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by Clair G. Wood

Soapmaking may be the second oldest chemical reaction known, first place honors going to the fermentation of grape juice to make wine. The origins of soapmaking are unknown, but it probably started by accident when one of our ancestors boiled animal fat contaminated with campfire ashes and discovered a white curd floating on top of the mixture. Both the Greeks and the Romans knew about soap. In the ruins of Pompeii (destroyed in 79 A. D.), archaeologists have unearthed a soap factory. The Romans probably didn't use soap for washing; most likely, they mixed it with perfumes to make hair dressings, cosmetics, and ointments for dressing burns and wounds. Eventually its value for cleaning the body was recognized.

Soft soap

For centuries, soapmaking was done at home and was a regular chore for women and children. A common sight in the yard was the leaching barrel, a large cask placed on supports with a drain hole near the bottom. It was someone's task to fill it with ashes, then pour bucket after bucket of warm water into the barrel. Eventually a coffee-colored extract began to dribble from the drain hole and was collected in a stoneware crock. The strength of this "lye" solution was tested with an egg. If the egg sank, it meant the solution was too weak and had to be poured through the barrel again. If it floated too high, the solution was diluted with water before use. A 50-gal. barrel of ashes would produce about four pails of lye strong enough to make soap. Next, about 12 lb of beef fat or pork suet was melted in a large cast-iron kettle over a fire. The lye solution was added and the mixture was stirred with a wooden paddle. As the fat and lye reacted, a viscous white layer formed on top, with large bubbles slowly breaking the surface. This was soap. Each soapmaker had a different technique for determining when the batch was ready; but even if the measurements and timing were not exact, the crude soap would still work. Soap made this way was called "soft soap" because it inevitably contained a liquid by-product, glycerin, that prevented it from hardening. Hard soap was made from the soft variety by stirring salt into the kettle; this caused the soap to separate from the glycerin. Either way, the soap was usually harsh to both skin and fabric because it contained excess lye.

Modern commercial soapmaking is not greatly different from this ancient process, though the ingredients are now pure and are mixed to an exact formulation. The basic ingredient, animal fat, may be supplemented or replaced by vegetable oils. Especially valued are coconut oil from the Philippines, palm oil from Africa, and olive oil from the Mediterranean. Sodium hydroxide, the modern equivalent of the frontier homemaker's lye, can now be obtained in pure solid form or in strong solutions. Modern soaps made for everyday use are colored by dyes and perfumed by essential oils. Soaps made for special purposes may contain finely ground pumice, antiseptics, or emollients such as lanolin. Modern additives aside, soapmaking today is essentially the same process that went on in that Pompeiian soap factory nearly 2000 years ago.

Soapmaking

The chemical reaction that produces soap is *saponification,* in which fat or oil is reacted with a strong base (sodium hydroxide or potassium hydroxide) to produce glycerin and soap (Figure 1). Fats are large molecules that some people consider to be made of four smaller molecules. The smallest of these component molecules is *glycerin,* an alcohol with three hydroxyl (OH) groups. It is combined with three *fatty acids,* which may be identical molecules or may all be different. The base attacks the fat where the component molecules were joined and produces one molecule of glycerin and three molecules of *modified* fatty acid—soap.

The variation among different soaps—other than the added perfumes, dyes, and emollients—is due to the different fatty acids used in their preparation. If the soap is to be used in saltwater or other "hard" water, it will produce a better lather if made with a high percentage of coconut oil. Palm oil soaps give small, long-lasting bubbles and are very mild to the skin. Each performance objective requires soapmakers to formulate a soap base with a different blend of fatty acids. In this respect, soapmaking is as much an art as it is a science.

Bathtub debate

"But do we have to wash with *soap*? Why can't we just use water?" Generations of parents have been confronted with this question while persuading a child to wash his face. The reply sometimes contains more tradition than reason, "Because it helps you get clean . . . now wash behind your ears!" In fact, the chemistry of soap favors the parents' side of the dispute. It *is* difficult to clean the body with plain water; much of the dirt just won't wash off. This is because, as the old adage goes, water and oil don't mix. Your body is constantly exuding oil, which forms a thin layer over your skin. When dirt and bacteria settle on your skin, they are covered by this oily film. The oil rubs onto your clothes, trapping dirt there as well. If you wash with plain water, the water simply slides over the layer of oil without penetrating to the dirt below, like water rolling off a duck's back.

If you didn't have any soap, it might be better to wash with plain *oil* than plain water because oil can mix with, and wash off, the body's dirty oil film. Strange as it sounds, this was once standard practice. The Egyptians and

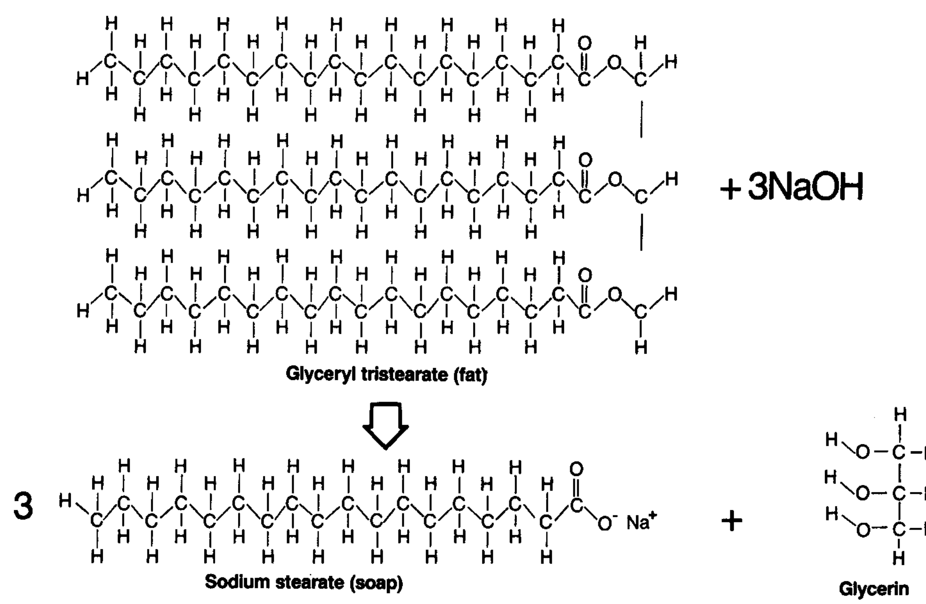

Figure 1. **The conversion of a fat, glyceryl tristearate, to a soap, sodium stearate. Technically, soap is defined as a water-soluble metallic salt of a fatty acid. In the example above, a metal ion, Na^+, has joined with the fatty acid by an *ionic bond* (like the bonds in salt), making it electrically charged and thereby capable of dissolving in water**

Romans were famous for their public baths, but bathing was far different from what we practice today. In the days of Cleopatra, the bather was rubbed with sweet-smelling oils and then worked up a sweat in a steam bath. Then the oils—and, we hope, the dirt—were scraped off by an implement called a strigil. The bath was finished with a quick dip in a pool of cool water. No doubt Cleopatra smelled nice at the end of this lengthy ritual, but today you can get cleaner by spending five minutes in the shower with a bar of modern soap.

Oil and water *can* mix

How does soap work? It works by making oil mix with water, so that the water can wash off the oil, taking with it the dirt and bacteria. To understand this, let's first look at a common chemical that naturally mixes with water. Ethyl alcohol is a good example because it dissolves easily in water; water and alcohol are said to be *soluble* in each other.

Ethyl alcohol (beverage alcohol) has strong similarities to water. A molecule of water, H_2O, has a partial positive charge on the hydrogen atoms and a partial negative charge on the oxygen. Alcohol also has a small molecule containing an OH group with positive charge on hydrogen and negative charge on oxygen. The attraction of opposite charges and the structural similarities make water and alcohol soluble (Figure 2).

In contrast, oil, fat, and grease—the dirt trappers—are *hydrocarbons,* consisting of carbon and hydrogen. A typical lubricating oil, for example, might have the general formula $C_{20}H_{42}$. This molecule, because it has no charges and is structurally unlike water, is not soluble.

To get the oil to mix with water, some means must be found to increase their mutual affinity. This is the task of the soap molecule. A close look at a typical soap molecule, sodium stearate, reveals that it consists of two parts: a hydrocarbon portion, which is structurally similar to oil and thus soluble in it, and a charged portion, which is extremely soluble in water. This dual nature of the soap molecule allows it to couple the oil and water together, thus rendering them compatible with each other (Figure 3).

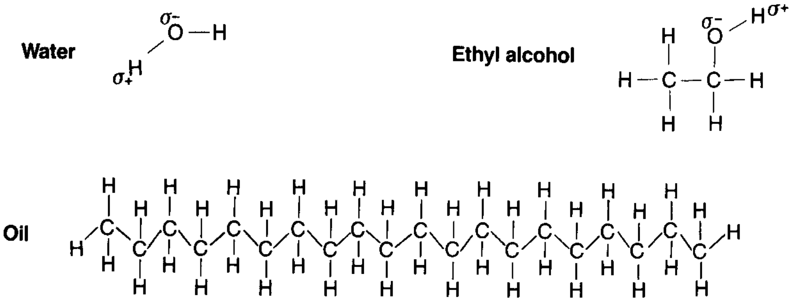

***Figure 2.* A water molecule has a negative electrical charge on oxygen and positive charges on hydrogen. Ethyl alcohol contains similarly charged atoms. Oil molecules do not have these charges. The greek letter (small delta) indicates *partial* charges, weaker than the charge on an ion**

When we wash with a solution of soap and water, we rub and scrub to break up the oil into small droplets. The soap molecules dissolve their oil-like ends into these droplets, leaving their charged ends sticking into the surrounding water. The soap molecules form a kind of shell around the oil droplet. This small sphere, with a captured oil drop in the center, is called a *micelle.* The soap camouflages the oil droplet, making its exterior attractive to water. The micelle—disguised with its oil and dirt—is easily washed away (Figure 4).

To summarize, soaps increase the compatibility between water and hydrocarbons by *partly* dissolving in hydrocarbons and *partly* dissolving in water thereby linking these two dissimilar liquid materials together.

Bathing in the nude!

Today, we accept the idea of washing our bodies and clothes with soap and don't realize that, historically, it is a custom of recent origin. Throughout the Dark and Middle Ages, no one, lord or serf, was very inclined to bathe. Queen Isabella of Spain (1451-1504) boasted of taking only two baths in her lifetime, once when she was born and another on her wedding day. By contrast, Queen Elizabeth I of England (1558-1603) was a bathing enthusiast; her chronicles record that "she hath a bath every three months whether she needeth it or no." In addition to the lack of hot water, soap, and social pressure, bathing was also discouraged by strong religious compunctions. Until well into the 19th century bathing nude was considered sinful—an ancient practice of the pagan Greeks and Romans.

The present practice of bathing with soap and water owes its existence to the Sanitary Movement that began in London as a backlash against the widespread filth that was slowly recognized as the cause for cholera and typhoid epidemics. Sewers were constructed, garbage was carted away, public drinking fountains were isolated from sources of contamination, and people were encouraged to wash themselves and their clothes. In 1846, the British government passed a Public Baths and Wash House Act that established public baths and laundries for the working class of London. The movement spread to Europe, then to the U.S., and, by the turn of the century, bathing was a habitual practice of millions.

References

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An article on the chemistry of detergents will appear in Chem Matters, *April 1985.*

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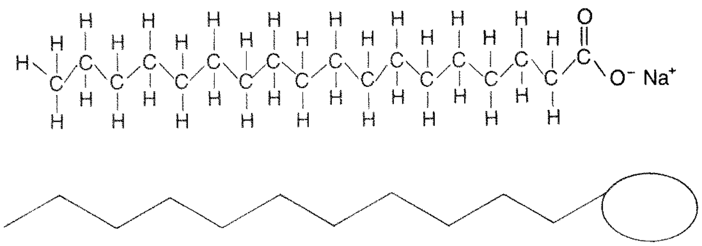

Figure 3. **Sodium stearate (top) is a typical soap molecule. Most of the molecule is composed of hydrogen and carbon, making it similar to oil and grease. The atoms on the right end (shaded) have various degrees of electrical charge, making them attractive to water. The lower illustration is a symbolic representation of a soap molecule**

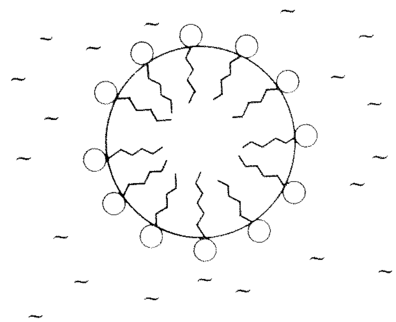

Figure 4. **A soap micelle, with an oil droplet in its center, can remain suspended in water indefinitely. Without soap, the droplet would merge with others of its kind, making a large pool of insoluble oil**

The soap box

- According to Roman legend, soap got its name from Mt. Sapo, a site of animal sacrifice. Women washing clothes at the foot of the mountain found that the mixture of tallow and ashes in the streams made their clothes cleaner.
- In 1806, William Colgate opened a shop to produce soap in bulk: 45,000-pound batches. It was sliced and sold by the pound like cheese. In 1872 Colgate & Company introduced a perfumed toilet soap in individual bars called Cashmere Bouquet and promoted it with national advertising. Other manufacturers quickly followed suit, and the contest between highly advertised specialty soaps was under way.
- Soapmaking and candlemaking were kindred professions because both used tallow. William Procter, soapmaker, and James Gamble, candlemaker, joined forces to sell their products door to door. One day in 1875, an employee left a soap mixer running when he went to lunch. He returned to find the soap overmixed—so full of air that it would float, so pure that it was white. Procter and Gamble decided to test it on the market. Harley Procter, William's son, remembering a verse from the 45th psalm, named it Ivory.
- Soap manufacturers have always competed by using different formulations. One soap, made of palm oil and olive oil, was so successful that the names of the ingredients were used in the company name—Palmolive. Through a series of mergers, the company eventually became Colgate–Palmolive.
- Expanding into the American soap frontier, the English firm Lever Brothers offered Lifebuoy in 1895. The new soap smelled like disinfectant and was not a big seller. Lever Brothers responded by calling it a health soap and pointed out that people who didn't use it would have body odor! Advertising made B.O. into a social curse, responsible for the loss of jobs, friends, and Friday night dates—problems that could be cured, of course, by Lifebuoy.
- Detergents are cleaning agents made from a petroleum base instead of fat or vegetable oil. They were first produced in quantity during World War II when fats and oils were in short supply and the Navy needed a cleaning agent that would work in seawater. Detergents work better in mineral-rich (hard) water because the mineral ions cause soaps to precipitate out of solution leaving a film or scum.
- Glycerin, the by-product of soapmaking, is a valuable industrial chemical; it is added to hand cream as an emollient and is used in the manufacture of dynamite.