In clinical dermatology, few questions are asked more commonly than “What is the best way for me to clean my skin or hair?”

The modern dermatologist needs to be familiar with the physiologic action of cleansing products available on the market. This familiarity should include chemical composition, application, cosmetic benefits, and safety, as well as potential hazards. This knowledge must be acquired from objective, independent, peer-reviewed scientific literature, and not from promotional sheets or biased, pseudoscientific articles that are distributed in great quantity by the cosmetic companies, which have heavily vested commercial interests. It is our hope that this chapter will be such an objective and evenhanded source of information for guiding practicing dermatologists.

Historical Perspectives

It would appear that soap has been used for personal hygiene and for washing clothes since the beginning of time. All major religions observe strict guidelines and instructions for maintaining cleanliness in holy sites. Cleanliness is also found in prayer, signifying purity of body and soul.

The origins of the word “soap” and the first chemical saponification are obscure. According to one Roman legend, soap was discovered accidentally near Mount Sapo, an ancient location for animal sacrifice not far from Rome. Animal fat mixed with wood ashes (the ancient source of alkali) and rainwater created an excellent soap mixture. Roman housewives noticed that the strange yellow mixture of the Tiber’s waters made their clothes cleaner and brighter than ordinary water.1,2

Soapmaking became an art during the time of the Phoenicians (600 BCE) and underwent significant advancement in the Mediterranean countries, where local olive oil was boiled with the alkali ashes.

In the Middle Ages, Marseilles became the first soapmaking center in Europe, followed by Genoa, and eventually Venice. In Germany, soap was manufactured but not widely used as a cleansing agent. For several centuries, the industry was limited to small-scale production using mainly plant ashes containing carbonate; the ashes were dispersed in water, then mixed with fat and boiled until the water evaporated. The reaction of fatty acid with alkali carbonate of the plant ashes formed the final product.3

The real breakthrough in industrial soap production was made by a French chemist and physician, Nicolas Leblanc, who invented the process (Leblanc process, 1780) of obtaining soda (Na2CO3) from common salt.2 This process increased the availability of alkali at reasonable cost, transforming soapmaking from a cottage industry into a huge commercial one. Soap, which had been a luxury item affordable only by royalty and the very rich, became a household item for the personal hygiene of mainstream citizens as well.

Throughout the 19th century and the beginning of the 20th century, physicians realized the value of soap as a medicinal agent. Perhaps the best known protagonist of soap was Ignaz Philipp Semmelweis who, in 1847, discovered the infectious etiology of puerperal fever and thus required all medical students to wash their hands before examining patients.3–6 His words, “I am not asking anything world shaking. I am asking you only to wash. . . For God’s sake, wash your hands,” and, “Unless everything that touches you is washed with soap and water and then chlorine solution, you will die and your child with you!”3,5 are immortal. Some of the great figures of dermatology of the 19th century (Ferdinand von Hebra, Paul Gerson Unna) advocated the use of soaps for the treatment of various dermatoses.1

Soap was also recommended for preventing skin infections and reducing the incidence of sepsis originating from minor skin injuries.7–9

The use of soap reached its zenith at the beginning of the 20th century, and the maxim “cleanliness is next to godliness” held sway.

During World War II, sailors who spent months at sea under severe freshwater restrictions had to use
The Chemistry of Soaps, Shampoos, and Detergents

Soaps, shampoos, and detergents generally comprise a mixture of ingredients that can be classified according to their function (Table 1).

Surfactants are the essential cleaning substances and they determine the cleaning and lathering characteristics of the soap, as well as its mushiness, plasticity, skin compatibility, and other features.

Table 1. Ingredients of Soap

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Percent of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactants</td>
<td>30–70</td>
</tr>
<tr>
<td>Plasticizers and binders</td>
<td>20–50</td>
</tr>
<tr>
<td>Lather enhancers</td>
<td>0–5</td>
</tr>
<tr>
<td>Fillers and binders</td>
<td>5–30</td>
</tr>
<tr>
<td>Water</td>
<td>5–12</td>
</tr>
<tr>
<td>Fragrance</td>
<td>0–3.0</td>
</tr>
<tr>
<td>Opacifying agents</td>
<td>0–0.3</td>
</tr>
<tr>
<td>Dyes and pigments</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Table 2. Anionic Surfactants Used as Active Ingredients in Cleansing Bars

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium carboxylate (soap)</td>
<td>RCOONa</td>
</tr>
<tr>
<td>Sodium alkyl sulfate</td>
<td>ROSO₃Na</td>
</tr>
<tr>
<td>Disodium alkyl sulfoacetate</td>
<td>ROCOCH(SO₃Na)₃CH₂COONa</td>
</tr>
<tr>
<td>Disodium amido sulfoacetate</td>
<td>RNHCOCH(SO₃Na)₃CH₂COONa</td>
</tr>
<tr>
<td>Sodium acyl taurate</td>
<td>RCON(CH₂)₃CH₂CH₂SO₃Na</td>
</tr>
<tr>
<td>Sodium acyl isethionate</td>
<td>RCOOCH₂CH₂SO₃Na</td>
</tr>
<tr>
<td>Sodium alkyl sulfoacetate</td>
<td>ROCOCH₂SO₃Na</td>
</tr>
<tr>
<td>Sodium alkyl sarcosinate</td>
<td>RCON(CH₂)₃CH₂COONa</td>
</tr>
<tr>
<td>Disodium acyl glutamate</td>
<td>RCONHCH(COONa)₃CH₂CH₂COONa</td>
</tr>
<tr>
<td>Disodium monoglyceride sulfate</td>
<td>ROCOCH₂CH(OH)CH₂OSO₃Na</td>
</tr>
<tr>
<td>α-sulfo fatty acid esters</td>
<td>RCH(SO₃Na)COOCH₃</td>
</tr>
<tr>
<td>Sodium dodecyl benzene sulfonate</td>
<td>RC₆H₄SO₃Na</td>
</tr>
<tr>
<td>Sodium alkyl ether sulfate</td>
<td>ROC₂H₄SO₃Na</td>
</tr>
<tr>
<td>α-olefin sulfonate</td>
<td>RCH(CH₂CH₂O)₃SO₃Na</td>
</tr>
</tbody>
</table>

Surfactants are compounds that have a dual affinity; they are both lipophilic and hydrophilic. Their molecule consists of a lipophilic tail group, which links to greasy soil, and a hydrophilic polar head group, which renders it water-soluble and helps disperse and rinse away greasy soil. The balance between hydrophobic and hydrophilic features governs the application of the surfactant as a detergent, wetter, or emulsifier.

There are four main types of surfactants, classified by the nature of their hydrophilic head: anionic, cationic, amphoteric, and nonionic. The first three are charged molecules. Anionic surfactants possess a negative charge that has to be neutralized with an alkaline or basic material before the full detergent capacity is developed, whereas cationic surfactants are positively charged and have to be neutralized by acids. Amphoteric include both acidic (negative) and basic (positive) groups, and nonionics contain no ionic constituents. Natural soap is the simplest anionic surfactant and, like it, the majority of surfactants used in personal cleansing bars and shampoos contain anionic head groups. A list of anionic surfactants (including soap) that are used as active ingredients in cleansing bars is given in Table 2.

Table 2 shows that almost all anionic surfactants are sodium or potassium salts of the negatively charged head of the hydrocarbon chains; thus, the ubiquitous slogans, “alkali free” or “soapless soap” are misnomers. Most soaps and shampoos contain a mixture of 2 to 4 surfactants and lather enhancers. The list of chemicals presented in Table 2 represents only a few of the thousands of synthetic surfactants. In addition, there are innumerable plasticizers, binders, moisturizers, and fillers available for formulating syndets. Constructing the formula of a syndet is extremely complicated and requires imagination, inspiration, and an extensive knowledge of chemistry and engineering. The contemporary formulation of soaps is the result of research and
development, as well as trial and error, performed for many years by large research teams. It is as much an art as it is a science, requiring a long learning experience. It should not be surprising, therefore, that a brief review can reveal only a small fraction of the “secrets” of this huge industry, especially as this chapter is intended for physicians who are not familiar with the highly sophisticated chemistry and equipment involved in this multi-million dollar business.

The Washing Process

The target of cleansing is the outermost layer of tissue of our body, the keratinizing epithelium. It is composed of a cornified cell envelope, which is an extremely tough protein/lipid polymer structure. Akin to a wall built from bricks and mortar, the cornified layer also consists of hard building blocks (the individual corneocytes) stuck together with space-filling mortar (intercorneocyte lipids). This hard and lipophilic layer of the epidermis would not easily retain dirt without the intervention of an outer hidrolipid film that covers it and picks up particles of soil. This outer natural film of lipids entraps and glues environmental dust, pollutants, smoke, greases, keratinous debris, organic and inorganic compounds of the sweat, cosmetics, and other substances that come in contact with it.

The process of washing consists of the removal of the outer layer of grease in which the soil (no matter what kind) is embedded. It is a complex physicochemical phenomenon that involves the following steps:

1. Weakening the binding forces between the keratin and the grease by reducing the surface tension between the water and the water-resistant oil/grease. Because of reduced surface tension, water and, with it, the molecules of the surfactants can penetrate into the finest wrinkles of the skin. In this way, more and more interface is occupied by surfactants, and the adhesiveness of the soil is weakened, a process that is facilitated by mechanical rubbing.
2. Transferring the oil into the aqueous vehicle. This process is facilitated by the fact that the micelles that had been created when the soil was emulsified have a negatively charged surface and are rejected by the negative charge of the keratin of the skin surface.
3. Dispersing/suspending the oil and dirt particles in the foam and preventing it from being redeposited on the surface preparing for being washed off.

Thus, cleansing will always remove fat from the skin, simply because the soil to be removed is embedded in the sebum of the skin. As a result, the methods for measuring the cleansing capacity of soaps are based mainly on testing their ability to remove fat. One frequently used method is based on a specially designed skin-washing machine. This machine simulates the washing process by moving its arms back and forth over human skin covered by two chambers containing the washing solution being tested. The “soil” or “dirt” is represented by a water-in-oil emulsion in which a color is incorporated. The reduction in color that is measured after the washing process by means of the washing machine represents the ability of the soap to remove fat, and this correlates with its cleansing capacity. Our group developed another method, based on the same principles, but with some modifications. As in the method described above, we used a fat-based ointment to emulate dirt. Instead of using the complicated washing machine, however, we placed the examined region (the dorsum of the hand), which had previously been covered with dirt (a measured amount of ointment over a marked circle), in a rotating soap solution at standardized conditions (speed, temperature, concentration of the solution, etc.). The capacity of various soaps to remove the dirt was assessed by comparing sebumeter readings before and after the washing process.

The Interaction of Soaps with the Skin

Although Blank pointed out some 30 years ago that “in producing inflammation a cleanser must diffuse through the stratum corneum,” dermatologists continued to adhere for years to the belief that irritation and damage provoked by surfactants were directly related to extraction of lipids from the stratum corneum surface. Although the final word on this assumption is not yet in, reports appearing during the last decade indicate that surfactants cause significant damage to both lipid and protein structures of the stratum corneum and alter its barrier properties. There is a positive correlation between the roughening and irritating effects of surfactants, their absorption/penetration through the stratum corneum, and their ability to damage biological membranes.

Studying the irritation by sodium lauryl sulfate (SLS) ultrastructurally and functionally indicated that SLS altered the permeability barrier by mechanisms that were different from the process induced by an organic solvent. Whereas with acetone the extraction of stratum corneum lipids was the main cause of barrier disruption and barrier recovery improved very quickly, the situation with detergents was more complex. It was suggested that detergents may possibly cause more extensive damage, such as the denaturation of proteins, which would result in alterations that cannot be ameliorated by providing externally applied lipid mixture alone. It was shown that SLS did not extract lipids as had been shown after application of acetone, but rather caused extensive damage to deeper nucleated layers of the epidermis. In this study, the upper stratum corneum showed regular lamellar arrangements of lipids after exposure to SLS for 24 hr. This corroborated with
previous biochemical studies that had shown that in experimentally SLS-treated skin, the amount of ceramides did not differ from that in healthy control skin with only a 4–7% removal of lipids. Ultrastructurally, the surfactant did not alter the existing lipid structure, but rather the processing of new epidermal lipids.

Although considerable efforts have been expended in investigating the effects of soaps on the skin, leading to significant progress of our understanding of surfactant–skin interactions, there are many as yet poorly understood aspects of this complex issue. What is now clear is that the drying, roughening, and irritating effects of detergents are not simply due to removal of fat from the outer layer of the skin, but a more profound effect on membrane structures and lipid–protein matrix of the stratum corneum.


After the introduction of the soap chamber test of Frosch and Kligman in 1979, many other tests were designed to evaluate the irritation potential of various soaps, often in conjunction with instrumental methods of evaluating skin reactions. All those tests had a common purpose: to achieve extreme conditions that would provide greater sensitivity and discriminating power and thereby accentuate the differences between soaps as much as possible; the greater the discrimination and differences between the products, the more efficient and useful the test. In a recent issue of Clinics in Dermatology on soaps and detergents, three sections were devoted to tests involving tens of different methods for assessing the irritancy potential of soaps in contrast to only one chapter concerned with the cleansing capacity of soap in which three methods were described.

As noted earlier, the introduction and publication of tests for evaluating the irritancy of soaps brought with it an upheaval in our approach to the sought-after qualities in a soap. Which came first is as shrouded in mystery as the chicken or the egg. Did the development of effective tests for irritancy result in that property becoming the key issue, or did the fear of the toxic and irritant effects of soap result in the search and development of effective tests to evaluate these qualities? We propose a third possibility: that the new concepts and fashions have been created primarily under the influence of the soap manufacturers, and that the various tests were designed and aimed first and foremost for their interests. A perusal through the advertisements in dermatological journals reveals that each company presents its choice method of analysis in which, to no one’s surprise, its soap ranks highest in mildness. As expected, the number of opinions as to which test is the most relevant, which method is “closest to nature” and reflects the soap’s quality most accurately, and which one would allegedly best serve the needs of the consumers is equal to the number of tests available!

The Bottom Line

Is this new approach to soap quality—the trigger for introducing all these tests—justified? Is a soap that scored well in irritancy tests really the best soap? What really constitutes a good soap? Which property of soap is the most important? In short, which soap should we recommend to our patients?

In the issue of Clinics in Dermatology devoted to soaps, all the experts agreed that the act of washing and the use of soaps contribute to a feeling of well-being and comfort as well as to improving the appearance and smell of the skin, but not to promoting health. As Kligman put it, “All soaps are potentially damaging to the skin. Modern middle-class people are too obsessed with cleanliness. Less washing is better. The skin doesn’t care whether it is clean or not—unlike in former days, when dirty skin spread contagion.”

On the other hand, the irritant, toxic, and harmful effects of soaps have been highly exaggerated, and the pendulum has swung back to where it was after World War II, when the emphasis was placed on the negative, damaging, and hazardous effects of soaps. Contemporary dermatologists seem to be too much influenced by the results of the various tests that are performed under extreme and nonphysiologic conditions, or by sophisticated irritancy assays that are sent to them by manufacturers. They seem to have ignored the simple fact that had been emphasized by distinguished dermatologists (Suskind, Stoughton, Buttleley, Blank, and others) more than 30 years ago: with ordinary use for general personal hygiene, the majority of the consumers will tolerate any kind of soap without any harm. So, in answer to the question of which soap to recommend, to paraphrase the song, just about anything goes!

Although washing with soap makes no contribution to the promotion of health, Semmeleweis notwithstanding, its importance lies in the feeling, appearance, and scent it imparts to the skin. People like to wash because the process gives them a sense of well-being for several hours. Dermatologists should not discourage them or deny them this pleasure.

The great majority of consumers have no need for the very high degree of mildness of modern soaps and certainly not the sophisticated systems that have been invented to rate them. It is to be hoped that the pendulum, now poised at the extreme in favoring mildness over cleanliness in its position next to godliness, will finally reach a balance in favor of the consumer, and only of the consumer!
References