1.2. Protecting sensitive skin

Sun and environmental pollutants are as common triggers of skin sensitivity symptoms as cosmetics. As they also contribute to damage to the skin barrier, individuals with sensitive skin are advised to use skin protective products. However, there are nuances here because, for example, many chemical sunscreens can irritate even the healthy skin as they degrade in the sun and can form potentially toxic compounds.

The 1st generation UV filters such as benzophenone-3 (aka oxybenzone), benzophenone-4, para-aminobenzoic acid (PABA), butyl methoxydibenzoylmethane (Avobenzone), and octocrylene, which have irritant potential and other potentially adverse effects, should be avoided by most individuals, especially those with sensitive skin (Diffey B., 2020). Newer filters like bis-ethylhexyloxyphenol methoxyphenyl triazine (Tinosorb S) have undergone much more research before entering the market and are thus considered more stable and much safer. Moreover, they protect against a wide range of radiation.

In general, physical UV filters such as titanium dioxide and zinc oxide are preferred, as these microparticles reflect radiation in the UVA and UVB spectral range without undergoing chemical transformations. In addition, the irritating potential of physical UV filters is lower than that of chemical filters, which act by absorbing UV rays. However, unlike microparticles, the nanoparticles comprising physical filters have been shown to penetrate the *stratum corneum*, and can leave a whitish film on the skin and even initiate oxidation reactions (Young A.R. et al., 2017).

UV filters based on cerium (Ce) phosphates and oxide/dioxide particles have also been developed. a comparison of the photoprotective properties of cerium oxide with titanium dioxide and zinc dioxide shows an even more pronounced filter efficacy. However, despite the initial hopes of non-toxicity, cerium oxide nanoforms, like other physical filters, are also characterized by potential cytotoxicity and pro-oxidant activity (Miri A. et al., 2020). Thus, micronized forms of all these filters, "packed" in a special shell, are currently considered the safest.

Those with sensitive skin are advised to use sunscreen with a UV index of two or higher. As the UV index (which characterizes the sunlight intensity) is broadcast by many information resources, it is always possible to choose individual sun protection based on the anticipated exposure. For the product to provide the declared photoprotection (sun protection factor [SPF] index), it should be applied at 2 mg/cm^2 rate and renewed every 2 h (or earlier if the skin was exposed to water in the interim). However, most consumers use about 0.5 mg/cm^2, rendering sun protection at least four times weaker. All this suggests that SPF is not a guarantee but only a reference point for choosing a product, while noting that the best sunscreen is clothing, hat, and shade.

Sunscreen formulations include substances that impart additional properties to the finished product, such as moisturizing components, anti-inflammatory agents, antioxidants (usually fat-soluble vitamin E), and even immunomodulators (yeast polysaccharides, chitosan), but should still be applied in moderation. As a rule, the higher the degree of photoprotection, the smaller the share of additional "active" components. There is a valid explanation for this relationship: a sunscreen product with a high SPF restrains the "pressure" of UV rays for hours, which means that everything that can potentially increase skin photosensitivity must be avoided. Fragrances and dyes are also highly undesirable, especially for sensitive skin.

Another nuance pertains to the anti-inflammatory agents in sunscreens. Since the only sign of pronounced photodamage to the skin is the appearance of erythema, and anti-inflammatory agents "take it away," there are concerns that their addition to the formula may give people a sense of false security.

On the other hand, the use of photostable antioxidants in the formula is highly recommended, given that they do not reduce the sun protection ability of the product and strengthen the skin's defense against UV free radicals. Moreover, vitamin E directly protects cells from forming cyclobutane pyrimidine dimers in deoxyribonucleic acid (DNA) (Delinasios G.J. et al., 2018).

Ideally, sun exposure between 10 am and 4 pm should be avoided, as this is the period when the sun is at its peak. It should also be remembered that UV exposure increases in the mountains due to the presence of reflective surfaces (snow, water, etc.). Once again, the best sun protection is clothing, hat, and shade.

Products used should also offer protection against environmental pollutants, such as particulate matter (PM), organic compounds, nitrogen, sulfur oxides, etc. Environmental pollution is a huge urban problem, and some experts believe that it also contributes to the sensitive skin epidemic. As extant research shows that most pollutants act by triggering oxidative stress and inflammation (Parrado C. et al., 2019), antioxidant and anti-inflammatory agents are currently considered the main anti-pollution agents.

1.3. Cleansing sensitive skin

Gentle cleansing is perhaps one of the most "vulnerable" steps of caring for sensitive skin, as many triggers of this condition are found in cleansing products.

Still, not washing your skin to avoid the symptoms of skin sensitivity is not an option. The face should be cleaned at least twice a day to remove excess sebum, impurities, microorganisms, as well as cosmetic residues, while avoiding scrubs, sponges, or other mechanical tools that can traumatize the skin. In other words, it is necessary to choose the right cleansers with minimal irritating potential.

1.3.1. Factors determining the irritant potential of a cleanser

pH range

The main irritant factor of a cleanser is the pH. Thanks to the active advertising of cosmetics with a pH of 5.5, many consumers have already memorized that this is the pH of the skin surface. However, recent studies show that the actual pH value is even lower depending on the skin area, and normal pH on the face can be as low as 4.5.

First, what is pH? It is a convenient measure of acidity, calculated as the inverse decimal logarithm of the concentration of hydrogen ions (protons) in a solution. The higher the proton concentration, the greater the acidity. But since the logarithm is inverse, the "numbers" are the opposite: the lower the pH value, the higher the acidity. As neutral solutions have the pH value of 7.0, the pH of acidic solutions is below, and that of alkaline ones is above this value.

The cells of the human body (including skin cells) live in a slightly alkaline environment with the pH 7.1–7.4. Extracellular fluid, intracellular cytoplasm, and blood plasma have normal pH values within slightly alkaline values. However, the skin surface is covered with a layer of dead cells that protect it, like a lizard is protected by its scales. It is only here, in the *stratum corneum*, where there are no living cells, that the pH value is below neutral. The acidic pH on the skin surface is created and maintained by special ingredients of the hydrolipid mantle (Chan A., Mauro T., 2011):

1. Substances secreted to the skin surface as sebum and sweat, such as lactic and butyric acids from sweat, cholesterol sulfate, and free fatty acids (FFA) from sebum. FFA are converted from phospholipids by secretory phospholipase A2*.
2. Metabolic products of natural moisturizing factor (NMF) components such as sodium pyroglutamate and urea.
3. Substances released by microorganisms living on the skin, e.g., *Lactobacillus* bacteria produce lactic acid.
4. Protons generated by Na^+/H^+ antiporters (sodium–hydrogen exchanger-1, NHE1).
5. Carbon dioxide, some amount of which directly escapes from the epidermis and dissolves in the hydrolipid mantle to form carbon dioxide.

In recent years, academic interest in the hydrolipid mantle has grown substantially, as it has become clearer why it is so important to skin health. Studies have shown that the pH gradient through the *stratum corneum* (pH 4.5–5.5 at the surface and 7.0 at the border with the granular layer) regulates keratinization and desquamation. The point is that different enzymes work at different depths of the *stratum corneum*. The surface proteases break down corneodesmosomes (protein "bridges" that bind horny scales to each other), and this is necessary for the scales to exfoliate in time. In deeper layers of the *stratum corneum*, extracellular lipid structures are formed, and other enzymes work in this area. The peculiarity of any enzyme is pH sensitivity; for each enzyme, there is a specific pH range at which it is most active. For instance, for enzymes that regulate desquamation

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* Phospolipase A2 has been shown to play a central role in the formation of the "acid mantle" in the early maturation of the epidermis postnatally.

near the surface of the *stratum corneum*, the optimal pH value is close to 5.0. For more deeply located enzymes, the optimum shifts to the alkaline direction and becomes about 6.0–7.0. Thus, the **pH gradient is a kind of "switch" that strictly controls the activity of enzymes at different depths of the *stratum corneum***. If the physiological pH gradient is impaired, a failure in the well-balanced mechanisms of maturation and desquamation will occur, leading to a violation of the *stratum corneum* structure. This happens due to exposure of the skin to acidic preparations (based on fruit acids) or washing with alkaline soap. In such cases, the work of enzymes is disturbed and, after some time, visible scaling and increasing dryness of the skin will emerge. If the damaged skin is irrigated with a solution of neutral pH, the restoration of the barrier will be slowed down. Conversely, with a slightly acidic solution, barrier repair will be faster.

In sensitive skin, where not only a barrier but also increased sensory reactivity is involved, both acidic and alkaline environments can activate TRP channels and free nerve endings, causing itching, burning, and other symptoms.

The hydrolipid mantle regulates the microbial community of our skin. A pH of 4.5–5.5 is of evolutionary importance, as it supports a healthy microbiome. In alkalinization, the microbiological balance is disrupted, immediately affecting the skin condition. Specifically, in persons that suffer from acne, a surface pH is about 6.0, which favors excessive growth of *Cutibacterium acnes*. In atopic dermatitis, the surface pH is often elevated, and the microbiome is different from the healthy. When the pH is elevated, a favorable environment for developing purulent bacteria and fungi is created.

Experiments have shown that the surface pH is most noticeably affected by washing and applying cosmetics. After washing with tap water, it takes the skin an average of four hours to regain its pH. If soap is used in washing, this time increases. The use of cosmetic products with a pH greater than 6.0 or less than 4.0 also shifts the pH gradient in the *stratum corneum*, sometimes on purpose.

The question of whether it is advisable to influence the skin by changing the pH gradient in the *stratum corneum* is resolved at other stages of cosmetic care. This is not the task of cleansers, so their pH should not affect the surface pH.

Surfactants

Even if the pH of the cleanser is within the physiological range, the product may still not be 100% safe because surfactants are the main functional ingredients in most formulations, given that the cleanser will not work without them. Surfactants are a mandatory component of cleansers due to their ability to dissolve (emulsify) fats. Still, since both the membranes of living cells and the lipid ctructures of the epidermal barrier contain lipids, we can surmise that **all products that clean the skin well have the potential to damage the epidermal barrier and cell membranes**.

Surfactants are compounds with **amphiphilic structure**, i.e., their molecules have a polar "head" (hydrophilic component: functional groups –OH, –COOH, –O–, etc.) and a non-polar tail (hydrophobic/lipophilic component: hydrocarbon chain). In an aqueous environment, the lipophilic "tail" is embedded in sebum and hydrophobic residues on the skin surface. On the other hand, the hydrophilic "head" faces the water so that the insoluble contamination masses are detached from the skin surface, passed into solution, and washed off (**Fig. IV-1-1**).

Surfactants differ in molecular length, charge, and strength of emulsifying action. The "strongest" surfactants are detergents with high foaming action. Even if the skin is characterized by increased sebum production, prolonged contact with surfactants should be avoided, as its barrier structures and acid mantle may be impaired otherwise.

As surfactant-based cleansers can only work in combination with water, it is no exaggeration to say that **water is the main activator of the cleanser**.

Some surfactants decompose into ions in aqueous solution: anionic surfactants carry a negative charge, cationic surfactants carry a positive charge, and amphoteric surfactants carry both charges. Other surfactants dissolve in water without ionizing (these are so-called

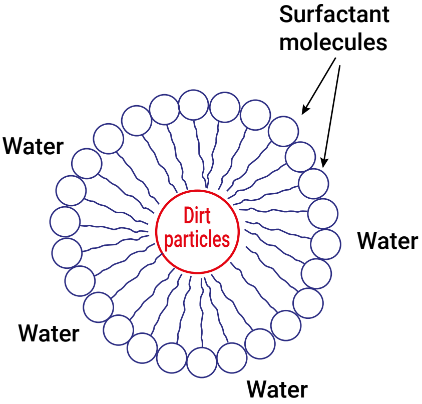

Figure IV-1-1. Solubilizing (dissolving) effect of surfactants: a contaminant particle coated with surfactant molecules in aqueous medium