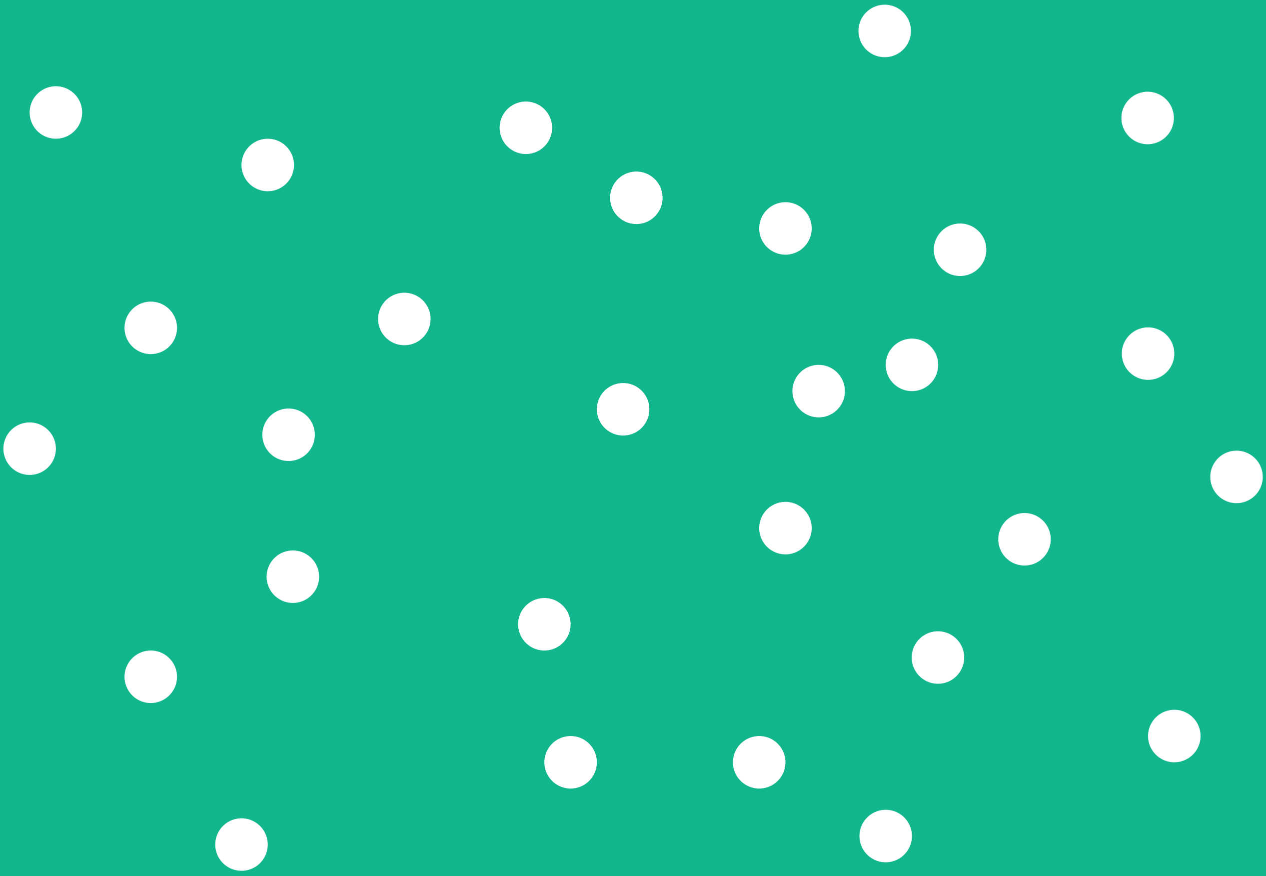
Cosmetic emulsions



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Cosmetic emulsions

Monograph

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ABBREVIATIONS

W/O – water in oil emulsion
O/W – oil in water emulsion
INCI – International Nomenclature of Cosmetic Ingredients
IPR – internal phase ratio
γ – surface or intenterfacial tension, J/m^2
W – work input required to increase the phase surface by the unit, J
A – interface (phase boundary), m^2
ΔG_{form} – free energy of emulsion formation, J
ΔA – total surface area, m^2
T – absolute temperature, K
ΔS – entropy, J/K
HLB – hydrophile-lipophile balance
HLB_r – required HLB number of an oil phase
M_H – molecular mass of hydrophilic groups
M_C – molecular mass of the whole emulsifier
SN – saponification number
AN – neutralization number of fatty acids
E – percentage content (wt.) of ethylene oxide in the molecule
P – percentage content (wt.) of other hydrophilic groups in the molecule
PEO – polyethylene oxide
M_L – molecular mass of lipophilic group
m_p – mass of polyglycerol used in the synthesis of the polyglyceryl ester
m_a – mass of carboxylic acids used in the synthesis of the polyglyceryl ester
Cw – surfactant concentration equilibrium in water
Co – surfactant concentration equilibrium in oil
PIT – phase inversion temperature
NMR – nuclear magnetic resonance
GC – gas chromatography
IP – polarity index
SP – solubility parameter, $mPa^{1/2}$
ΔH_V – heat of evaporation, J/mol
V_M – molar volume, cm^3/mol
E_i – free energy of molecular attraction
V_L – molar volume of the lipophilic part, cm^3/mol
V – flow rate of the droplets in a viscous medium, m/s
a – (a) droplet radius, m
ρ_D, ρ_C – internal and continuous phase density, kg/dm^3
g – apparent gravity, m/s^2

η – continuous phase viscosity, Pas
F – van der Waals forces, kJ/mol
UV – ultraviolet radiation
UVA – Ultraviolet A (320–400 nm)
UVB – Ultraviolet B (280–320 nm)
UVC – Ultraviolet C (200–280 nm)
SPF – Sun Protection Factor
MED – minimal erythemal dose
TEWL – transepidermal water loss
NMF – natural moisturizing factor
SC – stratum corneum
PABA – para-aminobenzoic acid
DHA – dihydroxyacetone
α–MSH – α-melanocyte-stimulating hormone
cAMP – cyclic adenosine monophosphate
ETO – ethylene oxide
PEG – polyethylene glycol
PVA – polyvinyl alcohol
EO – ethoxy group
PO – propoxy group
EUFA – essential unsaturated fatty acids
AHA – alpha-hydroxy acids
BHAs – beta-hydroxy acids
SC-CO_2 – supercritical carbon dioxide
SLS – Sodium Lauryl Sulfate
COSMOS – Cosmetics Organic and Natural Standards
BHT – butylated hydroxytoluene
BHA – buthylated hydroxyanisole
EDTA – ethylene diamine tetra acetic acid
CPNP – Cosmetic Product Notification Portal
C.I. – Colour Index
PAO – Period After Opening
BCOP – Bovine Cornea Opacity & Permeability Test
RBCT – Red Blood Cell Test
HET-CAM – test or tests on reconstructed human skin or porcine skin

1. INTRODUCTION

Current European laws on cosmetic products (Regulation (EC) no. 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products), define cosmetic products as "any substance or mixture intended to be placed in contact with the external parts of the human body (epidermis, hair system, nails, lips and external genital organs) or with the teeth and the mucous membranes of the oral cavity with a view exclusively or mainly to cleaning them, perfuming them, changing their appearance, protecting them, keeping them in good condition or correcting body odours" [1].

Depending on the intended use and contained ingredients, cosmetic products may vary in physicochemical forms. They are available in the form of multiphase systems, such as emulsions (creams, lotions, hair conditioners), suspensions (toothpastes, facial masks, make-up cosmetics) and foams, or in the form of single-phase systems i.e. solutions, (tonics, toilet waters). Color cosmetics, including face powders or make-up foundations, may appear in the form of mixtures of powdered solids.

The most popular systems employed in the manufacture of cosmetics are emulsions. They are a class of disperse systems consisting of two immiscible liquid phases, comprising multiple substances, including hydrocarbons, fats, waxes, odoriferous substances, water, and hydrophilic substances. Therefore, emulsions maintain water-lipid balance of epidermis and effectively moisturize the skin. Additionally, the systems demonstrate an ability to transport active ingredients (polar and nonpolar alike) into deeper layers of the skin; this effect increases the efficacy of cosmetics.

The classification of emulsion systems depends on the applied criteria. Considering as classification criterion the nature of the dispersed phase, emulsions with water are classified into water in oil systems (W/O) or oil in water emulsions (O/W). The oil is a synonym of a water-non-soluble organic phase which can be a mixture of any hydrophobic ingredients: silicones, paraffin hydrocarbons, fatty alcohols, fatty acids, fatty acid esters, waxes, or plant oils. The polar phase is water or a water solution of hydrophilic substances, such as polyols, alpha hydroxylic acids, amino acids, protein hydrolysates or saccharides [2–6].

Considering the cosmetic products effect on the skin, a general classification of the emulsions includes cleansing, moisturising and protective cosmetics. Depending on the time of cosmetics application, during a day, the creams can be classified as day creams (quick-breaking, instant-absorbing products with no greasy after feel) and night creams (generally with higher levels of occlusive emollients, containing nutrients). According to an application place, cosmetic emulsions may be classified into facial creams (including eye crams), hand creams, foot creams, and body emulsions. Cosmetics are also dedicated for different customer profiles e.g. facial creams for problematic skin (sensitive skin, cera with telangiectasias, greasy, acne skin), anti-cellulite and stretch mark cosmetics, or baby cosmetics [3–6].

The raw materials are chosen according to the intended use of the cosmetic product. The selection of ingredients for oil and water phases must follow the required functional properties of the finished product. A cosmetic product should be easily spread and absorbed, leaving a comfortable "non-greasy" sensation on the skin. The fragrance and colorants should also be appealing. A cosmetic product should be safe for human health when used under normal or reasonably foreseeable conditions of use, so no irritation, allergic response or carcinogenic action is permitted. In order to the cosmetic emulsions stability during storage and use in the formulations, supplementary components such as preservatives and antioxidants should be added [3–6]. The quantitative and qualitative composition and the emulsification processing parameters largely affect the quality of the finished formulation.

The ability to create emulsions is an integral part of the cosmetic formulator's skill set. Aside from a formula elaboration (determination of the product structure and selection of raw materials) the manufacture of cosmetic emulsions includes other critical stages, such as selection of process parameters, and a quality assessment of raw materials and the finished product.

2. EMULSIONS – THEORETICAL BACKGROUND

Becher [7] defines emulsion as a system of two or more immiscible liquid phases, with one dispersed in the form of droplets in the other. According to the definition, an emulsion system comprises two clearly distinguish phases:

- an internal phase (the dispersed one); the phase which is present in the form of finely divided droplets,
- an external phase (the continuous dispersing one); the phase which forms the matrix in which those droplets are suspended.

The classification of emulsion systems varies with the classification criteria. One of the distinctions consists in noting which component is the continuous and which the disperse phase (Fig. 1):

- water in oil (W/O), if the external phase is oil and the internal (dispersed phase) is water;
- oil in water (O/W), if the external phase is water and the internal (dispersed phase) is oil.

As already indicated in the background, in cosmetic emulsions, oil is synonym of the water-non-soluble organic phase which can be a mixture of any two or more hydrophobic ingredients: silicones, paraffin hydrocarbons, fatty alcohols, fatty acids, fatty acid esters, waxes or plant oils. The polar phase is either water or a water solution of hydrophilic substances, such as polyols, AHA, amino acids, protein hydrolysates, simple sugars, and polysaccharides.

Ostwald described the mutual relation between both of the phases in a theory by which the critical volumetric ratio between the continuous phase and the dispersed ones in an emulsion is 26:74. If the dispersed phase is present in an emulsion in the form of perfectly round globules which are packed as densely as possible, the volume occupied by the droplets is approximately 74% of the total volume of the vessel filled with the emulsion. The dispersing medium occupies 26% of the vessel's volume. A practical conclusion is that if the concentration of one liquid is < 26% by volume, only one emulsion type is viable and the liquid is the dispersed phase; whereas the concentration of the same liquid is between

26 and 74% of volume, two types of emulsion could be formed [8]. In real-life practice, however, it is possible to pack the droplets of dispersed phase more densely, since they are heterogeneous in size and deformable. An example of a specific W/O emulsion, in which the dispersed phase of water is at > 90% of volume, are gel emulsions.

Aside from the classic emulsions, Beher's definition includes multiple emulsions. In multiple emulsions, it is difficult to explicitly determine the exact disperse phase, since every phase of the emulsion contains droplets of the opposite phase. They can generally be determined as "emulsions in emulsion" and classified as follows by the mutual relation of phases:

- W/O/W: systems with the W/O emulsion dispersed in the water phase (Fig. 1),
- O/W/O: systems with the O/W emulsion dispersed in the oil phase.

Multiple emulsions are known in which the individual emulsion phases are multiple mutually enclosed (W/O/W/O, O/W/O/W).

Multiple systems in cosmetic preparations exhibit many advantages over classic emulsions; they combine the moisturising action of a W/O emulsions with good sensory properties of an O/W emulsions. Moreover, they are systems that improve the stability of easily-oxidised ingredients and allow to controlled delivery of active ingredients to the skin.

In thermodynamic terms, emulsions are unstable systems which can be decomposed over time due to different physicochemical mechanisms, including creaming, flocculation, or Ostwald ripening [9–13]. Formation of a stable emulsion system requires a necessary additive, an emulsifier; a substance increasing the emulsion stability by interfacial action, facilitating

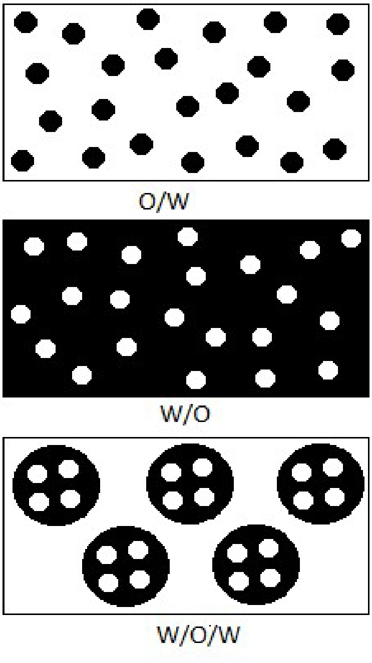


Fig. 1. Classical emulsion systems

dispersion and preventing coalescence of the internal phase particles. The emulsifier is also a determinant of the type of emulsion obtained. Mainly, in cosmetic emulsions, surfactants (surface active agents) are applied as the emulsifiers [14]. Other substances used for stabilizing cosmetic emulsion systems include polymers and solid particles (in the so-called Pickering emulsions [15]). Considering a structure of the emulsion-stabilizing surfactant, emulsions can be classified as cationic, anionic, and amphoteric emulsions.

W/O and O/W emulsions can also be differentiated by the internal phase ratio (IPR) into the following:

- low IPR emulsions (IPR < 30% of the composition), where the system properties depend mainly on the external phase,
- medium IPR emulsions (30% ≤ IPR ≤ 70%), where long-term stability is difficult to obtain (by phase inversion),
- high IPR emulsions, so-called concentrated emulsions (IPR > 70%), which are highly viscous and require specific manufacturing process parameters.

Depending on the degree of internal phase dispersion (the size of internal phase droplets), emulsions are classified as follows [3]:

- macroemulsions, which comprise classic emulsions, where systems include dispersed particles with a diameter > 500 nm,
- microemulsions, in which the diameter of internal phase particles is < 500 nm,
- nanoemulsions, which is the latest emulsion class with extremely fine dispersed phase droplets diameter ranging between 20 and 200 nm.

The size of the dispersed phase droplets affects the appearance of an emulsion (Table 1), since light waves are scattered by the droplets larger in diameter than the incident light wave length. The visible light waveband is 390 to 750 nm. Classic emulsions in which the droplet diameter exceeds 500 nm are white in appearance, since the entire visible light spectrum is scattered when it passes the dispersion medium. Microemulsions and nanoemulsions, where the droplet diameter is less than 500 nm, may pass visible light without scattering, by which the emulsion systems look semitransparent [16]. Nanoemulsions are often mistaken for microemulsions and vice versa, due to their similar appearance. The essential difference between the two emulsion systems is the content of surfactants. Unlike semitransparent nanoemulsions, which require special manufacturing equipment, microemulsions are formed spontaneously by solubilization of oil particles with a mixture of surfactants. The surfactant concentration required to achieve solubilization in a microemulsion is several times higher than in nanoemulsions and highly exceeds the concentration of the dispersed phase [16].

Refinement of the internal phase is not the only discriminant between macroemulsions and microemulsions; the emulsion life must also be considered. Microemulsion is a term coined by Hoar and Schulman for apparently homogeneous mixtures of water and oil with high surfactant content (and where the selection of appropriate emulsifiers is critical). Unlike macroemulsions, microemulsions are formed spontaneously and become thermodynamically stable systems with relatively low viscosity values [14]. At room temperatures, microemulsions form liquid systems with an oily consistency and which

Table 1

Effect of internal phase droplets size on emulsion appearance

Droplets diameter (μm)	**Emulsion appearance**
> 1	Milky white
0.5 to 1	Blueish white
0.2 to 0.5	Semitransparent
< 0.2	Transparent

can be translucent or opalescent (since the internal phase droplets are highly refined, < 500 nm, and do not scatter the visible light). Microemulsions exposed to low or high temperatures become opaque and form dense and viscous systems; the original structure of a microemulsion is restored when brought back to a room temperature. Microemulsions exhibit properties characteristic of both: emulsions and solutions.

Nanoemulsions are a relatively novel form of cosmetic products. Reference literature often defines nanoemulsions as emulsions with extremely fine and homogeneous size of internal phase particles. Depending on the reference, nanoemulsions are defined as systems with the particle size of the internal phase between 10 and 500 nm [17]. Not unlike microemulsions, a characteristic feature of nanoemulsions is their system, which is optically transparent or semitransparent and with a blueish tint. Many reference sources state that nanoemulsions are among the most promising physicochemical forms of cosmetic formulations which increase the percutaneous penetration and bioavailability of active ingredients. With relatively large interfaces and low surface and interfacial tension values, nanoemulsions have a higher absorption of active ingredients [17–22].

Note that the classification based on Becher’s definition of emulsion does not include micellar systems or liquid crystal systems; both forms have seen an increased use in latest cosmetic products.

2.1. STABILITY OF EMULSION SYSTEMS

Classic emulsions, comprising immiscible liquids, are thermodynamically unstable. Mixing two liquids of different polarity into an emulsion is not a spontaneous process and requires an energy input (work) (eq. 1).

$$W = \gamma \cdot A \tag{1}$$

where:

γ – surface tension, (J/m^2),
W – work input required to increase the phase surface by the unit, (J),
A – interface (phase boundary), (m^2).

Consider a case (Fig. 2) in which a large drop of oil (2) is dispersed by mixing in a continuous medium, water (1). The emulsification process produces a large number of small droplets (2) with an increase of the total surface area of the oil (A). An effect of this is an increase in the interfacial tension at the phase boundary (γ).

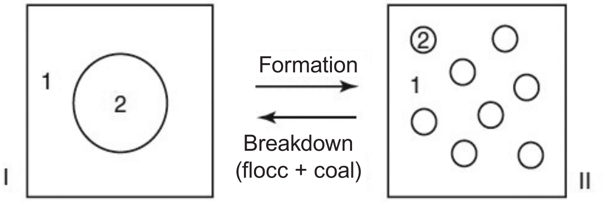


Fig. 2. Diagram of emulsion formation and destabilization (1 – water phase; 2 – oil phase) [23]

The change in the free energy during the transition from state I to state II results from two contributions: a surface energy term (which is positive) which is equal to $\Delta A\gamma$ (with $\Delta A = A_{II} - A_{I}$). An entropy of dispersions term which is also positive (since the production of a large number of droplets is accompanied by an increase in configurationally entropy, which is equal to $T\Delta S$). According to the second law of thermodynamics, the total free energy of an emulsion formation (ΔG_{form}) is described by equation 2.

$$\Delta G_{form} = \Delta A \cdot \gamma - T \cdot \Delta S \tag{2}$$

where:
ΔG_{form} – free energy of emulsion formation (J),
ΔA – total surface area (m^2),
γ – interfacial tension (J/m^2),
T – absolute temperature (K),
ΔS – entropy (J/K).

In most cases, the surface energy is higher that the entropy of the dispersion ($\Delta A\gamma >> T\Delta S$); the free energy is positive, so the emulsion formation is non-spontaneous and the system is thermodynamically unstable. In the absence of any stabilization mechanism, the emulsion will breakdown by flocculation and coalescence, Ostwald ripening or a combination of all these processes (Fig. 3).

The presence of a stabilizer (a surfactant or a polymer) creates an energy barrier between the droplets; hence, the inversion from state II (the dispersed system, in which a large number of small droplets is dispersed) to state I (with large droplets in the continuous phase) is discontinuous, as shown in Fig. 4 [23].

The system becomes kinetically stable if the energy value exceeds the energy barrier that inhibits the breakdown of the emulsion. The energy barrier can be formed, for example, by electrostatic or steric repulsions which exceed the attraction by Van der Waals forces [23].

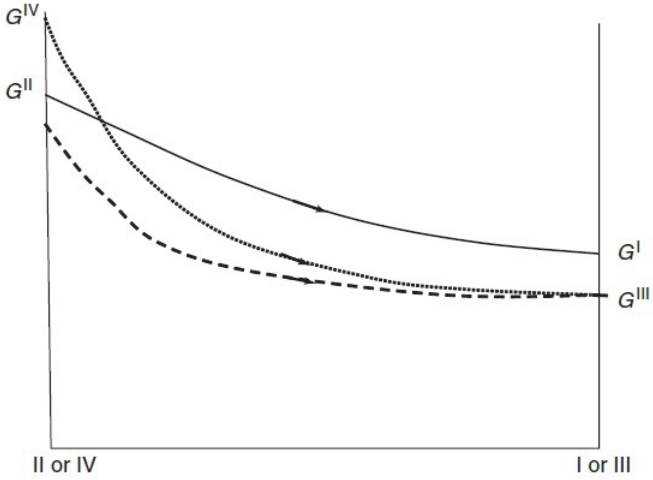


Fig. 3. Free energy transfer in an emulsion breakdown process
(with: – flocculation + coalescence; – - – - – flocculation + coalescence + sedimentation;
····· flocculation + coalescence + Ostwald ripening) [23]

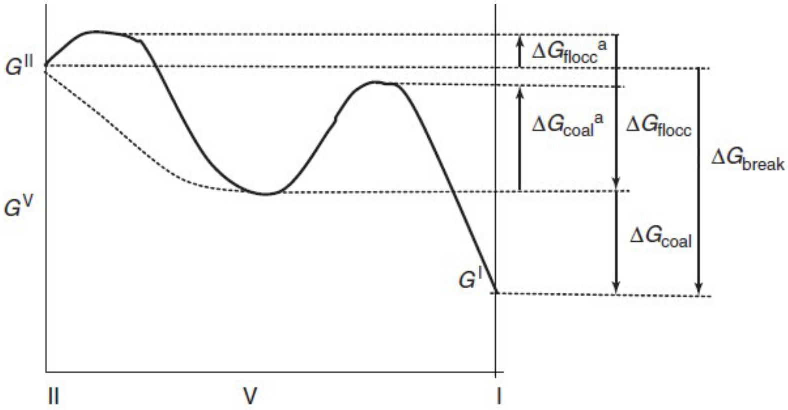


Fig. 4. Free energy path in the breakdown of the emulsion system [23]

2.2. ROLE OF EMULSIFIERS IN EMULSIONS STABILIZATION

Emulsifiers (surfactants) play an important role in the formation of stable emulsions. Due to their amphiphilic character emulsifiers reduces the interfacial tension and facilitated dispersion of the internal phase with an overall stability of the system [14, 23–25, 38].

Amphiphilic character means that an emulsifier molecule contains a polar/ hydrophilic part (the so-called “head”) with a nonpolar/ lipophilic part (the so-called “tail”) (Fig. 5).

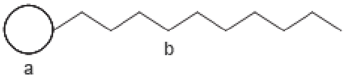


Fig. 5. Schematic structure of an emulsifier molecule (a – hydrophilic part; b – lipophilic part)

The hydrophobic part of the emulsifier particle has an affinity for oils. Usually it is a long, straight or branched chain of hydrocarbons (with 8 to 18 atoms of carbon). The hydrophilic part has an affinity for water and other polar liquids. In the molecules of classic emulsifiers, the hydrophilic part usually contains a fragment the nature of which resembles an acidic group (carboxylic (-COOH), sulphate ($-OSO_3H$), sulphonic ($-SO_3H$), or phosphatic ($-OPO(OH)_2$)) or an alkaline group (primary, secondary and tertiary amine groups and quaternary ammonia groups $[-NR_3]^+$). Surfactant molecules may also feature other hydrophilic groups which do not form salts, such as alcohol groups (-OH), ethoxy groups ($-CH_2CH_2O-$) or propoxy groups ($-CH(CH_3)CH_2O-$), as well as formations which bind the molecular compounds: ester groups (-COOR-), amide groups (-CONH-), or ether groups (-O-).

At the interfacial surface of the emulsion system, emulsifier is absorbed in the specific manner. Its lipophilic part is dissolved in the oil phase and reacts with nonpolar molecules of the lipid phase, whereas the hydrophilic parts are solvated by water (Fig. 6).

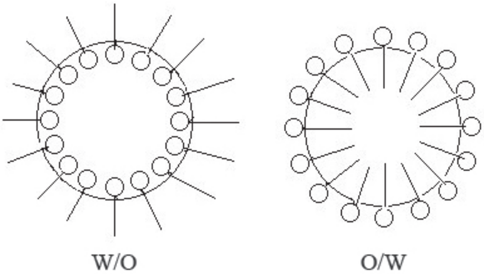


Fig. 6. Orientation of emulsifier molecules at an interfacial surface

There are several theories elaborated to explain the role of emulsifiers in emulsion systems formulation process. The Bancroft rule states that the type of emulsion depends largely on the properties of the emulsifier and the phase in which an emulsifier is more soluble is the continuous phase. Bancroft considered the effect of the protective film, formed by particles of emulsifiers at the interfacial surface. He was assuming that the protective film should be considered as a third phase of an emulsion, with different values of the interfacial tension relative to water and oil phase. As an effect of the interfacial tension differential on both its sides, the protective film of the emulsifier is curved and concave at the phase boundary at the higher interfacial tension (Fig. 7).

The Harkins theory (or the geometric theory) states that the shape of a surfactant molecule resembles a wedge. When the hydrophilic end of an emulsifier has a radius larger than the hydrocarbon chain (RCOONa), the oil/water phase boundary shall be curved and

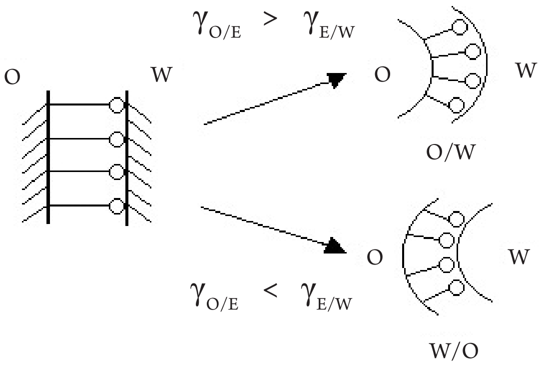


Fig. 7. Conventional directions of phase boundary curving in emulsions [6]. $\gamma_{O/E}$ – oil/emulsifier interfacial tension; $\gamma_{E//W}$ – emulsifier/water interfacial tension

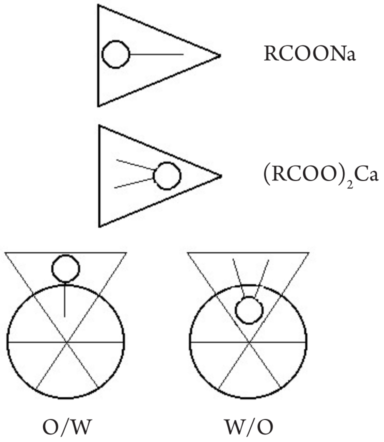


Fig. 8. Effect of emulsifier molecules geometry on the oil/water phase curvature

convex toward the water phase. This promotes the formation of oil droplets and an O/W emulsion. And conversely ($(RCOO)_2Ca$), when the polar surfactant end is smaller in radius than the hydrocarbon chain, W/O emulsion is formed (Fig. 8) [6].

Davies and Rideal provided a kinetic-based approach to the problem [23]. Davies and Rideal proved that the first stage, which follows the mixing of the oil phase with the water phase, creates both types of emulsion with an insignificant durability due to the input of mechanical work. In the second stage, one type of the emulsion is stabilized and it depends on the relative coalescence rate of liquid droplets. If the coalescence rate of water droplets is higher than the coalescence rate of oil droplets, an O/W emulsion is formed. The coalescence rate depends on the structure of the applied emulsifier and the coverage ratio of the emulsifier molecules on the surfaces of the droplets of the phase dispersed by the emulsifier, i.e. the concentration of the emulsifier.

Emulsifiers suitable for use in cosmetic products include surfactants (ionic and non--ionic ones), macromolecular substances (hydrophilic polymers, both synthetic and natural, such as polypeptides and polysaccharides), and solids (e.g. powdered forms of Al_2O_3, $MgSO_4$ or $MgCO_3$).

2.2.1. MECHANISM OF EMULSION STABILIZATION

The list of marketed cosmetic emulsifiers is very extensive and novel and more effective substances are kept being proposed. Different emulsifier groups can be distinguished, depending on the classification criteria. If the classification criterion of surfactants is the ion-forming properties, emulsifiers can be distinguished in two primary groups: non--ionic emulsifiers (which do not dissociate into ions in water) and ionic emulsifiers (which dissociate into ions in water) [14].

Non-ionic emulsifiers include:

- C_{12}–C_{22} fatty acid esters with glycols, glycerin, pentaerythritol, sorbitol and saccharose,
- polyoxyethylene glycol derivatives,
- polyglyceryl derivatives.

Ionic emulsifiers can be classified further according to the nature of the ion with amphiphilic part of the molecule:

- anionic emulsifiers, which include alkaline soaps (Na^+, K^+, NH_4^+), metallic soaps (Ca^{2+}, Mg^{2+}, Al^{3+}), alkyl sulphates ($ROSO_3Na$), alkyl sulphonates (RSO_3Na), and orto--phosphoric acid esters,
- cationic emulsifiers, which include amine salts, and salts of quaternary ammonium and pyridine salts,
- amphoteric emulsifiers, which include derivatives of betaine or lecithin.

The emulsion stabilization mechanism depends on the chemical structure of the applied surfactant. Apart from reducing the interfacial tension, an emulsifier takes part in other phenomena which contribute to stabilization of an emulsion: formation of a complex film on the dispersed phase droplet surfaces, formation of an electric layer around the emulsion droplets, and formation of liquid-crystallic structures, for example.

Non-ionic emulsifiers create hydrogen bonds and spatial obstacles which prevent dispersed droplets from approaching one another (Fig. 9). Introduction of an ionic emulsifier creates an electrically charged film on the surfaces of the dispersed phase droplets; this effect repels the droplets from one another (Fig. 10). Another method of emulsion stabilization is to increase the number of surfactant molecules with a defined orientation at the interface. This is achieved by increasing the emulsifier phase; however, in more frequently used method, a mixture of emulsifiers with different character (oil-soluble emulsifiers and water-soluble one) is applied (Fig. 11). Polymers applied in the function of emulsifiers stabilise emulsions with the steric effect (Fig. 12); hydrophilic polymers also stabilize O/W emulsions by increasing the viscosity of the external phase.

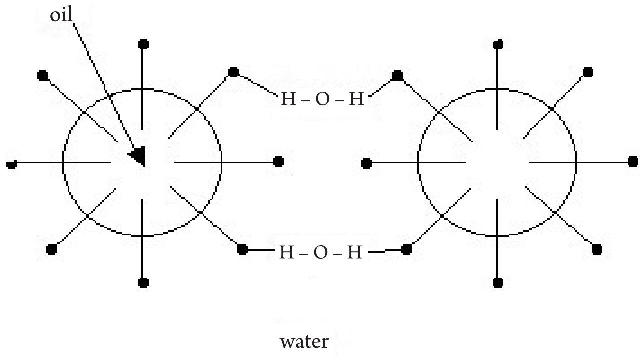


Fig. 9. O/W emulsion stabilization with non-ionic emulsifier molecules [6]

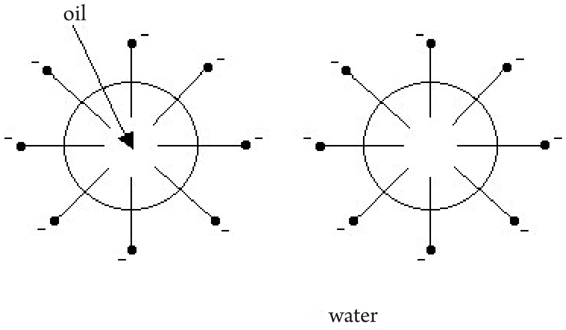


Fig. 10. O/W emulsion stabilization with ionic (anionic) emulsifier molecules [6]

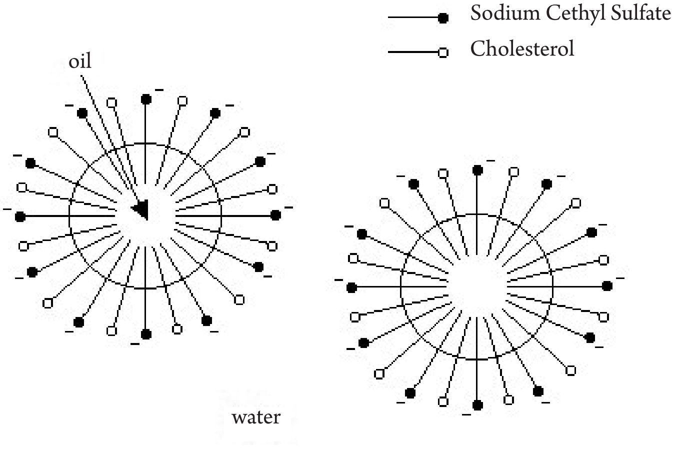


Fig. 11. O/W emulsion stabilization with a mixture of emulsifiers [6]

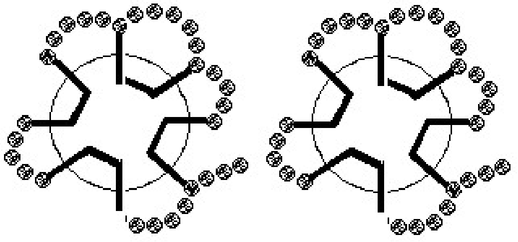


Fig. 12. O/W emulsion stabilization with polymer molecules

2.2.2. HYDROPHIL-LIPOPHIL BALANCE (HLB)

The hydrophile-lipophile balance (HLB) concept was developed by Griffin in 1949, nowadays it is widely used for classifying surfactants. Griffin developed a semiempirical method for determination of the hydrophile-lipophile balance for non-ionic surfactants [14, 26, 27]. According to Griffin, HLB number determines the ratio of the hydrophilic portion of emulsifier molecule to its total molecular mass (eq. 3).

$$\mathrm{HLB} = 20\,(M_H/M_C) \tag{3}$$

where:

M_H – molecular mass of hydrophilic groups,

M_C – molecular mass of the whole emulsifier.

Griffin created a conventional numerical scale for HLB, from 0 to 20, and classified surfactants assigning specific integer values on the scale to specific surfactant groups. HLB number is assigned to each surface active agent, and is related by a scale to the suitable applications (Table 2).

The HLB scale comes very helpful in characterizing emulsifiers as a general indicator of what emulsion the emulsifier will form. As can be seen, only those materials with HLB numbers in the range of 3 to 6 are suitable as emulsifiers for W/O emulsions, while only those with HLB numbers in the range 10 to 18 are suitable for preparation of O/W emulsions. Compounds with HLB in different ranges possessing others surface-active properties but cannot be applied as emulsifying agents. A large ratio of hydrophilic groups in the molecule of a surfactant makes it a good solubilizer, with a good cleaning and foaming performance.

The HLB number gives an indication of the relative affinity of a surfactant molecule for the oil and aqueous phase. In practical terms, however, knowing the HLB number of a surfactant greatly helps in pre-determining its application for a specific purpose; surfactant manufacturers also provide HLB numbers in product technical data publications.

Table 2

Surfactant applications vs. HLB number

HLB	Water solubility	Application
1.5 to 3	No dispersion in water	Anti-foaming agent
3 to 6	Poor dispersion in water	W/O emulsifier
7 to 9	Milky dispersions	Wetting agent
10 to 18	Stable milky dispersions	O/W emulsifier
13 to 15	Near-clear dispersions	Detergent
> 15	Clear solution	Solubilizer

Griffin's HLB determination method provides approximate characterization of surfactants but it does not consider the influence of their molecular structure on HLB numbers. Therefore, in reference literature there are many proposed empirical formulas for HLB numbers determination of different surfactants types, mainly non-ionic ones [7, 26, 27]. Equations 4 to 11 show some of these proposals.

For emulsifiers based on esters of higher fatty acids and polyhydric alcohols (polyols), the HLB numbers can be calculated follows – eq. 4.

$$\mathrm{HLB} = 20\,(1 - \mathrm{SN}/\mathrm{AN}) \tag{4}$$

where:
SN – saponification number of the tested compound,
AN – neutralization number of fatty acids.

For example, for glyceryl monostearate, SN = 161 and AN = 198, according to equation 4 its HLB number is 3.8 (suitable for a W/O emulsion).

For a simple alcohol ethoxylate, the HLB number can be calculated from the weight percentage of ethylene oxide (E) and polyhydric alcohol (P) – eq. 5.

$$\mathrm{HLB} = (E + P)/5 \tag{5}$$

where:
E – percentage content of ethylene oxide in the molecule,
P – percentage content of other hydrophilic groups in the molecule.

If a surfactant contains polyethylene oxide (PEO) as the only hydrophilic group, the contribution from one OH group can be neglected (eq. 6).

$$\mathrm{HLB} = E/5 \tag{6}$$

For the non-ionic surfactant $C_{12}H_{25}{-}O{-}(CH_2{-}CH_2{-}O)_6{-}H$, HLB is 12 (suitable for stabilization of O/W emulsion).

Other non-ionic surfactant HLB calculation methods exist, including the Kawakami equation [14, 27] (eq. 7).

$$HLB = 7 + \log (M_H/M_L) \tag{7}$$

where:
M_H – molecular mass of hydrophilic groups,
M_L – molecular mass of lipophilic groups.

For non-ionic surfactants from the group of polyglycerol fatty acid esters can be calculated follows – eq. 8[28].

$$HLB = (m_p/(m_p+m_a)) \cdot 20 \tag{8}$$

where:
m_p – the mass of polyglycerol used in the synthesis of the ester,
m_a – the mass of carboxylic acid mixture used in the synthesis of the ester.

For example, esterification of 100 g polyglycerol with 100 g fatty acids would result in an HLB of (100 g/(100 g+100 g)) · 20 = 10, independent of the degree of polymerization.

Cocbaina and McRoberts [14, 27] proposed a calculation of HLB for surfactants with the water/oil phase partition coefficient (eq. 9).

$$HLB = 7 + 0.36 \log (C_W/C_O) \tag{9}$$

where:
C_W – surfactant concentration equilibrium in water,
C_O – surfactant concentration equilibrium in oil.

Griffin's theory was also expanded by ionic hydrophilic compounds which can undergo different conversions in a solution (e.g. dissociation or hydration), resulting in an increase of hydrophilicity. This expansion extended the HLB scale maximum limit to 40. A widely used semiempirical method of calculating the HLB number, also for ionic surfactants, was defined by Davis [7, 14, 27, 29]. The HLB number of a surfactant can be calculated based on the chemical groups of it molecule, from knowledge of the number and type of hydrophilic and lipophilic groups it contains (eq. 10).

$$\begin{aligned} HLB = 7 &+ \Sigma\,(\text{hydrophilic group numbers}) + \\ &+ \Sigma\,(\text{hydrophobic group numbers}) \end{aligned} \tag{10}$$

The group numbers have been assigned to many different types of hydrophilic and lipophilic groups (Table 3, 4).

Table 3

Selected HLB group numbers

Group type	**Group number**
Hydrophilic groups	
-$SO_4^-Na^+$	38.7
-COO^-K^+	21.1
-COO^-Na^+	19.1
-N≡(tertiary amine)	9.4
-COO- (sorbitan ester)	6.8
-COO- (free ester)	2.4
-COOH	2.1
-OH (free)	1.9
-OH (sorbitan ring)	1.3
-O-	0.5
Hydrophobic groups	
-CH_3	–0.475
-CH_2-	–0.475
=CH-	–0.475
-CF_3	–0.870
-CF_2-	–0.870
Benzoic ring	–1.662
Group derivatives	
-OCH_2CH_2- (ethoxy group)	0.33
-$OCH_2CH(CH_3)$- (propoxy group)	–0.15

The conference materials of the AKZO Nobel Company there is a table (Table 4) with modified Davies HLB group numbers [30].

Table 4

HLB group numbers proposed by AKZO Nobel [14]

Hydrophilic groups	**Group number**	**Hydrophobic groups**	**Group number**
-SO_3Na	+20.7	-CH_3	–0.475
-OSO_3Na	+20.8	-CH_2-	–0.475
-COOK	+21.1	=CH-	–0.475
-COONa	+19.1	-CF_3	–0.870
-NH_3Cl	+20.0	-CF_2-	–0.870

$=\mathrm{NH_2Cl}$	+20.0	benzene ring	−1.662
$-\mathrm{N(CH_3)_3Cl}$	+22.0		
$=\mathrm{N(CH_3)_2Cl}$	+22.5		
$=\mathrm{N(CH_3)\text{-}CH_2\text{-}ArCl}$	+19.7		
$=\mathrm{N(CH_3)_2\text{-}CH_2\text{-}ArCl}$	+19.2	Other groups	
$-\mathrm{N(CH_3)(EO)_2Cl}$	+24.9	$-\mathrm{OCH_2CH_2}-$	+0.33
$-\mathrm{NH(EO)_2Cl}$	+21.9	$-\mathrm{OCH_2CH(CH_3)}-$	−0.15
$-\mathrm{N(CH_3)_2}\rightarrow\mathrm{O}^*$	+38.0	$-\mathrm{NH_2^+\text{-}CH_2CH_2CH_2\text{-}NH_3^+\cdot 2Cl^-}$	+38.6
$-\mathrm{N(EO)_2}\rightarrow\mathrm{O}^*$	+23.8	$-\mathrm{N^+(CH_3)_2\text{-}CH_2CH_2CH_2\text{-}N^+(CH_3)_3\cdot 2Cl^-}$	+43.5
-N (tertiary amine)	+9.4	$-\mathrm{NH^+(EO)\text{-}CH_2CH_2CH_2\text{-}NH^+(EO)_2\cdot 2Cl^-}$	+41.4
-COO- (in sorbitan ester)	+6.8	$-\mathrm{N^+(CH_3)_2\text{-}CH_2\text{-}COOH\cdot Cl^-}$	+21.4
-COO- (in free ester)	+2.4	$-\mathrm{N^+(CH_3)_2\text{-}CH_2\text{-}COO^-}$	+38.0
-COOH	+2.1	$-\mathrm{NH\text{-}CH_2CH_2CH_2NH_2}$	+17.4
$-\mathrm{CONH_2}$	+9.6	$-\mathrm{CH_2CH_2OH}$	+0.95
-OH (free hydroxyl group)	+1.9		
-OH (in sorbitan ring)	+1.3		
-O-	+0.5		
$-\mathrm{NH_2}$	+9.4		
=NH	+9.4		
$-\mathrm{N(CH_3)_2}$	+8.5		
$-\mathrm{N(EO)_2}$	+11.3		
EO = $-\mathrm{CH_2CH_2O}-$ * at pH=3.0			

Compared to the classic method by Griffin, the data produced by determination of specific physicochemical properties is usually a better foundation for the determination of HLB numbers. Aside from the aforementioned HLB calculation methods, many experimental methods were proposed for the determination of HLB number [14, 27]. The methods are based on the determination of surfactant properties, including: adsorption heat [27], foaming performance [31], wetting angle [32], interfacial tension [33], critical micellar concentration [33], and phase inversion temperature (PIT) [35]. The rather often applied experimental methods of HLB determination include: the emulsion method [36], NMR spectroscopy [37], and gas chromatography [38].

The determination of emulsifier HLB based on "emulsion method" requires knowledge of the required HLB number (HLB_r) of the oil phase.

The required oil phase HLB_r is determined with the following relationship (11):

$$HLB_r = HLB_x X_t + HLB_y Y_t \tag{11}$$

where:
HLB_r – required oil phase HLB number,
HLB_x, HLB_y – HLB of standard emulsifiers (X, Y),
X_t, Y_t – mass fractions of standard emulsifiers corresponding to the most stable emulsion.

The method consists in the determination of the required HLBr number for different oil phases with standard surfactants (which have known HLB number). The experimental determination consists in formulating several emulsions with specific quantities of both phases (e.g. 20% of the oil phase and 80% of water in the case of O/W) and 2% of mixture of standard emulsifiers (differ in mass ratios) and then monitoring the emulsions stability. The emulsifier mixtures consist of two-surfactants with known HLB numbers. Based on the emulsion breakdown time, the area of the required HLB_r numbers of oil phases is determined.

Next, the HLB_r is used to determine the HLB of the emulsifier of interest by applying equation (12):

$$HLB_z Z_t = HLB_r - HLB_s Z_s \tag{12}$$

where:
HLB_z – surfactant HLB of interest,
HLB_r – required oil phase HLB number,
HLB_s – standard surfactant HLB number,
Z_t, Z_s – mass fractions of the surfactant corresponding to the most durable emulsion.

NMR (nuclear magnetic resonance) is a method for a quick characterization of the molecular structure of a chemical compound by measuring the intensity of a proton peak. In this method, an emulsifier specimen is exposed to electromagnetic radiation to measure the response of the hydrophilic and hydrophobic groups of the tested compound. NMR can be applied for the identification of non-ionic surfactants and the determination of the hydrophilic/lipophilic group ratio in the molecule (eq. 13). NMR can also help identify the mean hydrocarbon chain length, the degree and types of chain branches, and the aromatic substitution type.

$$HLB = (A \cdot H)/5(A \cdot H + B \cdot L) \tag{13}$$

where:
A – constant, equal to 15,
B – constant, equal to 10,
H – hydrogen response values of the hydrophilic groups,
L – hydrogen response values of the hydrophobic groups.

The number of ethoxylated segments (n_{TE}) in the products of alcohol or fatty acid ethoxylation is calculated in the HNMR method follows equation 14.

$$n_{TE} = (31 \cdot A_2/A_1 - 3)/4 \tag{14}$$

where:
A_2, A_1 – integration curve height in the areas 0.4–2.35 ppm (A_1) and 2.35–4.9 ppm (A_2),
31 – number of hydrogen atoms in the lipophilic radical.

Hydrophilic-lipophilic balance of surfactants can also be studied with gas chromatography based on their polarity index calculation (eq. 15).

$$IP = 100 \cdot \lg (C - 4.7) + 60 \tag{15}$$

where:
IP – polarity index,
C – carbon number.

The carbon number is the numerical value on a hydrocarbon scale. It corresponds to the number of carbon atoms that the n-alkane would have to have a retention time corresponding to the methanol retention time on the chromatographic column containing the tested surfactant as a stationary phase.

As already discussed here, the HLB determination system is based on the ratio of the molecular weight of the water-soluble hydrophilic head to the oil-phase-soluble lipophilic tail of the surfactant. Beerbower [39] improved the discussed technique and demonstrated that molecular attraction of the hydrophilic parts to water and the lipophilic parts to the oil phase determines the stability and efficacy of the surfactant interphase. This improved and so-called cohesive energy helps form the internal phase of an emulsion.

The solubility parameter is a thermodynamic function of the cohesive energy field (eq. 16).

$$SP = \sqrt{\Delta H_V / V_M} \tag{16}$$

where:
SP – solubility parameter, ($mPa^{1/2}$),
ΔH_V – heat of evaporation, (J/mol),
V_M – molar volume, (cm^3/mol).

The free energy of molecular attraction (E_i) can be viewed as a result of reactions between the two areas.

$$E_i = \left(\Delta H_V / V_M\right)_a \left(\Delta H_V / V_M\right)_b \tag{17}$$

$$E_i = SP_a^2 SP_b^2 \tag{18}$$

The cohesion is at its maximum when the solubility parameters of interacting substances are equal; hence:

$$E_i = SP_{ab}^4 \tag{19}$$

The optimized energy effect depends on the function of solubility parameters. The optimized energy effect is further optimised with an empirical function which is proportional to the interaction of the surfaces in an O/W emulsion and to the HLB scale, a result of which is equation 20.

$$\text{Required HLB}\left(\text{HLB}_r\right)=\left[\left(SP+7\right)/8\right]^4 \tag{20}$$

The equation 20 predicts relatively stable oil in water (O/W) emulsions for single or multiple ingredient internal phases. Folding of linear aliphatic chains was found to affect predictive results. The stability of the boundary layer in a surfactant requires maximum cohesion of the oil phase required to equalize the hydrophilic attraction and expressed as the surface tension (eq. 21).

$$SP = \sqrt{\gamma/0.0715V_L^{1/3}} \tag{21}$$

where:
SP – solubility parameter,
γ – surface tension, (mN/m),
V_L – molar volume of the lipophilic part, (cm^3/mol).

This empirical relationship defines how the solubility parameter of oil represents the tension on the lipophilic end of a surfactant. The cohesive energy of the lipophilic part opposes the attraction of the hydrophilic parts and equalizes their attraction to water. Hence, the reactions are proportional to the HLB_r number [39].

Table 5 shows HLB number for some of commercial emulsifier [40].

Table 5

HLB values for selected commercial Croda emulsifiers

INCI	HLB
Sucrose Distearate	3.0
Sorbitan Sesquioleate	3.7
PEG-5 Castor Oil	3.9
Sorbitan Oleate	4.3
Sorbitan Stearate	4.7
PEG-7 Hydrogenated Castor Oil	5.0
Glyceryl Oleate	5.0
Polyglyceryl-3 Diisostearate	5.0
Oleth-2	5.0

Ceteth-2	5.3
Polyglyceryl-4 Isostearate	5.5
Glyceryl Myristate	5.8
Sorbitan Palmitate	6.7
Sorbitan Laurate	8.6
Oleth-5	9.0
Lecithin	9.7
PEG-8 Stearate	11.0
Glyceryl Stearate + PEG-100 Stearate	11.0
Polyglyceryl-4 Laurate	11.0
Glyceryl Stearate Citrate	12.0
Oleth-10	12.4
Cetoleth-10	12.5
PEG-40 Castor Oil	13.0
Sucrose Stearate	14.5
Polyglyceryl-4 Laurate/Succinate	14.5
Polysorbate 60	14.9
Polysorbate 80	15.0
PEG-60 Maracuja Glycerides	15.0
Polysorbate 40	15.6
Isoceteth-20	15.7
PEG-20 Stearate	16.0
Polysorbate 20	16.7
PEG-50 Stearate	17.9
PEG-100 Stearate	18.8
PEG-80 Sorbitan Laurate	19.1

2.2.3. SELECTION OF EMULSIFIER

Even when the HLB number of a surfactant is known, it is still unknown if the surfactant will be an effective emulsifier in a specific emulsion system. The efficiency of emulsification of the oil phase components depends on their hydrophilic or lipophilic nature (i.e. the chemical structure and polarity). The specific substances comprising the emulsion oil phase demonstrate individual HLB numbers, or so called the required HLB numbers (HLB_r) (Table 6). The HLB_r numbers depend on the lipophilic substances present and the emulsion type. To obtain a stable emulsion, an emulsifier or a mixture thereof must be chosen with an HLB number approximate to the HLB_r number of the emulsion oil phase.

Table 6

HLB_r of selected lipophilic components used in cosmetic emulsion composition [14]

Component (INCI)	**HLB_r**	
	W/O emulsion	O/W emulsion
Decyl Alcohol	–	15
Lauryl Alcohol	–	14
Cetyl Alcohol	–	13
Stearyl Alcohol	–	14
Oleyl Alcohol	–	13.5
Lauric Acid	–	16
Myristic Acid	–	11.7
Palmitic Acid	–	11.4
Stearic Acid	6	11.1
Oleic Acid	–	11
Isopropyl Myristate	–	11.5
Lanolin	8	10
Vegetable oils	ca. 5	ca. 10
Paraffin oil	5	12
Paraffin	4	11
Petrolatum	5	12
Beeswax	4	12
D4 Cyclomethicone	–	8

When the composition of the oil phase and the percentage of each of its component are known, HLB_r can be calculated. What follows (eq. 22) is an example of the HLB_r calculation of an O/W emulsion wherein the oil phase consists of 28% of paraffin ($HLB_r = 11$), 52% of jojoba oil ($HLB_r = 6.5$) and 20% of isopropyl myristate ($HLB_r = 11.5$).

$$HLB_r = 0.28 \cdot 11 + 0.52 \cdot 6.5 + 0.20 \cdot 11.5 = 8.76 \tag{22}$$

Hence, the HLB of the emulsifier must be equal to approx. 8.76 to produce a stable O/W emulsion with such the oil phase. Mixtures of emulsifiers are usually applied to produce emulsions. HLB is an additive value; equations 23 and 24 are used to calculate the ratios of the selected emulsifiers A and B in a mixture with $HLB_r = X$.

$$\%A = \frac{100\left(X - HLB_B\right)}{HLB_A - HLB_B} \tag{23}$$

$$\%B = 100 - \%A \tag{24}$$

Example: test if a mixture of surfactants, containing oleyl alcohol, ethoxylated with 2 mols of ethylene oxide, (HLB = 5) and triethanolamine stearate (HLB = 20) can be applied as an emulsifier mixture for the emulsion system mentioned above (eq. 25 and 26).

$$\%A = \frac{100(8.76 - 20)}{5 - 20} = 74.9 \tag{25}$$

$$\%B = 100 - 74.9 = 25.1 \tag{26}$$

While the HLB_r is determined, the problem of formulating a stable emulsion is not yet solved. The final effect of a properly composed mixture of emulsifiers depends on the following: the emulsification process conditions, the oil phase to water phase volume ratio, and the oil phase to emulsifier mass weight ratio.

Problem:

"Table 7 specifies the formulation of O/W emulsion (a moisturizing cream). Based on the known HLB_r of oil phase components choose the emulsifiers type and their concentration".

Table 7

Formulation of moisturizing emulsion (O/W)

Phase	INCI	Wt (%)
A (oil phase)	Avocado Oil	15
	Paraffin Oil	5
	Shea Butter	5
	Jojoba Oil	10
	Lanolin	10
	Isostearyl Lactate	5
B (water phase)	Glycerin	10
	Camellia Sinensis Leaf (Green Tea) Extract	2
	Aqua	up to 100
C	Emulsifier	5
D	Ascorbyl Palmitate	0.2
	Sodium benzoate	0.5
	Parfum	0.3

First, the HLB_r of the oil phase shall be calculated (Table 8).

Table 8

Calculation of the oil phase HLB_r

INCI	% in the oil phase	HLB_r	Actual HLB
Avocado Oil	30	7	$0.3 \cdot 7 = 2.1$
Paraffin Oil	10	12	$0.1 \cdot 12 = 1.2$
Shea Butter	10	8	$0.1 \cdot 8 = 0.8$

Jojoba Oil	20	6.5	$0.2 \cdot 6.5 = 1.3$
Lanolin	20	10	$0.2 \cdot 10 = 2.0$
Isostearyl Lactate	10	10.5	$0.1 \cdot 10.5 = 1.05$
TOTAL required HLB of the oil phase 8.45			

The proposed emulsifier mixture include: Polysorbate 80 (A, $HLB_A = 15$) and Glyceryl Oleate (B, $HLB_B = 5$).

Calculating of % content of each of the emulsifier in the mixture is as follows:

$$\%A = 100\,(8.45 - HLB_B)/(HLB_A - HLB_B) = 34.5$$

$$\%B = 100 - \%A = 65.5$$

2.2.4. PHASE INVERSION TEMPERATURE

Phase Inversion Temperature (PIT) method was developed by Shinoda [35] et al. PIT methods is strictly related to HLB. Shinoda assumed that many O/W emulsions stabilized with non-ionic surfactants at the critical temperature, i.e. the phase inversion temperature (PIT) undergo phase inversion.

The PIT can be determined by following the emulsion conductivity (where a small amount of electrolyte is added to increase the sensitivity) as a function of temperature. The conductivity of the O/W emulsion increases with the temperature rising until the PIT is reached, above which there will be a rapid reduction in conductivity (the W/O emulsion is formed). The PIT is influenced by the HLB number of the surfactant. The size of the emulsion droplets was found to depend on the temperature and the HLB number of emulsifiers.

The HLB number of surfactants and PIT are connected. This dependence is shown in Fig. 13 of a cyclohexane/water emulsion stabilized with different non-ionic surfactants.

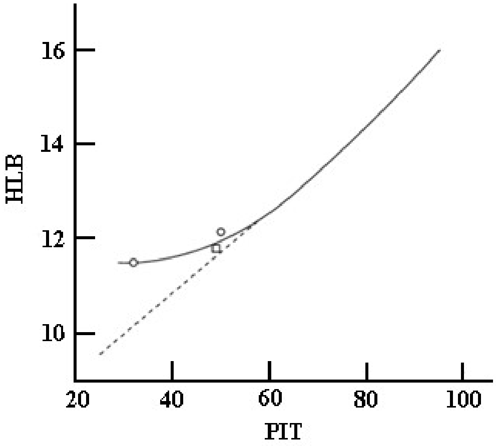


Fig. 13. Correlation of surfactant HLB and PIT [41]

The researchers also found that the emulsion droplet size depend on temperature at which the emulsification process is conducted and HLB number of the emulsifier.

Emulsions prepared at the temperature just below the PIT, followed by rapid cooling, generally have smaller droplet sizes. This can be understood if one considers the change of interfacial tension with temperature (Fig. 14).

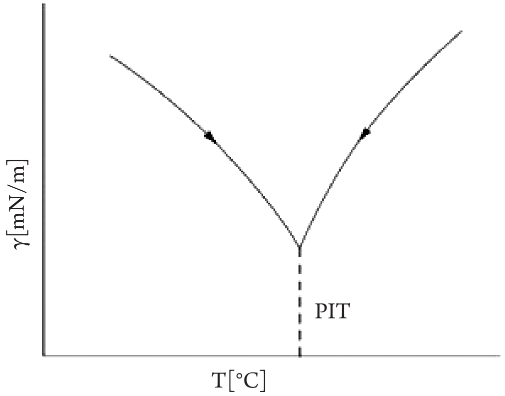


Fig. 14. Effect of temperature on interfacial tension [41]

The interfacial tension decreases when temperature increases, reaching a minimum close to the PIT, after which the interfacial tension grows. Relatively stable O/W emulsions could be obtained when the PIT of the system is 20–65°C above the storage temperature. The PIT method can be used to prepare nanoemulsions [20, 42].

2.3. OTHER FACTORS INFLUENCING EMULSION STABILITY

Although that cosmetic emulsions are unstable by nature, it is essential to find ways to keep the product in a minimally reasonable "steady state" or a "metastable state" until the end of its shelf life. It is very important, therefore, to understand the nature and type of stability we encounter in cosmetic emulsions. Three important categories of stability it must be face in cosmetics manufacturing: microbial stability, chemical stability and physical stability. To control microbial and chemical stability of cosmetic products appropriate raw materials are applied in formulation process: preservatives and antioxidants respectively.

Physical instability is mostly caused by gravitational force, or slow changes in crystalline structure of certain ingredients, or changes in products viscosity. The most often emulsion physical destabilization processes include: creaming and sedimentation, both of them can be reversed by blending / mixing the system to restore the emulsion (Fig. 15). Emulsion breaking or cracking (deemulsification), preceded by flocculation and coalescence, is irreversible (Fig. 16).

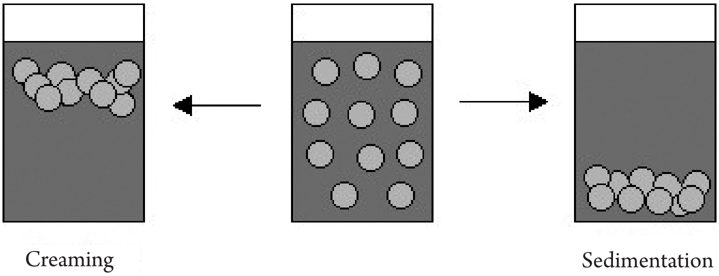


Fig. 15. Emulsion creaming and sedimentation [6]

Creaming and sedimentation are processes of forming two distinct layers within the volume of an emulsion, with one of the layers with more of the dispersed phase. Depending on the density difference between the two phases and the mass of globules, the globules accumulate in the upper layer (which essentially is creaming) or in the lower layer (which is sedimentation). An example of creaming is the formation of cream on the surface of milk; the cream has more fat globules than the remaining volume of milk. Creaming of cosmetic products most often occurs in cosmetic lotions, especially those with a high-water phase ratio.

The phenomenon observed during creaming and sedimentation of an emulsion can be described with an equation derived from the law of hydrodynamics, namely the Stokes law of rectilinear motion of a ball in a viscous medium (eq. 27).

$$V = \frac{2a^2 (\rho_D - \rho_C) g}{2\eta} \tag{27}$$

where:
V – velocity of motion of the drop flow rate of the droplets in a viscous medium lets, m/s,
a – droplet radius, m,
ρ_D – internal phase density, kg/dm^3,
ρ_C – continuous phase density, kg/dm^3,
g – apparent gravity, m/s^2,
η – continuous phase viscosity, Pas.

As demonstrated in equation 27, the risk of creaming or sedimentation can be reduced by: minimizing the diameter of dispersed phase droplets (since the creaming and sedimentation rate is directly proportional to the droplets size), use liquids with a relatively low difference of density, and produce a relatively high viscosity of the continuous phase (since the creaming and sedimentation rate is inversely proportional to the viscosity of the medium).

Another symptom of an unstable emulsion is the **phase inversion** process, in which an O/W emulsion is converted into a W/O emulsion, and vice versa. The factors contributing to this change in an emulsion include: excessively high concentration of the internal phase (systems with similar ratios of both phases display optimum stability), the type and concentration of the emulsifier, and the presence of electrolytes (NaCl, NaOH, or $Al_2(SO_4)_3$) – if the emulsifier is a ionic compound or a mixture of ionic and non-ionic compounds. Temperature is among significant emulsion destabilization contributors. Emulsions, especially those stabilized with non-ionic emulsifiers are sensitive to variations in temperature. Increasing temperature breaks the hydrogen bonds and reduces the efficacy of the emulsifier.

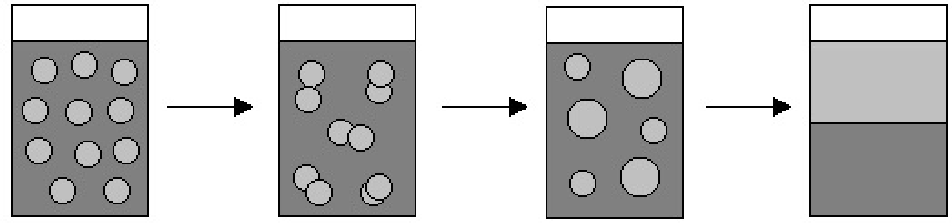


Fig. 16. Flocculation, coalescence and emulsion breaking/cracking [6]

Breaking (or cracking) is an irreversible emulsion destabilization process and comprised two stages. The first stage is **flocculation**, during which the internal phase droplets begin forming larger aggregates. The aggregation process is still reversible; the sedimentation of the aggregates can be avoided by changing the emulsifier or increasing the emulsifier concentration. In the second stage, the aggregates are transformed into large, isolated droplets (this is called **coalescence**). Ultimately, the droplets coalesce and the internal phase is separated (Fig. 16). The forces driving flocculation and coalescence include the van der Waals forces (eq. 28), Brownian motions (eq. 29), and the Ostwald ripening.

According to equation 28, the van der Waals forces are directly proportional to the radius of the droplets and inversely proportional to the distance between the droplets of the internal phase. By increasing the degree of fineness of the internal phase, the diameter of the dispersed liquid droplets can be reduced while increasing their spacing; this reduces the risk of emulsion destabilization.

$$F \sim \frac{a}{h} \tag{28}$$

where:
F – van der Waals forces, kJ/mol,
a – droplet radius, m,
h – droplet spacing, m.

Coalescence occurs usually when an emulsion is made with an insufficient quantity of the emulsifier. Hence, some dispersed phase droplets are devoid of the protective film. Brownian movements cause periodic collision of the droplets, during which they coalesce into larger droplets. According to equation 29, the oscillation path of the particles of the dispersed phase is inversely proportional to the viscosity of the continuous phase and the radius of the internal phase droplets. A careful selection of the emulsifier, a fine granulation of the dispersed liquid particles, and a high viscosity of the medium will reduce the risk of coalescence.

$$d = \sqrt{\frac{2tkT}{6\pi\eta a}} \tag{29}$$

where:
d – distance covered by a particle, m,
a – radius of the internal phase droplet, m,
η – external phase viscosity, Pas,
T – temperature, K,
t – time, s,
k – Boltzmann constant, m^2 kg s^{-2} K^{-1}.

The Ostwald ripening, an effect of heterogeneity in the internal phase droplets, has a negative impact on the stability of emulsion systems. The dispersed phase droplets migrate through the continuous phase to one another, forming larger aggregates; in this mechanism, smaller droplets tend to migrate toward the larger ones. The phenomenon can be reduced by a good homogenization of the emulsion.

To sum up, the stability of an emulsion system is affected by (i) the emulsifier type and its concentration, (ii) the degree of dispersion and homogeneity of dispersed phase particles, and (iii) the external phase viscosity. The stability can also be affected by processing factors, including agitation (the stirrer type and the time and speed of mixing), the emulsification temperature, and the cooling process.

2.4. STABILITY STUDY OF COSMETIC EMULSIONS

A stability study is designed to provide evidence on how the quality of a cosmetic product varies with time under the influence of a variety of environmental factors such as temperature, humidity, and light, and which enables recommended storage conditions, retest periods, and shelf lives to be established. There are several stability conditions which are commonly utilized in determining the stability of cosmetics. Currently available standard stability testing methods include freeze/thaw, incubation at different temperatures and centrifugal method, which is used as a first stage to eliminate the less stable formulations.

The centrifugal method is based on the effect of gravity force coupled with the density differential between the two phases of an emulsion. The separation of an emulsion can be accelerated by increasing the force of gravity by centrifugation. An emulsion specimen in placed in a heat dish of a centrifuge and spun at 3500 rpm for 10 to 15 minutes. Next, the emulsion is visually inspected for any changes from centrifugation. Centrifugation can only break up the least stable of emulsions.

The different temperature method (accelerated stability study) – a stability measurements conducted under exaggerated conditions, in an attempt to accelerate the aging process, i.e., the rate of chemical degradation and/or physical change. For cosmetic products the most commonly used accelerated stability storage conditions are 5°C, 20/25°C, 37/40°C, and 50°C. The measure of emulsion durability in the method is the time to achieve emulsion breaking. A similar determination can be made by pressurizing the specimen in an autoclave at a constant test temperature.

Freeze / Thaw Stability Study – a study that is conducted for 24 hours, at minus temperature ($T < -10°C$) followed by $T = 40°C$ (no humidity control) to determine the effect that freezing and subsequent thawing has upon the stability of a product. Such studies may be conducted with single or multiple freeze/thaw cycles, with three cycles being the most commonly used.

During pilot batch studies very valuable in troublemakers identification could be Turbiscan stability analyser. The apparatus enables fast identification of destabilization mechanisms like: creaming, sedimentation, flocculation or coalescence. At controlled temperature the instrument allows either monitoring the product stability or accelerating destabilization process, up to 200 times faster compared to visual testing [43].

As it was mentioned above, the stability assessment of an emulsion should also consider the emulsion resistance to oxidation, and microbiological stability tests according to applicable reference standards [1].

3. TECHNOLOGY OF COSMETIC EMULSIONS

The technology of cosmetic emulsions comprises several stages, including formula development, product structure determination, selection of raw materials and emulsifiers, selection of process parameters, and quality assessment of raw materials and the finished product.

Cosmetic emulsions are a group of products which vary in rheological properties and viscosity from ten-odd to over 100,000 mPas. Cosmetic emulsion forms include pastes, gels, creams, semiliquid systems (lotions or balms) and liquids. The basic principle of cosmetic emulsion manufacturing is to increase the interfacial boundary surface with mechanical and thermal inputs (namely, stirring and heating of raw materials). The addition of an emulsifier helps reduce the energy input and stabilize the obtaining systems. The stability of an emulsion is affected not just by the emulsifier, but also by the type and quantity of all ingredients used in the emulsion system, and by the method of their mixing, which is the sequence of addition of ingredients, the mass ratio of solid ingredients to liquid ingredients, and the emulsification time and temperature.

The actual emulsification process is preceded by batching the formula ingredients at mass ratios. Fig. 17 shows a scheme of forming emulsion systems.

In the first stage of the process, raw materials are batched to the mixers (separately for the oil phase and the water phase). The ingredients of both phases are pre-mixed and, depending on the specific ingredients in use, preheated to the required temperature

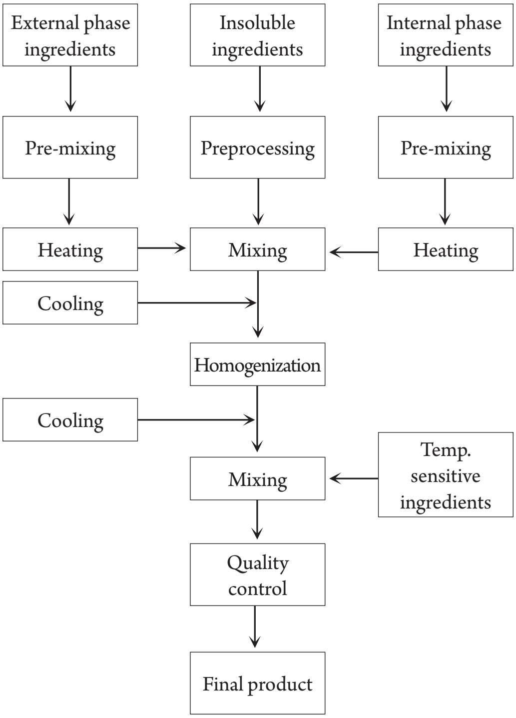


Fig. 17. General scheme of an emulsion technology by hot-hot method [6]

(usually 10°C above the melting point of the solid components of the oil phase). Insoluble ingredients are separately pre-processed by refinement or surface modification. The pre-processed ingredients of both phases are mixed together; the internal phase is dispersed within the external phase. The insoluble ingredients are added to the mixed mass at this stage. Homogenization follows to finely break up the dispersed phase into droplets identical in size.

The process is usually held at 70 to 80°C before the homogenization. The elevated processing temperature helps reduce the viscosity of the system and facilitate the mixing and dispersion of the phases. The system is cooled down to 40 to 50°C before adding heat-sensitive ingredients; following their addition, the emulsion is remixed. (The cool down process is sometimes completed before homogenization, depending on the ingredient types.) Sometimes only a part of the dispersing phase is heated and diverted to the first mixing stage, with the remainder added during the remixing. This is usually due to cost efficiency, reduced wear and tear of processing machines, and reduced energy inputs for heating, cooling and mixing. Hot processing is not the only viable option for manufacturing of emulsions; there are cosmetic emulsions formed by hot-cold processing, in which the water phase at the room temperature (20 to 25°C) is added to the oil phase held at 75 to 80°C. The emulsification process is held at a high temperature or a gradually reduced temperature while the water phase is being fed to the mixture.

Before the finished product is complete, the emulsion is post-processed e.g. by sterilization or staging. The finished product is sampled for quality control. The last production stage is packaging: the emulsion is placed in unit containers. Cosmetic products are usually packed in glass or plastic containers. Plastic containers can only be used if it is confirmed that no cosmetic ingredient will react with or destroy the plastic material. Each unit container can hold a predefined quantity of the cosmetic product, e.g. 35 cm^3, 50 cm^3 or 75 cm^3. Emulsions are automatically packed by high-performance filling and packing lines with measures for protection against foreign body contamination (like dust) or microbiological contamination (the product is distributed into unit containers in an inert gas atmosphere).

3.1. COSMETICS MANUFACTURING EQUIPMENT

State-of-the-art cosmetic manufacturers use dedicated apparatus and equipment with regulated heating, mechanical mixers, controlled atmospheres, and a very wide gamut of additional controls and monitoring features, all designed for sterile/clean room operation.

Cosmetic emulsions are manufactured both in batch and continuous duty apparatus; given the sheer scale of production output, batch mixers are most often used (Fig. 18).

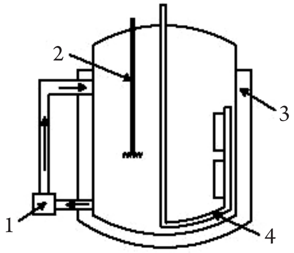


Fig. 18. General diagram of a mixer used for manufacturing of cosmetic emulsions: 1 – homogenizer; 2 – disperser; 3 – water jacket; 4 – main stirrer (agitator) [6]

Mixers used in cosmetic emulsion manufacturing usually equipped with following elements:

- the main stirrer, which a low-speed implement, usually in the form of a single or two-arm anchor, with plastic paddles in each case to scrape the emulsion of the mixer tank walls and provide heat transfer throughout the emulsion mass; double or triple-vane propeller agitators are alternatively used. The main stirrer runs usually from ten-odd to several hundred rpm (revolutions per minute);
- the disperser, which is a high-speed implement to eliminate the dead volume within the mixer's tank and disperse insoluble substances (such as pigments, colouring agent, or UV filters);
- the water jacket, which heats or cools the emulsion mass.

The type, capacity and power output of the mixer must be properly balanced. The emulsification efficacy depends on the stirrer type and vane angle. Low-viscosity liquids, water solutions and light oils are mixed with singe-vane stirrers, while high-viscosity emulsions required double-vane stirrers.

The homogenizer is an important part of every mixer, since the device provides proper refinement of the internal phase droplets. A homogenizer is most often a high-speed turbine agitator (working at 1,400 to 4,000 rpm) or colloid mills. The first descriptions of colloid mills and the production of homogenized emulsions were provided by Frazer and Walsch. By applying a pressure of 21 MPa, both researchers produced durable emulsions with a homogeneous size of internal phase particles (0.5 μm) and only a little of an emulsifier.

The general operating principle of a colloid mill (Fig. 19a) is to force a liquid, which contains large droplets of the internal phase, between a high-speed rotor and a stationary stator. The gap between the rotor and the stator can always be adjusted, even with the colloid mill running. Colloid mills provide the effect of hydraulic shearing with breaking and compression of the liquids; the concomitant phenomena depend on the rotor form and the design of a specific colloid mill. Today, colloid mills can be replaced with more efficient homogenizers to achieve better refinement and homogenization of the internal phase (even at high emulsion viscosities). These apparatus include pressure homogenizers and ultrasonic homogenizers (Figs. 19b and c).

Pressure homogenizers refine the internal phase by applying pressure the value of which may reach 20 MPa. Ultrasonic homogenizers refine the internal phase with a very sharp and fast blade, which generates an ultrasonic field and breaks up the dispersed phase into very fine and uniform droplets. Homogenizers can produce much finer particles than colloid mills, although they require much more energy. It has been an industrial practice to combine modern homogenizers with colloid mills.

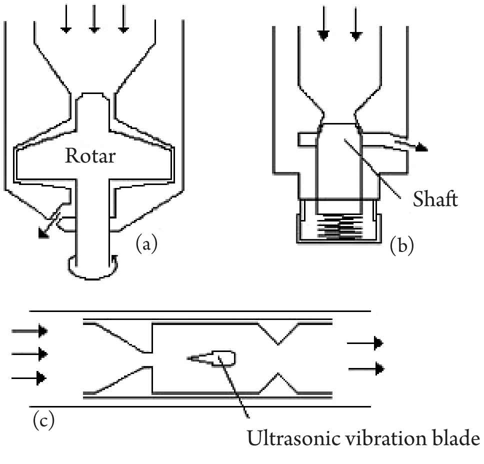


Fig. 19. Homogenizer types: (a) colloid mill; (b) pressure homog.; (c) ultrasonic homogenizer [6]

Fully equipped cosmetics production line consists of:

- water treatment plant, usually includes series of filters and reverse osmosis system, (water quality is an important technological parameter),
- storage tank for pure water,
- emulsifying mixer (Fig. 20), include main pot (of volume from 30 up to 2000 dm^3), water and oil pots,
- storage tank for mixer,
- filling machine,
- capping machine,
- labelling machine,
- inkjet printer.

Fig. 20. Hydralic lifting vacuum emulsifying mixer machine (consists of emulsifying mixing tank, water tank, oil tank, hydraulic lifting system, control system, homogenizer, mixing system and vacuum system), Guangzhou Ailusi Machinery Co., Ltd [44]

As was discussed above the quality and a stability of emulsions, among others, is affected by processing factors, including agitation process (the stirrer type and the time and speed of mixing). Mixing is a dynamic process whose driving force is the pressure difference in various tank regions that is produced by a rotating impeller therefore mixing systems usually are complex. In the case of mixer machine showed in the figure 20 the mixing systems include single-way agitator, double-way agitator and helical ribbon impeller.

3.2. MANUFACTURING OF W/O EMULSIONS

W/O emulsions is only about 20% of the market of cosmetic products. One of the reasons of such a situation is that the production of stable W/O emulsions is rather difficult process. This is due to many factors. It is crucial to properly develop the composition and choose the right emulsifier, the self-emulsifying base, and proper emollients.

The most popular emulsifiers for stabilization of W/O emulsions include non-ionic surfactants [45–49]:

- polyglycerol derivatives: *polyglyceryl-3-polyricinoleate*, *polyglyceryl-4- diisostearate*, or *polyglyceryl-3-pentaolivate*,
- fatty acid monoesters: *sorbitan monoolivate*, *glyceryl oleate*, or *glyceryl stearate*.

These surfactants provide the best stability to the systems with the oil phase between 25 and 35%. The water phase is usually between 20 and 60%. The systems with the water phase concentration at approximately 74% are known as "HIPE" (*High Internal Phase Emulsion*). Research demonstrates that the water phase concentration is a key parameter of emulsion viscosity and emulsion stability. The higher the water phase concentration is, the higher the viscosity of the system is [47, 48]. The stability of W/O emulsions can be greatly improved with the addition of dedicated stabilizers. The most popular stabilizers include paraffin wax and microcrystalline wax [46, 47]; natural stabilizers with the best efficacy include beeswax and lanolin. Fatty alcohols, such as cetyl alcohol and stearyl alcohol are also among popular W/O emulsion stabilizers [6].

Another significant parameter of W/O emulsion stability is the polarity of the oils phase. The lower the polarity of the oil is (as in e.g. squalene or hexadecane), the easier it is to produce a stable W/O emulsion [48, 49]. Polar oils feature, to a certain degree, an affinity to the water phase, which facilitates their diffusion (mass transfer) in the water phase. The effect of this situation is the destabilization of the system caused by the Ostwald ripening [49]. Table 9 presents a comparison of polarity of selected cosmetic emollients.

Given that the chemical potential of water is much higher in smaller droplets, the transport to larger droplets occurs, causing the Ostwald ripening. An addition of electrolytes in the water phase reduces the force of attraction between the water phase droplets and prevents coalescence [48]. Another group of researchers [50] states that the force of attraction (related to the effect of the van der Waals forces) between two water phase droplets in an oil phase is minimised when the refractive index and/or the dielectric constant of both emulsion phases are very similar. An increase of the electrolyte concentration in the water phase will increase the refractive index and reduce the dielectric constant of the water phase, thus reducing the difference between these values in the two phases.

Marquez Medrano et al. [50] were tested the effect of calcium chloride on the stability of a W/O emulsion based on sunflower seed oil and used polyglycerol polyricinoleate as the emulsifier (INCI: *Polyglyceryl-4 Polyricinoleate*). The research proved that the electrolyte used by Marquez et al. reduce the tension at the oil/water phase boundary, which facilitated

Table 9

Classification of cosmetic emollients by polarity [47]

Oil polarity	Examples
Nonpolar	Paraffin oil, petrolatum, squalene, dicapryl ether, and isohexadecane
Medium-polar	Isopropyl myristate, isopropyl isostearate, silicone oil, and caprylic/capric triglycerides
Polar	Wheat germ oil, shea butter, octyldecanol, PPG-15 Stearyl Ether, and C_{12}–C_{15} Alkyl Benzoate

adsorption of most emulsifier molecules at the interface. They explained the observed effect by the interaction of the electrolyte with the ionized surface-active components of the emulsion (such as free fatty acids) from the emulsifier or the sunflower oil. They also suspected that the calcium chloride cations could affect the reaction between the hydrophilic chains of the polyglycerols (i.e. the negative charge of the hydroxyl groups). These authors also compared the effect of 3 different calcium salts on emulsion stability. The effect was related with the degree of dissociation of the salt: carbonates < lactates < chlorides. Calcium chloride and calcium lactate reduced the interfacial tension more than calcium carbonate did; the two former compounds produced more stable emulsion systems.

The effect of electrolyte concentration (e.g. magnesium sulphate) on the stability of emulsion system with cetyl dimethicone copolyol as the emulsifier (INCI: *Cetyl Dimethicone Copolyol*) was tested by Park et al. [48]. Park et al. found that the increase of the electrolyte concentration (from 0.0 to 0.5%) was inversely proportional to the refractive index. However, an emulsion with an intermediate electrolyte concentration (0.3%) was the most durable in terms of kinetic stability. This proved that electrolyte concentration is not the only factor of emulsion stability, although it definitely improves it at optimal values for the specific quantitative and qualitative composition of the preparation [48].

In conclusion, it is critical to use electrolytes in W/O emulsions which will provide the latter with an additional protection against coalescence of droplets, aside from selecting a proper emulsifier. The concentration levels of both emulsion phases are also critical. The higher the concentration of the water phase is in an emulsion system, the more viscous and stable the emulsion system can be produced. Use of non-polar oils, such as squalene, largely reduces the migration of droplets in the internal phase. If, despite these measures, an emulsion system continues to be unstable, a homogenization process should be applied to assure a uniform dispersed phase, both in terms of droplet size and droplet form; this will improve the stability. Increasing the homogenization speed significantly reduced the internal phase particle size and the polydispersity of the emulsion system [51–53]. The reduction of the particle size increased the viscosity of the overall emulsion system [52]. Homogenization process has a significant impact on the improvement of W/O emulsion stability.

4. EMULSION AS A PHYSICOCHEMICAL FORM OF COSMETIC PRODUCTS

As was mentioned in chapter 1, according to the definition in Regulation 1223/2009 [1] "'cosmetic product' means any substance or mixture intended to be placed in contact with the external parts of the human body (epidermis, hair system, nails, lips and external genital organs) or with the teeth and the mucous membranes of the oral cavity with a view exclusively or mainly to cleaning them, perfuming them, changing their appearance, protecting them, keeping them in good condition or correcting body odours". Following this definition cosmetic products are classified into 4 basic categories:

1. personal hygiene products
   - washing and bathing products, shampoos,
   - deodorants,
   - shaving products,
   - oral hygiene products,
   - other;
2. care products
   - skin care products (moisturising, anti-age, problematic skin),
   - body care products (firming, cellulite, stretch marks, sunbathing protection),
   - foot, hand, nail care products,
   - hair care products,
   - special cosmetics – baby care cosmetics etc.;
3. beauty cosmetics
   - colour cosmetics (fluids, make-up products, products for beautifying eye area etc., lipsticks, permanent make-up),
   - products for hairstyling and changing the hair structure,
   - hair dying products,
   - nail polishes, artificial nails;
4. perfumery
   - perfumes,
   - toilet water,
   - cologne,
   - other perfumed products.

However, on the cosmetic market certain marketing trends are clearly visible. Apart from the classical cosmetic emulsions for skin care, maintaining water and lipid balance of the skin, there are new groups of products responding to the market needs, such as:

- personalised cosmetics – based on the skin diagnosis,
- cosmetics inspired by aesthetic medicine procedures,
- photo-ready cosmetics which immediately cover skin imperfections,

- nutricosmetics – a combination of cosmetics and dietary supplements,
- anti-pollution cosmetics.

In the search for innovation, certain trends are also observed regarding the ingredients. For many years natural cosmetics, based exclusively on the raw materials of plant origin or obtained in biotechnological processes, have been very popular. New sources of ingredients are sought in the plants of tropical forests, e.g. the Amazon jungle, high mountains, the sea, i.e. the regions still free from the harmful activity of man. The novelties regarding cosmetic ingredients also include:

- ingredients improving application and the sensation the cosmetics leave on the skin (emulsifiers and emollients),
- alternative options for traditions preservatives and silicones,
- substitution of fatty alcohol sulphates (SLS, SLES) in cosmetics for washing with mild surfactants such as alkyl polyglucosides, saponin ingredients, sugar surfactants or amino acid derivatives (glycine, sarcosine, glutamic acid),
- using natural ingredients (salt, sugar, fragmented plant parts) as an alternative for polyethylene.

4.1. RAW MATERIALS USED IN SKIN CARE EMULSIONS

The role of the ingredients present in cosmetic emulsions is to support the intercellular cement, a natural barrier reducing the loss of water from the skin. The binder of the *stratum corneum* (SC) cells has a liquid crystal structure, and is composed of alternate layers of polar lipids and the water areas. The lipid barrier protects the skin against water loss, reducing its diffusion from the live epidermal layers to the surface of the skin. Only a small quantity of water, i.e. transepidermal water loss (TEWL) may pass through this semi-permeable structure.

The lipids found in the intercellular cement include: ceramides, sterols, free fatty acids and certain amounts of hydrocarbons (Table 10). The liquid crystal structure of the cement is affected by non-polar interactions between the fat chains, and the hydrogen bonds between the polar fragments of lipids and the water molecules. However, ceramides play the most important role, providing the scaffolding for the entire structure.

Table 10

Composition of the *stratum corneum* lipids [54]

Type of lipids	Content Wt (%)
Ceramides	40
Cholesterol and its derivatives	25
Free fatty acids	18
Hydrocarbons (including squalene)	11
Other	6

The mean water content in the *stratum corneum* is approximately 10%. Components of the natural moisturising factor (NMF), hydrophilic compounds (humectants) demonstrating the ability to bind water, are responsible for the proper degree of hydration in the intercellular binder. They are found in the water areas of the *stratum corneum* intercellular cement. It is a combination of free amino acids, pyroglutamic acid, lactic acid and theirs sodium salt, urea and other substances (Table 11).

Table 11

Composition of the natural moisturising factor (NMF) [54]

Compound	**Content Wt (%)**
Free amino acids	40.0
Pyroglutamic acid	12.0
Lactates	12.0
Urea	7.0
Sugars, organic acids and peptides	8.5
Organic nitrogen compounds	1.5
Chloride ions	6.0
Phosphate ions	0.5
Sodium and potassium ions	9.0
Calcium and magnesium ions	3.0
Citrates and other organic salts	0.5

The role of skin-care cosmetics is to improve the condition and feel of the skin what is a function of its softness and flexibility. The main purpose of cosmetic emulsions application is to restore and maintain the water-lipid balance in the *stratum corneum* of the epidermis, therefore they contain substances similar to those naturally found in the SC.

Table 12 presents a general composition of a cosmetic emulsion. Apart from functional ingredients, affecting the skin condition, (emollients, humectants), there are also raw material used to maintain microbial, chemical and physical stability of emulsions (auxiliary components).

Depending on what additional, specific effect of cosmetic products on the skin is expected some optional raw materials, (such UV filters, plant extracts, acne treatment components), are added to main formulation.

Table 12

General composition of a cosmetic emulsion

Ingredients	**Content Wt (%)**
Emulsifier	2–6
Functional ingredients	
Emollients	10–35

Humectants	1–8
Auxiliary components	
Water	q.s.
Preservatives	0.2–1
Consistency agents	1–6
Antioxidants	0.01–0.05
pH regulators	q.s.
Optional ingredients	
Active substances	0.1–2
UV filters	0.01–0.5
Chelating agents	0–0.02
Fragrance	0.1–1
Dyes	q.s.

4.1.1. SELECTED GROUPS OF COSMETIC EMULSIFIERS

As was mentioned before, the concentration and the emulsifier structure significantly influence the consistency and stability of cosmetic emulsions. Especially, the chemical structure of the emulsifier is critical to the properties of the emulsion system [14, 23, 41]. The list of marketed cosmetic emulsifiers is very extensive and novel and more effective substances are kept being proposed. Emulsifiers can be classified by certain criterion for an easier understanding of this cosmetic raw materials group.

Considering origin as the classification criterion, emulsifiers are classified as follows [3, 6]:

- natural organic substances:
    - proteins, including casein, gelatin, and whey proteins,
    - polysaccharides, including starch, cellulose, rubber, slimes, and pectins,
    - lecithins and sterols,
    - waxes, e.g. lanolin;
- natural inorganic substances:
    - bentonite,
    - silica gel,
    - magnesium carbonate;
- synthetic:
    - synthetic derivatives of natural substances: methylcellulose, carboxymethylcellulose, or sulphated oils and fats,
    - synthetic polymers, including products of acrylic acid polymerization and silicone copolymers,
    - synthetic ionic and non-ionic surfactants.

Considering the ion formation properties as the classification criterion, emulsifiers are distinguished as follows:

- non-ionic,
- ionic:
  - anionic,
  - cationic,
  - amphoteric,
  - complex.

The most useful is a classification of cosmetic emulsifiers which is based on the formation properties of specific emulsion types. According to the Bancroft law, the type of the emulsion formed depends largely on the properties of the emulsifier applied. Water soluble emulsifiers (HLB > 10) stabilize O/W emulsions. Oil soluble emulsifiers (HLB < 10) stabilize W/O emulsions. HLB number of selected emulsifiers is presented in Table 5.

The group of cosmetic emulsifiers applied in the formation of stable O/W emulsions includes non-ionic emulsifiers (which are the largest and most diverse group of these products) and ionic emulsifiers (which mostly include anionic emulsifiers) [2–7].

4.1.1.1. NON-IONIC O/W EMULSIFIERS

Non-ionic emulsifiers are the most significant group of cosmetic emulsifiers. The constituents of non-ionic emulsifiers include hydrophobic hydrocarbon chains and hydrophilic groups which do not undergo electrolytic dissociation (most usually these are alcoholic hydroxyl groups or ester groups which are hydrated in water).

Non-ionic O/W emulsifiers are mostly polyoxyethylene polyol derivatives. Polyoxyethylene chains have a strong affinity to water, by which they form hydrogen bonds between the water molecules and the oxygen atoms of the ethoxylated groups; this stabilizes the system. Depending on the degree of ethoxylation (where n is the number of ethylene oxide molecules attached to the hydrophobic chain), the compounds vary in polarity and HLB numbers. Hydrophilic emulsifiers are highly ethoxylated (where n is between 8 and 20).

In general, non-ionic emulsifiers characterized by good properties: they are no toxic or irritating substances in relation to the skin, and they are universally compounds: insensitive to pH variations or addition of electrolytes. The compounds are also compatible with ionic emulsifiers, and the two classes can be combined. Note, however, that polyoxyethylene substances reduce the anti-microbial action of the preservatives used in cosmetic emulsions, including sorbic acid, benzoic acid, or PHBA esters. The emulsions stabilized with polyethoxylated substances are less stable at higher temperatures.

There is a few groups of polyoxyethylene non-ionic emulsifiers. Some of them are presented below.

Ethoxylated fatty alcohols (Fig. 21).

$$R–O–(CH_2–CH_2–O)_n–H$$

Fig. 21. Ethoxylated fatty alcohols ($R = C_{10}–C_{20}$, $n = 8–23$)

Cosmetic products usually contain ethoxylated fatty alcohols with 8 to 23 ethoxylate groups, with an alkyl residue, which can be straight, branched, saturated, or unsaturated hydrocarbon chain. INCI name (International Nomenclature of Cosmetics Ingredients) of the compound suggests its structure after abbreviation of alcohol's name there is the suffix "eth". *Ceteth-20,* stand for cetyl alcohol ethoxylated with 20 molecules of ethylene oxide (ETO). Other popular examples include: *Oleth-10* (oleyl alcohol ethoxylated with 10 ETO groups), *Ceteareth-20* (a mixture of cetyl alcohol and stearyl alcohol ethoxylated with 20 ETO groups), or the relatively popular lauryl alcohol ethoxylated with 7 to 10 moles of ETO (e.g. *Laureth-10*).

This group of emulsifiers has a very good wetting properties and surface activity. It is compatible with most surfactants. Ethoxylated fatty alcohols are used in cosmetic products as emulsion stabilizers, solubilizers of essential oils, or emollients.

Ethoxylated fatty acid esters (Fig. 22), or polyethylene glycol (PEG) ester derivatives.

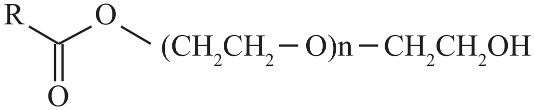


Fig. 22. Ethoxylated fatty acid esters ($R = C_{10}–C_{20}$, $n > 10$)

Ethoxylated fatty acid esters with ETO > 10 are used as O/W emulsifiers. Their emulsifying action aside, they have a good wettability and antielectrostatic performance. The trade names of PEG fatty esters usually characterise the structures of the compounds; *PEG-40 Stearate*, for example, is ester of stearic acid and PEG-40 glycol.

Ethoxylated sorbitan fatty esters (Fig. 23), or ethoxylation products of sorbitan fatty acid monoesters, are ether-ester bonds components. The trade names of these ethoxylated derivatives include Tweens and Polysorbates, such as Tween 20 stand for polyoxyethylene (20) sorbitan monolaurate.

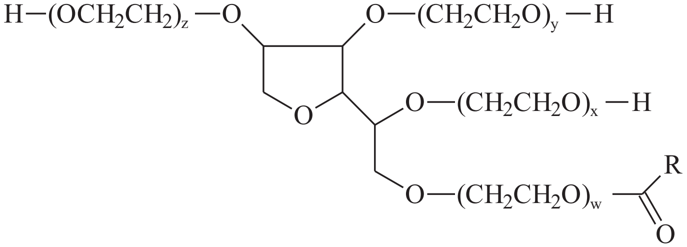


Fig. 23. Ethoxylated sorbitan fatty monoesters (R is the alkyl residue of fatty acids)

Ethoxylated sorbitan fatty monoesters are used in the cosmetic industry as O/W emulsifiers, wetting agents, solubilizers for essential oils and emulsion oil components, where they exhibit an emollient action.

Derivatives of mannite and pentaerythrite are also cosmetic hydrophilic emulsifiers in the group of ethoxylated polyol esters.

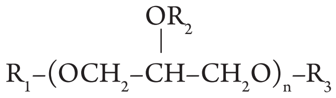
Other examples of non-ionic O/W emulsifiers include:

- **ethoxylated glycerin monoesters**, usually found in body lotions, where they also provide an emollient and moisturizing action without a greasy sensation after the application, e.g. ethoxylated glycerine monolaurate with 8 ETO groups (INCI: *PEG-8 Glyceryl Laurate*),
- **ethoxylated castor oil derivatives** with over 20 ETO moles per molecule; these substances are well soluble in water and organic solvents, resist alkalis, acids and hard water, emulsify fats and waxes very well, and provide an excellent softening action, e.g. hydrogenated castor oil ethoxylated with 40 ETO moles (INCI: *PEG-40 Hydrogenated Castor Oil*),
- **ethoxylated derivatives of rapeseed oil** and other oils without free hydroxyl groups. The ratio of oil to the hydrolysing agent and the number of attached ETO determine the dispersing, emulsifying and softening action. These compounds are very popular in cosmetic products, and most popular in the food industry, including rapeseed oil sterols ethoxylated with 10 ETO moles (INCI: *PEG-10 Rapeseed Sterol*),
- **ethoxylated lanolin**, the derivatives of which used in the cosmetic industry have 6 to 75 ETO molecules per chain; the attachment of 75 ETO moles to one mole of lanolin results in a water-soluble derivative of lanolin with HLB at 17,
- **ethoxylated polyglyceryl esters**, e.g. *PEG-10 Polyglyceryl-2 Laurate*.

Currently on the market of cosmetic products is evident interest in natural products. Natural and organic cosmetics have had ample growth rates for years. The five major European organic and natural cosmetics standard-setting organisations, bodies like the Ecocert, came together to harmonize their respective standards. In 2010 they introduce COSMOS stands for "Organic and Natural Cosmetic", which sets certification requirements for organic and natural cosmetics products in the Europe. The standard covers all aspects of the sourcing, manufacture, marketing and control of cosmetic products [55]. According to the COSMOS standards non-ionic surfactants from the group of ethoxylated substances are not allowed as emulsifiers in natural cosmetics. Ideal raw materials for natural cosmetics are polyglycerol fatty acid esters or alkyl polyglucosides. These two groups of non-ionic surfactants meet the criteria for "PEG-free" products and compliant with the COSMOS could be use in the natural cosmetic products.

Polyglycerol fatty acid esters (Fig. 24), e.g. ester of stearic acid and polyglyceryl-5 (INCI: *Polyglyceryl-5 Stearate*), or *Polyglyceryl-4 Caprate, Polyglyceryl-4 Laurate* are formed by reacting polymerized glycerols with edible fats, oils, or fatty acids; degree of polymerization varies, and is specified by a number (such as tri-) that is related to the average number of glycerol residues per polyglycerol molecule. By varying the proportions as well as the nature of the fats or fatty acids to be reacted with the polyglycerols, a large and diverse class of products is obtained. Depending of structure the polyglycerol esters are water or oil soluble and with an HLB from about 4 to about 13 [28, 56, 57].

The use of hydrophile polyglycerol fatty esters gives an outstanding, non-sticky feeling to the skin. The liquid form allows these O/W emulsifiers to be processed cold, enabling for example the manufacture of lotions in spray form.



$$R_1-(OCH_2-\overset{OR_2}{\overset{|}{CH}}-CH_2O)_n-R_3$$

Fig. 24. Polyglycerol fatty acid esters (R_1, R_2 and R_3 each may be a fatty acid moiety or hydrogen, n is about 3–5)

Alkyl polyglycosides (APG), such as cetearyl glucoside (INCI: *Cetearyl Glucoside*), are very efficacious surfactants with a high compatibility with other surface-active agents and a gentle action on the skin. When combined with selective emollients, they can form O/W emulsions of great stability and performance. They are produced by proton-catalysed, preferably of glucose, or by butyl polyglucoside with fatty alcohols. Chemically the alkyl polyglycosides are acetals. The hydrophilic headgroup is characterized by the (average) number of glucose units (n) present in the saccharide moiety. The hydrophobic residue may vary in the number of carbon atoms (x) of the alkyl chain (Fig. 25) [58].

$$H-(C_6H_{10}O_5)_n-O-C_xH_{2x+1}$$

Fig. 25. Empirical formula of alkyl polyglucosides
(n is usually between 1 and 5, x is about 6–18 carbon atoms)

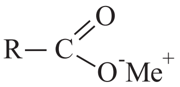
4.1.1.2. ANIONIC O/W EMULSIFIERS

An anionic emulsifier dissociates in a water solution into an anion with the hydrophilic and lipophilic parts of the molecule and a cation, which is usually a metal, an amine group or an ammonium group. The emulsifying action of this group consists in formation of an electric layer around the droplets of the dispersed phase, which prevents coalescence.

There are far fewer anionic emulsifiers than non-ionic emulsifiers. While they can form very stable emulsions in neutral or slightly alkaline media, their main weakness is the high sensitivity to acidity modifier and electrolytes.

The most popular anionic O/W emulsifiers are **alkaline soaps**. Alkaline soaps are salts of fatty acid with a hydrocarbon chain length between C_{12} and C_{18} (Fig. 26). Alkaline soaps with less than 12 carbon atoms display an overt hydrophilic action and lose their emulsification potency. The most popular alkaline soaps in use are sodium salts, potassium salts, triethanolamine salts, stearic acid salts, palmitic acid salts, and lauric acid salts [2].

Anionic emulsifiers are usually used in the formulation of stearic creams. The emulsions have an alkaline reaction. During emulsification process, stearic acid is neutralized with

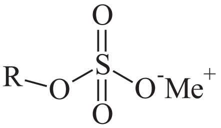


$R = C_{12}$ to C_{18}
$Me = Na^+, K^+, NH(CH_2-CH_2-OH)_3$

Fig. 26. O/W emulsifiers with soapy structures

potassium or sodium hydroxide or triethanolamine and as a result, soaps are formed. The pH value of the emulsions is reduced by adding an excess of fatty acids to the raw material composition. A weakness of fatty acids salts, including stearic acid, is the skin whitening effect; this, however, can be prevented by adding silicone oil to the recipe. Note that alkaline soaps are sensitive to calcium and magnesium ions and $pH < 7$; these factors result in precipitation of water-insoluble fatty acids. As already mentioned, soap solutions are alkaline, which may cause skin irritation. In comparison organic amine salts of fatty acid, like the triethanolamine stearate, are less irritant then alkali soaps.

Fatty alcohol sulphates are another group of anionic O/W emulsifiers. Fatty alcohol sulphates are sulphuric acid esters of fatty alcohols (Fig. 27).



$R = C_{12}$ to C_{18}
$Me = Na^+, K^+, NH_4^+$

Fig. 27. O/W emulsifiers with a structure of fatty alcohol sulphates

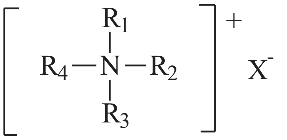
These compounds are highly hydrophilic and usually used in combination with low--HLB emulsifiers. The most popular compound in the group is sodium cetearyl sulphate (INCI: *Sodium Cetearyl Sulfate*). Fatty alcohol sulphates are insensitive to calcium and magnesium ions, and display an excellent performance as surfactants, wetting agents, and foaming agents which give stable foams. Not unlike alkaline soaps, a weakness of fatty alcohol sulphates includes a risk of skin irritation; hence, the industry has moved to more delicate and milder compounds, such as the following:

Isethionates (e.g. INCI: *Sodium Cocoyl Isethionate*): these compounds are among the most gentle emulsifiers with an excellent surfactant, wetting, dispersion and suspension performance; they are used in cosmetic products, liquid soaps and solid soaps;

Alkyl phosphate salts, e.g. potassium cetyl phosphate (INCI: *Potassium Cetyl Phosphate)* and **ethoxylated derivatives thereof**, e.g. phosphate of ethoxylated with 10 ETO moles oleic alcohol (INCI: *Oleath-10 Phosphate*). Phosphate esters and ether-esters feature a good surfactant performance. The compounds remain active already at very low concentration.

4.1.1.3. CATIONIC O/W EMULSIFIERS

A cationic emulsifier dissociates in a water solution into a cation with the hydrophilic and lipophilic parts of the molecule and an anion, usually an acid radical ($X = Br^-, J^-, Cl^-$, or SO_4^{-2}) (Fig. 28). Structure-wise, the compounds are most often quaternary ammonium salts.



$$\left[R_4 - \overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_3}{|}}{N}} - R_2 \right]^+ X^-$$

$R_1 = C_{12}$ to C_{18}

$R_2 = R_3 = R_3 = CH_3$

Fig. 28. Cationic emulsifiers, derivatives of quaternary amines

Due to a high irritating action, these compounds are rarely used in skin care cosmetics, in which they are usually replaced with anionic or non-ionic emulsifiers. They have found use, however, in hair care products, as secondary surfactants, conditioning substances and anti-static agents, which prevent tangling and electrostatic charging of hair.

An advantage of quaternary ammonium salts is their stability in acidic or alkaline media and a certain antibacterial activity. The weaknesses include a high irritating action, are incompatibility with anionic compounds, and zero tolerance to hard water. Emulsion-based cosmetics including *Distearylammonium Chloride*, forms soft, pleasant to touch emulsions and reduces the stickiness sensation caused by glycerol.

4.1.1.4. AMPHOTERIC EMULSIFIERS

Amphoteric emulsifiers feature molecules with two groups each: one acidic and one alkaline. Depending on the pH reaction, an amphoteric emulsifier can have a positive or negative charge, or form dual (amphoteric) ions (a.k.a. zwitterions). In acidic media, amphoteric emulsifiers act like cationic emulsifiers; in alkaline media, they act like anionic emulsifiers.

A major advantage of amphoteric emulsifiers is that they can be combined with anionic, cationic and non-ionic compounds. Amphoteric emulsifiers do not irritate the skin; it was demonstrated that they can inhibit the irritating effects of other chemicals. Amphoteric surfactants exhibit a good performance as detergents, foaming agents, and antistatic agents; they feature a relatively low toxicity and are highly degradable, and can form ion calcium complexes. These properties helped amphoteric surfactants find a widespread use in cosmetics, including formulas for shampoos, aerosols, shaving products, toothpastes, as well as body lotions, creams and emulsions.

The most popular amphoteric emulsion compounds are based on **betaine derivatives**: alkyl betaines, amidoalkyl betaines, sulphobetaines, and acyl amino betaines. Amphoteric surfactants also include imidazoline derivatives, amino carboxylic acids, proteins, and lecithin.

Lecithins are naturally occurring emulsifiers. In chemical terms, lecithins are esters of glycerophosphoric acid, in which two hydroxide groups are esterified with fatty acids, whereas phosphoric acid is ester-bonded with choline, an organic base (Fig. 29).

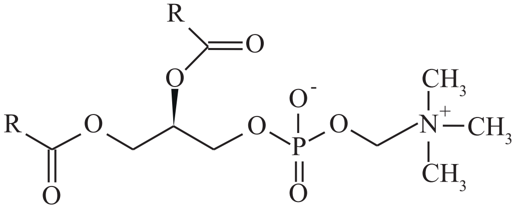


Fig. 29. Lecithin (R is the fatty acid alkyl residue)

The type of fatty acid residue in lecithins depends on the raw material origin. Lecithins can be derived from stearic acid, palmitic acid, oleic acid, linoleic and linolenic acid. Lecithin is most usually produced by hydration of plant oils (from rapeseed or soy oils).

Commercial lecithin is a yellowish, wax-like and hygroscopic substance soluble in ether and ethanol, partially miscible with plant oils and animal fats, and swelling in water. Aside from pure lecithin, commercially available lecithin formulations include phospholipids, triacylglycerols, free fatty acids, sterols, and carbohydrates. Lecithin is an amphoteric emulsifier which can be anionic or cationic in action, depending on the pH value of the medium. Pure lecithin stabilizes O/W emulsions; raw lecithins fomulations with the aforementioned compounds can stabilize W/O emulsions. Its emulsifying effects aside, lecithins exhibit other properties important in formulation of cosmetic products. Lecithin softens the skin, facilitates resorption and penetration of active cosmetic ingredients, and inhibits greasing of the skin [2, 3, 76].

4.1.1.5. NON-IONIC W/O EMULSIFIERS

W/O emulsifiers are hydrophobic compounds and are better solved in fats than water; they stabilize emulsions with oil as the external phase. W/O emulsifiers are less popular than hydrophilic emulsifiers (O/W). Cosmetic W/O emulsifiers include lanolin and its derivatives, castor oil and its derivatives, polyalcohol esters, sorbitan esters, and multivalent cation fatty acid salts.

Lanolin (wool fats) is a secretion of sebaceous glands in many animals. Lanolin produced by centrifugation of wash water from raw sheep wool has found practical applications. Pharmaceutical-grade lanolin is produced from this raw material by purification (depigmentation and deodorization) [59].

Commercial lanolin is a light yellow-brownish, thick, ductile, greasy and sticky mass with a weak specific odour. It is not soluble in water; it is poorly soluble in ether, benzene, toluene, petroleum ether and ethanol. Lanolin is miscible with most oils, fats, waxes, petroleum products (paraffin, petrolatum and paraffin oil) and synthetic wax; it is an excellent W/O emulsifier and an auxiliary O/W emulsifier. When ground with water, lanolin can absorb at twice its quantity, without losing its greasy consistency.

The composition of lanolin may vary with origin and extraction method. In chemical terms, lanolin is a mixture of fatty acid esters and lanolin alcohols. The primary components include macromolecular esters, diesters and hydroxyesters of lanolin acids (C_7–C_{41}) with lanolin alcohols (C_{12}–C_{36}). The composition of the latter is generally dominated by sterols (mainly cholesterol, dihydrocholesterol, and trimethyl sterols). The fatty acids are represented by straight-chain bonds (either saturated or unsaturated), branched acids (iso acids), and hydroxy acids, including lanoceric acid ($C_{29}H_{59}COOH$), lanopalmitic acid ($C_{15}H_{31}COOH$), carnauba acid ($C_{23}H_{47}COOH$), myristic acid ($C_{13}H_{27}COOH$), stearic acid ($C_{17}H_{35}COOH$), and oleic acid ($C_{17}H_{33}COOH$) [58]. Lanolin also contains some quantity of free alcohols, lanolin acids, and hydrocarbons (Table 13).

Table 13

Chemical composition of lanolin [59]

Chemical compound	Content Wt (%)
Esters	90.0
Free alcohols	9.50
Free acids	0.30
Hydrocarbons	0.20

Lanolin is widely used in cosmetic formulations as a solvent for a broad selection of fats and waxes, a plasticizer of waxes and adhesion films, an efficient W/O emulsifier, an dispersing and wetting agent, and last but not least, a softener in cosmetic emulsions. It is also used as an emollient in soaps, syndets and shampoos, as well as an intermediate for cream bases, such as eucerin. Chemical or physical conversion of lanolin can provide a number of valuable input materials for cosmetics, pharmaceuticals, and home care products.

Steroid alcohols, based on a four-cyclic system of cyclopentanoperhydrophenanthrene, occur in the animal and plant kingdoms. The W/O emulsions in this group include cholic acid salts and sterols. Here, sterols are usually represented by cholesterol, $C_{27}H_{46}OH$. **Cholesterol** is usually found in animal fats, suint, and egg yolk, from the hen, for example. Industrial-scale production of cholesterol relies on lanolin, from which it is produced. The commercially available form is clear crystals, which are insoluble in water and poorly soluble in alcohol, petrolatum, paraffin oil, and plant oils. The predominant lipophilicity from condensed rings and the hydrocarbon chain makes cholesterol a W/O emulsifier and, if combined with higher fatty alcohols, an auxiliary emulsifier.

Secondary emollients in washing products, tonics and shampoos are ethoxylated derivatives of cholesterol, which are well soluble in water.

Esters of fatty alcohols and fatty acids This group includes beeswax, cetaceum, cetyl palmitate, and lanolin (as discussed above). These substances are rather poor emulsifiers in general and have found use as auxiliary emulsifiers in formulations of cosmetic ointments and creams.

Fatty alcohols are used as auxiliary compounds in complex emulsifiers, e.g. mixtures of cetyl alcohol and stearyl (or sometimes cetearyl) alcohol.

Ethoxylated castor oil Castor oil and its derivatives are used to form W/O emulsions in cosmetic products. The most popular variety includes ethoxylated castor oil derivatives with less than 10 ETO moles, e.g. castor oil ethoxylated with 5 ETO moles (INCI: *PEG-5 Castor Oil*) and ethoxylated hydrogenated castor oil derivatives (e.g. INCI: *PEG-7 Hydrogenated Castor Oil*). In cold processing, these emulsifiers can give stable emulsions with excellent sensory properties.

Polyalcohol esters are a group of surfactants which is most widely used in cosmetics as W/O emulsifiers. The emulsions they produce are stable, non-greasy, and with very good sensory properties. Another advantage is their natural origin, ready biodegradability, and a high tolerance of the skin. The most prominent compounds in the group are monoglycerides (e.g. glycerol monooleate or glycerol monolaurate, INCI resp.: *Glyceryl Oleate, Glyceryl Laurate*) and hydrophobic polyglycerol fatty acid esters (e.g. INCI: *Poliglyceryl-2-Polyhydroxystearate* or polyglycerol diisostearate, INCI: *Polyglyceryl-3 Diisostearate*) [58]. These high-performance **hydrophobic polyglycerol esters** enable the manufacture of especially light and easily spreadable emulsions with a water content of up to 75%. The liquid form of the emulsifiers allows the W/O obtaining by cold processed emulsification. Concentrations of just 2% are effective, and most emulsions can be manufactured without the addition of a coemulsifier [57].

Sorbitan esters are one of the most popular W/O emulsifier groups among the esters of fatty acids and polyols [2,6]. The group includes sorbitan palmitate, sorbitan oleate, and sorbitan stearate. Esters of sorbitan are available under the trade name Span (Fig. 30). Span preparations are very gentle to the skin, non-toxic, and non-irritating; they are often used in baby formulations and hypoallergenic products.

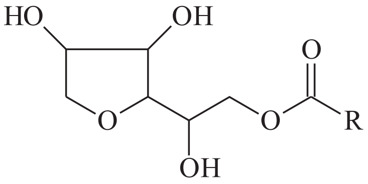


Fig. 30. Sorbitan fatty esters, Spans (R is the fatty acid alkyl residue)

Sorbitan esters are used in production of W/O emulsions; the HLB numbers of the components ranges from 2 to 8 inclusive and depends on the degree of esterification and the structure of the acyl residue (RCO-).

Among the esters of fatty acids and polyols, mannite fatty esters, such as *mannite monooleate*, are used in cosmetic formulations [2, 3, 6].

4.1.1.6. ANIONIC W/O EMULSIFIERS

Multivalent cations fatty acid salts are calcium, magnesium, zinc or aluminium salts of fatty acids with a hydrocarbon chain length from C_{10} to C_{20} (e.g. *Calcium or Magnesium Palmitate*). They are used to stabilize W/O emulsions and as consistency factors in cosmetic emulsions. The compounds cannot be used in combination with alkaline soaps, otherwise their properties are neutralized and emulsion stability is lost.

4.1.1.7. POLYMERS AND INSOLUBLE SOLIDS

Alternatives to popular surfactants applied as cosmetic emulsifiers include polymers and highly refined insoluble solids [2, 6].

Macromolecular compounds prevent coalescence of the dispersed phase; the relatively large molecular mass prevents the compounds from migrating into the skin and irritating it. Polymers, such as hydroxypropyl methylcellulose are often added to the continuous water phase to increase its viscosity and achieve a higher stability of the emulsion.

Polymers fit for the purpose must not include homopolymers comprising mers of the same kind, such as PVA (polyvinyl alcohol) or PEO (polyethylene oxide), since these substances are soluble in water and adsorbed on the surface of emulsion droplets, providing a coalescent effect, instead of an isolating one. Emulsifiers fit for the purpose include polymers the structures of which include parts adsorbed on the surface of the internal phase droplets and parts soluble in the dispersing phase. These structures are made from two different mers and called “copolymers”. Copolimers are amphiphilic structures with the notation AAAABBBB. Regarding O/W emulsions, the hydrophilic chain can be poly(ethylene oxide), while the hydrophobic chain can be 12-hydroxystearic acid copolymer. Much more effective copolymeric surfactants include three blocks: AAAAABBBBBAAAAA. An example of the system can be a block copolymer of polystyrene-poly(ethylene oxide)-polystyrene.

Poloxamers (EO/PO copolymers) are an interesting group of non-ionic polymeric surfactants. Poloxamers are formed by ethoxylation of both terminal hydroxyl groups in 1,2-polypropylene glycol. Poloxamers have a very good performance in cosmetic products: they are stable over a wide pH range, and mild to the skin, the mucous membranes, the eyes, and hair. It is possible to adjust the surface properties of EO/PO copolymers by altering the molecular structure of these compounds (i.e. the molecular mass and the ratio of both polymers) (this varies HLB from 1 to 30 inclusive). Poloxamers are used in cosmetic preparations as emulsifiers and dispersing agents; they can also adjust viscosity.

Wetting agents and emulsifiers of cosmetic products can also comprise **silicone polyether copolymers**. Silicone copolyols exhibit properties typical of non-ionic surfactants.

Pickering emulsions are a different kind of emulsion formulations. A stable systems can be produced by densely packing solid grains on the interfacial surface [15]. The key criterion of use of these compounds as emulsion stabilizers is their wettability by the oil phase and the water phase. A mechanical barrier which inhibits coalescence of droplets is formed by solid grains ten times smaller in diameter than the dispersed droplets, a proper angular alignment of solid grains to the phase surface, and a constant concentration of solid grains. Examples of these stabilizers include aluminium oxide (W/O), bentonite (O/W), magnesium aluminium silicate (O/W), magnesium oxide (W/O), magnesium sulphate (W/O), magnesium silicates (W/O), TiO_2 (O/W and W/O), and ZnO (O/W). The last two compounds are used in sun protection formulations, due to their UV--protection performance.

4.1.2. EMOLLIENTS

The main role of emollients is to moisturise, soften, and smoothen the skin. Depending on their chemical composition and properties, we may distinguish substances that reduce TEWL by creating a hydrophobic, protective occlusive layer on the skin, and polar emollients which can penetrate the epidermal corneal layer, and build into the structures of SC lipid layers as a result of *stratum corneum* regeneration [60].

The ingredients of the oil phase (so-called wax-oil base) of the emulsion systems determine the usability properties of the product, including consistency, stability, application and distribution, or proper pH. Their selection is of great importance for the effectiveness and mode of action of the cosmetic product. The right choice of emollients affects the usability characteristics of emulsion [61, 62].

The ingredients of the wax-oil base that demonstrate occlusive properties and create a protective film on the skin include paraffin hydrocarbons, lipids, waxes and silicones.

4.1.2.1. PARAFFIN HYDROCARBONS

Paraffin hydrocarbons are ingredients of mineral origin, obtained as a result of petroleum processing. They are combinations of compounds with various hydrocarbon chain lengths and degrees of branching, which result is different physical properties (liquids, solids). The following can be found in cosmetics: vaseline oil (INCI *Paraffinum Perliquidum*), paraffin oil (INC: *Paraffinum Liquidum, Mineral Oil*), white vaseline (INCI *Petrolatum*), or paraffin (INCI: *Paraffinum*). Moreover, ozokerite, a combination of branched chain hydrocarbons of large molecular masses, melting at 72 to 85°C (a white or yellowish, fine crystalline substance), ceresin, (INCI: *Ceresin*), or ozokerite (INCI: *Ozokerite*) can be found, as well as microcrystalline wax (INCI: *Cera Microcristallina*), a combination of aliphatic hydrocarbons and branched isoparaffins with the molecular weight of 450–1,000.

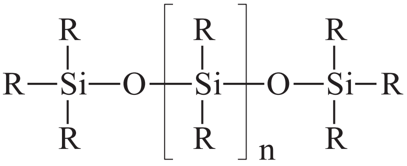
All the above substances are non-polar and insoluble in water or ethyl alcohol. The mix with organic substances, oils and fats, creating mixtures of various consistencies. They are very pure, easily absorbed, chemically passive (do not react with acids and alkali). Paraffin hydrocarbons are resistant to light, water and air, do not change during storage, are easily scented, odourless and neutral for the skin.

In cosmetic emulsions they play the role of oiling and protective substances, as they cover the skin with a thin protective layer, thus preventing excessive evaporation of water. This is how they accelerate hydration of the keratinised layer of the epidermis [63]. However, the film they create on the skin surface is too dense, and if their content in emulsion is too high, they may prevent penetration of the active substances and block the sebaceous and sweat glands, resulting in inflammatory lesions. An important disadvantage of mineral ingredients is that they leave a visible and perceptible oily layer on the skin. In a more recent generation of "oil free" cosmetics they are substitute by silicones.

Solid paraffin hydrocarbons (vaseline, paraffin or ceresine) are also used as binding agents, emulsion stabilisers, opacifying substances, and viscosity regulators in W/O emulsions.

4.1.2.2. SILICONES

Silicones are synthetic organosilicon polymers, polysiloxanes. The siloxane skeleton is composed of alternating atoms of silicon and oxygen. Various function groups are attached to this skeleton with carbon-silicon bonds (Fig. 31). Depending on the method of production (degree of polymerisation) and intended use, silicones may have a straight, branched or cyclic structure [64].



$R_3Si{-}O{-}[SiR_2]_n{-}O{-}SiR_3$

Fig. 31. Structure of silicone polymers (R may be hydrogen, alkyl or aryl groups)

As cosmetic ingredients, silicones are well-tolerated by the skin, and demonstrate softening, oiling and protective properties. They create an invisible, thin, hydrophobic film on the skin, resistant to removal with water. They spread well on the skin surface, and do not leave the oily sensation or shine on the skin. Due to very good mixing with other ingredients of emulsion, they improve the penetration of dermatologically active components into the skin, and protect it against aggressive substances. The most frequently used are volatile liquids, cyclic polydimethylsiloanes (INCI: *Cyclomethicone)*. Apart from cyclic silicones, skincare products sometimes contain methylsilicone oils (INCI: *dimethicone*), liquids of various viscosity. They are used as ingredients of the oil phase, and demonstrate softening and protective properties. They make the skin soft and delicate, without the oily feeling. Adding small amounts of silicones, 1–5%, significantly improve the usability characteristics of cosmetic products: cream spreadability, pigment dispersion (in make-up fluids), increased resistance to water (water-resistant mascaras, sunbathing products). Polymethyl alkyl siloxanes, mainly stearyl dimethicone and cetyl dimethicone used in products with UV filters, offer thixotropic properties, increasing the product's viscosity and resistance to radiation [2, 6].

Glycol silicone copolyols, polyester siloxanes (INCI: *Dimethicone Copolyol*), due to the presence of hydrophobic and hydrophilic groups in the molecule, demonstrate surfactant properties. They are used as foam stabilizers and as mild surfactants in shower gels, shaving foams and baby shampoos. Usually the formulation contains no more than 2–3% of these substances. Used in O/W cosmetic emulsions as co-emulsifiers, they reduce the irritating effect of anionic detergents. In W/O emulsions, addition of copolyol and dimethicone combination eliminates stickiness, and makes the skin dry and gentle to the touch [65].

4.1.2.3. FATTY ALCOHOLS

Fatty alcohols are important ingredients of cosmetic emulsions. The length of the hydrocarbon chains in alcohols used in cosmetics is usually C_{12} to $C_{18.}$ Fatty alcohols are neutral for the skin, and their consistency varies from liquid (branched and unsaturated compounds) to solid (Table 14). In cosmetic emulsions fatty alcohols are used as stabilisers, consistency regulators in O/W emulsions (*cetyl alcohol, cetaryl alcohol* – mixture a of cetyl and stearyl alcohol), as skin oiling and softening substances.

Table 14

Examples of fatty alcohols used in cosmetic emulsions

Alcohol	INCI name	Formula	Physical state
2-Octylododecanol	*Octyldodecanol*	CH_3- C_9H_{18}-CH(C_8H_{17})-CH_2 -OH	Liquid
Stearyl alcohol	*Stearyl Alcohol*	$C_{17}H_{35}CH_2OH$	Solid
Cetyl alcohol	*Cetyl Alcohol*	$C_{15}H_{31}CH_2OH$	Solid
Oleyl alcohol	*Oleyl Alcohol*	C_8H_{17}-CH=CH-C_8H_{16}-OH	Liquid

4.1.2.4. FATTY ACIDS

Both saturated and unsaturated fatty acids are used in cosmetic emulsions (Table 15).

Saturated fatty acids are primarily skin oiling and moisturising agents, in addition providing the emulsion with the mother-of-pearl shine. They also affect the stability and consistency of emulsion. In reaction with alkali they form salts, which are also used in cosmetics. Sodium and potassium salts are soluble in water, demonstrate excellent washing and emulsifying properties, and stabilise O/W emulsions. Salts of divalent metals (calcium, magnesium, zinc) are insoluble in water, and are mostly used for production of W/O emulsion emulsifiers. The saturated fatty acids most frequently used in cosmetic emulsions include: stearic acid, palmitic acid and stearin (a combination of stearic and palmitic acids).

Unsaturated fatty acids, especially those with C_{18} chains (linoleic, linolenic) belong to the group of EUFA (essential unsaturated fatty acids), and are very important ingredients of cosmetic emulsions. Apart from their moisturising effect due to strengthening of the epidermal lipid barrier, they demonstrate biological activity, accelerate epidermal regeneration, eliminate inflammation, inhibit the development of allergies, and improve the immune system.

Table 15

Essential unsaturated fatty acids

ω-6 fatty acids		**ω-3 fatty acids**	
Common name	Structure	Common name	Structure
Linoleic (LA)	18:2(9,12)	α-Linolenic	18:3(9,12,15)
γ-Linolenic (GLA)	18:3(6,9,12)	Stearidonic	18:4(6,9,12,15)
Arachidonic	20:4(5,8,11.14)	Eicosapentaenoic	20:5(5,8,11,14,17)
Adrenic	22:4(7,10,13.16)	Docosapentaenoic	22:5(7,10,13,16,19)
Docosapentaenoic	22:5(4,7,10,13,16)	Docosahexaenoic	22:6(4,7,10,13,16,19)

4.1.2.5. ESTERS OF FATTY ACIDS WITH ALCOHOLS

Esters of fatty acids and branched alcohols, such as isopropyl, isobutyl or isoamyl alcohol are of particular importance in the formulation of cosmetic emulsions. They easily spread on the skin and penetrate the epidermis. They demonstrate cosmetic effects by strengthening the lipids of the intercellular cement and increasing epidermal hydration, thus moisturising and softening the skin. In addition, they improve the usability properties of emulsion, reduce the oily feeling caused the presence of paraffin hydrocarbons, and improve the spreadability of the cosmetic on the skin.

These substances are characterised by low density, chemical stability and can be easily combined with hydrophobic ingredients of the emulsion. They enable introducing large quantities of lanolin and other waxes, as well as mineral oils to the wax-oil base.

Quite often esters of myristic acid are used, e.g. isopropyl myristate, as well as oleic acid esters, e.g. oleyl oleate.

In the group of ester emollients we can distinguish compounds originating in the esters of medium-chain, unbranched alcohols (e.g. hexyl, decyl, or myristic alcohol), with straight--chain fatty acids (lauric and myristic), e.g. myristyl myristate.

Apart from the broadly used fatty acid esters, also lanolin and the products of its modification demonstrate a softening effect on the epidermis. For instance, the result of transesterification of lanolin with isopropyl alcohol is a product combining lanolin, lanolin alcohols and isopropyl esters of lanolin acids. The product maintains the beneficial characteristics of lanolin, demonstrates a lower melting point and better solubility, and its viscosity is significantly lower compared to lanolin. The obtained isopropyl esters of lanolin acids considerably increase penetration of lanolin and other ingredients of the wax-oil base [59].

4.1.2.6. TRIGLYCERIDES

Another important group of cosmetic emollients are esters of fatty acids and glycerine – triglycerides. Their effect consists in skin hydration through building into the lipid structures of the intercellular cement, and increasing lipophilicity of the epidermal *stratum corneum*, reducing TEWL as a result.

The main sources of triglycerides, used in cosmetics, are plant oils. The physicochemical properties and biological value of plant oils is determined by the type of fatty acids found in them. They may be saturated acids, e.g. stearic acid (C_{18}) or palmitic acid (C_{16}), or unsaturated acids of various lengths and location of double bonds, e.g. oleic acid ($C_{18:1}$), linoleic acid ($C_{18:2}$), or linolenic acid ($C_{18:3}$) (Table 16).

Table 16

Approximate composition [%] of fatty acids in plant oils used in cosmetic emulsions

Oil	**Type of fatty acid**				
	C_{16}	C_{18}	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$
Cocoa butter	25	35	38	2	–
Olive	10	2	77	9	–
Avocado	10	–	70	15	–
Black currant seed	7	2	10	49	30
Borage	9	3	14	38	25
Corn	11	2	30	55	1
Oenothera	6	2	8	71	12
Grapeseed	6	2	25	69	–
Peanut	10	2	48	40	–
Sesame	10	5	40	45	–
Soybean	11	4	25	55	5
Sunflower	6	4	15	75	–
Wheat-germ	13	3	14	58	8

The demands of the modern market regarding cosmetic products are increasingly high. There is a growing need for multifunction, safe, innovative ingredients, especially of natural origin. Therefore, the popularity of plant oils, demonstrating not only hydrating properties, but also nutritional, regenerative, anti-inflammatory or antimicrobial effects, is increasing. The rich offer includes new, effective, often exotic plant oils: e.g. moringa, tamanu, karanja, kukui, buriti, cupuacu, passion fruit, and pomegranate or watermelon oils.

The oils obtained from berries, such as black currant, raspberry, strawberry, blackberry or chokeberry can be classified as emollients providing active lipids. The pomace left as a by-product of fruit processed for juices contains 10–30% of fat. Recovery of the fat from the post-production waste is in line with the ecological trend, applying also to cosmetic ingredients. Berry seed oils contain triglycerides of essential unsaturated fatty acids, as well as bioactive substances such as phospholipids, tocopherols, carotenoids, phytosterols or phytohormones [66–68].

The content of individual biologically active ingredients in oils is determined by many factors, especially by the plant the oil is obtained from. However, the method of oil extraction is also very important. Traditional technologies of obtaining plat oils include the processes of cold pressing and/or extraction with the use of selective solvent, e.g. isohexane. An interesting alternative for the ingredients obtained with the traditional methods is supercritical carbon dioxide (SC-CO_2) extraction of oils. The parameters of the extraction process allow to obtain products of very high purity, free from the contamination with conventional solvents. Moreover, relatively low temperatures and oxygen-free atmosphere allow to prevent oxidation and thermal degradation of the bioactive ingredients in the extracts [69, 70, 72].

Table 17 presents the profile of fatty acids selected in oils obtained from berry seeds via supercritical CO_2 extraction.

Table 17

Structure of fatty acids in SC-CO_2 extracts from strawberry (St), black currant (BC), blackberry (BB) and chokeberry seeds (C) [71, 74]

Numerical symbol of the fatty acid	**Name of the acid**	**% (w/w) of the total acid content in oils**			
		St	**BC**	**BB**	**C**
C16:0	Palmitic	3.7±0.1	5.6±0.1	11.5±0.9	4.5±0.1
C16:1	Palmitoleic	0.2±0.0	–	–	–
C18:0	Stearic	1.4±0.1	1.7±0.0	3.7±0.3	0.9±0.1
C18:1n-9	Oleic	15.7±0.4	12.2±0.2	10.9±0.1	16.4±0.0
C18:2n-6	Linoleic	46.3±0.2	44.7±0.2	44.3±1.5	68.8±0.0
C18:3n-3	γ-linolenic	31.5±0.3	16.0±0.1	25.1±0.1	7.8±0.0
C18:3n-6	α-linolenic	–	14.9±0.3	–	–
C18:4n-3	Stearidonic	–	3.5±0.1	–	–
C20:0	Arachidic	0.8±0.1	0.2±0.0	2.3±0.1	–
C20:1	Eicosenoic	0.3±0.0	1.2±0.0	2.1±0.0	–

The studies reported in the literature demonstrate [73, 74] that using strawberry seed or black currant seed oils (in the form of extracts obtained by supercritical CO_2 extraction process) in a washing formulation had beneficial effects on the characteristics of the cosmetic products. Only 0.5% of oils were sufficient to reduce significantly the degreasing effect of sodium lauryl sulphate (SLS). The skin after cleansing with cosmetics containing oils was smooth and better moisturised. Figure 32 presents the effect of the strawberry seed oil content in the formulation of cleansing cosmetic emulsion on the skin hydration, comparing the situation after using a cosmetic product without oil (C0%St) and after the use of products containing various concentrations of oil, from 0.5% (C0.5%St) to 2% (C2%St) [74].

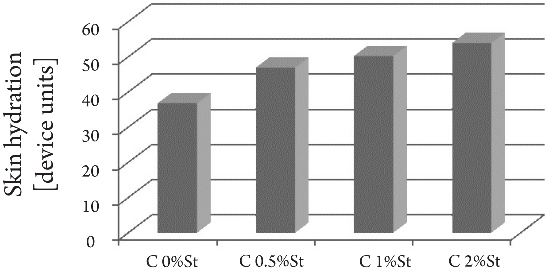


Fig. 32. The effect of SC-CO_2 extracted strawberry seed oil (0–2.0%) on the degree of skin hydration [74]

Apart from the fatty acids bound in triglycerides, the cosmetic usefulness of the oil is determined by another group of ingredients, i.e. the unsaponifiable fraction (a combination of ingredients which, contrary to glycerides, are not hydrolysed). The non-glyceride fraction includes aliphatic hydrocarbons (e.g. squalene), phytosterols and lecithins, as well as vitamins (tocopherols and carotenoids). As a result, plant oils are used in cosmetic products as emollients in creams, lotions, bath lotions, shampoos and hair conditioners. In these formulations they play the role of moisturisers, softening, regenerating and smoothening substances, and in addition, they affect the consistency and usability properties of the products.

4.1.2.7. CERAMIDES

Natural ceramides are sphingolipids, i.e. long-chain amine-alcohols acylated with fatty acids (Fig. 33). Ceramides are biosynthesised in the cells of the epidermal *stratum spinosum* and *stratum granulosum*, where glycoceramides are formed first (a combination of ceramides with galactose). During the enzymatic transformations in the skin the sugar residue is separated from the molecule. As a result, in the outermost corneal layer of the epidermis mostly ceramides are found, and only trace amounts of glycoceramides are present. Ceramides in the human skin differ in fatty acid content, length of the aliphatic chains, and the degree of unsaturation of amine-alcohols. Natural sphingolipids found in the skin are composed of over 100 various compounds, of which a few were identified and marked with Arabic digits (1, 2, 3, 4, 5, 6I, 6II).

Along with age and due to unfavourable external factors (environmental pollution, UV radiation) the amount of ceramides in the skin decreases. Skin damage and reduced amount of lipids necessary for the proper function of the lipid barrier lead to water loss, adversely affecting the general condition of the skin. The dried skin is flaking, the rate of cellular renewal is reduced, and the skin aging processes start.

Figure 33 presents a ceramide molecule (N-acylsphingosine).

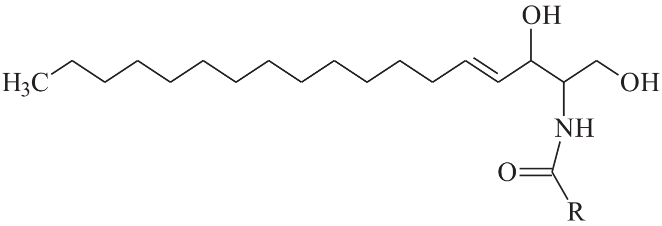


Fig. 33. N-acylsphingosine (R = C_{30} and C_{32} – *Ceramide 1*, R = C_{18}, C_{24} and C_{26} – *Ceramide 2*, R = C_{16}, C_{24} and C_{26} – *Ceramide 4+5*)

Ceramides used in cosmetics easily penetrate the epidermis and build into the damaged layers of the intercellular cement, providing proper skin hydration. The skin becomes smooth and supple.

4.1.2.8. PHOSPHOLIPIDS

Phospholipids are ingredients of natural origin (they were mentioned before in chapter concerning amphoteric surfactants). From the chemical point of view, they are esters of glycerophosphoric acid, where two hydroxy groups are esterified with fatty acids, and the phosphoric acid is ester-bound with an organic alkali, choline.

Depending on the degree of purity, they stabilise O/W emulsions, whereas unpurified lecithin, containing fatty acids, triglycerides and sterols, can fix W/O emulsions. Apart from its emulsifying effect, lecithin demonstrates a number of other properties important in cosmetics.

Phospholipids demonstrate a skin softening effect; they build into the lipid structures of the intercellular cement, increase the degree of epidermal hydration, thus facilitation resorption and penetration of active ingredients of a product, and reduce excessive sebum production. Moreover, due to the amphiphilic character, phospholipids are used for preparation of liposomes, topical delivery systems for biologically active substances.

4.1.2.9. WAXES

Natural waxes in cosmetic emulsions are used as emollients, but primarily they were applied as emulsifiers, stabilising and consistency agents.

Natural waxes can be divided into animal waxes (beeswax, spermaceti, lanolin, Chinese wax) and plant waxes (Carnauba wax, Candellia wax, Japanese wax, fruit waxes), and they are mainly solids. However, there are waxes with a low melting point, so-called „liquid waxes". Jojoba oil is an important liquid wax in the cosmetic industry [75, 76].

The aim of waxes in cosmetic formulations is to stabilise emulsion, and to improve the viscosity of the system. Many natural waxes additionally demonstrate antibacterial, antifungal and antioxidant properties. Waxes, similarly to other lipids, have a moisturising effect on the skin.

Less often used plant waxes include exotic products: Java wax (from the milk of a plant called *Ficus variegata*), Mohwa butter (with anti-inflammatory properties, rich in linoleic acid), Sal butter (containing arachidonic acid), Kokum butter (with astringent effect, used in anti-acne products) [75].

4.1.3. HUMECTANTS

Water in cosmetic emulsions is used as solvent (base) for hydrophilic substances (soluble in water). According to the molecule size, hydrophilic substances used in cosmetics can be divided into two categories:

- small-molecule water-binding substances, providing and binding water in the skin to ensure a proper degree of epidermal hydration, and reducing the risk of the product drying out:
  - polyhydroxy alcohols: propylene glycol, glycerine, sorbitol,
  - lactic acid, lactates, urea,
  - pyroglutamic acid and AHA,
  - biotin, provitamin $B_{5,}$
  - protein hydrolysates, amino acids,
- hydrophilic film-forming substances – their moisturising effect is due to formation of a hydrophilic film on the skin surface; in addition, they increase the density of the aqueous phase of products (viscosity regulators):
  - polypeptides, protein hydrolysates,
  - hyaluronic acid and its salts,
  - polyglycols,
  - propylene polyglycol, ethylene polyglycol,
  - polyglycerol,
  - polysaccharides,
  - chitosan, chitin, plant mucus, gums.

Humectants have an affinity for water, help binding water to the skin and resist evaporation from the skin. Moreover, humectants have been shown to be valuable not only in hydrating the *stratum corneum*, but also improving viscoelastic behaviour of it [3].

4.1.3.1. POLYHYDROXY ALCOHOLS

Polyhydroxy alcohols: propylene glycol, glycerine, sorbitol are used as moisturisers and substances preventing drying out of preparations, so-called humectants. They absorb moisture from the air and supply water in a controlled manner to deeper layers of the epidermis. Hygroscopic properties are also demonstrated by polyoxyethylated polyhydroxy alcohols: polyoxyethylated glycerol, polyoxyethylated glycol, polyoxyethylated sorbitol.

4.1.3.2. PROTEINS

Most proteins used in cosmetics are products of partial or complete enzymatic, alkaline or acid hydrolysis of natural proteins. Hydrolysates of natural proteins of animal origin (milk, eggs and silk), and derived from plants (wheat, soy, corn and almonds) are used in cosmetic products. Proteins in cosmetics are used as: ingredients affecting the usability properties of cosmetic products, rheological regulators, consistency agents, stabilisers of O/W emulsions and active ingredients, nutrients, hydrating and protective substances, reducing the irritating effects of surfactants.

The cosmetic effectiveness of proteins is only slightly associated with their origin (plant proteins demonstrate similar effects to animal proteins), but it depends on their composition (amino acid content) and the degree of hydrolysis. Individual hydrolysates differ in the ability to absorb and retain water, in membrane-forming properties and affinity to epidermal keratin, which determines the durability of the produced protective membrane. According to the degree of hydrolysis, we can distinguish the following categories:

– amino acids with the mean molecular weight of 100–150, able to retain moisture; they demonstrate hydrating effect and intensify the hydrating effect of other ingredients;
– hydrolysates of proteins with the mean molecular weight of 1,000–10,000; they demonstrate membrane-forming properties and help to retain water;
– proteins with the mean molecular weight of 125,000–300,000; they demonstrate a strong membrane-forming effect, are able to retain moisture, and increase the viscosity of the aqueous phase.

Recently, more interest is paid to peptides, also amino acid polymers but with shorter amino acid chains. Naturally occurring human peptides are known for cellular communication, such as protein regulation, cell proliferation, cell migration, inflammation, angiogenesis, and melanogenesis [77], which results in a broad variety of physiological processes including defense, immunity, stress, growth, homeostasis, and reproduction [78]. Topical cosmeceutical peptides can be classified as signal peptides, carrier peptides, neurotransmitter inhibitor peptides, and enzyme inhibitor peptides. Some of the peptides like Palmitoyl pentapeptide-4 or Carnosine are known as anti- aging actives. Others have been proven in their efficacy through clinical skin trials. Well-known and documented peptides like copper tripeptide are still under research to obtain more details on their effectiveness, and for the development of new treatments [79].

4.1.3.3. HYDROXY ACIDS

Hydroxyl acids used in cosmetics include: alpha-hydroxy acids (AHA) and beta-hydroxy acids (BHA). AHA are hydroxy acids in which the hydroxyl group is attached to the same carbon atom as the carboxyl group.

AHA are highly hygroscopic, and have a moisturising effect, as they compete the NMF components. In addition, they demonstrate a keratolytic effect, consisting in loosening and breaking the chemical bonds between the cells in the epidermal *stratum corneum* and the intercellular cement, which facilitates exfoliation of the corneal cells, and accelerates the process of cellular regeneration. Removal of the layer of dead, keratinised cells shows new, healthy cells, improving the structure and colour of the skin. Similar properties are revealed by salts of certain hydroxy acids, especially the lactic acid. Moreover, AHA have a whitening effect, and help to remove discolourations and small acne scars. Thanks to keratolytic properties, they reduce fine superficial wrinkles, and improve skin elasticity [80, 81].

Hydroxyl acids are found in fruits, so they are also referred to as fruit acids. The most frequently used cosmetic ingredients in this group include:

- glycolic acid – $CH_2(OH)COOH$, the smallest of the fruit acids, obtained from sugar cane,
- lactic acid – $CH_3CH(OH)COOH$ – from sour milk,
- malic acid – $HOOCCH_2CH(OH)COOH$, from apples,
- tartaric acid – $HOOCCH(OH)CH(OH)COOH$, obtained from grapes,
- citric acid – $HOOCCH_2C(OH)COOHCH_2COOH$, from citrus fruits.

From the above acids, the most frequently used are lactic acid and glycolic acid, as they have the smallest molecules, and are the best absorbed by the skin, demonstrating the highest effectiveness. AHA acids are soluble in water, so, contrary to BHA acids, cannot pass through the layer of sebum and penetrate into deeper skin layers or clear the pores.

Due to their irritating properties, the concentration of fruit acids in skin care products is $< 4\%$. At higher concentrations they may be used only in professional cosmetic salons. Products containing these acids are recommended not only for the face, but the entire body.

In the group of beta-hydroxy acids, only salicylic acid is used in cosmetics. It is obtained from the willow bark, and in chemical synthesis. The general effect of salicylic acid is very similar to that of AHA acids. It regulates the cellular renewal of the skin, and exfoliates by loosening the intercellular bonds, removing the unnecessary layers of keratinised epidermal cells. Salicylic acid has a milder effect than alpha-hydroxy acids. Its use is associated with less frequent adverse effects such as burning, stinging, or excessive skin flaking. Salicylic acid is soluble in fats, so it may pass though the layer of sebum, deep into the epidermis. It unblocks pores, and prevents formation of inflammatory lesions, as well as helps to remove comedones, which become less visible [82]. Products with salicylic acid are recommended for acne-prone skin with blocked pores. The effective concentration of salicylic acid is 1–2%. Another aromatic hydroxyl acid, mandelic acid, demonstrates similar properties and indications to salicylic acid [83].

4.1.4. PRESERVATIVES

Microbiological purity of cosmetics and resistance to infections is a complex problem, determined by: the quality and purity of ingredients (especially the quality of water), hygiene of the technological process (organisation of the production, cleanliness of the devices used), physicochemical properties of the final product, type of the packaging and packaging materials, or the presence of microbial inhibitors, i.e. preservatives. Preservatives are ingredients added to cosmetics to protect the consumer and prevent microbiological contamination during a normal and expected use of the cosmetic product. They demonstrate an antimicrobial effect, and when added to cosmetic, they inhibit the growth of bacteria, mould and fungi, thus extending the shelf-life. Annex V to the EU Directive 1223/2009 contains a list of 55 compounds approved for use as preservatives in cosmetics [1]. The effect of preservatives is determined by the presence in their molecules of chemical groups or structures able to bind with the components of cellular membranes or proteins of microorganisms. Considering the chemical structure, cosmetic preservatives may be classified as follows:

- organic acids and their salts
    - sorbic acid (2,4-hexadienoic) and its salts, e.g. potassium sorbate,
    - benzoic acid, its salts and esters, e.g. sodium benzoate,
    - p-hydroxy benzoic acid and its esters, commonly known as parabens, e.g. *Methyl Paraben*;
- alcohols and phenols
    - *2-phenoxyethanol,*
    - Bronopol (INCI: *2-Bromo-2-Nitropropane-1,3-Diol)*;
- heterocyclic compounds
    - Germall 115 (INCI: *Imidazolidynyl Urea*);
- quaternary ammonium salts
    - *Quaternium-15* (Methenamine 3-chloroallylochloride).

Preservatives are necessary ingredients of cosmetic formulations, but they are considered, next to aromas and dyes, as the most common reasons for allergies and irritations caused by cosmetic products New market trends (interest in cosmetics without preservatives, especially visible in the case of parabens), as well as modifications in the legal regulations regarding natural cosmetics [76, 84] motivate manufacturers to seek alternative preservative agents.

4.1.4.1. ALTERNATIVE PRESERVATIVES

Glycols with longer hydrocarbon chains are alternatives for conventional preservatives, and they provide an effective protection of cosmetics against bacterial and fungal infections. Glycols are popular groups of cosmetic ingredients, offering a multidirectional effect (they are moisturising agents, humectants, solvents for active ingredients, skin penetration enhancers, and preservative boosters). Introducing various glycols in cosmetic formulations we may modify the sensory characteristics of skincare products, at the same time providing a proper level of protection against infections with microorganisms [84]. The antimicrobial effect depends on the glycol structure and concentration. For instance, to protect a cosmetic product against a microbiological infection, it is necessary to use 5% of pentylene glycol, whereas glycols C_8 (MinaCareOctiol) and C_{10} (MinaCareDeciol) ensure microbiological stability of the product already at the alcohol concentration of less than 1% [85].

The offer of e.g. Minasolve company includes also multifunctional glycine derivatives (INCI: Capryloyl Glycine) with the ECOCERT certification, introduced as a multifunctional ingredient for toiletries applications and formula protection (anti-dandruff, deodorant, anti-acne, anti-microbial) [85]. The list of preservatives identical with the natural ones approved by the COSMOS standards is relatively short [55]:

- benzoic acid, its salts and ethyl ester,
- salicylic acid and its salts,
- sorbic acid and its salts,
- dehydroacetic acid and its salts,
- anisic acid,
- benzyl alcohol,
- phenylethyl alcohol.

Apart from glycols, the alternatives to conventional preservatives include essential oils containing phenols, such as thymol, eugenol or carvacrol. The main representatives of this group used in cosmetics are thyme oil (*Thymus vulgaris*) and clove oil (*Syzygium aromaticum*). Oils that do not contain phenols also demonstrate strong antimicrobial effects. They include: tea tree oil *(Melaleuca alternifolia*), passiflora incarnata oil (*Passiflora incarnata),* lavender oil (*Lavandulla officinallis*), cinamon oil (*Cinnamomum ceylanicum*), sage oil (*Salvia sclarea*), witch-hazel oil (*Hamamelis Virginiana* L.), or the less popular in Poland oils from manuka (*Leptospermum scoparium*) and kanuka *(Kunzea ericoides)* [86].

As alternative for preservatives, the cosmetic industry also uses compounds rich in di- and triterpenoids, tannins, or polyphenols, e.g. extracts from thyme (*Thymus Vulgaris*), goldenseal (*Hydrastis Canadensis Citrus*), citron *(Medica Limonum),* lavender (*Lavandula Augustifolia*), cinnamon *(Cinnamomum Zeylanicum Bark*), rosemary (*Rosmarinus Officinalis*), olive (*Olea Europaea*), oregano *(Origanum Vulgare)* or mint (*Mentha Piperita*). Properly selected and used at concentration of 0.5–2.5%, these substances demonstrate a high antimicrobial potential [86, 87].

4.1.4.2. CRITERIA FOR PRESERVATIVES SELECTION

Preservatives used in cosmetic products must meet a number of basic requirements [2–6]:

- demonstrate activity against a wide spectrum of microorganisms,
- be effective at low concentrations,

- concentrations to be applied need to demonstrate good dermatological characteristics, absence of toxic, allergising and irritating effects,
- present a relatively good solubility in water, and an optimal partition coefficient between the aqueous phase and the oil phase.

Moreover, as all other cosmetic ingredients, they need to demonstrate thermal stability in production, be easy to introduce to the system, be compliant with other components of the formulation and the packaging, and their scent, colour and taste must be imperceptible.

The preservatives are selected for every formulation on individual basis. The factors to be considered while making the choice include: the type of physicochemical system (emulsion type, pH), active substances in the formulation (they may reduce or intensify the effect of a preservative), and other ingredients that may be a medium for a given group of microorganisms.

Acidity of the formulation is an important factor affecting the physicochemical stability and effects of the cosmetic product. It often determines the choice of preservatives. Preservatives containing acidic groups (acids, phenol derivatives, parabens) demonstrate activity only in the acidic environment (in non-dissociated forms), whereas in the products with alkaline pH they dissociate and lose their activity. Conversely, cationic preservatives cannot be used in the environment with $pH < 7$. Many compounds disintegrate in specific environments. One of preservatives sensitive to changes in pH is 2-bromo-2-nitro-1,3-propanadiol (Bronopol). The products of its disintegration (formaldehyde and bromine derivative) are characterised by a significantly lower activity compared to the starting compound.

On the other hand, certain substances reveal antimicrobial activity only after destabilisation (regulated by pH), e.g. formaldehyde donors. Methenamine (hexamethylenetetramine) in aqueous environment slowly disintegrates to ammonia and formaldehyde, demonstrating preservative effects.

Another important factor that determines the activity of a preservative is its solubility in water and the partition coefficient between the aqueous phase and oil phase. Microorganisms in emulsions grow in the aqueous phase or between the phases. Migration of the preservative from the aqueous phase to the oil one may reduce the agent's concentration below the level ensuring effectiveness.

Preservatives may also deactivate as a result of reduced concentration in the aqueous phase of emulsion. It is caused by solubilisation due to the presence of surfactants in the formulation (e.g. interaction between polysorbates and preservatives).

Presence of certain natural substances such as peptides, protein lyophilizates or polysaccharides also affects the effectiveness of the preservative system (e.g. 3% of tragacanth gum neutralises the antibacterial effect of benzoic acid esters).

Finally, one more factor affecting the microbiological quality of the product should be taken into account: the packaging. The packaging with a small contact surface between the cosmetic and the air (bottles with dispensers, flip-top caps) are at a lower risk of contamination during the product use. While selecting the packaging, it is also important to consider the sorption of the preservative on the surface of the packaging.

The preservation test, required by regulations, provides a final confirmation of the proper choice of the substance protecting the cosmetic product from contamination [1, 87, 88]. Preservation tests, referred to as load tests, simulate secondary contamination that may occur while the product is used by a consumer. The test consists in a controlled, single contamination of the product samples with selected test strains (calibrated inoculum), and then following the number of microorganisms at fixed time intervals (48 h, 7, 14, 28 days) and at a set temperature. The following microorganisms are used as test strains: *Pseudomonas aeruginosa*, *Staphylococcus ureus, Escherichia coli, Candida albicans*, and *Aspergillus brasiliensis* [89].

4.1.5. ANTIOXIDANTS

The preservatives discussed in the previous section are to provide microbiological stability of cosmetic products. The chemical stability and protection from light or oxygen in the air (oxidation processes) during the product's storage and use is the role of antioxidants. Cosmetic emulsions contain many substances characterised by low resistance to external factors that may adversely affect the product, modifying its colour, consistency or odour. This group of ingredients includes the previously mentioned unsaturated fatty acids, terpenoids, plant oils rich in unsaturated compounds or phospholipids.

Oxidation processes are among the main causes of limited durability and quality of cosmetics. They follow the mechanism of free-radical reactions, whose rate is determined e.g. by the chemical structure of the oxidised compound, light, temperature, presence of certain metal ions (in particular the iron and copper ions), a developed contact surface between the interphase and oxygen etc.

Antioxidants, also known as inhibitors of free radical reactions, are used to reduce the process of free radical oxidation. Their mechanism of action consists in capturing and neutralising free radicals that initiate the oxidation process. Used in cosmetics at 0.001–0.01%, they effectively deactivate free radicals.

Antioxidants in cosmetic emulsions not only inhibit the oxidation of cream ingredients, but by the contact with the skin surface they may have a direct effect on *stratum corneum*, and delay the skin aging process.

However, complete protection against the oxidation processes requires also the implementation of other measures regarding cosmetic products: the access to oxygen and light should be limited by using hermetic packaging, the products should be stored in the inert gas atmosphere, and oxidants or oxidation-promoting compounds should be eliminated (metal ions, chlorophyll etc.).

According to their origin, the antioxidants used in cosmetics can be classified as:

- synthetic antioxidants – compounds in the phenol group, aromatic amines or their derivatives, tert-butylphenol derivatives: butylated hydroxytoluene (BHT), tert-butylhydroquinone (BHA),

- natural antioxidants – vitamin E (tocopherols), vitamin C (ascorbic acid), carotenoids, Q10 co-enzyme, gallic acid, plant extracts containing polyphenol compounds, tannins, catechins, flavonoids,
- semi-synthetic derivatives of natural ingredients – vitamin C esters (ascorbyl palmitate), esters of gallic acid (propyl gallate, dodecyl gallate),
- synergents – compounds acting in synergy with antioxidants; they can form complexes of metal ions with varying valence: citric acid, lactic acid and its salts, EDTA or phosphonic acid derivatives.

4.1.5.1. NATURAL ANTIOXIDANTS

As with the previously discussed ingredients used in cosmetic emulsions, also in the case of antioxidant, natural ingredients are widely popular. The antioxidants most frequently used in cosmetics are vitamins E (INCI: *Tocopherol*) and C (INCI: *Ascorbic acid*), often combined due to their synergistic action [54]. Apart from vitamins (E and C) and carotenoids, polyphenol compounds are largely represented: phenol acids, flavonoids, anthocyanins, proanthocyanins or catechins. These compounds often demonstrate not only antioxidant properties, but also bactericidal or fungicidal activity. It applies especially to flavonoids and polyphenol acids. Natural antioxidants are usually complexes of related compounds, and due to their synergistic activity, they are effective even at low concentrations, as illustrated by the extracts of green tea, ginkgo biloba, olive leaves or lemon balm. Table 18 presents the sources of plant substances with antioxidant properties.

Table 18

Sources of the most important natural antioxidants

Substance	**Sources of the antioxidants**
Tocopherols	oils from germinating cereals, e.g. germs of wheat, rosehip seeds, tomato seeds, pumpkin seeds, grapeseeds, buckthorn, corn oil, avocado oil, rice oil, grapefruits
Flavonoids	hawthorn fruit, chokeberries, rose-hips, leaves of ginkgo, spearmint, blueberry, yarrow, pansy, borage, field horsetail, bistort, flowers of lemon tree, arnica, camomile, parsley root, dill, willow bark, common hop
Quercetin	onion, pedunculate oak bark, hawthorn fruit, borage herb
Anthocyanins	chokeberry fruit, elderberries, blueberries, rowanberries, black currants, pansy herb, cornflowers
Polyphenols	hawthorn fruit, chokeberries, ginkgo leaves, lemon balm leaves, green tea (catechins)
Rosmarinic acid	herbs of sage, rosemary, mint, lemon balm
Curcumin	turmeric rhizome

4.1.5.2. SEMI-SYNTHETIC ANTIOXIDANTS

The structure of the natural antioxidant molecule is modified to increase the lipophilic character of the hydrophilic substances, and to increase their solubility in lipids. Semi--synthetic derivatives used in cosmetic emulsions include gallic acid esters (Fig. 34), both with small-molecule alcohols and with fatty alcohols. Gallates of small-molecule alcohols (methyl, ethyl or isopropyl alcohol) are soluble in ether and alcohol, poorly soluble in water, and they are soluble in fats and oils only in high temperatures. Conversely, gallates of fatty alcohols, e.g. octyl gallate or dodecyl gallate demonstrate a good solubility in water.

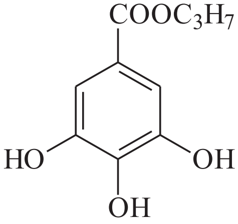


Fig. 34. Isopropyl gallate (INCI: *Propyl gallate*)

Esters of gallic acid and fatty acids in addition reveal an antifungal activity. However, due to their sensitivity to polyvalent metal cations, they require an additional use of chelating agents.

The vitamin C molecule is also esterified to obtain esters of ascorbic acid (e.g. ascorbyl palmitate – Fig. 35) which demonstrate a much higher solubility in oils and fats compared to pure vitamin C.

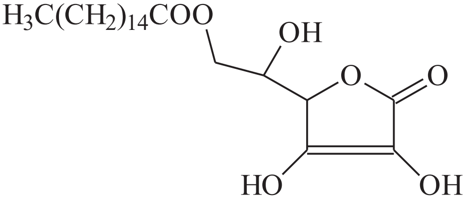


Fig. 35. Ascorbyl palmitate

As mentioned in the case of the gallic acid esters, the antioxidative effect of certain antioxidants requires the use of synergistic compounds, chelating the polyvalent metal cations (sequestrants). These substances can bind the cations of metals with varying valence that catalyse the self-oxidation processes into non-dissociating complexes. Thus, they inhibit the oxidation processes. The substances most frequently used in cosmetic products are citric acid, lactic acid and its salts, and EDTA (Fig. 36) and its salts.

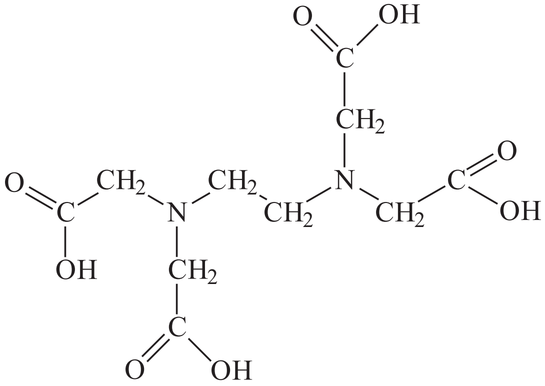


Fig. 36. Ethylenediaminetetraacetic acid (INCI: *Disodium EDTA*)

4.1.6. RHEOLOGY MODIFIERS

Cosmetic products, including emulsions, can have a different consistency, from liquids of various viscosity (semi-liquid lotions, emulsions), to gel systems, to semi-solid creams. The term "consistency" refers to rheological properties of the products, such as viscosity, plasticity and elasticity. All these physical characteristics are determined by the presence of certain ingredients. They may also be modified by addition of consistency agents (rheology regulators, viscosity regulators, thickening agents).

It should be emphasised that the rheology of cosmetic products plays an important role. Not only does it affects the physical stability of the system, but also determines its usability properties, and is a marketing element. Obtaining the right consistency of the product is a very complex problem, as cosmetic preparations are multi-component and multi-phase systems, and individual ingredients interact to a higher or lesser degree.

The proper consistency of hydrophobic emulsions (W/O) is obtained by using natural waxes (beeswax, lanolin), solid paraffin hydrocarbons (paraffin, vaselines, microcrystalline wax) and stearate salts, including magnesium stearate, calcium stearate and aluminum stearate. In hydrophillic emulsions (O/W) the following are used: glycerol monostearate, cetyl alcohol, stearyl alcohol, stearin, spermaceti and natural and synthetic hydrocolloids.

The hydrocolloids used as thickening agents in cosmetics may be classified into the following categories [2–6]:

- natural polymers – hydrocolloids of plant origin (mucus, gums, resins, starch, dextrins, pectins, protein preparations), of animal origin (polypeptides, e.g. gelatine, casein, whey proteins etc.);
- biosynthetic hydrocolloids produced by microorganisms, e.g. dextran, xanthan;

- synthetic polymers – modified with the use of chemical and physical methods derivatives of cellulose, starch or poliacrylic acid;
- inorganic compounds – minerals in the group of aluminosilicates (bentonite), colloidal silica.

Most hydrocolloids form solutions (not only aqueous) are with the characteristics of pseudoplastic liquids, whose viscosity increases along with the concentration. The final products demonstrate high stability, high thermal durability, good dispersion properties, and provide pleasant sensation after application on the skin.

Derivatives of acrylic acid play an important role in the group of synthetic polymers used as thickening agents (Carbomers – Fig. 37). They are obtained in the process of polymerisation of acrylic acid. After neutralisation they form a viscous fluid, pleasant to the touch. The viscosity of aqueous solutions of carbomers increases after, they are neutralised with alkalis (triethanolamine, sodium hydroxide), reaching maximum values at pH of 6.0–10.

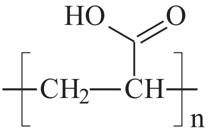


Fig. 37. Polyacrylic acid (INCI: *Carbomer*)

Polyacrylic resins are non-toxic, non-irritating and durable. They are used as thickening agents and dispersants in shampoos and toothpastes, as well as stabilisers of O/W emulsions. They create non-newtonian, shear diluted systems, with a high flow limit, which results in stabilisation of emulsion systems, and increases their resistance to temperature.

4.1.7. ACIDITY REGULATORS

The skin pH oscillates between 4.5 and 6.5. It depends on the composition of the hydrolipid layer on the skin surface – the skin's lipid coat.

Most skincare cosmetics (creams, lotions, balms) have a slightly acidic pH, close to the physiological pH of the skin. The products characterised by intensive effect on hair, skin and nail keratin, demonstrating a softening or keratolytic activity (removing the keratinised epidermis) have an alkaline pH. The highest pH is found in cosmetic products for softening and removing the cuticles, or hair removal products; their pH is 10–12. A slightly lower pH of 8–9 is observed in soaps and shaving creams. Facial tonics, aftershave products or hair regenerating preparations have an acidic pH of 3–5.

A proper pH in cosmetics may be obtained by using acidity regulators such as organic acids, including both: hydroxy acids and fatty acids. Apart from their neutralising effect, the organic acids used in cosmetics also demonstrate cosmetic properties: they act as astringents, brighten the skin, have keratolytic and moisturising effect (AHA), reveal keratolytic and deodorising characteristics (e.g. salicylic acid), can oil and hydrate the skin (fatty acids), or provide skin care and regeneration (EUFA).

The most often used as acidity regulators in cosmetic emulsions are hydroxy acids: lactic and citric acids.

4.2. FORMULATIONS OF COSMETIC EMULSIONS

The main role of cosmetic emulsions for skin care is to maintain the physiological water and lipid balance in the epidermis and to protect the skin from external factors, e.g. UV radiation. Appropriate selection of the components taking both the physicochemical and cosmetic properties of the finished product into account is one of the most important aspects of creating the formula.

It is difficult to make a clear classification of the emulsion preparations. Considering the effect on the skin, a general classification of cosmetic emulsions includes cleansing, moisturising, and protective emulsions. If the basic classification criterion is the time of day of application, creams can be classified as fast-absorbing day creams and much heavier night creams which feature nutrients. Yet another set of classification criteria is associated with the application site: facial care creams (including eye creams), hand creams, foot creams, and body creams. While, taking the consumer group into account, we can distinguish creams for problematic skin (e.g. sensitive skin, atopic skin or acne skin), anti-aging cosmetics and baby products.

4.2.1. UNIVERSAL CREAM BASES

Cream bases are ready made absorptive bases consisting in a mixture of fatty substances, emulsifiers and hydrophilic substances. The base components are selected in such a way that they ensure the creation of a stable and durable emulsion with very good sensory properties. An example of cream base for O/W emulsion, with semi-liquid consistency and creamy-white colour, is Lekobaza (Table 19), amphiphilic base from Fargon Pharma Cosmetics [90].

Table 19

The formulation of Lekobaza [90]

INCI name of compounds	Wt (%)
Paraffinum Liquidum (Mineral Oil)	3.0
Petrolatum	32.0
Glyceryl Monostearate	3.0
Cetearyl Alcohol	9.0
Polisorbat 40	7.0

Caprilic/Capric Triglicerides	2.0
Propylene Glycol	5.0
Silica	0.1
Sorbic Acid	0.2
Water	up to 100

Similarly, readymade cream bases are produced for W/O emulsions. The basic components of hydrophobic bases are: vaseline, paraffin, ceresin, microcrystalline waxe, mineral oil, cholesterol, sorbitan esters, fatty alcohols, lanolin alcohols. The most basic example of a hydrophobic cream base is "Eucerin", the mixture of white *Vaseline* (95%), *Cetyl alcohol* (3%) and *Cholesterol* (2%). Another example is the pharmacopoeial lipophilic base "Cold Cream" (Table 20) [91] – white, homogeneous, soft mass. The formulation presented in Table 20 is slightly different from the first cream formulation described in literature, in 2 BC, by Galen from Pergamon. His cream consisted of bee wax, olive oil and rose water.

Table 20

The formulation of "Cold Cream" [91]

INCI name of compounds	**Wt (%)**
Beeswax	8.0
Cetaceum	15.0
Soybean Oil	62.0
Sodium Borate	0.5
Water	up to 100

On the cosmetics raw materials market, ready-mixed emulsifier mixtures are also available. These kind of self-emulsification systems enable formulation of the emulsions with a wide range of consistency.

One of the example of such the systems is NatraGem™ EW, (INCI: *Glyceryl Stearate (and) Polyglyceryl-6 Palmitate/Succinate (and) Cetearyl Alcohol*), emulsion base from Croda [92]. According to the producer declaration this is a highly effective emulsifying wax, with an excellent electrolyte tolerance and compatibility with both high and low polarity oils, can create pourable lotions to high viscosity creams. It is approved natural by Ecocert. Applications of NatraGem™ EW include skin care, hair care, sun care, colour cosmetics, baby care, and natural creams and lotions.

Another example of raw materials supplied by Croda Company is Versaflex™ V-175 (INCI: *Sucrose Palmitate (and) Glyceryl Stearate (and) Glyceryl Stearate Citrate (and) Sucrose (and) Mannan (and) Xanthan Gum*). Versaflex™ V-175 is a unique technology developed to stabilise oil-in-water emulsions, whilst offering mildness and superior skin feel to a variety of applications. It is suitable for formulation different oil-in-water emulsions, containing various kind of oils or oil-soluble actives. This grade is 100% plant derived and free from ethylene oxide (EO), making it suitable for formulators who wish to use only natural ingredients [93].

MixXIN™ ME (INCI: *Caprylic/Capric Triglyceride (and) Glycol Stearate (and) PEG-3 Glyceryl Cocoate (and) Steareth-7*) is offered by Croda for cold-process complete emulsion system. It is possible to achieve a variety of skin feel with the use of emollient esters and other sensory modifiers like silicones and oils. MixXIN™ ME can be formulated into various forms, from milks to lotions and creams [94].

On the other hand, Coast Southwest Company proposed PEG-free, and derived entirely from natural raw materials emulsifiers mixture such as Olivatis series. For examples, Olivatis™18 (INCI: *Olive Oil Polyglyceryl-6 Esters (and) Sodium Stearoyl Lactylate (and) Cetearyl Alcohol*) is a mild, O/W emulsifier used in a wide range of applications from butters to hair and skin lotions [95]. Olivatis™ 12C, (INCI: *Olive Oil Polyglyceryl-6 Esters (and) Polyglyceryl-6 Pentaoleate*) is PEG-free and palm-free, liquid crystal-promoting, non-ionic, W/O emulsifier. Emulsions formulated with Olivatis™ 12C are easily absorbed and rich in natural oily substances without being greasy or sticky. Olivatis™ 12C is Ecocert-certified. It is ideal for use in lip glosses, lip sticks, moisturisers, sunscreens, and baby products [96].

One more example of self-emulsification base is the product of Synergia – Phytocream®2000 (INCI: *Potassium Palmitoyl Hydrolysed Wheat Protein, Glyceryl Stearate, Cetearyl Alcohol*) is plant origin anionic/non-ionic, PEG-free, O/W emulsifier. It is giving stable emulsions systems with a wide range of consistency [97].

The use of such the ready-mixed emulsifying systems makes it much easier to obtain stable emulsion forms.

4.2.2. CLEANSING COSMETICS

All cosmetic market players offer cleansing cosmetic for make-up removal in their cosmetic lines, i.e. creams and emulsions that clean the skin without using soap and other alkaline agents, so that it does not lose the natural protective lipid coat and retains the proper, slightly acidic pH.

Emulsion cleansing products should spread easily on the skin, and after removal leave the skin softened, slightly moisturised without the feeling of greasiness. Cosmetics for the treatment of particularly sensitive eye area also often contain plant oils rich in essential unsaturated fatty acids (avocado, evening primrose or sesame oil), as well as anti--inflammatory and anti-allergic ingredients (vitamins, proteins, plant extracts).

Cleansing creams, although they are derived from cold creams (Table 20), may take the form of both O/W emulsion (Table 21) and W/O emulsion (Table 22), most of them come in the form of cosmetic milk or liquid cream.

Table 21

Formulation of cleansing cream O/W [6]

INCI name of compounds	Wt (%)
Polyglyceryl-4 Oleate	2.6
Sulfated Castor Oil	0.4
Mineral Oil	10.0
Isopropyl Myristate	5.0
Urea	3.0
Xanthan Gum	0.6
Water	78.1
Parfum	0.3
Preservative	q.s.

Table 22

Formulation of Light W/O Lotion [98]

Phase	INCI name of compounds	Wt (%)
A	Water	up to 100
	Glycerin	7.0
	Levulinic Acid and Sodium Levulinate	0.5
	Magnesium Sulfate	1.0
	Sodium Hydroxide (sol. 1%).	0.9
B	P-Anisic Acid	0.2
	Polyglyceryl-3 Polyricinoleate	3.0
	Polyglyceryl-3 Diisostearate	2.0
	Caprylyl Glycol	0.2
	Butylene Glycol Dicaprylate/Dicaprate	9.0
	Hexyldecanol, Hexyldecyl Laurate	10.0
	Magnesium Stearate	0.50
	Hydrogenated Castor Oil	1.00
	Tocopherol, Helianthus Annuus (Sunflower) Seed Oil	0. 5
C	Parfum	0.30

Manufacturing Procedure:

1. Heat phase A up to 78°C.
2. Adjust pH-value to pH 5.0–5.5 with NaOH sol. 1%.
3. Heat phase B to 78°C. P-Anisic Acid should be completely dissolved.
4. Emulsify phase A slowly to phase B under stirring.
5. Homogenize for 1–2 min. using an high shear homogenizer.
6. Start to cool down to 32°C under stirring. Add perfume.

In the group of cleansing cosmetics there are also **acne products** (special cosmetics for seborrheic and acnetic complexion). Table 23 shows formulation of oil and acne skin care cream. Preparations of this type contain substances regulating the secretion of sebaceous glands. Primarily, zinc salts: zinc alginate, zinc laurate, zinc pyrithionate, zinc pyroglutamate, triclosan or salicylic acid. Among the natural substances: linseed oil, methyl and butyl esters of avocado oil, licorice extracts, erysipelas, extract from the African tree *Enantia chlorantha* (containing high levels of the protoberberine alkaloid, which reduces the secretion of sebum and regulates the proliferation of fat cells). In cosmetics intended for the care of oily skin, there are also components regulating epidermal keratosis (retinol, B vitamins, AHA) and soothing irritations, such as: panthenol, allantoin, bisabolol, or a number of plant extracts: from rosebay willowherb, epilobium, peony, birch, burdock or aloe). Another important group are matting components, e.g. kaolin, bentonite, calcium carbonate, zinc oxide, polyacrylates or modified starch (e.g. aluminum starch

Table 23

Formulation of oil and acne skin care cream [6]

Phase	INCI name of compounds	Wt (%)
A	Water	63.60
	Potato Starch Modified	0.80
	Steareth-21	2.00
	Polyaminopropyl Biguanide	0.30
	Sodium Lactate	3.60
	Glyceryl Stearate/PEG-100 Stearate	3.20
	Aluminum Starch Octenylsuccinate; Acrylates Polymer; Magnesium Carbonate	3.00
	Corn Starch Modified	3.00
	Propylene Glycol	8.00
	Glycerin	1.00
B	Salicylic Acid	0.50
	Steareth-2	3.00
	Caprylic/Capric Triglyceride	8.00

Manufacturing procedure:

1. prepare the water phase (A), disperse all starch components in water, while stirring vigorously (700 rpm),
2. add the rest of water phase ingredients under stirring,
3. weigh out and mix the oil phase (B),
4. add to the oil phase with stirring, (500 rpm),
5. homogenize for 3 minutes using a rotor / stator system at approx. 10,000 rpm.

octenyl succinate, magnesium carbonate starch) and astringents (extracts from hamamelis virginiana, sage, chestnut, multiflora rose fruit or willow). A very important element of the formulation of this group of cosmetics is the selection of emollients. The raw materials used in cosmetics intended for oily skin should quickly penetrate the skin and leave no fatty film. The use of pore-blocking substances should be avoided. These substances include hydrocarbons: isoparaffins, squalane, squalene and oils: coconut, nut, almond, sunflower or lanolin and its derivatives.

The physicochemical form has an impact on the effectiveness of this group of cosmetics. W/O formulations are not used; only light O/W emulsions, gel emulsions or gels containing mild emulsifiers and a minimum amount of oil phase.

4.2.3. MOISTURISING PRODUCTS

Proper functioning of the skin, kinetics of physiological and biochemical processes in the skin are strongly depend on water contents in the skin. The degree of skin hydration is responsible for the proper structure of skin proteins and, consequently, its flexibility and elasticity. The skin has natural barriers that inhibit water loss (e.g. intercellular cement that connects the corneocytes in the *stratum corneum* or the hydro-lipid film of the outer skin layer), however, they are often damaged by various external factors and their properties are also affected by the physiological aging of the skin [99, 100].

The role of moisturisers is to restore and maintain the skin in a good-looking, fully moisturized condition, reduce the loss of water from the epidermis and to strengthen natural barriers reducing the transepidermal water loss.

Therefore, in moisturising cosmetics, an important role is played by components that create an impermeable barrier on the skin surface, making it resistant for the water evaporation. In particular, the hydrophobic film forming organic substances ought to be mentioned here. They include waxes, paraffin hydrocarbons or silicones as well as the substances forming a hydrophilic film on the skin surface, i.e. proteins, mucopolysaccharides, polyglycols and polysaccharides. The second category of moisturising raw materials are substances that have the ability to penetrate the skin and strengthen the lipid barrier of the skin (triglycerides, phospholipids, sphingolipids, fatty alcohols, fatty acids or sterols) and substances that provide water to the deeper layers of the epidermis and facilitate its binding by the skin (polyols, alpha-hydroxy acids, including lactic acid and its salts, simple sugars, pyroglutamic acid, protein hydrolysates or amino acids).

Moisturising cosmetics are usually emulsions, either O/W and W/O. There are two most popular forms of moisturizers: creams (semi-solid emulsions) and lotions (flowable emulsions). Moisturizing cosmetics are differentiated not only by their emulsion type but also by their functional use. There are facial, hand and body creams and lotions, with low oil phase content (10 to 40%) and night creams rich in oil phase content (30–70%), which have additional occlusive and protective properties.

Moisturising cosmetics for face care include delicate components for softening and smoothing of the epidermis (plant oils rich in essential unsaturated fatty acids triglycerides: avocado, sesame, evening primrose, borage, wheat germ, berry seed oils), moisturising protein hydrolysates, components that protect the skin barrier against oxidation – antiradical substances (vitamins C, E, Coenzyme Q_{10}), and anti-inflammatory and anti-allergic plant extracts. What is more, creams intended for delicate under-eye skin care may contain skin lightening and blood vessel sealing components such as vitamin C, vitamin K and retinol, as well as plant components that improve the circulation of blood (rich in saponin glycosides or flavonoids). Sensory impressions play a significant role in the perception of face care cosmetics. In the development of facial care emulsion formulations, the main focus is on the product texture. The most desired products are light and well absorbed creams living the skin after their application smooth and flexible.

The composition of body moisturising emulsions is usually similar to the composition of facial products. However, in this group of cosmetics, sensory impressions such as slightly greasy feeling or slower absorption are not as important. Moisturising lotions and milks contain waxes and vegetable fats, fatty alcohols, polyols, phospholipids and sphingolipids, as well as components that soothe irritations such as panthenol or allantoin. Whereas, hand moisturising emulsions should additionally exert a protective effect. Therefore, they often contain silicones and paraffin hydrocarbons forming a protective film on the skin. Tables 24 to 27 present sample formulations of moisturising emulsions.

Table 24

O/W Macadamia Milk (Natural cosmetic, cold/ cold process) [101]

Phase	INCI name of compounds	Wt (%)
A	Polyglyceryl-4 Oleate	2.6
	Sulfated Castor Oil	0.4
	Macadamia Oil	10
	Cetearyl Ethylhexanoate (and) Isopropyl Myristate	5.0
	Parfum	0.3
B	Urea	3.0
	Xanthan Gum	0.6
	Water	78.1
	Preservative	q.s.

Manufacturing procedure:

1. prepare the water phase (B), add the Xanthan gum while stirring vigorously until firm, (and remove air using a vacuum, where possible),
2. weigh out and mix the oil phase (A) in the sequence shown above,
3. add to the water phase without stirring,
4. homogenize for 3 minutes using a rotor / stator system at approx. 10,000 rpm.

Table 25

Formulation of moisturizing body cream [98]

Phase	INCI	Wt (%)
A	Polyglyceryl-4 Isostearate	2.7
	Aluminium Stearate	0.1
	Magnesium Stearate	0.8
	Isohexadecane	4.7
	Dioctylcyclohexane	2.7
	Decyloleate	4.6
	BHT (and) Glyceryl Stearate (and) Glyceryl Oleate (and) Ascorbyl Palmitate (and) Citric Acid (and) Propylene Glycol	0.05
B	Urea	9,0
	Magnesium Sulfate	0.4
	Preservative	q.s.
	Water	up to 100
C	Parfum	0.30

Manufacturing procedure:

1. weight out the oil phase (A) in the sequence shown above,
2. heat to approx. 100°C until the phase is clear,
3. then cool phase A to approx. 75°C,
4. heat phase B to approx. 75°C,
5. next add the water phase (B) within approx. 20 minutes while stirring, keeping the temperature at a minimum 70°C,
6. after adding, cool the mixture to 50–60°C and homogenise for 3 minutes using a rotor/stator system at approx. 10,000 rpm,
7. next cool to approx. 35°C, add perfume and homogenise again for 1 minute using the rotor/stator system,
8. continually cool to approx. 25°C under stirring.

Table 26

Formulation of long lasting moisturizer- daily use facial cream [102]

Phase	INCI name of compounds	Wt (%)
A	PEG-100 Stearate and Glyceryl Stearate	5.5
	Paraffinum Liquidum (Mineral Oil)	5.00
	Caprylic/Capric Triglyceride	2.00
	Cetearyl Alcohol	2.50
	Dimethicone	0.50
	Sweet Almond Oil	5.00
	BHT	0.10
B	Aqua (Water)	up to 100
	Xanthan Gum	0.40
	Disodium EDTA	0.10
	Allantoin	0.10
	Acrylates C10-30 Alkyl Acrylate Crosspolymer	0.20
C	Cyclopentasiloxane, Cyclohexasiloxane	1.50
	Tocopheryl Acetate	0.20
	Retinyl Palmitate	0.05
	Vitamin F – Gliceric Ester	1.50
	Parfum (Fragrance)	0.35
D	Preservative	0.20
	Aqua (Water)	3.00
	Galactomannan and galacto-mannose oligosaccharides (5–7%)/ Hydromanil	10.00
E	Triethanolamine	q.s.

Manufacturing Procedure:

1. heat phase A up to 65°C,
2. heat phase B + D to 65°C, adjust pH-value to pH 5.0–5.5 with triethanolamine,
3. add phase A slowly to the mixture of phase B+D, under stirring,
4. next the obtained emulsion homogenize for 1–2 min. using an high shear homogenizer,
5. start to cool down to 40°C and then add phase C under stirring.

Table 27

Soft Cream [98]

Phase	INCI	Wt (%)
A	Aqua	up to 100
	Glycerin	3.0
	Caprylyl Glycol	0.5
	Levulinic Acid	0.2
	Panthenol and Aqua	2.0
	Allantoin	0.2
A1	Carbomer	0.2
B	Glyceryl Stearate Citrate	0.5
	Polyglyceryl-3 Stearate	1.5
	Glyceryl Stearate	4.0
	Stearic Acid and Palmitic Acid	2.0
	Isoamyl Laurate	7.0
	Butylene Glycol Dicaprylate/Dicaprate	2.0
	Triheptanoin	5.0
	Tricaprylin	5.0
	Tocopherol, Helianthus Annuus (Sunflower) Seed Oil	0.5
C	Sodium Hydroxide (sol 1%)	q.s.
D	Parfum	q.s.

Manufacturing Procedure:

1. heat phase A up to 78°C and strir strongly until be completely dissolved,
2. disperse phase A1,
3. heat phase B to 78°C,
4. emulsify phase B into phase A/A1while stiring,
5. homogenize for 2 min. using an high shear homogenizer,
6. start to cool down to 32°C under stirring and add perfume oil,
7. adjust pH value with D if necessary.

4.2.4. PROTECTIVE CREAMS

Protective creams are intended to protect the skin against external factors such as: industrial pollution (lubricants, aqueous solutions of acids and bases, petrol, oils), chemical products used in the household, as well as against ultraviolet radiation. After spreading, protective hand creams should leave a tin protective layer on the skin surface. It should be characterised with considerable chemical resistance adapted to the type of hazard. They are produced in the form of either O/W or W/O emulsions, with an average (up to 40%) oil phase content. The main components of the oil phase are paraffin hydrocarbons, vegetable oils, synthetic liquid waxes as well as lanolin and its derivatives. The moisturising substances most often used in these creams are glycerol and glycols.

A special group among protective cosmetics are sunscreen preparations containing UV--filters. In order to minimize the negative effects of UV radiation on the skin, ultraviolet filters are used in cosmetic preparations, not only in the ones intended for sunbathing, but also in coloured cosmetics and daily used cosmetics and hair care. The purpose of the sun protection agents is to extend the time of sunbathing and protect the skin from against and the harmful effects of UV radiation.

Ultraviolet radiation is divided into three ranges according to its biological activity: UVC (200–280 nm), UVB (280–320 nm), UVA (320–400 nm). UVC is high energy radiation but does not reach the earth surface and does not affect our body. UVB radiation has a relatively high energy. In smaller doses it causes erythema, while in larger doses it can even cause serious burns leading to the destruction of the epidermis (that is why it is labelled UVB, for burning UV radiation). As the wavelength of light increases, the skin's reddening effect decreases, and, at the borderline between UVB and UVA, it decreases sharply. UVA penetrates the skin to the level of the dermis. It causes so-called direct pigmentation, which occurs immediately after irradiation and stimulates the release of melanin from melanosomes. It does not cause erythema at normal doses; however, it contributes to the formation of free radicals and the effects of its action are visible with delay. It causes cumulative effects of photoaging of the skin (accelerating the degradation of collagen fibres). It acts as a mutagenic and carcinogenic agent (causing changes in nucleic acids) [99, 100].

The sunscreens used in cosmetics are substances whose task is to extend the time of sunbathing and protect the skin against the harmful effects of UV radiation. The list of UV filters approved for use in cosmetics is included in Annex VI to the Regulation of the European Parliament and of the Council (EC) No. 1223/2009 [1]. Sunscreen actives are generally classified as organic sunscreens or inorganic ones. Organic sunscreens absorb strongly at specific wavelengths and are transparent to visible [103, 104]. Inorganic sunscreens work by reflecting or scattering UV radiation.

Organic sunscreens are classified according to the effectiveness of protective filters that absorb UVB and UVA radiation or so-called wide-range filters (UVA + UVB).

The UVB filters absorb radiation in the wavelength range corresponding to UVB light [6], there are some examples of them:

- paraaminobenzoic acid (PABA) and its esters, (e.g. *Octyldimethyl PABA*),
- cinnamic acid esters, (e.g. *Octyl Methoxycinnamate*),
- salicylic acid esters (e.g. *Octyl Salicylate*),
- terpenic compounds, camphor derivatives (*Camphor Benzalkonium Methosulfate*).

Examples of UVA filters include:

- dibenzoylmethane derivatives (e.g., *Butyl Methoxy Dibenzoylmethane – BMDM*),
- benzophenone derivatives: 2-hydroxy-4-methoxybenzophenone-5-sulphonic acid and its sodium salt (INCI: *Benzophenone-4 and Benzophenone-5,* respectively).

UVA + UVB filters include (2-hydroxy-4-methoxyphenyl)-phenylmethanone, (INCI: *Benzophenone-*3) or triazine derivatives, (INCI: *Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine*).

Plant extracts that contain flavonoids and anthocyanins, ferulic acid and its derivatives as well as m-digallic acid in its composition are included in natural filters. Some of the extract examples showing the UV protective properties include: extracts of mountain arnica, black chokeberry, hamamelis virginiana or walnut.

The most popular physical (inorganic) filter is titanium dioxide (INCI: *Titanium Dioxide).*

For measuring the effectiveness of sunscreen the Sun Protection Factor (SPF) was proposed in 1978, by North American regulatory agency (FDA). The Sun Protection Factor can be defined as the numerical ratio between the minimal erythemal dose (MED) of sunscreen-protected skin, applied in the amount of 2 mg/cm^2 and the minimal erythemal dose of unprotected skin, a mathematical relation that can be represented by the eq. 30.

$$\text{SPF} = \text{MED (protected skin)} / \text{MED (unprotected skin)} \tag{30}$$

The FDA and European COLIPA methodologies have become a reference for determining the Sun Protection Factor (SPF); other countries and regions have proposed or issued similar regulations and guidelines in line with the EU and FDA; owing to consumer confusion over the real degree and duration of protection offered, labelling restrictions are now in force in several countries. According to European Union (EU) Council Directive 76/768/EEC of 27 July 1976 on the approximation of the laws of the Member States relating to cosmetic products ("Cosmetics Directive 76/768/EEC"); Commission regulation (EU) No. 344/2013 of 4 April 2013, amending Annexes II, III, V and VI to Regulation (EC) No. 1223/2009 [105] of the European Parliament and of the Council on cosmetic products – sunscreen products are cosmetic products. In the EU, sunscreen labels can only go up to SPF 50+. Tables 28 to 29 present sample formulations of UV protective cosmetics.

Table 28

Daily Protection Skin Care Cream (O/W emulsion, SPF 30) [98]

Phase	INCI name of the compounds	Wt (%)
A	Aqua	64.75
	Sodium Phytate, Aqua	0.10
	Glycerin	3.00
	Caprylyl Glycol, Glyceryl Caprylate, Glycerin, Phenylpropanol, Aqua	1.00
B	Xanthan Gum	0.20
	Magnesium-Aluminium Silicate	0.50
C	Titanium Dioxide, Silica	2.00
D	Glyceryl Stearate Citrate, Cetearyl Alcohol, Glyceryl Caprylate	5.00
	Isoamyl Laurate	8.00
	Squalane	3.00
	Benzophenone-3	3.00
	Ethylhexyl Methoxycinnamate	7.00
	Tocopherol, Helianthus Annuus (Sunflower) Seed Oil	0.05
E	Parfum	0.40
	Aqua, Melissa Officinalis, Disodium Rutinyl Disulfate, Hordeum Distichon	0.50
	Alcohol, Aqua, Glycerin, Hydrolyzed Wheat Protein, Ilex Aquifolium, Sodium Ursolate, Sodium Oleanoate	1.50

Manufacturing Procedure:

1. Heat phase A up to 78°C. Disperse B i C.
2. Heat phase D to 78°C, next add phase D to phase A/B/C under stirring.
3. Homogenize for 1–2 min. using a high shear homogenizer.
4. Start to cool down to 32°C under stirring. Add ingredients of phase E.

Table 29

O/W Sun protection cream (SPF 15) [98]

Phase	INCI	%
A	Aqua	68.35
	Glycerin	3.50
	Caprylyl Glycol, Glycerin, Glyceryl Caprylate, Phenylpropanol	0.80
	Sodium Polyacrylate	0.20
	Xanthan Gum	0.25
B	Glyceryl Stearate Citrate, Cetearyl Alcohol, Glyceryl Caprylate	5.00
	Butyrospermum Parkii	2.00
	Squalane	2.00
	Butylene Glycol Dicaprylate/Dicaprate	3.00
	Tricaprylin	5.00
	Polydecene	4.00
	Butyl Methoxydibenzoylmethane	1.00
	Ethylhexyl methoxycinnamate	2.50
	Dimethicone	0.20
C	Cyclopentasiloxane	2.00
D	Parfum	0.20
	Sodium Hydroxid	q.s.
	Citric Acid	q.s.

Manufacturing Procedure:

1. Heat phase A up to 78°C and disperse polyacrylate and Xanthan gum.
2. Heat phase B up to 78°C.
3. Emulsify phase B into phase A under stirring.
4. Homogenize for 1–2 min. using a high shear homogenizer.
5. Cool down to ca. 60°C under stirring and add C.
6. Cool down slowly to 30°C and add D. Adjust pH value if necessary.

Apart from sun protective cosmetics, containing UV filters on the market there are sunless tanning substances produce a tanning effect without exposure to ultraviolet radiation. A safe and effective method of sunless tanning is consumption of certain carotenoids. Among self-tanning substances, the most popular is dihydroxyacetone (DHA), it cause a chemical reaction with the amino acids of the stratum corneum giving on the skin surface tanning effect. Others examples are a synthetic α-melanocyte-stimulating hormone (α-MSH) analogue and tanning accelerator – tyrosine, an amino acid which stimulate and increase of melanin formation [106]. Table 30 shows a self-tanning formulation contains forskolin as a natural substance to obtain a healthy tan.

Table 30

Self-tanning formulation [107]

Emulsion phase	INCI Ingredient Name	Wt (%)
oil phase	Caprylic/Capric Triglceryde	30.6
	Isohexadecane	3.4
surfactants	Steareth-2	3.6
	C_{13}–C_{15} Pareth-7	0.4
water phase	Water	up to 100
active	Coleus Forskohlii Root Extract (Forskolin)	0.075

Manufacturing procedure:

1. dissolve Forskolin in the oil phase prior to the emulsion formation,
2. add the oil phase do the mixture of surfactants,
3. add water to oil/surfactant mixtures, at 28°C,
4. in order to obtain emulsions with small droplet size use a high shear homogenizer.

Forskolin is a diterpenoid, extracted from the root of *Coleus forskohlii* plant (the only natural source of this substance). Forskolin is a molecule commonly applied to raise the intracellular levels of cyclic adenosine monophosphate (cAMP) by direct activation of the enzyme adenylyl cyclase. Forskolin or the *Coleus forskohlii* extract are applied in anticellulite cosmetic products, for stimulating lipolysis and haematic flow at microvascular level. Recently, the potential of forskolin as a natural substance to obtain a healthy tan and to protect the skin from the side effects of UV radiation, (apoptosis of keratinocites, DNA damage or melanoma), has been reported [108–110].

4.2.5. ANTI-AGING COSMETICS

Anti-aging cosmetics constitute a large group of the skin care cosmetics market. Originally, this group included only products intended for mature skin to reduce the appearance of wrinkles and other signs of skin aging. The role of modern anti-aging cosmetics is not only to improve the appearance of the skin by stimulating and regenerating natural physiological processes that improve the skin condition, but also to protect the skin against factors causing skin aging [99, 111–113].

Cutaneous aging is the result of the interaction between endogenous and exogenous factors. However, approximately 80% of skin aging-associated changes can be attributed to extrinsic factors such as ultraviolet (UV) light, environmental pollution, chemicals or atmospheric temperature. There are a few theories explaining aging process. The oxidative theory (free radicals damage of tissues) is the most popular in the public's mind. This is understandable if we look at the structure of the skin. Most of the lipids in the *stratum corneum* are unsaturated and therefore they are sensitive to damage by free radicals [113–115].

Therefore, anti-aging cosmetics include substances neutralizing free radicals: vitamins E and C, coenzyme Q10, carotenoids, or the ones contained in plant extracts, like polyphenols and flavonoids (the plants that are especially rich in these substances are ginkgo biloba, green tea, ginseng, medical calendula, chamomile or grape seed extracts). The second group of raw materials present in anti-aging cosmetics are substances that protect against solar radian (UV filters) [111, 113].

The basic group of anti-aging components are of course substances that stimulate cell renewal processes and biosynthesis of structural skin proteins [99]. Modern cosmetics regenerating and delaying skin aging include nucleic acids, protein hydrolysates, algae extracts rich in microelements, vegetable oils, which constitute a source of essential unsaturated fatty acids (especially cereal germ oils, evening primrose oil, borage oil) or hydroxy acids with keratolytic and softening properties. A valuable component of anti-aging products is so called vitamin of youth – vitamin A and its derivatives, regulating the renewal of the epidermis and the synthesis of collagen and elastin, reducing skin discolouration and improving its colour. Recently, fashionable ingredients include: phytohormones, cytokines, steam cells extracts or bioactive peptides. The hydration status of the *stratum corneum* is of special importance for the improvement of the elasticity and smoothness of the skin. Therefore, the products that delay the skin aging processes additionally contain ingredients that affect the water content in the *stratum corneum* and delay transepidermal water loss (i.e. amino acids, urea, pyroglutamic acid, especially its sodium salt, minerals, hyaluronic acid and mucopolysaccharides) [99, 111–113].

4.2.5.1. PLANT MATERIALS AS ACTIVE COMPONENTS OF ANTI-AGING COSMETICS

Products of plant origin are used either in the form of extracts: water, water-glycolic, glycolic (propylene and butyl glycols), oil, alcohol (ethyl and isopropyl alcohols), or in the form of pure compounds isolated using various methods. They are complex mixtures, which include a number of biologically active substances and physiological plant products: glycosides, alkaloids, tannins, azulenes, essential oils and terpenes, balms and resins, mucus and pectin, silicon compounds, organic acids, carbohydrates, fats, proteins, minerals, phytohormones and phytosterols. They exert various effects on the skin: astringent, toning, anti-inflammatory, regenerative, moisturising, smoothing or UV-protective [76, 112].

The astringent and firming effects are exerted by extracts of birch bark, cinquefoil root, *Hamamelis virginiana herb*, black cranberry, aloe, tea, horsetail and ivy. The above-mentioned raw materials mainly include tannins, acid saponins and silicic acids.

The toning (nutritional) effect is exerted by extracts of marigold, avocado, aloe, carrot, cucumber and sea-algae, which are rich in vitamins, minerals, phytosterols and plant proteins that strengthen the skin cells.

Moisturising and smoothing effects used in various types of cosmetic masks, compresses, creams and lotions are exerted by extracts that are rich in polysaccharides and slimes, e.g. hibiscus extract, linden blossom, mallow, elderberry flower or Icelandic moss.

Extracts of ginkgo biloba, lemon balm, rosemary, lavender, ginseng or chestnut, containing triterpene saponins, essential oils rich in sesquiterpenes and flavonoids, have a stimulating effect on the circulatory system and blood vessel sealing.

The regenerative effect that accelerates the healing of the skin is characteristic for extracts of ginseng, marigold, St. John's wort, chamomile or pansy flowers, i.e. raw materials rich in flavonoid glycosides, triterpene saponins and slimes.

A special group of substances used in anti-aging cosmetics are flavonoids, a group of natural substances with variable phenolic structures. They were found in fruits, vegetables, grains, bark, roots, stems, flowers, tea and wine. Most often occur in the form of glycosides. These substances are characterized by a large variety of chemical structure. Their skeleton consists of two aromatic rings joined by a heterocyclic system (Fig. 38). The flavonoid compounds differ in the number and positioning of the hydroxyl groups at both aromatic rings and the type of glycosidic linkage with sugars. The sugar part of flavonoid glycosides are most often simple sugars, like glucose, galactose, rhamnose, arabinose or disaccharides (rutinose, glucuronic acid) [116].

The most famous flavonoids include: quercetin (Fig. 39), found in onion skins, oak bark or arnica flowers and its glycoside – rutin (from herb rue or green tea).

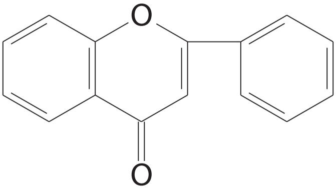


Fig. 38. The basic skeleton structure of flavonoids

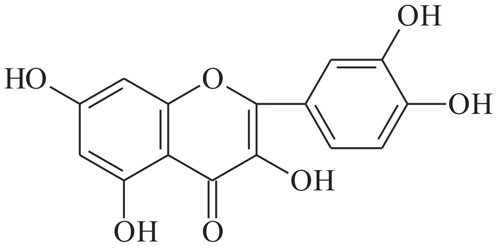


Fig. 39. The structure of quercetin

Flavonoids demonstrate a wide spectrum of biological activity [116, 117], they:

- relax the blood vessels, preventing them from cracking (bruises, micro-extravasation) and dilation (a net of small blood vessels on the facial skin),
- show antioxidant properties, neutralize free radicals responsible for aging and degeneration of tissues,
- absorb UVA and UVB radiation,
- stabilize vitamin C, which has a beneficial effect on collagen biosynthesis and improves the quality of connective tissue,
- have an anti-allergic effect,
- they are anti-inflammatory and antiseptic compounds.

Table 31 presents selected plant materials that are especially rich in flavonoids.

Table 31

Selected plant raw materials used in cosmetics as a source of flavonoids

Plant	Important flavonoids
Horsetail herb	Isoquercetin, galuteolin, apigenin, coffee acid
Linden	Derivatives of quercetin, kaempferol, acacetin
Ginkgo biloba	Derivatives of quercetin and kaempferol, bilobetin
Green tea	Quercetin, kaempferol, catechin gallate, epigallocatechin gallate, tearubigin, rutin
Grapes (seeds, skins, leaves)	Gallocatechin, epicatechin gallate, kaempferol
Viola tricolor (pansy)	Rutin, quercetin, luteolin, scoparine
St. John's wort	Hyperosite, rutin, quercetin

4.2.5.2. PLANT STEM CELLS AS A RAW MATERIAL OF ANTI-AGING COSMETICS

In the past few years, plant stem cell extracts have obtained a special place among raw materials used in anti-aging cosmetics. The declared effects of plant stem cells include protection of human stem cells, stimulation of skin regeneration, regeneration and prevention of skin aging processes. Stem cells differ from other cells due to their extraordinary properties, such as the ability to proliferate (multiply continuously) and differentiate into specialized cells (depending on the organ in which they occur), and also the offered potential for growth and repair of tissue damage [118, 119].

In 2008, as the first company in the world, Mibelle Biochemistry implemented apple stem cells (PhytoCellTec Malus Domestica) using PhytoCellTec technology. [120]. This active ingredient is a revolutionary technology designed to protect human skin stem cells with the help of stem cells from a rare Swiss apple. The clinical trials conducted by the Company showed that 100% of the participants saw a reduction in fine lines and wrinkles after using a solution containing 2% PhytoCellTech Malus Domestica. The apples are rich in phytonutrients, proteins and long-living cells. Thanks to a novel technology, plant stem cells are obtained and incorporated into skin care products to enhance the longevity of skin cells [118].

Mibelle Biochemistry's subsequently implemented raw materials include extracts from argan tree stem cells (PhytoCellTec™ Argan) that delay the depletion of dermal stem cells. Moreover, the company's offer includes the Alpine rose stem cells (PhytoCellTec Alp Rose) that protect the skin against oxidative stress induced by UV radiation and increase the vitality of skin cells; comfrey stem cells, (PhytoCellTec Symphytum) that improve the regeneration and renewal of epidermal stem cells; stem cells from grapes (PhytoCellTec Solar Vitis) that protect epidermal stem cells against UV radiation [119].

Stem cell extracts are used as cosmetic raw material. The offer of ACT Co, whose exclusive distributor in Poland is Alfa Sagittarius company, includes stem cell extracts of: grapes (Acostem Grape) and green tea (Acostem Green Tea) with antioxidant activity, hydroponic ginseng (Acostem H-Panax Ginseng) improving skin elasticity, Korean ginseng (Acost EKG) with anti-wrinkle effect, paper mulberry bark (Acostem paper Mulberry) and Siebold magnolia (Acostem MagnolSi) with brightening and whitening effect on the skin [121].

Sederma company also has plant stem cells, recommended as raw materials for anti--aging and anti-pollution cosmetics, in their portfolio (including stem cells from Edelweiss or sea holly) [122].

Nowadays, plant stem cells are being increasingly added to the emulsion cosmetics for mature skin care: creams, masks, highly concentrated serums, and as a base for specialist treatments. They are completely safe for the skin and do not cause side effects. Their efficacy has been confirmed in both in vitro and in vivo tests.

4.2.5.3. SELECTED FORMULATIONS OF ANTI-AGING COSMETICS

Tables 32 to 36 show examples of anti-aging formulations.

Table 32

Formulation of Anti Aging Light Day Cream [98]

Phase	INCI	Wt (%)
A	Aqua	56.30
	Glycerin	3.00
	Sodium Phytate, Aqua	0.10
	Caprylyl Glycol, Glycerin, Glyceryl Caprylate, Phenylpropanol	0.80
A1	Sodium Polyacrylate	0.20
	Xanthan Gum	0.30
B	Glyceryl Stearate Citrate, Cetearyl Alcohol, Glyceryl Caprylate	5.00
	Butyrospermum Parkii	2.50
	Squalane	5.00
	Isoamyl Laurate	8.00
	Cyclopentasiloxane, Cyclohexasiloxane	3.00
	Dimethicone	1.00
	Diethylamino Hydroxybenzoyl Hexyl Benzoate	2.80
	Ethylhexyl Methoxycinnamate	5.20
	Tocopheryl Acetate, Helianthus Annuus (Sunflower) Seed Oil	0.50
C	Water, Glycerin, Linum Usitatissimum Seed Extract	4.00
	Water, Cyathea Medullaris Leaf Extract	2.00
D	Parfum	0.30
	Sodium Hydroxide	q.s.

Manufacturing Procedure:

1. Heat Phase A up to 78°C and disperse ingrediens of A1.
2. Heat phase B up to 78°C.
3. Emulsify phase B into phase A under stirring. Homogenize for 1–2 min. using a high shear homogenizer.
4. Start to cool down under medium stirring.
5. Add C and D below 40°C and cool down under stirring. Adjust pH value if necessary.

Linum usitatissimum (linseed) seed extract used as an actives in the formulation above-mentioned offers anti-inflammatory, antiacne, antiwrinkle, antioxidant, emollient, healing, stimulates cellular growth and moisturizing properties. Flaxseed is very rich in unsaturated fatty acids, mainly in alpha-linolenic acid [123]. Moreover, it is a rich source of valuable protein, soluble fibre, lecithin, lignans and minerals [124, 125]. The other ingredients Cyathea medullaris (black tree fern) extract is the rich source of polysaccharides [126] therefore offers anti-inflammatory and moisturizing properties [127].

Table 33

A moisturizing natural anti-aging lotion with plant extracts [100]

Phase	INCI names of the compounds	Wt (%)
A	Chrondus Crispus (Carrageenan)	0.8
	Xanthan Gum	0.4
	Glycerin	5.0
	Aloe Barbadensis Leaf Juice	0.2
B	Water	q.s.
	Cetyl Alcohol	7.0
	Butyrospermum Parkii (Shea Butter)	1.0
	Dicaprylyl Ether	3.0
	Olea Europaea (Olive) Fruit Oil	3.0
	Tocopherol	0.1
D	Carthamus Tinctorius (Safflower) Oleosomes + Water	5.0
E	Preservative	q.s.
	Hydrolyzed Corn Protein + Glycerin + Water	1.0
	Citrullus Vulgaris (Watermelon) Fruit Extract + Pyrus Malus (Apple) Fruit Extract + Lens Esculenta (Lentil) Fruit Extract + Sodium Lactate + Sodium PCA + Glycerin + Water	3.0
	Hydrolyzed Soybean Fiber + Water	2.0
	Parfum	0.2
	Citric Acid	q.s.

Manufacturing procedure:

1. Mix together Phase A and add under strong agitation into Phase B. Mix 30 minutes.
2. Heat to 55 to 60°C.
3. Weight together Phase C and heat 55 to 60°C.
4. Add Phase C to Phase AB and homogenize 10 minutes at 4000 rpm.
5. Add Phase D and homogenize at 2000 rpm for 10 minutes while maintaining the temperate at 55–60°C.
6. Cool down using side scraper for mixing.
7. At 45°C add phase E mixing well between each addition.
8. Adjust the pH between 5.5–6.0. Continue cooling.

Butyrospermum Parkii Butter used as an active ingredient in the formulation above-mentioned is the fat obtained from the nuts of the African Shea Tree. The fat is primarily comprised of triglycerides of saturated and unsaturated fatty acids. It is typical fatty acid profile consists of palmitic acid, stearic acid, oleic acid, linoleic acid, eicosanoic acid, eicosenoic acid. The most interesting part is its unsaponifiable fraction, containg vitamins A, E, phytosterols, phospholipids and triterpene alcohols, (alpha-amyrin, beta-amyrin, lupeol and butyrospermol), most of which present as acetate or cinnamyl ester. Used in anti-aging cosmetics it acts as a skin moisturizing, conditioning and regenerating agent. It helps retain moisture and lessen the loss of water by forming a barrier on the skin's surface. Moreover, the fat works to reduce the appearance of rough patches and dry flakes on the skin. Additionally shea butter absorbs some UV light and imparts anti-inflammatory actions [128].

Aloe Barbadensis Leaf Juice can soothe skin and serve as an anti-inflammatory. It can be efficiently used topically, because of its burn healing effects, scar reducing and wounds healing properties. Aloe contains aloin, which can protect the skin from ultraviolet rays

Table 34

A moisturizing natural anti-aging lotion with effective anti-aging Tetrapeptide-21 [100]

Phase	INCI name of componds	Wt (%)
A	Polyglyceryl-3 Methylglucose Distearate	3.00
	Glyceryl Stearate	2.00
	Stearyl Alcohol	1.00
	Caprylic/Capric Triglyceride	9.50
	C_{12-15} Alkyl Benzoate	9.50
B	Tetrapeptide-21 (and) Glycerin (and) Butylene Glycol (and) Water	3.00
	Glycerin	3.00
	Water	69.00
C	Preservative	q.s.
	Parfum	q.s.

Procedure:

1. Separately, combine A and B and heat to 70–75°C.
2. Add A to B with stirring and homogenize.
3. Cool with gentle stirring.
4. Note: If A has to be charged into the vessel first, B must be added without stirring.

damage. The extract is a reach source of number of vitamins, including A, B1, B2, B3, B5, B6, B12, C, E, choline and Folic Acid. These vitamins are great for protecting the skin from free radicals, rejuvenate aged tissues and promote healthy skin.

Citrullus Vulgaris (Watermelon) Fruit Extract is rich in moisturizing complex, (i.e. proteins, lipids, carbohydrate), mineral salts and antioxidants (vitamin C and E, citrulline and licopene), keeping skin hydrated, soft and supple [129].

Esculenta (Lentil) Fruit Extract contains vitamin B5, trisaccharides and phenolic compounds it moisturizes a skin and help increases it intracellular hydration, reducing the look of fine lines and wrinkles, works as an antiradical scavering agent [130].

Table 35

Anti-aging O/W emulsion with Magnolia Siebolda Callus Culture Extract

Phase	INCI name of componds	Wt (%)
A	Aqua	10
	Glycerin	3
	Xantam Gum	0.20
A1	Aqua	up to 100
	Sorbitan Stearate (and) Sucrose Cocoate	2.50
	Sodium Levulinate, Sodium Anisate	0.50
	Sodium Benzoate	0.50
	Citric Acid	q.s.
B	Glyceryl Stearate (and) Polyglyceryl-6 Palmitate/Succinate (and) Cetearyl Alcohol	4.50
	Oeonthera Biennis (Evening Primrose) Seed Oil	10.0
	Isopropyl Myristate	5.00
	Tocopherol	0.60
C	Magnolia Sieboldii Callus Culture Extract, Butylene Glycol, Phenoxyethanol, Ethylhexylglycerin	2.00

Manufacturing procedure:

1. Disperse Xantam Gum in Glycerin and next add the water (phase A1).
2. Add phase A to A1.
3. Heat Phase A+A1 up to 70°C.
4. Heat phase B up to 70°C.
5. Add under strong agitation Phase B into Phase A. Mix together 30 minutes.
6. Cool down, at 50°C add Phase C to Phase AB and homogenize 10 minutes at 4000 rpm.
7. Adjust the pH between 5.5–6.0. Continue cooling.

Tetrapeptide-21 mentioned above in the formulation of anti-aging lotion (Table 34) is an example of new active substances currently applied in cosmetic products. In cosmeceuticals the bioactive peptides are used for collagen stimulation, wound healing, "Botox-like" wrinkle smoothing, as well as antioxidative, antimicrobial and whitening effects. They are classified as signal peptides, carrier peptides, neurotransmitter inhibitor peptides, and enzyme inhibitor peptides [131–134], Tetrapeptide-21 is a cell communicating (signal) peptide is a type of synthetic peptide compound which combines several chains of amino acids. Its amino acid sequence is glycine-glutamic acid-lysine-glycine (Gly-Glu-Lys-Gly). This peptide demonstrated in in vitro studies, an increase of collagen (Type I) production on the protein level and mRNA level and hyaluronic acid synthase, which lead to an increased elasticity and a decreased volume of wrinkles and fine lines [135].

Magnolia Sieboldii Callus Culture Extract contains sesquiterpene lactones, has unique features that help in the treatment of inflammation and hyperpigmentation caused by inflammation, shows excellent anti-oxidizing and antibacterial properties [136].

Table 36

Anti-aging O/W emulsion with Elderberry flower extract [137]

Phase	INCI name of componds	Wt (%)
A	Aqua	up to 100
	Xantam gum	0.20
	Sorbitan Stearate (and) Sucrose Cocoate	2.50
	Levulic Acid	0.80
	Sodium Benzoate	0.50
	Glycerin	3.0
	Elderberry Flower Extract	8.0
B	Glyceryl Stearate (and) Polyglyceryl-6 Palmitate/Succinate (and) Cetearyl Alcohol	5.0
	Linum Usitatissimum (Linseed) Seed Oil	10.0
	Ribes Nigrum (Black Currant) Seed Oil (SC-CO_2)	10.0
	Isoamyl Laurate	5.00
	Ascorbyl Palmitate	0.10
	Tocopherol Acetate	0.10
	Phenylethyl Alcohol	0.3
	Elderberry Flower SC-CO_2 Extract	0.3

Manufacturing procedure:

1. Disperse Xantam Gum in Glycerin and next add the water and the rest of ingredints of phase A.
2. Heat up to 60°C and mix together Phase A.
3. Heat up to 60°C and mix together Phase B.
4. Add under agitation phase B into Phase A. Mix 30 minutes, at T = 60°C.
5. Cool down and homogenize 10 minutes at 4000 rpm.
6. Continue cooling.

Elderberry inflorescence is rich source of glycosides, di and triterpenes, phenolic compounds, flavonoids, tannins and coumarins. Moreover, it contains essential oil and sixteen of amino acids, including exogenous amino acids such as: valine, threonine, methionine, isoleucine, leucine, lysine, histidine, and phenylalanine. The elderberry extract, due to the composition, shows antioxidant activity, by deactivating free radicals, it effectively inhibits skin aging processes [138].

4.2.5.4. EMULSIONS AS A FORM OF HAIR-CARE PRODUCTS

Shampoos, as products for cleansing and care of skin and hairs, are most often produced in the liquid form of a clear solution or emulsions. They usually contain 40–80% water and primary and secondary surfactants. The shampoo formulations contain also other ingredients such as: foam stabilizers and boosters, thickeners, conditioning agents, preservatives, pH regulators, colours and perfumes.

Today, more than ever, cosmetic industry is focused on the high quality and safety products, containing multifunctional ingredients, fulfilling several requirements in a single product. In the case of washing products apart from good cleansing and foaming properties, non-irritant to eyes, mucous membrane and skin, also moisturizing action is required. Commonly used in personal-care products, alkyl and/or alkylether sulfates, as main surfactants, increase cleansing performance and exhibit good foaming properties but could damage the skin by removing skin lipids, resulting in transepidermal water. In order to minimize such the side effects mild surfactants and emollients are added to shower/both products [139,140]. Frequently as moisturizing agents vegetable oils are used [76].

Formulation of cleansing cosmetics in form of O/W microemulsion is presented in table 37.

Strawberry seeds oil, used in the formulation mentioned above, was obtained by supercritical CO_2 extraction. *Fragaria ananassa l.* seeds oil contained triglycerides of linoleic and linolenic acid, tocopherols, phytosterols, antioxidants, when is added to the cleansing products formulation it showed a moisturizing effect [141].

Table 38 shows formulation of shampoo dedicated for weak or damaged hair also containing the strawberry seeds oil. The formulation is based only on mild surfactants, (BASF products), eco-friendly alternative to sulphate-based surfactants.

Table 37

Moisturizing shampoo in a form of O/W microemulsion [141]

INCI name of componds	Wt (%)
Sodium Cocoamphoacetate	17
Disodium Laureth Sulfosuccinate	10
Sodium Lauryl Sulphate	3
Cocoamide DEA	2
Cocoamidopropyl Betaine	5
Glycerin	2
Sodium Benzoate	0.5
Cytric Acid	q.s.
Sodium Chloride	q.s.
SC-CO_2 Strawberry Seeds Extract	1
Water	up to 100

Manufacturing procedure:

1. First SC-CO_2 strawberry seeds oil mix with glycerin and liquid surfactants, at room temperature, using the magnetic stirrer, at rotation rate = 250 rpm.
2. Parallel, Sodium Lauryl Sulphate and Sodium Benzoate dissolve in water by mixing at 50°C.
3. Next, to the mixture of the oil, glycerin and surfactants, step by step, add the water solution of SLS and Sodium Benzoate, cool to 25°C.
4. Next adjust the pH of the mixture up to 5.5 with addition of Citric Acid.
5. The product viscosity regulate to the desired value with Sodium Chloride.

Table 38

Shampoo for weak or damaged hair [142]

Phase	INCI name of compounds	Wt (%)
A	Water	up to 100
B	Sodium Cocoamphoacetate, Glycerin, Lauryl Glucoside, Sodium Cocoyl Glutamate, Sodium Lauryl Glucose Carboxylate	40.0
	Glycol Distearate (and) Laureth-4 (and) Cocamidopropyl Betaine	1.0
	Coco-Glucoside (and) Glyceryl Oleate	2.0
C	SC-CO_2 Strawberry Seeds Extract	1.0
E	Sodium Benzoate	0.5

F	Citric Acid	q.s.
G	Parfum	q.s.

Manufacturing procedure:

1. Add the extract (C) to the mixture of surfactants (phase B) and stir at room temperature until a homogeneous mixture will obtained.
2. Next, sodium benzoate dissolve in water and the obtained solution add, step by step, under stirring, to the mixture (B + C).
3. Adjust the pH of the mixture up to 5.0 with addition of citric acid.

Washing hair with even the most delicate surfactants can lead to their degreasing by washing out the lipid film covering the surface of the hair. In the case of undamaged hair, washing, even with delicate detergents, causes difficult combing and accumulation of electrostatic charges. To prevent this, conditioning substances are introduced into shampoos. The following are used for this purpose: protein hydrolysates, lipids, silicones, derivatives of tertiary ammonium salts (quats) or quaternized natural and synthetic polymers. The conditioning effect could be achieved by two methods. The first is related to the introduction of conditioning compounds into shampoos (Table 37, 38). The second method is to wash the hair with shampoo and then apply a conditioner in the form of a rinse emulsion. An example of conditioner formulation in emulsion form is presented in Table 39.

Table 39

Formulation of hair conditioner [143]

No.	INCI name of compounds	Wt (%)
1	Water	86
2	Dicetyl Dimonium Chloride	7
3	Myristyl Stearate	1.5
4	Amodimethicone (and) Trideceth-12 (and) Cetrimonium Chloride	3.0
5	Cetyl Trimethyl Ammonium Chloride	0.5
6	Hydroxypropyltrimonium Hydrolyzed Rice Protein (and) Oryza Sativa (Rice) Extract	1
7	Cranberry Seed Oil	0.3
8	Diazolidinyl Urea, Methyl Paraben, Propyl Paraben, Propylene Glycol	0.5
9	Fragrance	0.2

Manufacturing procedure:

1. Heat water (1) to 70–75°C.
2. Add in dicetyl dimonium chloride (2) and mix until uniform.
3. Add in myristyl stearate (3) and mix until uniform.
4. Add in the component no 4 and mix until uniform.
5. Add in the the component no 5 and mix until uniform.
6. Cool batch to 50–55°C and add in the the component no 8.
7. Cool batch to 45–50°C and add in the cranberry seed oil (7) and fragrance.

Cationic surfactants such as cetrimonium chloride or amodimethicone have a positive charge on their head group. The composition of the molecules can vary, but is typically a fatty, acid-derived, hydrophobic tail with a nitrogen-containing head group. The nitrogen-containing group can be either a tertiary or quaternary amine. Typically these surfactants are either alkyl amine salts or alkyl quaternary ammonium salts. The substances improve the ease of wet and dry combing, leaving a soft, silky feel for hair and a smooth, velvety feel for skin [3, 6].

5. REGULATIONS ASSOCIATED WITH COSMETIC PRODUCT MARKETING

5.1. ASSESSMENT OF THE COSMETIC PRODUCT SAFETY

In accordance with Regulation (EC) No. 1223/2009 of the European Parliament and of the Council of 30 November 2009, Chapter II "Safety, Responsibility, Free Movement", Article 3 "Safety" – "(…) A cosmetic product made available on the market shall be safe for human health when used under normal or reasonably foreseeable conditions of use, taking account, in particular, of the following: presentation including conformity with Directive 87/357/EEC [144], labelling, instructions for use and disposal, any other indication or information provided by the responsible person defined in Article 4 (…)" [1]. The production of cosmetic products should take place in accordance with Good Manufacturing Practice (GMP) and the production process is deemed to comply with good manufacturing practice if it complies with the relevant harmonized standards [145].

The quality assessment of the final product includes:

- study of physicochemical properties (including stability),
- microbiological testing,
- dermatological testing,
- sensory testing: ease of application and spreading, sensations after the cosmetic product application (no greasiness, stickiness, good absorption, smoothness, softening of the skin),
- final safety assessment.

Physicochemical examinations of cosmetic emulsions (care products) include:

- organoleptic assessment (appearance, colour, smell and consistency),
- pH determination both directly in the preparation and in water extract,
- determination of the emulsion type,
- determination of viscosity,
- determination of density,
- determination of physical stability.

Microbiological tests are carried out in accordance with the "Criteria for chemical and microbiological purity of cosmetics" [88, 89]. The quantity of aerobic microorganisms must not exceed 1000 cfu/g (cfu – colony forming units). A separate group are cosmetics used around the eyes and cosmetics for children, where the number of aerobic bacteria must not exceed 100 cfu/g. Moreover, cosmetic preparations must not contain any *Esherichia coli* bacteria or other coliforms, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Clostridium* anaerobic bacilli in 0.1 g of the product.

In order to confirm the resistance of cosmetics to microbial infection during use (confirmation of the right choice of substance that protects the cosmetic against microbiological instability) there is an obligation to perform "load tests" (maintenance tests), which are executed in accordance with PN-EN ISO 29621:2011 [88] or PN-EN ISO 11930:2012 [89]. The test consists in a controlled, single contamination of the product samples with selected test strains (calibrated inoculum), and then following the number of microorganisms at fixed time intervals (48 h, 7, 14, 28 days) and at a set temperature. The following microorganisms are used as test strains: *Pseudomonas aeruginosa*, *Staphylococcus aureus, Escherichia coli, Candida albicans, Aspergillus brasiliensis.* In accordance with the PN-EN ISO 29621:2011 standard, in terms of susceptibility to infection, cosmetics are divided into three groups: low, medium and high susceptibility to infection. Cosmetic emulsions are found in the group with high susceptibility to infection.

In order to assess the impact of a cosmetic product on the skin regarding its irritating or sensitizing properties, dermatological tests are conducted (so-called compliance tests). According to the current regulations [1], the cosmetic raw materials and cosmetic products cannot be test on animals, therefore alternative (*in vitro*) tests are used, including:

- BCOP test – Bovine Cornea Opacity & Permeability Test,
- RBCT test – Red Blood Cell Test,
- HET-CAM test or tests on reconstructed human skin or porcine skin.

Complementary research is performed on volunteers under the supervision of a dermatologist:

- test with single use of flakes,
- test with repeated use of flakes,
- test with intermittent exposure,
- test with continuous exposure.

The Safety Assessor is responsible for the evaluation of the safety of each product placed on the market, as well as for preparing a cosmetic product safety report in accordance with Appendix I to Regulation 1223/2009/EC [1]. This person should be a graduate of theoretical and practical university studies in pharmacy, toxicology, medicine or other similar field (e.g. chemistry) or a course recognized by the Member State as equivalent. The safety report is part of the cosmetic product documentation that consists of parts A and B, in which the following information is provided:

I.1. Intended use of the product
I.2. Qualitative and quantitative composition of the cosmetic product

PART A.
A.1. INFORMATION ABOUT THE PRODUCT COMPONENTS
A.1.1. Physicochemical properties of the raw materials
A.1.2. Microbiological purity of the raw materials
A.1.3.1. Toxicological properties of the commercial raw materials
A.1.3.2. Toxicological properties of the products according to INCI names
A.2. THE FINISHED PRODUCT
A.2.1. Qualitative and quantitative composition of the cosmetic product
A.2.2. Physical/chemical properties
A.2.3. Microbiological quality of the product
A.2.4. Stability of the cosmetic product
A.2.5. Impurities, trace amounts, excipients
A.2.6. Packaging
A.2.7. Normal and predictable usage
A.2.8. Exposure to the cosmetic product activity
A.2.9. The available toxicological data for the product
A.2.10. Adverse effects and serious adverse effects
A.2.11. Other

PART B. COSMETIC PRODUCT SAFETY REPORT
B.1. Conclusion of assessment, summary of physicochemical, microbiological and toxicological component properties
B.2. Systems Exposure Division (SED) and Margin of Safety (MOS)
B.3. Statement regarding cosmetic product safety in connection with Art. 3.
B.4. Reasoning
B.5. Warnings and instructions for use placed on the label

5.2. COSMETIC PRODUCT REGISTRATION

From January 11, 2012, according to the legislation in force, namely Article 13 of Regulation 1223/2009 [1], before placing on the market, each cosmetic preparation must be registered on-line in the Cosmetic Product Notification Portal (CPNP). It is an electronic system for reporting information about a cosmetic product that is marketed or made available on the European market. To report a product in CPNP, simply log in and provide basic product information (name, frame formulation, photos). Nevertheless, the product notification must be followed by the preparation of the cosmetic product dossier, that is, full documentation in accordance with Regulation 1223/2009, including safety report in accordance with Appendix I. Before you submit a product to the CPNP, you must prepare the necessary documents required for reporting [146]. These are:

- information about the packaging,
- safety report conforming with Appendix I to Regulation 1223/2009,
- MOS calculation,
- label content,
- pictures of the finished product.

5.3. LABELLING OF THE COSMETIC PRODUCT

Article 19 of Regulation 1223/2009 [1] sets out requirements for the labelling of a cosmetic product. The manufacturer of cosmetics is obliged to place the following information on each unit package:

- the trade name of the cosmetic product,
- the name and address of the manufacturer, the country in which the cosmetic product has been made,
- the volume of the cosmetic product in the package, in millilitres or grams, excluding packaging containing less than 5 grams or millilitres as well as free samples and single-use packaging,
- shelf life (expiration date) and if the minimum shelf life of the cosmetic is more than 30 months, the use-by date after opening the cosmetic product (in this case the packaging should be marked with the graphic sign PAO (Period After Opening), (Fig. 40a),
- special warnings regarding the use of cosmetics, present mainly on the packaging of preparations containing potent ingredients that, in the event of improper use, could pose a threat – e.g. exerting severe irritant effect,
- batch number allowing identification of the cosmetic product,
- information about the effect of the cosmetic product,
- list of ingredients in accordance with the International Nomenclature of Cosmetic Ingredients (INCI), given in descending order according to the ingredient's percentage in the cosmetic product, with components below 1% listed at the end of the list, in any

order; the colour numbers are preceded by the C.I. (Colour Index) abbreviation and the name of the fragrance composition.

If, because of the size or shape of the packaging, it is not possible to place all the above information on the packaging, they can be provided in the attached leaflet, which is indicated by a graphic symbol (Fig. 40b).

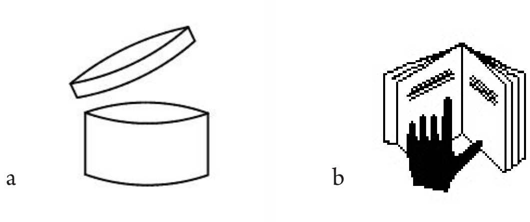


Fig. 40. Graphic signs placed on cosmetic product packaging

In addition to the PAO sign and a sign informing about the inclusion of the required information in the attached leaflet, we can also find other graphic signs on the packaging of cosmetic products. The “e” sign placed next to the weight of the cosmetic product stated on the package means the manufacturer’s guarantee that the packaging process is carried out under strict quality control. Indication of the type of packaging material used (LDPE, HDPE, PP). “Green point” – a sign informing about the manufacturer’s obligation to recycle packaging or a sign indicating that the packaging should go to the waste bin.

REFERENCES

[1] http://eur-lex.europa.eu/legal-content/PL/ALL/?uri=CELEX%3A32009R1223, online access 30.11.2017.

[2] Malinka W., *Zarys Chemii Kosmetycznej*, Volumed, Wrocław 1999.

[3] Williams D.F., Schmitt W.H., *Chemistry and Technology of the Cosmetics and Toiletries Industry*, Blackie Academic & Professional, Glasgow 1996.

[4] Draelos Z.D., *Kosmeceutyki*, Urban & Partner, Wrocław 2007.

[5] Molski M., *Chemia piękna*, PWN, Kraków 2009.

[6] Sikora E., Olszańska M., Ogonowski J., *Chemia i technologia kosmetyków*, Wydawnictwo PK, Kraków 2012.

[7] Becher P., *Emulsion. Theory and practice*, Reinold Publ. Corp, New York 1965.

[8] Gilewicz J., *Emulsje*, PWN, Warszawa 1957.

[9] Becher P., *Encyclopedia of Emulsion Technology*, Vol. 2, *Applications*, Dekker, New York 1985.

[10] Becher P., *Encyclopedia of Emulsion Technology*, Vol. 3, *Basic Theory, Measurement and Applications*, Dekker, New York 1988.

[11] Schramm L.L, *Emulsions: Fundamentals and Applications in the Petroleum Industry*, Am. Chem. Soc., Washington, D.C. 1992.

[12] McClements D.J., *Food Emulsions: Principles, Practice and Techniques*, CRC Press, Boca Raton 1999.

[13] Hunter R.J., *Introduction to Modern Colloid Science*, Oxford Univ. Press, Oxford 1993.

[14] Zieliński R., *Surfaktanty. Budowa, właściwości, zastosowania*, Wydawnictwo Uniwersytetu Ekonomicznego w Poznaniu, Poznań 2013.

[15] Pickering S.U., *Pickering Emulsion*, J. Chem. Soc., Trans., Vol. 91, 1907, 2001–2021.

[16] Bouchemal K., Briançon S., Perrier E., Fessi H., *Nano-emulsion formulation using spontaneous emulsification: solvent, oil and surfactant optimisation*, Int. J. Pharm, Vol. 280, 2004, 241–251.

[17] Jaworska M., Sikora E., Ogonowski J., *Nanoemulsje – charakterystyka i metody otrzymywania*, Przemysł Chemiczny, Vol. 93(7), 2014, 1000–1005.

[18] Tirnaksiz F., Akkus S., Celebi N., *Nanoemulsions as drug delivery system*, in: *Colloids in drug delivery*, Dekker, New York 2005.

[19] Solans C., Izquierdo P., Nolla J., Azemar N., Garcia-Celma M.J., *Nano-emulsions*, Curr. Opin. Colloid Interface Sci., Vol. 10, 2005, 102–110.

[20] Sadurní N., Solans C., Azemar N., Garcia-Celma M.J., *Studies on the formation of O/W nano-emulsions, by low-energy emulsification methods, suitable for pharmaceutical applications*, Eur. J. Pharm. Sci., Vol. 26, 2005, 438–435.

[21] Maestro A., Solè I., González C., Solans C., Gutiérrez J., *Influence of the phase behavior on the properties of ionic nanoemulsions prepared by the phase inversion composition method*, J. Coll. Int. Sci., Vol. 327, 2008, 433–439.

[22] Sonneville-Aubrun O., Simonnet J.T., L'Alloret F., *Nanoemulsions: a new vehicle for skincare products*, Adv. Colloid Interface Sci., Vol. 108, 2004, 145–149.

[23] Tadros T.F., Vincent B., *Encyclopedia of Emulsion Technology*, Vol. 1., P. Becher (ed), Dekker, New York 1983.

[24] Walstra P., *Encyclopedia of Emulsion Technology*, Vol. 1., P. Becher (ed), Dekker, New York 1983.

[25] Walstra P., Smolders P.E.A., *Modern Aspects of Emulsions*, B.P. Binks (ed), The Royal Society of Chemistry, Cambridge1998.

[26] Griffin W.C., *Calculation of HLB Values of Non-Ionic Surfactants*, J. Soc. Cosmetic Chem., Vol. 5(4), 1954, 249–256.

[27] Krugliakov P.M., *Hydrophile – Lipophile Balance of Surfactants and Solid Particles. Physicochemical Aspects and Applications*, Elsevier, Amsterdam 2000.

[28] Henning Wenk H., Kottke U., Ponder J.B., *Polyglycerol esters and their use*, Patent US 8227399B2, 24 July 2012.

[29] Davis J.T., *A quantitative kinetic theory of emulsion type. I. Physical chemistry of the emulsifying agent*, Proceedings of 2nd International Congress on Surface Activity, Vol. 1, 1957, 426–438.

[30] AKZO Nobel Surface Chemistry LLC, *HLB & emulsification. Description of hydrophil lipophil balance and use of HLB in producing emulsion*, 2011, za: Zieliński R., *Surfaktanty, budowa, właściwości, zastosowania*, Uniwersytet Ekonomiczny w Poznaniu, Poznań 2013.

[31] Badwan A.A., Cham T.M., James K.C., Pugh W.J., *A relationship between foaming and HLB value*, Int. J. Cosmetic Sci., Vol. 2, 1980, 45–51.

[32] Ross S., Chun E.S., Becher P., Ranauto J.J., *Spreading coefficient and hydrophile-lipophile balance of aqueous solutions of emulsifying agents*, J. Phys. Chem, Vol. 63, 1959, 1681–1684.

[33] Hayes M.E., El-Emary M., Schechter R.S., Wade W.H., *The relation between the EACNmin concept and surfactant HLB*, J. Colloid Interface Sci., Vol. 68, 1979, 591–592.

[34] Lin I.J., Friend J.P., Zimmels Y., J., *The effect of structural modifications on the hydrophile–lipophile balance of ionic surfactants*, Colloid Interface Sci., Vol. 45, 1973, 378–385.

[35] Shinoda K., Sagitani H., *Emulsifier selection in water/oil type emulsions by the hydrophile–lipophile balance–temperature system*, J. Colloid Interface Sci., Vol. 64, 1978, 68–71.

[36] Marszall L., *Cloud point and emulsion inversion point in the presence of additives*, J. Colloid Interface Sci., Vol. 59, 1977, 376–377.

[37] Rabaron A., Cavé G., Puisieux F.,Seiller M., *Physical methods for measurement of the HLB of ether and ester non-ionic surface-active agents: H-NMR and dielectric constant*, Int. J. Pharm., Vol. 99, 1993, 29–36.

[38] Broniarz J., Szymanowski J., Wiśniewski M., *Wyznaczanie i zastosowanie równowagi hydrofilno – lipofilnej związków powierzchniowoczynnych*, Przem. Chem., Vol. 51, 1972, 517–519.

[39] Vaughan C.D., Rice D.A., *Predicting O/W Emulsion Stability by the Required HLB Equation*, J. Dispersion Sci. Technol., Vol. 11(1), 1990, 83–91.

[40] Croda Personal Care Product Guide, Croda Europe Ltd, www.croda.com/europe/pc.

[41] Tadros F., *Applied Surfactants: Principles and Application*, Wiley-VCH, Weinheim 2005.

[42] Wang L., Dong J., Chen J., Eastoe J., Li X., *Design and optimization of a new self-nanoemulsifying drug delivery system*, J. Colloid Interface Sci., Vol. 330, 2009, 443–448.

[43] http://www.formulaction.com/en/products-and-technologies/product-range/turbiscan-lab, online access 19.03.2018.

[44] http://www.ailusi-e.com/ave-b-hydralic-lifting-vacuum-emulsifying-mixer.html, online access 19.03.2018.

[45] Le Révérend B.J.D., Taylor M.S., Norton I.T., *Design and application of water-in-oil emulsions for use in lipstick formulations*, Int. J. Cosmetic Sci., Vol. 33, 2011, 263–268.

[46] Beri A., Norton J.E., Norton I.T., *Effect of emulsifier type and concentration, aqueous phase volume and wax ratio on physical, material and mechanical properties of water in oil lipsticks*, Int. J. Cosmetic Sci. Vol. 35, 2013, 613–621.

[47] Haj-shafiei S., Ghosh S., Rousseau D., *Kinetic stability and rheology of wax-stabilized water-in-oil emulsions at different water cuts*, J. Coll. Interface Sci., Vol. 410, 2013, 11–20.

[48] Park Ch.I., Cho W.-G., Lee S.J., *Emulsion stability of cosmetic creams based on water--in-oil high internal phase emulsions*, Korea-Aust Rheol J., Vol.15 (3), 2003, 125–130.

[49] Chanamai R., Horn G., McClements D.J., *Influence of oil polarity on droplet growth in oil-in-water emulsions stabilized by a weakly adsorbing biopolymer or a nonionic surfactant.*, J Coll. Interface Sci., Vol. 1, 2002, 167–176.

[50] Márquez Medrano A.L., Panizzolo L.A., Wagner J.R., *Effect of calcium salts and surfactant concentration on the stability of water-in-oil (w/o) emulsions prepared with polyglycerol polyricinoleate*, J. Coll. Interface Sci., Vol. 341, 2010, 101–108.

[51] Silva T.M., Cerize N.N.P., Oliveira A.M., *The Effect of High Shear Homogenization on Physical Stability of Emulsions*, Inter. J. Chem., Vol. 8 (4), 2016, 52–61.

[52] Roland I., Piel G., Delattre L., Evrard B., *Systematic characterization of oil-in-water emulsions for formulation design*, Inter. J. of Pharma., Vol. 263, 2003, 85–94.

[53] Ghosh S., Pradhan M., Patel T., Haj-shafiei S., Rousseau D., *Long-term stability of crystal-stabilized water-in-oil emulsions*, J. Coll. Interface Sci., Vol. 460, 2015, 247–257.

[54] Majewski S., Arct J., Pytkowska K., *Kosmetyczne zastosowanie witamin A i E – pielęgnacja i suplementacja*, Wyższa Szkoła Zawodowa Kosmetyki i Pielęgnacji Zdrowia, Warszawa 2003.

[55] https://cosmos-standard.org/about, online access 19.03.2018.

[56] McIntyre, R.T., *Polyglycerol esters*, J. Am Oil Chem Soc., Vol. 56, 1979, 835A–840A.

[57] Natalie Duerr-Auster N., Gunde R. Windhab E.J., *Structure and Mechanical Properties of a Polyglycerol Ester at the Air–Water Surface*, Langmuir, Vol. 24(21), 2008, 12282–12289.

[58] Balzer D., Luders H., *Nonionic Surfactants. Alkyl Polyglucosides*, Dekker, New York 2000.

[59] Clark E.W., *Lanolin Book*, Ed. Paul Beiersdorf AG, Hamburg 1999.

[60] Salka B.A. *Emollients*, Cosmetics and Toiletries, Vol. 112, 1997, 101–106.

[61] Chao Ch. et al., *Emollients for cosmetic formulations: Towards relationships between physico-chemical properties and sensory perceptions*, Coll Surf. A, Vol. 536, 2018, 156–164.

[62] Douguet M. et al., *Spreading properties of cosmetic emollients: Use of synthetic skin surface to elucidate structural effect*, Coll Surf. B, Vol. 154, 2017, 307–314.

[63] Morrison D.S., Schmidt J., Paulli R., *The scope of mineral oil in personal care products and its role in cosmetic formulations*, J. Appl. Cosmetol., Vol. 14, 1996, 111–118.

[64] Rościszewski P., Zielecka M., *Silikony właściwości i zastosowanie*, WNT, Warszawa 2013.

[65] Hill R.M., *Silicone surfactants-new developments*, Curr Opin Colloid Interface Sci., Vol. 7, 2002, 255–261.

[66] van Hoed V., de Clercq N., Echim C., Andjelkovic M., Leber E., Dewettinck K., Verhé R., *Berry seeds: a source of specialty oils with high content of bioactives and nutritional value*, J. Food Lipids., Vol. 16, 2009, 33–49.

[67] Yang B., Ahotupa M., Määttä P., Kallio H., *Composition and antioxidative activities of supercritical CO2-extracted oils from seeds and soft parts of northern berries*, Food Res. Inter., Vol. 44, 2011, 2009–2017.

[68] Pieszka M., Migdał W., Gąsior R., Rudzińka M., Bederska-Łojewska D., Pieszka M., Szczurek M., *Native Oils from Apple, Blackcurrant, Raspberry, and Strawberry Seeds as a Source of Polyenoic Fatty Acids, Tocochromanols, and Phytosterols: A Health Implication*, J. Chem., 2015, doi.org/10.1155/2015/659541.

[69] Rój E., Dobrzyńska-Inger A., Kostrzewa D., Kołodziejczyk K., Sójka M., Król B., Miszczak A., Markowski J., *Extraction of berry seed oils with supercritical CO_2*, Przemysł Chemiczny, Vol. 88(12), 2009, 1325–1330.

[70] Rój E., *Supercritical CO_2 extraction and its application*, Polish Foundations of the Opportunities Industrialization Centers "OIC Poland", Lublin 2014.

[71] Michorczyk M., Ogonowski J., *Ekokosmetyki*, Wydawnictwo PK, Kraków 2016.

[72] Milala J. et al., *Changes of bioactive components in berry seed oils during supercritical CO_2 extraction*, J. Food Process Pres, 2017, DOI: 10.1111/jfpp.13368.

[73] Sikora E., Ogonowski J., Lulek P., *Use of supercritical CO_2 extracts from black currant and strawberry seeds in mild detergents*, Przemysł Chemiczny, Vol. 3, 2014, 339–342.

[74] Sikora E., Michorczyk P., Olszańska M., Ogonowski J., *Supercritical CO2 extract from strawberry seeds as a valuable, component of mild cleansing compositions*, Int J. Cosmet Sci., Vol. 37(6), 2015, 574–578.

[75] Warth A.H., *The Chemistry and Technology of Waxes*, Reinhold Publishing Corporation, New York 1960.

[76] Dweck A.C., *Formulating Natural Cosmetics*, Allured Publishing Corporation, Carol Stream 2011.

[77] Fields K., Falla T.J., Rodan K., Bush L., *Bioactive peptides: signaling the future*, J. Cosmet. Dermatol., Vol. 8, 2009, 8–13.

[78] Pai V.V., Bhandari P., Shukla P., *Topical peptides as cosmeceuticals*, Indian J. Dermatol. Venereol. Leprol., Vol. 83, 2017, 9–18.

[79] Schagen S.K., *Topical Peptide Treatments with Effective Anti-Aging Results*, Cosmetics, Vol. 4, 2017, 16–30.

[80] Morganti P. Ranadzzo S.D., Bruno C., *Alpha hydroxy acid in the cosmetic treatment of*

photo-induced skin aging, J. Appl. Cosmetol., Vol.14, 1996, 1–8.

[81] Morganti P., *Alpha hydroxy acid in the cosmetic dermatology*, J. Appl. Cosmetol., Vol. 14, 1996, 35–41.

[82] Arif T., *Salicylic acid as a peeling agent: a comprehensive review*, Clin. Cosmet. Investig. Dermatol., Vol. 8, 2015, 455–461.

[83] Taylor M.B., *Summary of mandelic acid for the improvement of skin conditions*, Cosmetic Dermatology, Vol. 6, 1999, 26–28.

[84] Pillai R. et al., *1,2-alkanediols for cosmetic preservation*, Cosmetics & Toiletries magazine, Vol. 123 (10), 2008, 53–61.

[85] Conference materials of Minasolve Company, https://minasolve.com/green-chemistry-company, online access 19.03.2018.

[86] Adaszyńska M., Swarcewicz M., *Essential oils as an active ingredients or preservativies in cosmetics*, Wiadomości Chemiczne, Vol. 66(1–2), 2012, 139–158.

[87] Sikora M., *Preservatives – necessity of use, traditional cosmetics, natural cosmetics*, Conference materials. Microbiological safety of cosmetic preparations. Modern preservatives, Warszawa 2011.

[88] PN-EN ISO 29621:2011, Cosmetics – Microbiology – Guidelines for risk assessment and identification of products with low microbial risk.

[89] PN-EN ISO 11930:2012, Cosmetics – Microbiology – Cosmetics – Microbiology – Evaluation of the antimicrobial protection of a cosmetic product.

[90] https://pl.fagron.com/pl, online access 25.03.2018.

[91] Pharmacopoeia Poland, Edition VI, Office for Registration of Medicinal Products, Warszawa 2003.

[92] https://www.ulprospector.com/en/eu/PersonalCare/Detail/1409/221368/NatraGem-EW, online access 25.03.2018.

[93] https://www.ulprospector.com/en/eu/PersonalCare/Detail/1409/120381/Versaflex-V-175, online access 25.03.2018.

[94] https://www.ulprospector.com/en/na/PersonalCare/Detail/134/204510/MixXIN-ME, online access 25.03.2018.

[95] https://www.ulprospector.com/en/na/PersonalCare/Detail/5303/739888/Olivatis-18, online access 25.03.2018.

[96] https://www.ulprospector.com/en/na/PersonalCare/Detail/5303/739384/Olivatis-12C, online access 25.03.2018.

[97] https://www.sinerga.it/en/raw-materials/products/emulsifiers/phytocream-2000, online access 25.03.2018.

[98] DrStraetmans – Company information materials, https://www.dr-straetmans.de/en/, online access 25.03.2018.

[99] Draelos Z.D., Pugliese P.T., *Skin physiology. Theory and practice*, MedPharm Polska, Wrocław 2014.

[100] Rhein L.D., Fluhr J.W., *Skin aging. Current therapeutic strategies*, MedPharm Polska, Wrocław 2013.

[101] https://www.personalcaremagazine.com/formulation-details/896/o-w-macadamia-milk-natural-cosmetic-cold-cold-process-1-97?companyid=2483, online access 30.03.2018.

[102] ProvitalGroup – Company information materials, https://www.provitalgroup.com/pl/products/skin-care/moisturizing/actives/hydromanil, online access 03.04.2018.

[103] Shaath N.A., *Sunscreens: Regulations and Commercial Development* third ed., CRC Press Inc., Boca Raton 2005.

[104] Draelos Z.D., *Cosmetic Dermatology: Product & Procedure*, Wiley-Blackwell, New York 2009.

[105] https://publications.europa.eu/en/publication-detail/-/publication/0ec06a83-a560-43bb-8607-f6690bdc06f7/language-en, online access 25.03.2018.

[106] Choquenet B., Couteau C., Paparis E., Coiffard LJ., *Foundations and self-tanning products: Do they provide any protection from the sun?*, J. Dermatol., Vol. 36, 2009, 587–591.

[107] Sikora E., Llinas M., Garcia-Celma M. J., Escribano E., Solans C., *Transdermal delivery of forskolin from emulsions differing in droplet size*, Colloids Surf., B., Vol. 126, 2015, 541–545.

[108] D'Orazio J.A. et al., *Topical drug rescue strategy and skin protection based on the role of Mc1r in UV-induced tanning*, Nature, Vol. 443, 2006, 340–344.

[109] Passeron T., Namiki T., Passeron H., Le Pape E., Hearing V.J., *Forskolin protects keratinocytes from ultraviolet (UV) B-induced apoptosis and increases DNA repair independent of its effects on melanogenesis*, J. Invest. Dermatol., Vol. 129, 2009, 162–166.

[110] Amaro-Ortiz A., Yan B., D'Orazio J.A., *Ultraviolet radiation, aging and the skin: prevention of damage by topical cAMP manipulation*, Molecules, Vol. 19, 2014, 6202–6212.

[111] Draelos Z.D., *Cosmeceuticals*, Urban & Partner, Warszawa 2007.

[112] Lamer-Zarawska E., Chwała C., Gwardys A., *Plants in cosmetics and anti-aging cosmetology*, PZWL, Warszawa 2012.

[113] Praca zbiorowa, *Antiaging: Physiology to Formulation*, Allured Publishing Corporation, Carol Stream 2006.

[114] Knott A. et al., *A novel treatment option for photoaged skin*, J. Cosmet. Dermatol., Vol. 7, 2008, 15–22.

[115] Baxter R.A., *Anti-aging properties of resveratrol: review and report of a potent new antioxidant skin care formulation*, J. Cosmet. Dermatol., Vol. 7, 2008, 2–7.

[116] Andersen O.M., Markham K.R., *Flavonoids: Chemistry, Biochemistry and Applications*, CRC Press, Taylor & Francis, Boca Raton 2006.

[117] Panche A.N., Diwan A.D., Chandra S.R., *Flavonoids: an overview*, J. Nutr. Sci., Vol. 5, 2016, 1–15.

[118] Trehan S. et al., *Plant stem cells in cosmetics: current trends and future directions*, Future Sci OA., Vol. 3(4), 2017, 226–231.

[119] Miastkowska M., Sikora E., *Anti-Aging Properties of Plant Stem Cell Extracts*, Cosmetics, Vol. 5(4), 2018, 55–61.

[120] Schmid D. et al., *Plant Stem Cell Extract for Longevity of Skin and Hair*, SOFW J., Vol. 134, 2008, 30–35.

[121] http://www.alfasagittarius.eu/substancje-aktywne-i-komorki-macierzyste, online access 04.04.2018.

[122] https://www.crodapersonalcare.com/en-gb/our-brands/sederma/irb-by-sederma, online access 04.04.2018.

[123] Hunter J.E., *ω-3 fatty acids from vegetable oils*, Am. J. Clin. Nutr., Vol. 51(5), 1990, 809–814.

[124] Bhatty R.S., Cherdkiatgumchai P., *Compositional analysis of laboratory-prepared and commercial samples of linseed meal and of hull isolated from flax*, J. Am. Oil Chem. Soc., Vol. 67, 1990, 79–84.

[125] Rubilar M. et al., *Functional ingredients from Flaxseed*, J. Soil Sci. Plant Nutr., Vol. 10(3), 2010, 373–377.

[126] Brooker S.G., Cambie R.C., Cooper R.C., *New Zealand medicinal plants*, Reed Publishing (NZ) Ltd., Auckland 1987.

[127] Tha Goh K.K., Matia-Merino L., Pinder D.N., Saavedra C., Singh H., *Molecular characteristics of a novel water-soluble polysaccharide from the New Zealand black tree fern (Cyathea medullaris)*, Food Hydrocolloids, Vol. 5, 2011, 286–292.

[128] Tomaszkiewicz-Potępa A. et al., *Shea butter (karite butter)*, Vol. III, *Application in the food, cosmetics and pharmaceutical industries*, Przemysł Chemiczny, Vol. 94(7), 2015, 69–73.

[129] https://www.centerchem.com/Products/DownloadFile.aspx?FileID=6943), online access 04.06.2018

[130] Zou Y., Chang S.K.C., Gu Y., Qian S.Y., *Antioxidant activity and phenolic compositions of lentil (Lens culinaris var. Morton) extract and its fractions*, J. Agric. Food Chem.,Vol. 59(6), 2011, 2268–2276.

[131] Fields K., Falla T.J., Rodan K., Bush L., *Bioactive peptides: Signaling the future*, J. Cosmet. Dermatol., Vol. 8, 2009, 8–13.

[132] Rahnamaeian M., Vilcinskas A., *Short antimicrobial peptides as cosmetic ingredients to deter dermatological pathogens*, Appl. Microbiol. Biotechnol., Vol. 99, 2015, 8847–8855.

[133] Gorouhi F., Maibach H., *Role of topical peptides in preventing or treating aged skin*, Int. J. Cosmet. Sci., Vol. 31, 2009, 327–345.

[134] Schagen S.K., *Topical Peptide Treatments with Effective, Anti-Aging Results*, Cosmetics, Vol. 4, 2017, 16–30.

[135] Farwick M., et al. *Bioactive tetrapeptide GEKG boosts extracellular matrix formation: In vitro and in vivo molecular and clinical proof*, Exp. Dermatol., Vol. 20, 2011, 602–604.

[136] Lee G.T. et al., *Cosmetic composition for skin whitening comprising the extract of Magnolia sieboldii as active ingredient*, Patent US8268295B2, 18 September 2012.

[137] Tabaszewska M., Sikora E., *Cosmetic formulation for skin care*, Patent PL224161B1, 30 November 2016.

[138] Śliwa K., Tomaszkiewicz-Potępa A., Sikora E., Ogonowski J., *Micelle-mediated extraction of elderberry blossom by whey protein and naturally derived surfactants*, Acta Biochim. Pol., Vol. 4, 2013, 803–809.

[139] Förster Th., Issberner U., Hensen H., *Lipid/Surfactant compounds as a new tool to optimize skin-care properties of personal-cleansing products*, J. Surf. Detergents., Vol. 3, 2000, 345–352.

[140] Beerling J., Gough T. *Clean and Green: A review of modern day surfactants and emulsifiers*, Cosm. & Toil., Vol. 8, 2013, 566–573.

[141] Sikora E., Michorczyk P., Olszanska M., Ogonowski J., *Supercritical CO_2 extract from strawberry seeds as a valuable, component of mild cleansing compositions*, Int. J. Cosmet. Sci., Vol. 37(6), 2015, 574–578.

[142] Olszańska M., Sikora E., Ogonowski J., *Study of properties of shampoos based on mild surfactant, containing strawberry seeds extract,* Polish Journal of Commodity Science, Vol. 2, 2014, 134–141.

[143] https://cosmetics.specialchem.com/formulation/hair-care-anti-oxidant-hair-conditioner, online access 29.11.2018.

[144] Council Directive 87/357/EEC of the European Parliament of 25 June 1987, *Official Journal of the European Union*, L.192/49, 1987.

[145] EN ISO 22716:2007, *Cosmetics – Good Manufacturing Practices (GMP) – Guide to Good Manufacturing Practices*.

[146] http://ec.europa.eu/consumers/sectors/cosmetics/files/pdf/cpnp_user_manual_pl.pdf, online access 20.05.2018.

STRESZCZENIE

Cosmetic emulsions stanowi opracowanie monograficzne poświęcone najbardziej popularnej formie produktów kosmetycznych, jaką jest emulsja. Książka podzielona jest na kilka rozdziałów, zasadniczą część technologiczną poprzedza rozdział obejmujący podstawy fizykochemiczne dotyczące układów emulsyjnych, w którym omówione zostały mechanizmy stabilizacji emulsji oraz rola, jaką odgrywa emulgator w procesie otrzymywania stabilnych formulacji. Rozdział 3 zawiera najważniejsze informacje dotyczące technologii wytwarzania emulsji oraz aparatury stosowanej w przemyśle kosmetycznym.

W rozdziale 4 czytelnik może poszerzyć swoją wiedzę na temat surowców stosowanych w emulsjach kosmetycznych. Najpierw scharakteryzowane zostały podstawowe grupy surowców obecne w recepturach, czyli emulgatory oraz emolienty i nawilżające substancje hydrofilowe. W kolejnych podrozdziałach omówiono substancje pomocnicze odpowiedzialne za stabilność fizykochemiczną i mikrobiologiczną emulsji oraz ich właściwości organoleptyczne, czyli substancje konserwujące, antyutleniacze, regulatory konsystencji i kwasowości.

W rozdziale 5 przedstawiono klasyfikację emulsji kosmetycznych. Omówiono właściwości, działanie i przykładowe receptury (wraz z metodyką wykonania) wybranych grup produktów, tj.: uniwersalnych baz emulsyjnych, kosmetyków oczyszczających, nawilżających, ochronnych (ze szczególnym uwzględnieniem środków promieniochronnych) oraz kosmetyków anti-age. W rozdziale poświęconym kosmetykom przeciwstarzeniowym uwagę zwrócono na rolę surowców pochodzenia naturalnego (surowce roślinne i otrzymywane w procesach biotechnologicznych) jako substancji biologicznie aktywnych. Ostatni rozdział monografii poświęcony jest obowiązującym regulacjom prawnym dotyczącym badania, produkcji i wprowadzania na rynek preparatów kosmetycznych.

SUMMARY

Cosmetic emulsions is a monograph concerning an emulsion – the most popular form of cosmetic products. The book is divided into several chapters, the main technological part is preceded by a chapter covering physicochemical fundamentals of emulsion systems, in which the mechanisms of an emulsion stabilization and the role of the emulsifiers in the process of obtaining stable formulations are discussed. Chapter 3 contains the most important information on emulsion technology and equipment used in the cosmetics industry.

In the fourth chapter, the reader can learn about raw materials applied in cosmetic emulsions. First, the basic groups of raw materials used in the formulations, i.e. emulsifiers and emollients and moisturizing hydrophilic substances, were characterized. The following subchapters discuss the auxiliary substances responsible for the physicochemical and microbial stability of the emulsions and their organoleptic properties, i.e. preservatives, antioxidants, consistency and acidity regulators.

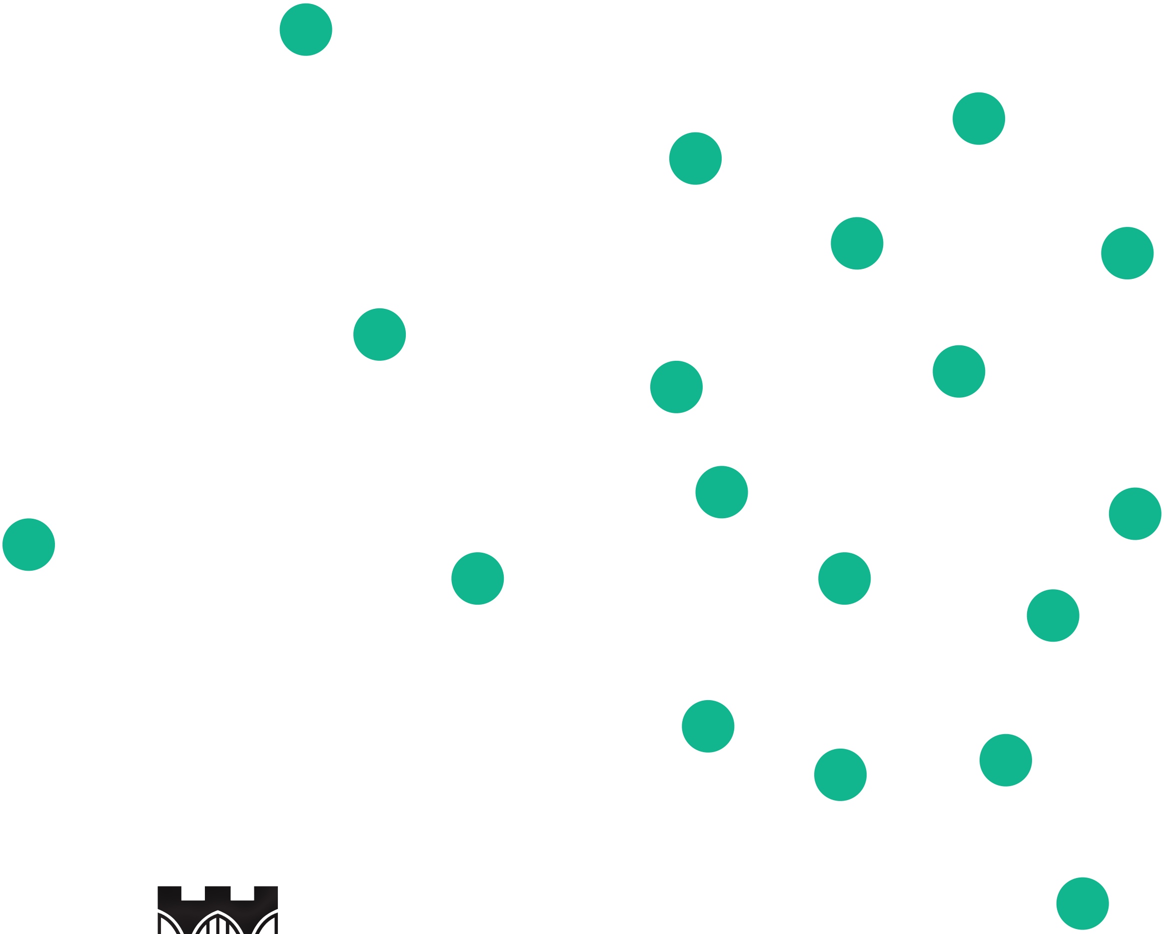
Chapter 5 presents the classification of cosmetic emulsions and characteristic of selected cosmetic product groups. The properties, example formulas and manufacturing procedures of universal cream bases, cleansing cosmetic, moisturizing products, protective creams (with particular emphasis on sunscreens) and anti-age cosmetics are described. In the chapter devoted to anti-aging cosmetics, a specially attention was paid to the role of raw materials of a natural origin, (vegetable raw materials and obtained in biotechnological processes), as the biologically active compounds. In the last chapter of the monograph the current legislations regarding the examination, production and marketing of cosmetic preparations are presented.

ZUSAMMENFASSUNG

Kosmetische Emulsionen ist eine Monographie, die der beliebtesten Form der kosmetischen Produkte gewidmet ist – der Emulsion. Das Buch ist in mehrere Kapitel unterteilt. Dem wichtigsten technologischen Teil ist ein Kapitel über physikalisch-chemische Grundlagen von Emulsionssystemen vorangestellt, in denen die Mechanismen der Stabilisierung der Emulsion und die Rolle der Emulgatoren bei der Herstellung stabiler Formulierungen diskutiert werden. Das 3. Kapitel enthält die wichtigsten Informationen zur Technologie der Emulsionsherstellung und der Apparatur in der Kosmetikindustrie.

Im vierten Kapitel kann der Leser etwas über Rohstoffe erfahren, die in kosmetischen Emulsionen verwendet werden. Zuerst wurden die Grund-Rohstoffgruppen charakterisiert, die in den Rezepturen zu finden sind d.h. Emulgatoren und Erweichungsmittel wie auch feuchtigkeitsspendende hydrophile Substanzen. In den folgenden Unterkapiteln werden die Hilfssubstanzen, die für die physikalisch-chemische und mikrobiologische Stabilität der Emulsionen und ihre organoleptischen Eigenschaften verantwortlich sind, diskutiert, d.h. Konservierungsmittel, Antioxidantien, Konsistenz- und Säureregulatoren.

Im 5. Kapitel wurde die Klassifizierung der kosmetischen Emulsionen vorgestellt. Es wurden Eigenschaften und Wirkung wie Rezepturen (samt Methodik der Ausführung) ausgewählter kosmetischer Produktgruppen besprochen, d.h. von universellen Cremebasen, Reinigungskosmetika, feuchtigkeitsspendenden Produkten, schützenden Cremes (mit besonderem Schwerpunkt der Sonnencremes) und Anti-Aging-Kosmetika. In dem Kapitel über die Anti-Aging-Kosmetik wurde besonders auf die Rolle von Rohstoffen natürlichen Ursprungs (pflanzliche Rohstoffe und in biotechnologischen Verfahren gewonnene) als biologisch aktive Verbindungen geachtet. Im letzten Kapitel der Monographie werden die geltenden Rechtsvorschriften zur Prüfung, Herstellung und Vermarktung kosmetischer Präparate vorgestellt.



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