

Cleaning is a familiar process which involves considerable chemistry and an understanding of numerous physical principles. Although the cleaning of a solid object—the removal of unwanted foreign matter from its surface—can be brought about by many ways such as blotting, abrasion, selective chemical reaction, or dissolution in an appropriate solvent, we generally think of cleaning as involving washing the object in a liquid bath, often water, containing substances which enhance the cleaning process. The action of the bath involves more than the dissolution of the “soil” or “dirt.” The bath liquid usually contains special solutes called detergents which act by changing the surface tension of the original bath liquid.

□ The Theory of Detergency

Consider water as the bath liquid. Pure water has a surface tension of 72 dynes per cm^2 which arises because of the unequal forces acting on water molecules in the surface compared with those which find themselves in bulk of the liquid. As illustrated in Figure 1a, the water molecules within the interior of the liquid experience interactions with other molecules in every possible direction, but the molecules at the surface only feel the presence of the molecules in the bulk of the liquid and in the surface. At a gas-liquid interface there are relatively few molecules (of any kind) above the surface so that the interactions in this direction are relatively small. The net result is that the surface molecules are pulled strongly into the liquid phase; which in the case of small amounts of water leads to the formation of a spherical drop.

Surface active molecules (surfactants), or molecules that spontaneously gather at liquid surfaces (Figure 1b) have a special geometry. Good surfactants are long molecules that carry polar groups at one end. The dissolution of a surfactant in pure water leads to the formation of a solution in which polar ends (hydrophilic) of the surfactant molecule are solvated by the water molecules in the surface. The long nonpolar part of the surfactant (hydrophobic end) is repelled by the water molecules. The surfactant molecules thus tend to reduce the surface tension of water by providing a means to oppose the attractive forces generated by the water molecules within the bulk of the liquid. As little as 0.2% of a surfactant can reduce the surface tension of water to 30 dynes/ cm^2 .

The action of a surfactant shown in Figure 1a also applies to the presently accepted ideas for the removal of any dirt from the surfaces of fabrics. Figure 2a illustrates the situation where pure water is in contact with an oily cotton fiber. As before, a surfactant dissolved in the water will still collect at the water interface—which in this case happens to involve water and oil. The nonpolar surfactant groups dissolve in the oily drop which helps lift the drop away from the fiber, and water (containing more surfactants) can creep between the drop and the fiber continuing the process of removal. Many fibers carry polar groups (like -OH on cotton fibers, NH and CO on Nylon) which tend to encourage water spreading (wetting) along the fiber.

Commercial detergents contain surfactants together with other substances which enhance detergency as described above.

□ Soaps

Soaps are the sodium (RCOO^-Na^+), potassium (RCOO^-K^+), or triethanolammonium ($^+\text{RN}(\text{CH}_2\text{CH}_2\text{OH})_3$)

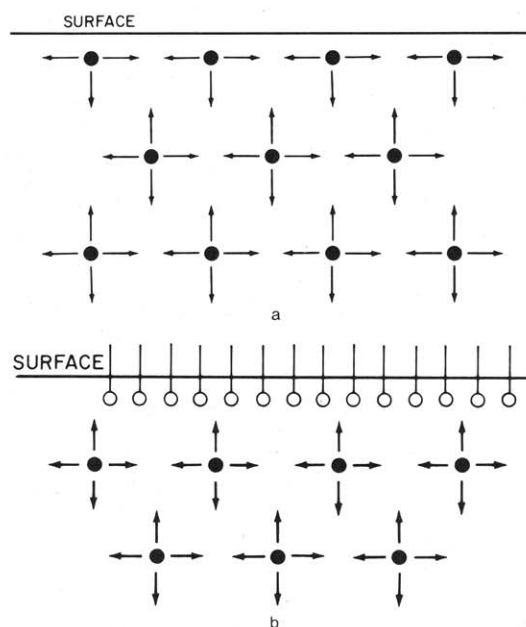


Figure 1. a, Surface tension of a pure liquid arises because of the unequal forces acting on molecules in the surface compared with those in the bulk liquid. b, Surfactant molecules collect at the surface of a liquid and change the surface tension.

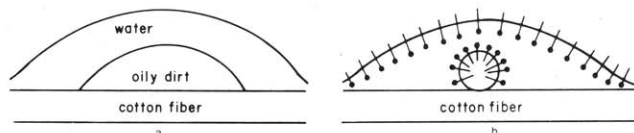


Figure 2. a, Pure water in contact with oily dirt on cotton. b, Interaction of surfactant with the oil and water. The dots represent the polar end of the surfactant molecule and the tails, the nonpolar.

salts of long chain organic acids; the organic chain is the hydrophobic end of the molecule while the carboxylate end ($-\text{CO}_2^-$) is hydrophilic. Other common metal salts of long chain organic acids tend to be less soluble and hence are poor surfactants; indeed, the presence of these ions, e.g., Mg^{2+} , Ca^{2+} , Al^{3+} , in washing water leads to the removal of the long chain organic acid anions making the soap less efficient per unit weight as a surfactant. When the ions occur naturally in water, we call it “hard water.” The triethanolammonium salts are interesting because they are soluble in organic solvents and can be used in dry-cleaning processes.

Historically, natural fats and oils have been the source of long chain carboxylic acids. Naturally occurring triglycerides (I) are esters of glycerol (II).

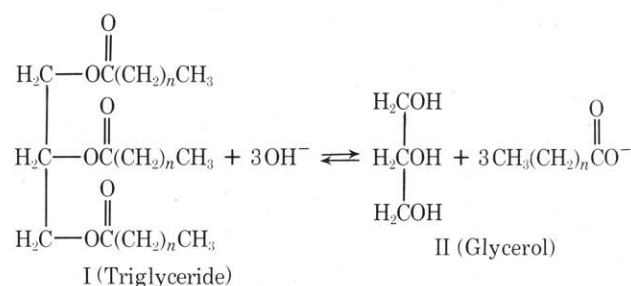


Table 1. Acids Obtained from Fats and Oils

Fat or Oil	(Percent Carboxylic Acid)							
	Caprylic	Capric	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic
Coconut	8.0	7.0	48.0	17.5	8.2	2.0	6.0	2.5
Babassu	6.5	2.7	45.8	19.9	6.9	...	18.1	...
Palm kernal	3.0	3.0	52.0	15.0	7.5	2.5	16.0	1.9
Palm	1.0	42.5	4.0	43.0	9.5
Olive	6.0	4.0	83.0	7.0
Peanut	7.0	5.0	60.0	21.0
Beef tallow	2.0	32.5	14.5	48.3	2.7
Lard	1.1	30.4	17.9	4.2	5.7

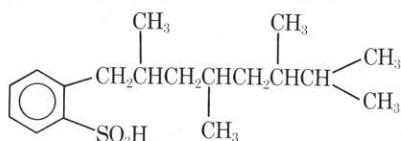
The ester link can be hydrolyzed in the presence of strong base to form the glycerol and the organic carboxylate. The chemistry described by the equation clarifies the classical soap-making processes. Wood ashes are leached with water, which produces a strongly basic solution. Soap is formed when fat is heated with this solution; home recipes call for the addition of rock salt (NaCl) to the mixture. This process causes the soap to precipitate, and, since it is less dense than the solution, it floats to the surface as a scum. The product contains 50–60% water and is pasty in consistency. The commercial and home processes for making soap are virtually identical except for questions relating to scale of production. Continued heating will reduce the water content to about 30% making a solid material that can be formed into cakes. Soap containing 10–15% water is suitable for making flakes, and soap powder is produced from a product containing 5–10% moisture.

Natural soaps are produced from a variety of fats and/or oils. These contain mixtures of long chain organic acid fragments; some typical analyses are shown in Table 1. Natural soaps can be fairly complex mixtures of organic acid salts (Table 2). Fortunately, acids with chain lengths greater than 9 carbon atoms are more or less equally good surfactants so that the composition of the natural fat or oil is not too critical. However, if the chain length is longer than 18 carbon atoms, the metal salts (soaps) become less soluble. The principal carboxylic acids obtained from natural sources all contain sufficiently long chains to be good surfactants.

□ Synthetic Surfactants

Although natural soaps are good surfactants, the availability of the raw materials and the need for detergents with better properties led to the development of synthetic substances. The first synthetic surfactant was produced in Germany during World War I as a result of tallow shortages. The first synthetic detergent (syndet) was produced commercially in this country in 1933, and since that time a variety of compounds have appeared. Like soaps, syndets have hydrophobic and hydrophilic ends. The hydrophilic ends may be anionic, cationic, or non-ionic. Generally the substances are derived from petrochemical stocks which, until now, have been relatively inexpensive. Some typical families of syndets are given in Table 3.

In 1947 the biodegradability of syndets became a major problem as was made obvious in Mt. Penn, Pennsylvania. A new detergent was distributed door-to-door in this city on Friday; by Monday morning mountains of foam appeared in the sewage treatment plant. The problem was traced to anionic syndets made from alkylbenzene sulfonic acids which carried branched hydrocarbon side chains.



Unfortunately, branched hydrocarbon chains are difficult for bacteria to biodegrade which has led to a relatively high concentration of syndets in water treatment plants. As little as 1 ppm of syndet will cause foaming in natural moving waters. This realization eventually led to legislation requiring that

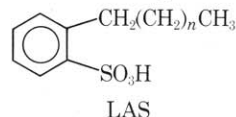
Table 2. Organic Acids Found in Natural Fats and Oils used to make Soap

		<i>n</i>	<i>mp</i> (°C)
$\text{CH}_3(\text{CH}_2)_n\text{CO}_2\text{H}$	Caprylic acid	6	16.3
	Capric acid	8	31.4
	Lauric acid	10	43.6
	Myristic acid	12	58.0
	Palmitic acid	14	62.9
$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$	Stearic acid	16	69.9
	Oleic acid	...	16
$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}=\text{CH}(\text{CH}_2)_2\text{CO}_2\text{H}$	Linoleic acid	...	9.5

Table 3. Typical Classes of Detergents

$\text{RCH}_2\text{SO}_3^-\text{Na}^+$	Anionic
$\text{RCH}_2\text{OSO}_3^-\text{Na}^+$	Alkylsulfonates
	Alkylsulfates
$(\text{C}_6\text{H}_5\text{CH}_2)_4\text{N}^+\text{Cl}^-$	Cationic
$\text{C}_{12}\text{H}_{25}$	Tetraalkylammonium chloride
$\text{C}_{17}\text{H}_{33}\text{CO}_2\text{C}_2\text{H}_4(\text{OC}_2\text{H}_4)_n\text{OH}$	Nonionic
$\text{C}_8\text{H}_{18}(\text{C}_6\text{H}_4)\text{OC}_2\text{H}_4(\text{OC}_2\text{H}_4)_n\text{OH}$	Esters
	Ethers

syndets be biodegradable. The technical solution to this problem was the development of syndets based on linear alkyl sulfonates (LAS) which are biodegradable.



The earlier detergents were less expensive because they could be prepared from petroleum wastes, whereas LAS-based detergents are more expensive because more "chemistry" must be accomplished to produce the linear side chain.

□ Detergents

Modern detergents are fairly complex mixtures that are compounded especially to produce desired effects.

"Builders" are substances added to complex ions such as Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} , that cause hardness. Builders are usually phosphates ($\text{Na}_5\text{P}_3\text{O}_{10}$ or $\text{Na}_4\text{P}_2\text{O}_7$), but carbonates, silicates, and borates have been employed. These substances also help create an alkaline condition in the water which helps stabilize suspended soil particles preventing them from depositing and helps dissolve acid soils.

Added emulsifiers such as carboxymethylcellulose ($\text{Cellulose-OCH}_2\text{CO}_2^-\text{Na}^+$) help prevent dirt particles from redepositing by placing a negative charge on dirt particles which then repel each other.

Often corrosion inhibitors like sodium silicate ($\text{Na}_2\text{Si}_3\text{O}_7$) are present in detergents to keep metal parts (washing machines, zippers, buttons) from corroding. Foaming agents are added because suds float suspended oil and dirt to the top of the water and keep it away from the items being washed. Finally, most detergent formulations contain a small amount of Na_2SO_4 which prevents caking of the product during storage.