

Soap and Detergents

The washing industry, usually known as the soap industry, has roots over 2000 years in the past, a soap factory having been found in the Pompeii excavations. However, among the many chemical process industries, none has experienced such a fundamental change in chemical raw materials as have the washing industries. It has been generally accepted that the per capita use of toilet soap is a reliable guide to the standard of living for any country.

HISTORICAL. Soap itself was never actually "discovered," but instead gradually evolved from crude mixtures of alkaline and fatty materials. Pliny the Elder described the manufacture of both hard and soft soap in the first century, but it was not until the thirteenth century that soap was produced in sufficient quantities to call it an industry. Up to the early 1800s soap was believed to be a mechanical mixture of fat and alkali; then Chevreul, a French chemist, showed that soap formation was actually a chemical reaction. Domeier completed his research on the recovery of glycerin from saponification mixtures in this period. Until Leblanc's important discovery producing lower-priced sodium carbonate from sodium chloride, the alkali required was obtained by the crude leaching of wood ashes or from the evaporation of naturally occurring alkaline waters, e.g., the Nile River.

The raw material shortages of World War I led the Germans to develop "synthetic soaps" or detergents. These were composed of short-chain alkyl naphthalene sulfonates, which were good wetting agents but only fair in detergent action. This sparked the interest worldwide in developing detergents, and new developments are continuing to the present time. From the original short-chain compounds the development has progressed through long chain alcohol sulfates in the 1920s and 1930s, through alkyl-aryl long chain sulfonates in the 1940s, to branched chain compounds in the 1950s and 1960s. During the 1960s the requirement of biodegradability became important and caused the return to linear long chains, because only the linear chains can be easily biodegraded.

USES AND ECONOMICS.¹ In 1981 the total value of surfactant and soap shipments was \$10,701 million. Of this, the value of household soap shipments was about \$1300 million and for household detergent products, \$4000 million. Out of a total demand of 3200 kt, soap represented 39 percent with a demand of 540 kt and detergents accounted for 840 kt.^{1a} Indus-

¹*U.S. Industrial Outlook, 1982*, U.S. Dept. of Commerce; Layman, Surfactants—A Mature Market with Potential, *Chem. Eng. News* 60 (2) 13 (1982); Moffet and von Hennig, Detergent Activities, *Soap Cosmet. Chem. Spec.* 57 (9) 29 (1981); Piellisch, Stronger Than Dirt: The Battle of the Detergent Chemicals, *Chem. Bus.* June 29, 1981, p. 33.

^{1a}t = 1000 kg; kt = 10³ kg.

trial uses accounted for the difference. Figure 29.1 and Tables 29.1 and 29.3 show the gradual replacement of soap by detergents in the household market.

Laundry products, toilet soaps, shampoos, dishwashing products, and cleaning products are the chief household uses of these materials. Industrial uses include cleaning compounds, specialty surfactants for hospital germicides, fabric conditioners, emulsifiers for cosmetics, flowing and wetting agents for agricultural chemicals, and rubber processing aids. A potentially large use is for enhanced oil recovery from presently "worked-out" oil wells.

DETERGENTS²

Detergents differ from soap in their action in hard water. Soaps form insoluble compounds with the calcium and magnesium ions present in hard water. These insoluble compounds precipitate out and reduce foaming and cleaning action. Detergents may react with the hard water ions, but the resulting products are either soluble or remain colloidally dispersed in the water. Table 29.2 illustrates the differences between soaps and detergents in composition and manufacture. Table 29.3 shows the consumption of surfactants in detergents.

Detergents have been divided into four main groups: anionic, cationic, nonionic, and amphoteric. The largest group consists of the anionics which are usually the sodium salts of

²Scientifically, the term detergent covers both soap and synthetic detergents, or "syndets," but it is widely used to indicate synthetic cleaning compounds, as distinguished from soap. It is so used in this book. The U.S. Tariff Commission reports on detergents under the name surface-active agents or surfactants under the broader class of synthetic organic chemicals.

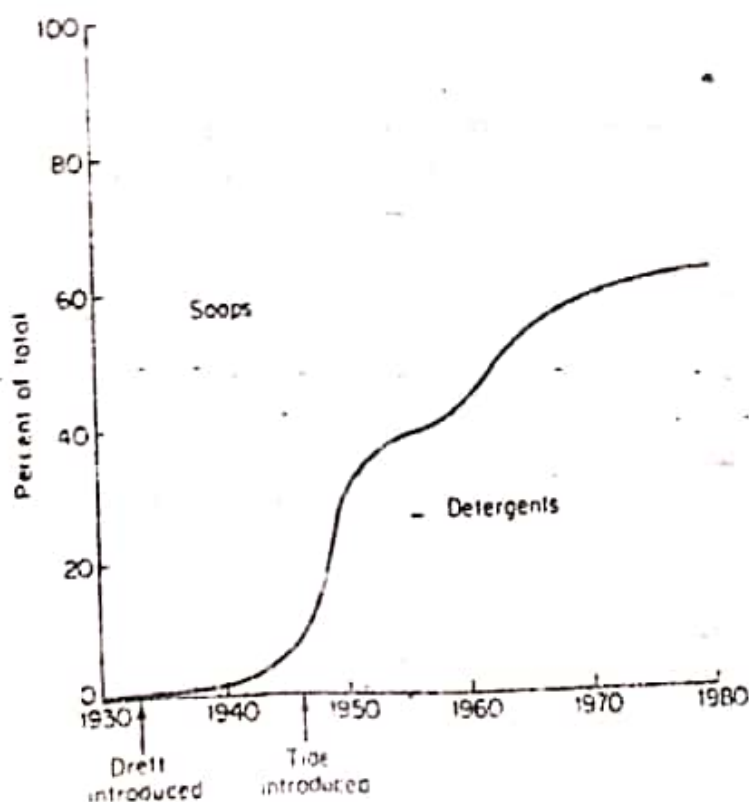


Fig. 29.1. Relative production of detergents and soap.

Table 29.1 Production and Sales of Soaps and Surfactants

	Soap		Surfactants		Total	
	10 ⁶ \$	kt	10 ⁶ \$	kt	10 ⁶ \$	kt
1940	313	1455	7	13	320	1468
1945	527	1717	35	68	562	1785
1950	540	1308	294	655	834	1963
1960	376	558	953	1789	1329	2347
1970	427	567	1379	2565	1806	3132
1980	1030	545	5430	2663	9460	3208

SOURCE: CPI 4, chap. 29. *U.S. Industrial Outlook, 1982*, U.S. Dept. of Commerce

an organic sulfate or sulfonate. Detergents can be formulated to produce a product of the desired characteristics ranging from maximum cleaning power, maximum cleaning/unit of cost, to maximum biodegradability. Usually commercial products are a compromise of the various desirable properties.

Soil removal is accomplished by wetting, emulsifying, dispersing, and/or solubilizing the soil by the cleaning agent. Detergent molecules can aggregate in water into spherical clusters called micelles. The hydrocarbon parts of the molecules gather together on the inside of the micelle and the polar groups are on the outside. Oil-soluble water-insoluble compounds, such as dyes, are often dissolved into the center of the micelle attracted by the hydrocarbon groups. This process is known as solubilization.³

Detergents and soaps have water-attracting (hydrophilic) groups on one end of the molecule and water-repelling (hydrophobic) groups on the other. These special properties are used in soil removal.

During the 1960s and 1970s, the composition of detergents underwent rapid changes because of environmental considerations.⁴ Evidence indicated that phosphates from deter-

³McGraw-Hill *Encyclopedia of Science and Technology*, 5th ed., vol. 18, McGraw-Hill, New York, 1982, p. 488.

⁴For Detergent Producers, the Question Is Which? *Chem. Week* 129 (4) 44 (1980).

Table 29.2 Soaps and Detergents

To Make Synthetic Detergents	
Alkylbenzene + oleum	→ alkylbenzene sulfonate
Tallow fatty alcohol + oleum	→ fatty alcohol sulfate
Sulfonate + sulfate + NaOH	→ sodium salts
Sodium salts + builders, etc.	→ detergents
To Make Soap	
Tallow + hydrolysis (splitting fats)	→ tallow fatty acid
Tallow fatty acid + NaOH	→ sodium salt of fatty acid
Salt of fatty acid + builder, etc.	→ soap

Table 29.3 Detergent Consumption of Surfactants (in metric kilotons)

	Powders	Liquids
Anionics		
Alkylbenzene sulfonate	148	43
Alcohol ethoxy sulfates	45	Small
Alcohol sulfates	22	—
Nonionics		
Alcohol ethoxylates	45	41
Alkyl phenol ethoxylates	5	5
Amines, amine oxides	5	5

SOURCE: *Chem. Week* 127 (26) 3 (1980).

gents may contribute to the eutrophication of lakes, so the use of phosphates in detergents was banned in some areas of the country. Many different substitutes were formulated into detergents, but some of these were found to be unsafe and were then banned. The position taken by the detergent industry has been that phosphates in wastewater can be removed by special treatment in sewage plants and, in view of the proved lack of toxicity of phosphates, their replacement may not be the most desirable solution. The soap and detergent industry and its suppliers face an enormous task in testing new materials for all possible effects on the environment, and extensive research will be needed before this complex problem can be solved.