History of detergents

Origins
Detergents are frequently used and essential products in our lives, thanks to their ability to remove dirt, thus contributing to the reduction of the presence of germs and to maintaining good personal hygiene. Soap, like all objects of daily use, has taken on an almost taken-for-granted connotation, yet its discovery and especially its use represented a true revolution in the history of our civilization. The widespread use of soap, along with personal hygiene practice, has been more effective than any antibiotic or anti-viral drug against the spread of severe diseases, such as typhoid, cholera and dysentery, to name just a few.

The history of soap has ancient origins: the first evidence of the manufacture and use of soap dates back to the Babylonian civilization. In Mesopotamia (now Iraq) clay cylinders dating back to 2800 BC have been found, containing traces of a substance similar to soap. Again in Mesopotamia, an old Sumerian tablet dating back to 2200 BC has been found, written with cuneiform characters, giving the recipe for making soap.

Table of the Sumerian era showing the recipe for making soap.

Soap Manufacturing Technology - Luis Spitz, 2009 AOCS Press, Urbana, IL 61802

The Ebers Papyrus, named after its European buyer, dating back to the Eighteenth Dynasty of Egypt, more precisely to the reign of Amenhotep I (1550 BC), describes the soap making method used by the Egyptians, who mixed animal fat or vegetable oils with a salt called “Trona” that was collected in the Nile valley. Other ancient Egyptian papyri mention soapy substances used in the preparation of wool. In Europe, the Gauls and the Teutons were the first people to make soap: a mixture of fats and ashes that was mainly used to dye the hair red. Gallic women were the first to discover that, by treating clothing with ash and fat, a stain removing effect was obtained. The Romans, on the other hand, were not able to produce soap: they preferred to go to the spa and use scented oils and curved implements (strigili) to scrape the skin and remove dirt. Nevertheless, the Romans knew about soap (in Latin *sapo*, probably from *sebum*, fat), as witnessed by Pliny the Elder in the first century AD, who in his *Historia Naturalis* describes its recipe of ashes and animal
fat, borrowed from the Gauls, albeit denouncing the excessive use these peoples made of it. The importance of the use of soap soon became clear. We know that the Greek physician Galen in the second century AD recommended the use of soap as a method of preventing certain diseases as well as for cleaning. The people who most contributed to the birth of modern soap, in its formulation, were the Arabs. The Arabs regularly produced soap from olive oil and Laurel or thyme. They were the first to use *caustic soda* (NaOH, sodium hydroxide, a strong alkali), and were therefore the inventors of modern soap. Fragrant and colourful soap, initially produced in Aleppo, rapidly spread throughout the Arab world and starting from 800 AD, in the wake of their expansion, the Arabs introduced soap into Sicily and Spain, from where it spread throughout Europe. The first soap factories in Europe were built in the twelfth century, in Castile (Spain) and in Italy (Savona, Venice), then in France where *Marseille soap* was born, which derives directly from that of Aleppo. But these were mainly artisan products, even if in considerable quantities for the time. Unfortunately, in the Middle Ages, general hygienic conditions rapidly declined and this contributed to the spread of certain serious diseases, such as the plague in the fourteenth century. Thanks to the Belgian Ernest Solvay, who in 1861 discovered a chemical process which, starting from sodium chloride and using ammonia, allowed sodium carbonate to be produced in large quantities, new and significant impetus was given to the manufacture of soap. These developments paved the way for the industrialisation of soap production.

Until the end of the nineteenth century, soap was the only detergent with surfactant properties. Other ingredients were added to soap bringing specific benefits: ash, for example, was used for laundry since it had a sequestering effect on water hardness, due to the presence of phosphorus and soda that contributed to increasing the alkalinity of the washing solutions. For dishes, on the other hand, sand was often added due to its abrasive power. For the products we use today we must reach very recent times. The history of synthetic detergents only began in the twentieth century and was marked by two dramatic events: the two World Wars. It was precisely the scarcity of some basic materials for the production of soap (fat and oil) which stimulated the search for synthetic alternatives. In 1946, the first totally "constructed" laundry product was introduced in the United States, containing a combination of synthetic surfactants.

**Soap as a chemist sees it!**

Have you ever wondered what soap is? Why were animal fat and ash needed to make it? In short, have you ever wondered what it is made of?

From the chemical point of view, soap is a salt obtained from a fatty acid and a strong base such as soda, potash or lime. Fatty acids, as their name already suggests, are contained in animal and vegetable fats, while soda or potash (commonly lye) are contained in ash. This explains the ancient recipe for the preparation of soap!

\[
\text{FAT} + \text{BASE} \rightarrow \text{SOAP}
\]

The reaction, called "saponification", occurs when the two reagents are heated. In practice, the animal fat (lard or suet) was purified to produce tallow and then mixed with the lye. The latter was obtained from ash, first subjected to a cleaning procedure; the ash suspended in water was filtered and the liquid obtained then underwent a kind of cooking. The liquid was again filtered and stored, also for prolonged periods, in glass containers. This traditional method was revived and re-used during the Second World War when, especially in small towns and in the countryside, there was a shortage of everything and therefore also of soap. Soap obtained in this manner, however, is useful for washing clothes: it is produced in the presence of an excess of base which, remaining partially incorporated in the soap, makes it too aggressive for our skin.
The industrial method substantially uses the same type of reagents: the difference lies mainly in the speed of execution of the reaction and in the possibility of dosing the reagents. On an industrial scale, the saponification reaction takes place continuously at high pressure and at a controlled temperature, in the presence of a catalyst which renders the chemical transformation fast and quantitative, and therefore the entire process is very efficient.

In the saponification reaction the fats, which are typically present in the form of triglycerides, are treated with a sodium hydroxide solution. The basic conditions hydrolyse the triglyceride and thus the salt, which constitutes our soap, and the glycerine, which in industrial processes is recovered and re-used in the cosmetic, pharmaceutical and also tobacco industry as a humidifying agent, is formed. Looking at the stoichiometry of the reaction we can observe that using 3 equivalents of base all the fat reacts and the reaction is quantitative. If we want a soap which is "more gentle" on the skin, we must use a quantity of sodium hydroxide lower than the stoichiometric quantity, so that not all of the fat reacts. For this reason, according to the use of soap (shampoo, shower, hands, face, clothes), a different percentage of "soda reduction" is performed. Soda reduction thus ensures that there is a part of unreacted fat in our soap: chemically speaking, the soda thus becomes the limiting reagent.

How does soap “work”? 

The soap molecule consists of two parts: a hydrophilic “head”, with a negative charge (let’s not forget that soap essentially consists of carboxylates) and a long lipophilic “tail” (a long chain of carbon atoms).

\[
\begin{align*}
\text{CH}_2\text{OOC} & - \text{R} \\
\text{CH} & - \text{OOC} - \text{R} + 3 \text{ NaOH} \rightarrow \text{CH}_2\text{OH} \\
\text{CH} & - \text{OOC} - \text{R} \\
\text{CH}_2\text{OH} & + 3 \text{ R} - \text{CO} \rightarrow \text{Na}
\end{align*}
\]

FAT CAUSTIC SODA GLYCERINE SOAP

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In other words, the soap molecule simultaneously has chemical affinity for both water, due to its hydrophilic head, as well as for fat (the dirt), due to its lipophilic tail. Moreover, soap molecules dissolved in water are organised so as to expose their hydrophilic part (polar) to the solvent and fold the lipophilic tails towards the inside of a spherical structure (micelle). Inside the micelles, the dirt is surrounded and absorbed by the lipophilic parts: in this way, the soap catches the fats and somehow “solubilizes” them, allowing them to be conveyed towards the water that takes them away.
"Modern" detergents

The formulations of detergents currently in use are complex and diversified depending on their intended use. If we consider laundry detergents, for example, they must be able to carry out their "cleaning" action on various types of fabrics and stains, at different temperatures and in different conditions of water hardness. For this reason, simple "soap" is no longer sufficient. All formulations include two main components: surfactants and hardness sequestrants (builders) which are the "backbone" of all detergents. Alongside these two functional families, detergents contain a series of adjuvants which confer specific characteristics and which differentiate the various formulations one from another.

Surfactants are foaming substances, which have the ability to reduce the "surface tension" of the water, thus allowing the dirt to be removed and avoiding that it redeposits, keeping it in suspension in the aqueous phase. Surfactants may be:

- **anionic**: these have a negative electrostatic charge and are the most common. Compounds such as alkyl benzene sulphonates, alkyl sulphates, alkyl ethoxy sulphates and alcohol ethoxy sulphates belong to this class;
- **cationic**: these have a positive electrostatic charge. Compounds such as quaternary ammonium salts and quaternary esters belong to this class;
- **non ionic**: these have no net electrostatic charge, so they are less sensitive to the hardness of the water. Polar compounds such as ethoxylated alcohols and alkylamine oxides belong to this class;
- **amphoteric**: these are able to assume a positive or negative electrostatic charge, depending on the type of solution in which they are present. Compounds such as betaines and alkylamino-oxides belong to this class.

Hardness sequestrants (builders) have the function of facilitating the performance of the surfactants by reducing the water hardness. The "historic" ingredients in this category are the polyphosphates. Following episodes of abnormal growth of algae (eutrophication) in the Adriatic Sea in the seventies, the use of phosphates in laundry detergents has been virtually eliminated in Italy since several decades, replaced by zeolites.

**Surface tension**: To understand what it is, we must consider liquids themselves at the molecular level. A molecule placed in a liquid is completely surrounded by other molecules: this means that it is subject to attractions in all directions which thus counterbalance each other. Conversely, molecules that are on the surface undergo attractive forces that only partially counterbalance each other. This happens because the number of molecules contained in the vapour phase above the surface of the liquid is significantly lower. The resultant of the forces of attraction is non-zero and is directed towards the interior of the liquid, causing the surface of the liquid to contract, becoming as small as possible. This is the reason why a drop of water has a spherical shape: the sphere is the geometric figure that for a given volume has the smallest surface.
The table below lists some of the ingredients and adjuvants and the type of products in which they are found:

<table>
<thead>
<tr>
<th>INGREDIENT</th>
<th>EXAMPLES</th>
<th>FUNCTION</th>
<th>PRODUCTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acids</td>
<td>Citric acid</td>
<td>Remove limescale, stabilise the pH of the product.</td>
<td>House cleaning</td>
</tr>
<tr>
<td>Abrasive agents</td>
<td>Silica, Carbonate</td>
<td>Remove dirt with a mechanical action, polishing.</td>
<td>Dishes, house cleaning</td>
</tr>
<tr>
<td>Anti-redepositants</td>
<td>CMC (Carboxymethyl cellulose)</td>
<td>Keep the dirt in solution during washing.</td>
<td>Laundry, dishes</td>
</tr>
<tr>
<td>Foam control agents</td>
<td>Soaps, Silicones</td>
<td>Maintain the right level of foam.</td>
<td>Laundry, dishes, house cleaning</td>
</tr>
<tr>
<td>Colour protection agents</td>
<td>PVP (polyvinylpyrrolidone)</td>
<td>Help keep colours more vivid and prevent pigment transfer</td>
<td>Laundry</td>
</tr>
<tr>
<td>Softening agents</td>
<td>Clay, Silicones, Cationic surfactants</td>
<td>Provide softness to the laundry</td>
<td>Laundry</td>
</tr>
<tr>
<td>Bleaches</td>
<td>Peroxide, Peroxide, Sodium Hypochlorite</td>
<td>Whiten and remove stains.</td>
<td>Laundry, dishes, house cleaning</td>
</tr>
<tr>
<td>Bleaching system activators</td>
<td>TAED</td>
<td>Facilitate the removal of oxidising stains at low temperatures</td>
<td>Laundry</td>
</tr>
<tr>
<td>Enzymes</td>
<td>Protease, Cellulase, Lipase</td>
<td>Break down the dirt into more easily removable parts.</td>
<td>Laundry, dishes</td>
</tr>
<tr>
<td>Optical bleaches</td>
<td>Various pigments</td>
<td>Improve the appearance of clothes making whites and colours brighter.</td>
<td>Laundry</td>
</tr>
<tr>
<td>Dyes</td>
<td>Various pigments</td>
<td>Improve product aesthetics. Can also act as brighteners.</td>
<td>Laundry, dishes, house cleaning</td>
</tr>
<tr>
<td>Perfume</td>
<td>Essential oils and other perfum ingredients</td>
<td>Gives a pleasant smell to the product, laundry and the home.</td>
<td>Laundry, dishes, house cleaning</td>
</tr>
</tbody>
</table>

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Recipe for homemade soap

**Ingredients**

- 900 grams of olive oil (not extra virgin, rather used frying oil)
- 115 grams of anhydrous caustic soda (also available in the supermarket, in solid form)
- 315 grams of water
What you need

- Scales
- A glass to weigh the caustic soda
- A heat-resistant glass container
- A stainless steel pan with double the capacity compared to the volume of oil used
- A second pan able to contain the stainless steel pan
- A wooden spoon
- Rubber gloves

Hot process
The hot process is longer than the cold one, but offers the advantage of being simpler. The result is usually better and the soap obtained has a shorter curing time. In addition, if you decide to add “accessory” ingredients to the soap to improve its characteristics (such as essential oils, dyes or perfumes), these will not be attacked and damaged by the caustic soda. Let’s start! After having accurately weighed all the ingredients, pour the water into a heat-resistant glass container. Slowly and carefully, add the caustic soda to the water (NEVER do the opposite!), stirring with a wooden spoon. Dissolution of the sodium hydroxide (caustic soda) in water is an exothermic process, i.e. develops heat. For this reason it is advisable to use a heat resistant container and a wooden spoon, which is both resistant to the sodium hydroxide and does not conduct heat. Then cover the container, with a saucer for example, and wait until the caustic soda solution has cooled down to about 45°C. Meanwhile, heat the oil in a stainless steel pan (with double the capacity compared to the volume of oil) to a temperature of about 45°C. At this point you can add the soda solution to the oil, mixing with the same wooden spoon. The oil will change colour, becoming opaque. Now you can start to emulsify the mixture with an immersion blender. As you proceed, the mixture becomes increasingly creamy and consistent until, after 5-10 minutes, its reaches the so-called “ribbon” texture. It is at this point that saponification can really start! The process is facilitated by heat, so the pan containing the emulsion must be immersed in a second, larger pan, containing water and heated up to a temperature of about 70-80°C. In practice, the water contained in the second, larger pan should just simmer. From time to time, stir with a wooden spoon. You will see that after half an hour of coming to the boil, the emulsion will start to become dark and transparent, taking on a gelatinous consistency. The cooking phase must last two hours, after which optional ingredients such as dyes or essential oils and perfumes can be added, to render our “homemade” soap more pleasant. Since the long cooking facilitates the elimination of any excess soda, you can also pour the soap into simple and convenient aluminium containers, where we will leave it to solidify for 2 to 3 days in a cool, dry place. At the end of this phase, the soap will be solid, but not perfumed (quite the contrary!!!!) and may still contain traces of soda. For it to take on more most pleasant characteristics, we must wait for the curing phase, i.e. store it in a cool, dry place and wait at least one month. After which your soap will be perfectly usable.

By Tiziana Perri

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