.

Other factors affecting the transfer are the concentration of the active in emulsion, the volume fraction, the droplet size, the possibility for the active to bind physically or chemically with a component within the emulsion, and the presence of inverse micelles or oil crystals ^{11,24}.

- **Release of a relative nonpolar molecule to a polar medium (D17).** It occurs as the active diffuses through the droplet, partition to the aqueous phase, and then diffuse to the polar medium. Molecules that are soluble in the oily phase are relatively nonpolar. They just transfer in low proportions from the droplet to the aqueous phase or to a polar medium. The main factor affecting this release is the active concentration. Other factors that may enhance or delay this release are the same as those presented above.
- **Release of a relative polar molecule (KOW<1) to a non-polar medium (D18)** It occurs as the active partitions to the non-polar medium. Molecules that are soluble in the aqueous phase are relatively polar and they diffuse to a non-polar medium in low proportions. The main factor affecting this release is the concentration of the active. Other factors are the possible binding of the active with components in the aqueous phase (which delay the release), a change in the polarity of the aqueous phase (by incorporating solvents or additives).
- **Release of a relative polar molecule to a polar medium (D19)** It occurs as the medium dilutes the emulsion and the active molecule diffuses due to the difference in chemical potential created by the dilution. This is the case, for example, of polar flavors in a O/W emulsion food diluted by saliva when eaten and transported by diffusion to the flavor receptors ¹¹. In this case partitioning is not relevant and diffusion is favored. Factors that may decrease transport include an increase in continuous phase viscosity.
- **Release of a relative polar volatile molecule to the air (D20).** When this occurs, the properties of the volatile molecule are the main factors determining its transport ¹¹. For example, as the molecular weight of the active increases, its volatility decreases ¹¹. Droplet size and volume fraction have a minimal effect on the release because the molecule is mainly in the aqueous phase.

- **Release of a relative nonpolar volatile molecule to the air (D21).** As in the previous case, the properties of the volatile molecule are the main factors determining its transport¹¹. Formulation factors that may affect its transport include the presence of binding molecules and micelles, the volume fraction and the droplet size (vapor pressure of a molecule within a droplet increases as the droplet size decreases, which is relevant, for example in nano emulsions).

S3. EXTENDED EXPLANATION OF SOLUTION STRATEGIES

S3.1. Aqueous phase (A): Water is the main ingredient in O/W emulsions; thus, its properties contribute greatly to the emulsion's behavior. Some of its characteristics can be implemented as solution strategies:

- **Water activity (A1)** is related to the capability of organisms to survive and growth. The smaller the water activity, the fewer the possibilities for organisms to live in the media²⁵. Water activity can be reduced by adding solutes such as sugar, salt, glycerin, propylene glycol and rheological modifiers, among others. It also decreases with temperature.
- **Polarity of the aqueous phase (A2)** is related to the capability of water to solubilize and transport substances. It can be modified by the addition of solutes. For example, the addition of glycerin, propylene glycol and/or ethanol reduces its polarity.
- **pH (A3)** has an important effect on almost all emulsion characteristics because it affects the behavior of molecules able to dissociate. It can be changed by the addition of an acid (for cosmetics, when it is required to reduce the pH, it is suggested to use a weak acid such as lactic or citric acid) or an alkali (such as sodium hydroxide, potassium hydroxide and triethanolamine) and it can be controlled with a buffer.
- **Electrolytes (A4)** are compounds that dissociate in water, such as salts. Their concentration affects the behavior of electrically charged species within the emulsion, which may be critical when ionic surfactants are used. In cases where it is necessary to increase electrolyte concentration, for example when a rheological modifier is activated with electrolytes or there is an active molecule that is also an electrolyte, attention must be paid not to exceed the minimum flocculation concentration to avoid instability.
- **Multivalent electrolytes concentration (A5)** has a much bigger effect than monovalent ion concentration. Thus, in emulsions stabilized with ionic surfactants, multivalent electrolytes should be avoided or used in very small concentrations. The use of distilled and deionized water is a common practice in the cosmetics industry to avoid product instability.

S3.2. Oily phase (B):

- **Polarity of oily phase (B6)** defines in part the relationship between the oily and aqueous phases. It also determines the solubility and transport of lipophilic actives. It can be changed by selecting a proper mix of oily compounds. Different oil types have different polarities. Hydrocarbons tend to have low polarity; esters have intermediate to high polarity and fatty alcohols tend to have very high polarity.
- The **degree of unsaturation of the oils (B7)** determines their tendency to oxidize. A low degree of unsaturation means a lower propensity to oxidation. Unsaturation is measured through the iodine number, which is high when the degree of unsaturation of the compound

is high. In some cases, oils with a relatively high iodine number are used in cosmetic formulations due to their function or nature. In this case, an additional strategy to avoid oxidation is recommended.

S3.3. Oily-aqueous phase (C):

- **The difference in the refractive index of phases (C8)** partially determines the emulsion's appearance; if it is zero, the emulsion turns transparent. The refractive index of water is normally lower than the refractive index of the oily phase. It is possible to increase the first by adding solutes to the aqueous phase such as salts, polysaccharides, alcohols and polyols¹¹. This will also change other aqueous properties²⁶. It is possible to change the oily phase refractive index by modifying the oily phase composition. Refractive index is also affected by temperature. It decreases as temperature increases. It is closely related and has an inverse behavior in relation to density²⁷. It is also related to the dielectric constant and consequently to colloidal interactions¹¹.
- **The difference in density between phases (C9)** can be decreased by selecting an oily phase with a relatively high density. Examples of some oily components with relative high density are waxes (of around 0.96 to 1) such as carnauba wax, candelilla wax and beeswax, which show relative high specific gravities²⁸. Natural oil and fats have densities of around 0.91¹¹. The presence of these components affects oily phase density, but also other important properties as the sensorial ones. Densities can be equated by changing composition, but this solution is only valid at a unique temperature¹⁶.
It can also be decreased by using weighting agents soluble in the oily phase. This solution is frequently used in food emulsions of low concentration to avoid separation by gravity¹¹. Weighting agents are molecules with a gravity greater than 1 that are soluble in the oily phase. Examples are brominated vegetable oil (BVO $\rho \approx 1330 \text{ kg m}^{-3}$), sucrose acetate isobutyrate (SAIB $\rho \approx 1146 \text{ kg m}^{-3}$), ester gum (EG $\rho \approx 1080 \text{ kg m}^{-3}$), damar gum (DG $\rho \approx 1050 - 1080 \text{ kg m}^{-3}$)¹¹.
It can also be decreased by increasing the portion of solid oils (fats) and/or using emulsifiers that form a thick interlayer which may increase droplet density¹¹.
- **The solubility of the disperse phase components in the continuous phase (C10)** is related to the instability of Ostwald ripening. It has been found experimentally that for O/W emulsions, the presence of components such as alcohols, or micelles in the continuous phase, increase the solubility of oils in water and in turn the Ostwald ripening rate²⁹. The effect of micelles formed by nonionic surfactants tends to be higher than for those of ionic surfactants, apparently because the latter generate an electrostatic repulsion³⁰. The solubility of the disperse phase can be also reduced by selecting a low polar oil, e.g., hydrocarbons and silicones instead of esters and fatty acids.

S3.4. Colloidal forces (D):

- **Electrostatic interactions (D11)** are generated in the emulsion by adding ionic surface-active agents, which adsorb on the oil-water interface. If they are in their ionized form (which depends on their pKa and the pH of the aqueous phase) a surface potential and a double layer is formed and droplets repel each other¹⁶. To assure emulsion stability, attention must be given to the factors that affect the spontaneous curvature of the surfactant. Factors that increase the curvature toward the oil droplets and consequently the stability of

O/W emulsions are: reduction of the electrolytes concentration and increase of temperature. Factors that decrease the spontaneous curvature towards the oily phase are: increase of the size of the surfactant chain, branching of the surfactant chain, presence of desorbing neutral species (i.g., sugar), oils with high polarity³⁰. An advantage of using ionic surfactants is that lower quantities are required in comparison to nonionic surfactants¹¹. A disadvantage is that their performance is highly dependent on pH and electrolyte concentration, thus flocculation may occur when surfactant isoelectric point is closed to emulsion pH. Additionally they have poor stability when emulsions is frozen and thawed¹¹.

- **Steric interactions (D12)** are generated when nonionic surfactants are added to the emulsion. Nonionic surfactants' molecules have two parts, one of them is highly soluble in the medium, and defines the curvature and the thickness of the interfacial layer. The other has a high surface activity and should absorb efficiently on the droplet interface¹⁶. Attention must be given to factors that affect the spontaneous curvature of the surfactant, because it has repercussions in emulsion stability. Factors that increase the curvature toward the oil droplets and consequently the stability of O/W emulsions are: higher size of the polar group and oils with a large chain³⁰. Factors that decrease the curvature and may destabilize emulsions are: a rise in temperature when the surfactants are dehydrated¹¹. Polymeric surfactants, such as the polysorbate type nonionic surfactant, have polymeric hydrophilic head groups that generate a better steric protection than the provided by small molecules¹¹. An advantage of using nonionic surfactants is that they are relative stable to pH changes and high electrolyte concentration¹¹. Some disadvantages are that they are needed in larger quantities in comparison to ionic surfactant, many of them are unstable at high temperatures although they may present a relative good stability to freeze and thaw¹¹.
- **Weak flocculation (D13)** is generated by the interrelation between attractive and repulsive forces. It may occur when forces acting between droplets create a configuration in which two potential energy minimums are presented. One of them is very deep and corresponds to a very close distance between droplets (primary minimum), and the second one corresponds to a larger distance where droplets can agglomerate reversibly (weak flocculation)¹¹. Weak flocculation can be selected as a strategy to increase emulsion viscosity and thinning behavior. In electrostatically stabilized systems it is possible to generate weak flocculation by controlling electrostatic repulsion. For example, by adding small amounts of electrolytes to the emulsions system¹⁸. In sterically stabilized emulsion, it is possible to generate a weak flocculation by a controlled reduction of the protecting layer. This can be done by reducing the molecular weight of emulsifier or changing the relation between the surfactant chains and the medium (for example by adding electrolytes)¹⁸. Weak flocculation can also be generated by the addition of a non-absorbed polymer or surfactant (surfactants such as Tween 20, sodium dodecyl sulfate, polysaccharides such as xanthan gum, and proteins, such as whey and caseinate¹¹). This action increases the osmotic pressure outside droplets and generate an attraction between them to compensate the pressure change¹⁸.

S3.5. Interface (E): Surfactants and amphiphilic compounds locate at the droplet – continuous phase interface. They are responsible for interfacial phenomena which are highly related to emulsion rheology and stability. Interface characteristics that can be tuned to define emulsion behavior include:

- **Surface charge density (electrolyte repulsion) (E14)** is defined as the amount of electrical charge on the droplet surface. It is mainly affected by the nature of the ionic compounds adsorbed on the droplet surface (ionic surfactants such as phospholipids, fatty acids, multivalent ions such as Ca^{2+} , Cu^{2+} , charged biopolymers and nanoparticles) as well as by the characteristics of the continuous phase such as the pH, ionic composition, temperature ¹¹. Depending on the nature of the adsorbed ion, electrical charge of droplets may increase, decrease or be inverted ¹¹. Monovalent ions in water in moderate concentrations screen electrostatic interactions but do not affect the electrical charge. Multivalent ions do affect electrical charge ¹¹.
- **Surfactant – solvent conditions (steric repulsion) (E15):** Steric repulsion is enhanced when surfactant chains are in good solvent conditions, that is, when the surfactant – solvent interaction is favored over the polymer-polymer interaction ¹⁸. Good solvent conditions can be encouraged by selecting an appropriate surfactant with a suitable HLB, by keeping low temperatures, or by changing the composition of the aqueous phase to enhance solvation (for example by adding a solvent in which the surfactant has a higher solubility than water).
- **Thickness (steric repulsion) (E16)** refers to the range of steric interactions. In practice, it can be increased by selecting surfactants with a longer hydrophilic chain. In addition, the strength of steric interactions increases with droplet size and depends on the interfacial layer characteristics such as viscosity and flexibility ¹¹.
- **The interfacial dilatational Gibbs elasticity (E17)** gives resistance to the interfacial layer against deformation and coalescence. It can be improved by the implementation of polymeric and biopolymeric emulsifiers such as proteins and polysaccharides ^{16,11}. It is also improved when the packaging of the interface is tight, which is why the use of a mixture of surfactants with different polymer lengths and different HLB is suggested ¹⁶.
- **Interfacial tension (E18)** indicates the free energy required to increase the interfacial area ¹¹. It is decreased when surfactants or polymers are adsorbed. It is also decreased when temperature is increased to reach a minimal value at a temperature point known as PIT. When emulsions are prepared at PIT, droplets are smaller than those prepared at lower temperatures ¹⁸.

S3.6. Microstructure (F):

- **Droplet size (F19)** is defined by components and process conditions. It can be decreased by increasing surfactant concentration, selecting a surfactant with a high adsorption rate (which is related to the surfactant's molecular weight), increasing processing temperature (which reduces the viscosity of phases) and by decreasing interfacial tension ^{11,31}. If enough emulsifier is added, droplet size is decreased by increasing the mechanical energy input. Energy input depends on the homogenizer and operating conditions. In a rotor-stator homogenizer, it increases with the rotation speed ¹¹.
- **Droplet size distribution (F20)** width is difficult to control and depends strongly on the homogenization process. Membrane and micro-channel homogenizers (which are not common on an industrial scale) generate narrow distributions, while high shear mixers, high-pressure valve homogenizers, colloid mills, micro-fluidizers, and ultrasonic homogenizers generate broader distributions ¹¹. Batch systems produce wider DSDs than continuous operation systems ³². A more viscous disperse phase generates a broader

distribution^{32,33}. This effect can be avoided by heating or changing the disperse phase composition. Interfacial tension: distribution becomes broader as interfacial tension is increased³³. Interfacial tension can be reduced by adding/changing the surfactant system.

- **Volume fraction (F21)** of the dispersed phase in O/W emulsions is increased by increasing the oily phase and/or particle concentration if the product contains suspended particles. When volume fraction is augmented, emulsion rheology, stability and appearance are importantly affected. For example, emulsion lightness increases, viscosity and viscoelastic behavior are enhanced, and stability against flocculation, coalescence and phase inversion may be affected. For O/W the increment of the oily phase carries higher costs.

S3.7. Emulsion protection (G):

- **The packaging (G22)** provides protection to the product. It can be designed with U.V. protection or in such a way as to limit oxygen inlet into the product. Special attention must be paid to the packaging material and its compatibility with the product components, as well as its performance in sustainability terms.

S3.8. Functional ingredients (H):

- **Antioxidants (H23)** are compounds that prevent oxidation, the formation of free radicals and thus the deterioration of skin cells.
- **Preservatives (H24)** are substances that inhibit the growth of organisms, preventing the product from getting damaged. Care must be taken with these substances because many of them can be toxic or controlled with a limited maximal concentration.
- **Chelating agents (H25)** are compounds capable of removing transition metals such as iron and copper from the vicinity of droplets²¹. An example of these agents is EDTA²¹.
- **Alcohols and solvents (H26)** This solution strategy refers to the addition of a low molecular weight alcohol (e.g. ethanol) or other solvent. In some cases, this can affect the spontaneous curvature of the surfactant system (from O/W to water in oil (W/O)), increase the solubility of oil in water, reduce surface tension, increase the water refractive index, enhance emulsion preservation, among other effects.
- **Fragrances (H27)** When selecting them, care must be taken with aspects such as toxicity, compatibility with other components, stability to pH and light, price, and in the case of cosmetics, compatibility with skin.
- **Colorants (H28)** are substances that give color to the emulsion. In their selection, it is necessary to pay attention to aspects such as solubility in the media (dyes are soluble, and pigments are not, i.e., the latter should be dispersed in the emulsion), resistance to pH, temperature changes, stability to light and chemical agents, and price, among others.
- **Rheological modifiers – continuous phase (H29)** are substances that change the rheological behavior of a phase and of the emulsion. They can increase viscosity or change the rheological profile to increase shear thinning behavior or enhance viscoelasticity.
- **Rheological modifiers – disperse phase (H30)** Rheological modifiers can also be added to the disperse phase, affecting the rheological behavior of the entire emulsion.

S4. EXTENDED INFORMATION – COSMETIC INGREDIENTS

Table S2. Commonly used cosmetic oils classified in families

International Nomenclature of Cosmetic Ingredients INCI	Polarity	Viscosity (qualitative)	Spreading	Emollience	After feel	Required HLB	State	Density	Origin
Esters: Compounds with a wide range of properties. Medium polarity between hydrocarbons and fatty alcohols. Typical required HLB between 10-12. Unstable at low and high pH.									
C12-15 Alkyl Benzoate	Very high ^(a, f)	Medium ^(a, f)	Low ^(a)	Medium to light ^(f)	Low oily sensation ^(f)	13 ^(k)	Liquid	0.92 ^(g)	Natural raw material ^(l)
Cetyl Ethylhexanoate	Medium ^(f)	Medium ^(f)	High ^(f)	Medium to light ^(f)	Low oily sensation ^(f)	11 ^(k)	Liquid	0.85	Natural and synthetic
Decyl Cocoate	Medium ^(f)	Low ^(g)	Low ^(f)	Light ^(f)	Smooth, oily residue ^(f)	10 ⁽ⁱ⁾	Liquid	0.85 ^(h)	Natural raw material ^(h)
Decyl Oleate	Medium ^(a)	Medium ^(a)	Medium ^(a)	NA	NA	10 ⁽ⁱ⁾	Liquid	0.86 ^(a)	Natural raw material
Ethylhexyl Palmitate	Medium ^(a, f)	Medium ^(a, f)	Medium ^(a)	Light ^(c, f)	Low oily sensation ^(c, f)	8 ^(g)	Liquid	0.86 ^(h)	Natural and synthetic ^(2, 4)
Ethylhexyl Stearate	Medium ^(a, f)	Medium ^(a, d, f)	Medium ^(g)	Medium to light ^(f)	Low oily sensation ^(f)	8 ^(g)	Liquid	0.86 ^(g)	Natural and synthetic ^(l)
Isoamyl Cocoate	Medium ^(f)	Low ^(f)	Medium ^(f)	Light ^(f)	Low oily sensation ^(f)	10 ⁽ⁱ⁾	Liquid	0.85 ^(h)	Natural raw materials ^(h)
Isopropyl Isostearate	Medium ^(b)	Low ^(b)	High ^(g)	Light ^(b)	Low oily sensation, silky ^(b)	9 ^(b)	Liquid	0.86	Natural and synthetic ^(g)
Isopropyl Myristate	Medium ^(a, f)	Low ^(a, d, f)	High ^(g)	Light ^(c, f)	Low oily sensation ^(f)	11.5 ^(k)	Liquid	0.86 ^(h)	Natural and synthetic ^(l)
Isopropyl Palmitate	Medium ^(a, f)	Low ^(a, f)	High ^(a)	Light ^(c, f)	Smooth ^(f)	10 ^(g)	Liquid	0.86 ^(h)	Natural and synthetic ⁽¹³⁾
Isostearyl Isostearate	Medium ^(b)	High ^(b)	Low ^(b)	Medium ^(b)	Smooth ^(b)	11 ^(b)	Liquid	0.87	Natural and synthetic ⁽²⁴⁾
Oleyl Erucate	Medium ^(a, f)	High ^(a, f, g)	Low ^(a)	Rich ^(a, f)	Smooth, lubricous ^(a, f)	13 ^(h)	Liquid	0.87 ^(h)	Natural raw materials ⁽¹³⁾
Cetyl palmitate	Medium ⁽ⁱ⁾	NA	NA	Heavy	Highly lubricous, waxy, smooth ^(g)	10 ^(k)	Solid	0.83	Natural raw material ^(l)
Fatty alcohol: Compounds with high polarity. They are frequently used as consistency agents. They have a required HLB between 14-15. Stable to pH changes and oxidation									

Hexyldecanol	Medium ^(a)	High ^(a)	Medium ^(a)	Light to medium ⁽ⁱ⁾	Smooth ^(j)	14 ⁽ⁱ⁾	Liquid	0.84 ⁽ⁱ⁾	Natural raw materials ^(l)
Octyldodecanol	High ^(a)	High ^(f)	Low ^(a)	Medium light ^(f)	Low oily sensation ^(f)	11 ^(k)	Liquid	0.84 ^(b)	Natural raw materials ^(l)
Stearyl Alcohol	High ⁽ⁱ⁾	NA	NA	Heavy	Highly lubricous, waxy, smooth ⁽¹¹⁾	15.5 ^(k)	Solid	0.81 ^(h)	Natural raw materials ^(l)
Cetyl Alcohol	High ⁽ⁱ⁾	NA	NA	Heavy	Highly lubricous, waxy, smooth ⁽¹¹⁾	15.5 ^(k)	Solid	0.81 ^(h)	Natural raw materials ^(l)
Hydrocarbons: Ingredients of low polarity, highly stable to pH and oxidation. Required HLB between 9-11.									
Mineral oil*	Low ⁽ⁱ⁾	Medium ^(e)	Medium ^(e)	Medium to rich	Smooth, lubricous	10 ^(k)	Liquid	0.86 ^(l)	Synthetic raw material ^(l)
Silicone: often used to give a soft and silky texture to emulsions. They have a low melting point. They are liquids with a wide range of viscosity giving different viscosities according to their molecular weight.									
Cetyl Dimethicone (very high viscosity, nonpolar)*	Low ⁽ⁱ⁾	Very high ^(f)	Low ^(f)	Rich ^(f)	Smooth ^(f)	NA	Liquid	0.93 ^(g)	Synthetic raw material ^(l)
Dimethicone*	Low ⁽ⁱ⁾	Very high ^(h)	Low ^(f)	Rich ^(f)	Smooth, oily residue ^(f)	NA	Liquid	0.96 ^(g)	Synthetic raw material ^(l)
Triglyceride: high polar, high viscous compounds with a high oily sensation. Low resistance to changes in pH and oxidation									
Caprylic/Capric Triglyceride	Medium ^(a)	High ^(a, d, f)	Medium ^(e)	Light to medium ^(f)	Low oily sensation ^(f)	11 ^(k)	Liquid	0.94 ^(h)	Natural raw material ^(l)
Triisostearin	High ^(b)	Very high ^(b)	Low ^(b)	Medium to rich ^(b, f)	Smooth ^(b, f)	8 ^(b)	Liquid	0.91 ^(h)	Natural raw material ^(l)
Avocado oil	NA	Very high ^(f)	NA	Rich ^(f)	NA	7 ^(k)	Liquid	0.92 ^(m)	Natural ^(l)
Shea butter	NA	NA	NA	Rich	Oily residue, smooth	8 ^(k)	Solid	0.95 ^(g)	Natural ^(l)
Olive oil	NA	NA	Low	Rich	Oily residue, smooth	7 ^(k)	Liquid	0.92 ⁽ⁿ⁾	Natural ^(l)
Almond oil	NA	NA	High	Light	Smooth	6 ^(k)	Liquid	NA	Natural ^(l)
Joboba oil	NA	NA	High	Light	Smooth	6 ^(k)	Liquid	0.86 ^(o)	Natural ^(l)
Olus Oil	Medium ^(a)	High ^(a)	Low	Rich	Smooth	NA	Liquid	NA	Natural
Passiflora Incarnata Seed Oil	Medium ^(a)	High ^(a)	Low	Rich	Smooth	NA	Liquid	NA	Natural
Fatty acids: Highly polar. They can increase the viscosity of emulsion. Required HLB 14-15. Unstable at high pH. For cosmetics, it is common to use their salts as emulsifier agents (Table 2)									

(NA) means not available. (*) means not biodegradable. (a) BASF. BASF emollients - choosing the right emollient. BASF Personal Care and Nutrition GmbH. 2016, (b) Croda. Emollients Your Essential Selection Guide. Seventh Edition. 2013, (c) Technical information -Crodamol TM (spanish). Croda, (d) Croda. Pigment Wetting Guid DS-120R-1. Croda February 25, 1999, (e)

Nonionic	POE Alkyl ethers	O/W	Ceteareth-25	16 ^(a)	X ^(b)	-	-		X ^(b)	X ^(b)	-	-	
Nonionic	POE Alkyl ethers	NA	Steareth-100	18.8 ^(d)									
Nonionic	POE Alkyl ethers	O/W and W/O	Steareth-2	4.9 ^(a)	X ^(e)	X ^(e)	X ^(e)		X ^(e)	X ^(e)		X ^(e)	X ^(e)
Nonionic	POE Alkyl ethers	O/W	Steareth-20	15.3 ^(a)	X ^(e)	X ^(e)	X ^(e)		X ^(e)	X ^(e)		X ^(e)	X ^(e)
Nonionic	Polyglycerol ester	W/O	Polyglyceryl-3 Diisostearate	4 ^(c)									
Nonionic	Polyglycerol ester	O/W	Polyglyceryl-3 Distearate	9 ^(c)	X ^(e)	X ^(e)	X ^(e)	- ^(c)	X ^(e)	X ^(c)	X ^(c)	-	X ^(c)
Nonionic	Polyglycerol ester	W/O	Polyglyceryl-3 Oleate	5 ^(a)									
Nonionic	Polyoxyethylene glycerides	O/W	PEG-100 Stearate	19 ^(a)	X ^(e)	X ^(e)			X ^(e)	X ^(e)			
Nonionic	Polyoxyethylene sorbitans	O/W	Polysorbate 60	15 ^(a)									
Nonionic	Polyoxyethylene sorbitans	O/W	Polysorbate 80	15 ^(a)									
Nonionic	Sorbitans	NA	Sorbitan isostearate	4.7 ^(d)									
Nonionic	Sorbitans	O/W	Sorbitan Laurate	9 ^(a)									
Nonionic	Sorbitans	NA	Sorbitan Monopalmitate	6.7 ^(d)									
Nonionic	Sorbitans	NA	Sorbitan Monostearate	4.7 ^(d)									
Nonionic	Sorbitans	W/O	Sorbitan sesquioleate	3.7 ^(d)									
Nonionic	Sorbitans	W/O	Sorbitan trioleate	1.8 ^(d)									
Nonionic	Sucrose ester	NA	Sucrose Distearate	3 ^(d)	X ^(d)				X ^(d)		X ^(d)		
Nonionic	Sucrose ester	O/W	Sucrose Stearate	14.5 ^(d)					X ^(d)	X ^(d)			

Notes: X means recommended used for. References: (a) Evonik industries. Personal Care Catalog of products. 2015, (b) Evonik Industries. Emulsifiers for Skin Care Applications. March 2008. Essen - Germany, (c) BASF. Emulsifiers & Cream Bases. May 2016, (d) Croda datasheet, (e) Evonik datasheet

Table S4. INCI names of surfactants used in Figure 6

Classification 1	Classification 2	Inci name	C in alkyl chain	POE groups	HLB	REF
Nonionic	Alkylglucosides	Cetearyl Glucoside	C16-C18		13	Basf datasheet
Nonionic	Monoglycerol esters of fatty acids	Glyceryl Stearate	C18		4	Croda datasheet
Nonionic	Monoglycerol esters of fatty acids	Glyceryl Oleate	C18 -oleate		3	Basf datasheet
Nonionic	POE Alkyl ethers	Laureth-4	C12	POE-4	9.7	Croda datasheet
Nonionic	POE Alkyl ethers	Laureth-23	C12	POE-23	16.9	Evonik datasheet
Nonionic	POE Alkyl ethers	Ceteth-2	C16	POE-2	5.3	Croda datasheet
Nonionic	POE Alkyl ethers	Ceteth-10	C16	POE-10	12.9	Croda datasheet
Nonionic	POE Alkyl ethers	Ceteth-20	C16	POE-20	15.7	Croda datasheet
Nonionic	POE Alkyl ethers	Isoceteth-20	C16 -isocetyl	POE-20	16	Evonik datasheet
Nonionic	POE Alkyl ethers	Ceteareth-20	C16-C18	POE-20	15	Basf datasheet
Nonionic	POE Alkyl ethers	Ceteareth-25	C16-C18	POE-25	16	Evonik datasheet
Nonionic	POE Alkyl ethers	Ceteareth-30	C16-C18	POE-30	17	Basf datasheet
Nonionic	POE Alkyl ethers	Oleth-10	C18 -oleyl	POE-2	4.9	Croda datasheet
Nonionic	POE Alkyl ethers	Oleth-2	C18 -oleyl	POE-10	12.4	Croda datasheet
Nonionic	POE Alkyl ethers	Steareth-2	C18	POE-2	4.9	Evonik datasheet
Nonionic	POE Alkyl ethers	Steareth-10	C18	POE-10	12.4	Croda datasheet
Nonionic	POE Alkyl ethers	Steareth-20	C18	POE-20	15.3	Evonik datasheet
Nonionic	POE Alkyl ethers	Steareth-100	C18	POE-100	18.8	Croda datasheet
Nonionic	Polyglycerol esters of fatty acids	Polyglyceryl-4 Laurate	C12		11	Basf datasheet
Nonionic	Polyglycerol esters of fatty acids	Polyglyceryl-4 Diisostearate	C18-iso-stearate		5	Evonik datasheet
Nonionic	Polyglycerol esters of fatty acids	Polyglyceryl-3 Diisostearate	C18-di-isostearate		4	Basf datasheet
Nonionic	Polyglycerol esters of fatty acids	Polyglyceryl-3 Distearate	C18-di-stearate		9	Basf datasheet
Nonionic	Polyglycerol esters of fatty acids	Polyglyceryl-3 Oleate	C18-oleate		5	Evonik datasheet
Nonionic	Polyoxyethylene glycerides	PEG-4 Sorbitan Monolaurate	C12	POE-4	13.3	Croda datasheet

Nonionic	Polyoxyethylene glycerides	PEG-20 Sorbitan Monolaurate	C12	POE-20	16.7	Croda datasheet
Nonionic	Polyoxyethylene glycerides	PEG-80 Sorbitan Laurate	C12	POE-80	19.1	Croda datasheet
Nonionic	Polyoxyethylene glycerides	PEG-20 sorbitan monopalmitate	C16	POE-20	15.6	Croda datasheet
Nonionic	Polyoxyethylene glycerides	PEG-4 sorbitan monostearate	C18	POE-4	9.6	Croda datasheet
Nonionic	Polyoxyethylene glycerides	PEG-8 Stearate	C18	POE-8	11.1	Croda datasheet
Nonionic	Polyoxyethylene glycerides	PEG-20 sorbitan monostearate	C18	POE-20	14.9	Croda datasheet
Nonionic	Polyoxyethylene glycerides	PEG-100 Stearate	C18	POE-100	19	Croda datasheet
Nonionic	Sorbitans	Sorbitan Monolaurate	C12		9	Croda datasheet
Nonionic	Sorbitans	Sorbitan Monopalmitate	C16		6.7	Croda datasheet
Nonionic	Sorbitans	Sorbitan Monostearate	C18		4.7	Croda datasheet
Nonionic	Sorbitans	Sorbitan sesquioleate	C18 - oleate		3.7	Croda datasheet
Nonionic	Sorbitans	Sorbitan trioleate	C18-tri-oleate		1.8	Croda datasheet
Nonionic	Sucrose fatty acid esters	Sucrose Distearate	C18-di-stearate		3	Croda datasheet
Nonionic	Sucrose fatty acid esters	Sucrose Polystearate	C18-polystearate		10	Basf datasheet
Nonionic	Sucrose fatty acid esters	Sucrose Stearate	C18 - mono-stearate		14.5	Croda datasheet

Table S5. List of some rheological modifiers frequently used in cosmetic emulsions

Thickener	Electrical nature (a)	Type (b)	Solvent (b)	Rheology (b)	Yield value (b)	Electrolyte stability (a)	Temperature stability (a)	Activation (a)	pH stability (a)
Cellulose gum	Nonionic, anionic	Aqueous thickeners	Water	Thixotropic	Yes	Yes	Excellent	NA	NA
Guar gum	Nonionic	Aqueous thickeners	Water	Pseudoplastic	No	Yes	NA	NA	Poor acid stability
Xanthan gum	anionic	Aqueous thickeners	Water	Pseudoplastic	Yes	Yes	Excellent	NA	Stable at low and relative high pH
Hydroxyethyl-cellulose	nonionic	Aqueous thickeners	Water	Pseudoplastic	No	Yes	NA	NA	NA

Methylcellulose	nonionic	Aqueous thickeners	Water	Pseudoplastic	Yes	Yes	NA	NA	NA
Hydroxypropyl methylcellulose	nonionic	Aqueous thickeners	Water	Pseudoplastic	No	Yes	NA	NA	NA
Carbomers	anionic	Aqueous thickeners	Water	Pseudoplastic	Yes	No	NA	Alkaline agent	NA
Acrylates / VA crosspolymers	anionic	Aqueous thickeners	Water	Pseudoplastic	Yes	No	NA	NA	Stable at high pH
Polyethylene glycols	nonionic	Aqueous thickeners	Water	Newtonian	No	Yes	NA	NA	NA
clays	NA	Aqueous thickeners	Water	Thixotropic	Yes	Yes	Excellent	NA	Stable at high and low pH
Polyethylenes	NA	Non-Aqueous thickeners	Oil	Pseudoplastic	Yes	NA	NA	NA	NA
Trihydroxystearin (organic)	NA	Non-Aqueous thickeners	Oil	Thixotropic	Yes	NA	NA	NA	NA
Organoclays	NA	Non-Aqueous thickeners	Oil	Thixotropic	Yes	NA	NA	Chemical (polar) activator	NA
Fumed silica	NA	Non-Aqueous thickeners	Oil	Thixotropic	Yes	NA	Excellent	NA	NA

Notes: NA means Not available. References: (a) Braun D. B., Meyer R. R., Rheology Modifiers Handbook, 1st Edition, Elsevier, 2000 (b) Laba, D., 2001. How Do I Thicken my Cosmetic Formula. Cosmet. Toilet. 116, 35–44

Table S6. List of UV filters approved by the FDA

UV Filter	CAS No	Maximum concentration FDA[%](e)	Protection range	log BCF	Toxicity NFPA	Fire-NFPA	Reactivity NFPA
Avobenzene(b),(d)	70356-09-1	3	UVA1	1.929	1	1	0
Ecamsule (d)	90457-82-2	3	UVA2	NA	NA	NA	NA
Meradimate (d),(g)	134-09-8	5	UVA2	3.968	0	1	0
Aminobenzoic acid(b), (d)	150-13-0	15	UVB	0.5	1	1	0

UV Filter	CAS No	Maximum concentration FDA[%](e)	Protection range	log BCF	Toxicity NFPA	Fire-NFPA	Reactivity NFPA
Cinoxate (d)	104-28-9	3	UVB	1.344	NA	NA	NA
Ensulizole(b), (d)	27503-81-7	4	UVB	0.5	1	1	0
Homosalate (d)	118-56-9	15	UVB	4.045	2	1	0
Octocrylene(b), (d)	6197-30-4	10	UVB	4.599	1	1	0
Octinoxate(b), (d)	5466-77-3	7.5	UVB	3.768	1	1	0
Octisalate(b), (d)	118-60-5	5	UVB	3.895	1	1	0
Padimate O (d), (f)	21245-02-3	8	UVB	3.739	1	1	0
Trolamine salicylate (d)	2174-16-5	12	UVB	NA	1	1	0
Dioxybenzone (d), (g),(h)	131-53-3	3	UVB, UVA2	2.6732	2	1	0
Oxybenzone(b), (d)	131-57-7	6	UVB, UVA2	1.378	1	1	0
Sulisobenzone (c),(d)	4065-45-6	10	UVB, UVA2	0.5	2	1	0
Titanium dioxide(b), (d)	13463-67-7	25	UVB, UVA2	-	1	0	0
Zinc oxide(c),(d)	1314-13-2	25	UVB, UVA2, UVA1	-	1	0	0

Notes: NA means Not available. References: (a) SPF for each ingredient and combinations at different concentrations can be found in the SPF simulator from BASF: https://www.sunscreensimulator.basf.com/Sunscreen_Simulator/Login_show.action (accessed 9.1.15)

(b) Merck. MSDS Merck <http://www.emdmillipore.com/US/en/support/safety/material-safety-data-sheets/lvmb.qB.TzsAAAFcXd4Xr74u.nav?bd=1> (accessed Aug 30, 2015).

(c) BASF. MSDS BASF <http://worldaccount.basf.com/wa/msds/na/search> (accessed Aug 30, 2015)

(d) Brooke, D. N.; Brund, J. S.; Crookes, M. J. UV-Filters in Cosmetics – Prioritisation for Environmental Assessment; Environment Agency UK: Rio Haus, 2008. (e) FDA.

CFR - Code of Federal Regulations Title 21. Food and Drug Administration

<https://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfCFR/CFRSearch.cfm?fr=201.327>

(accessed Mar 16, 2017).

(f) NTP. NTP Chemical Nomination - CAS 21245-02-3. US National Toxicology Program

https://ntp.niehs.nih.gov/ntp/htdocs/chem_background/exsumpdf/ethylhexyldimeth_508.pdf

(accessed Aug 30, 2015).

(g) SPharmacopeial. MSDS USPharmacopeial <http://www.usp.org/es/estandares-de-referencia/hojas-de-datos-tecnicos>

(accessed Aug 30, 2015).

(h) Li, M. Acute Toxicity of Benzophenone-Type UV Filters and Paraben Preservatives

to Freshwater Planarian, *Dugesia Japonica*. *Toxicol. Environ. Chem.* 2012, 94 (3), 566–

573.

References

- (1) Bernardo, F. P. Integrated Process and Product Design Optimization. In *Tools For Chemical Product Design: From Consumer Products to Biomedicine*; Martín Martín, M., Eden, M. R., Chemmangattuvalappil, N. G., Eds.; Elsevier B.V.: Amsterdam, 2016; pp 347–372. <https://doi.org/10.1016/B978-0-444-63683-6.00012-5>.
- (2) Bernardo, F. P.; Saraiva, P. M. A Conceptual Model For Chemical Product Design. *Am. Inst. Chem. Eng. J.* **2014**, 61 (3), 1–15. <https://doi.org/10.1002/aic>.
- (3) Arrieta-Escobar, J. A.; Bernardo, F. P.; Orjuela, A.; Camargo, M.; Morel, L. Incorporation of Heuristic Knowledge in the Optimal Design of Formulated Products : Application to a Cosmetic Emulsion. *Comput. Chem. Eng.* **2018**, 0, 1–10. <https://doi.org/10.1016/j.compchemeng.2018.08.032>.
- (4) Fung, K. Y.; Ng, K. M.; Zhang, L.; Gani, R. A Grand Model for Chemical Product Design. *Comput. Chem. Eng.* **2016**, 91, 15–27. <https://doi.org/10.1016/j.compchemeng.2016.03.009>.
- (5) Zhang, L.; Fung, K. Y.; Zhang, X.; Fung, H. K.; Ng, K. M. An Integrated Framework for Designing Formulated Products. *Comput. Chem. Eng.* **2017**, 107, 61–76. <https://doi.org/10.1016/j.compchemeng.2017.05.014>.
- (6) Conte, E.; Gani, R.; Ng, K. M. Design of Formulated Products : A Systematic Methodology. *AIChE J.* **2011**, 57 (9), 2431–2449. <https://doi.org/10.1002/aic>.

- (7) Conte, E.; Gani, R.; Cheng, Y. S.; Ng, K. M. Design of Formulated Products Experimental Component. *AIChE J.* **2012**, *58* (1), 173–189.
- (8) Kontogeorgis, G. M.; Mattei, M.; Ng, K. M.; Gani, R. An Integrated Approach for the Design of Emulsified Products. *AIChE J.* **2019**, *65* (1), 75–86.
<https://doi.org/https://doi.org/10.1002/aic.16363>.
- (9) Hada, S.; Herring III, R. H.; Eden, M. R. Mixture Formulation through Multivariate Statistical Analysis of Process Data in Property Cluster Space. *Comput. Chem. Eng.* **2017**, *107*, 26–36. <https://doi.org/10.1016/j.compchemeng.2017.06.017>.
- (10) Faust, J. M. M.; Henrichfreise, L.; Mhamdi, A.; Mitsos, A. Dynamic Optimization of an Emulsion Polymerization Process Using an Embedded Monte Carlo Model for Bimodal MWD. *Comput. Aided Chem. Eng.* **2020**, *48*, 1171–1176. <https://doi.org/10.1016/B978-0-12-823377-1.50196-8>.
- (11) McClements, D.-J. *Food Emulsions: Principles, Practices and Techniques*. Third Edit. CRC Press: Boca Raton 2016, p 702.
- (12) McClements, D. J. Emulsion Design to Improve the Delivery of Functional Lipophilic Components. *Annu. Rev. Food Sci. Technol.* **2010**, *1*, 241–269.
- (13) Chantrapornchai, W.; Clydesdale, F. M.; McClements, D. J. Understanding Colors in Emulsions. In *Color Quality of Fresh and Processed Foods*; Culver, Wrolstad, Eds.; ACS Symposium Series; American Chemical Society: Washington, 2008; Vol. 983, pp 364–387. <https://doi.org/10.1021/bk-2008-0983.ch026>.
- (14) Laba, D. *Rheological Properties of Cosmetics and Toiletries*. Marcel Dekker, Inc.: New York 1993, p 440.
- (15) Derkach, S. R. Rheology of Emulsions. *Adv. Colloid Interface Sci.* **2009**, *151* (1–2), 1–23. <https://doi.org/10.1016/j.cis.2009.07.001>.
- (16) Tadros, T. F. *Rheology of Dispersions: Principles and Applications*. Wiley-VCH: Weinheim, Germany 2010, p 216.
- (17) Cussler, E. L.; Wagner, A.; Marchal-Heussler, L. Designing Chemical Products Requires More Knowledge of Perception. *AIChE J.* **2010**, *56* (2), 283–288.
- (18) Tadros, T. F. *Emulsion Science and Technology*. Wiley VCH: Weinheim 2009, p 362.
- (19) Leal-Calderon, F.; Schmitt, V.; Bibette, J. *Emulsion Science Basic Principles*. Second Edi. Springer: New York 2007, p 227.
- (20) Brooks, B. W.; Howard, N. R.; Mohamed, Z. Phase Inversion and Drop Formation in Agitated Liquid-Liquid Dispersions in the Presence of Nonionic Surfactants. *Modern Aspects of Emulsion Science*. The Royal Society of Chemistry: Cambridge 1998, p 175.

- (21) McClements, D. J.; Decker, E. Lipid Oxidation in Oil-in-Water Emulsions: Impact of Molecular Environment on Chemical Reactions in Heterogeneous Food Systems. *J. Food Sci.* **2000**, *65* (8), 1270–1282. <https://doi.org/10.1111/j.1365-2621.2000.tb10596.x>.
- (22) Kabara, J. J.; Orth, D. S. Principles for Product Preservation. *Preservative-Free and Self-Preserving Cosmetic and Drugs*. Marcel Dekker: Basel 1997.
- (23) Draeos, Z. D. Cosmetic and Dermatological Problems and Solutions. A Problem Based Approach. third Edit. CRC Press: Boca Raton 2011, p 280.
- (24) Wiechers, J. W.; Kelly, C. L.; Blease, T. G.; Dederen, J. C. Formulating for Efficacy. *Int. J. Cosmet. Sci.* **2004**, *26*, 173–182.
- (25) Russell, N. J.; Leistner, L.; Gould, G. W. Solutes and Low Water Activity. In *Food Preservatives*; Russell, N. J., Gould, G. W., Eds.; Springer: Boston, 2003.
- (26) *CRC Handbook of Chemistry and Physics*, 84th edit.; Lide, D., Ed.; CRC Press, 2004.
- (27) Budwig, R. Refractive Index Matching Methods for Liquid Flow Investigations. *Exp. Fluids* **1994**, *17* (5), 350–355. <https://doi.org/10.1007/BF01874416>.
- (28) Iwata, H.; Shimada, K. Formulas, Ingredients and Production of Cosmetics. *Formulas, Ingredients and Production of Cosmetics*. Springer: Tokyo 2013, p 221.
- (29) McClements, D. J. Critical Review of Techniques and Methodologies for Characterization of Emulsion Stability. *Crit. Rev. Food Sci. Nutr.* **2007**, *47* (November), 611–649. <https://doi.org/10.1080/10408390701289292>.
- (30) Binks, B. P. Modern Aspects of Emulsion Science. The Royal Society of Chemistry: Cambridge 1998, p 430.
- (31) Chevalier, Y.; Bolzinger, M. A.; Puel, F. Émulsions. In *Conception des produits cosmétiques*; Pensé-Lhéritier, A. M., Ed.; Lavoisier: Paris, 2016; p 138.
- (32) Paul, E. L.; Atiemo-obeng, V. a; Kresta, S. M. Handbook of Industrial Mixing. John Wiley & Sons, Inc: New Jersey 2004, p 1140.
- (33) Vankova, N.; Tcholakova, S.; Denkov, N. D.; Ivanov, I. B.; Vulchev, V. D.; Danner, T. Emulsification in Turbulent Flow. 1. Mean and Maximum Drop Diameters in Inertial and Viscous Regimes. *J. Colloid Interface Sci.* **2007**, *312* (2), 363–380. <https://doi.org/10.1016/j.jcis.2007.03.059>.