

Chapter 3

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-

¹U.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 = 10⁶ kg.

trial uses accounted for the difference. Figure 3.1 and Tables 3.1 and 3.3 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 3.2 illustrates the differences between soaps and detergents in composition and manufacture. Table 3.3 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.

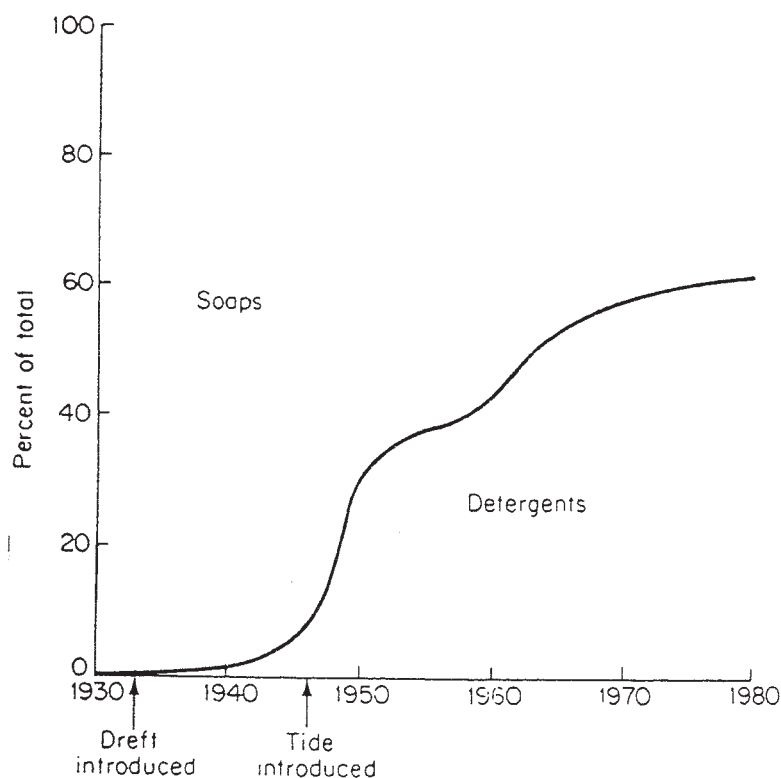


Fig. 3.1. Relative production of detergents and soap.

Table 3.1 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	2563	1806	3132
1980	1030	545	8430	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-

³*McGraw-Hill Encyclopedia of Science and Technology*, 5th ed., vol. 12, McGraw-Hill, New York, 1982, p. 488.

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

Table 3.2 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 3.3 Detergent Consumption of Surfactants (in metric kilotons)

	Powders	Liquids
Anionics		
Alkylbenzene sulfonate	148	43
Alcohol ethoxy sulfates	45	Small
Alcohol sulfates	23	—
Nonionics		
Alcohol ethoxylates	45	41
Alkyl phenol ethoxylates	5	5
Amines, amine oxides	5	5

SOURCE: *Chem. Week* 127:20-33, 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.

Raw Materials

A large volume of active organic compounds, or surfactants,⁵ for both detergents and soap are manufactured in final form by soap and detergent companies. Examples are linear alkylbenzene sulfonate (LAS) and fatty alcohol sulfate, which these companies manufacture in hundreds of millions of pounds. The same is true for fatty acids, the basic materials for soaps. Most of the inorganic materials, such as oleum, caustic soda, and various sodium phosphates and a large number of additives, the last mentioned amounting to 3% or less of the total product weight are purchased.

SURFACTANTS. These embrace "any compound that affects (usually reduces) surface tension when dissolved in water or water solutions, or which similarly affects interfacial tension between two liquids. Soap is such a material, but the term is most frequently applied to organic derivatives such as sodium salts of high molecular weight alkyl sulfates or sulfonates."⁶ The surfactants of both soap and synthetic detergents perform the primary cleaning and sudsing of the washing action in the same way through the reduction of surface tension. The cleaning process consists of (1) thoroughly wetting the dirt and the surface of the article being washed with the soap or detergent solution, (2) removing the dirt from the surface, and (3) maintaining the dirt in a stable solution or suspension (detergency). In wash water, soaps or detergents increase the wetting ability of the water so that it can more easily penetrate the fabrics and reach the soil. Then soil removal begins. Each molecule of the cleaning solution may be considered a long chain. One end of the chain is hydrophilic (water-loving); the other is hydrophobic (water-hating, or soil-loving). The soil-loving ends of some of these molecules are attracted to a soil particle and surround it. At the same time the water-loving ends pull the molecules and the soil particles away from the fabric and into the wash water. This is the action which, when combined with the mechanical agitation of the washing machine, enables a soap or detergent to remove soil, suspend it, and keep it from redepositing on clothes.

Classification. In most cases the hydrophobic portion is a hydrocarbon containing 8 to 18 carbon atoms in a straight or slightly branched chain. In certain cases, a benzene ring may replace some of the carbon atoms in the chain, for example, $C_{12}H_{25}-$, $C_9H_{19}\cdot C_6H_4-$. The hydrophilic functional group may vary widely and may be anionic, e.g., $-\text{OSO}_4^-$ or SO_3^{2-} ; cationic, e.g., $-\text{N}(\text{CH}_3)_3^+$ or $\text{C}_5\text{H}_5\text{N}^+$; or nonionic, e.g., $-(\text{OCH}_2\text{CH}_2)_n\text{OH}$.

In the anionic class one finds the most used compounds, namely linear alkylbenzene sulfonates from petroleum and alkyl sulfates from animal and vegetable fats (Fig. 3.2). Soap is

⁵Abbreviation for surface-active agents.

⁶Rose, *The Condensed Chemical Dictionary*, 6th ed., Reinhold, New York, 1961.

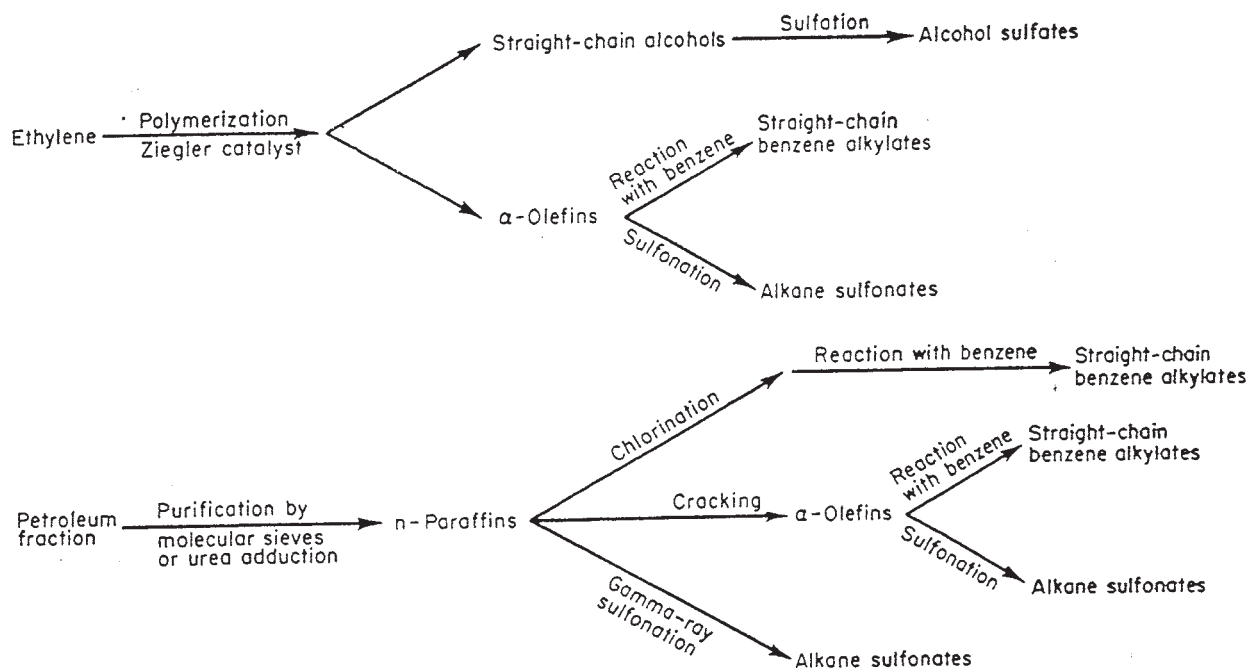
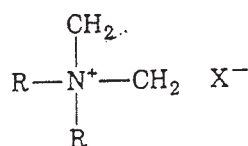
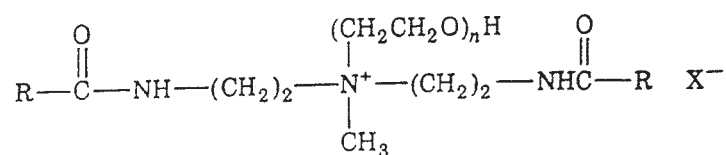


Fig. 3.2. Some possible paths to soft-detergent components. [*Chem. Eng.* 70 (18) 25 (1963).]

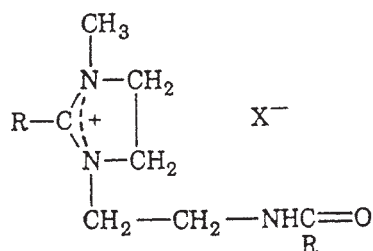
also anionic in character. Quaternary ammonium compounds comprise the cationic class. Three general types are used, mainly for fabric softeners. Type A is a dialkyl dimethyl quaternary ammonium compound



where X^- is either Cl^- or CH_3SO_4^- . Type B is a diamido alkoxyated quaternary ammonium compound, where X^- is CH_3SO_4^- .



Type C⁷ is an amido imidazolinium compound where X^- is CH_3SO_4^- .



⁷Williams, How to Choose Cationics for Fabric Softeners, *Soap Cosmet. Chem. Spec.* 58 (8) 28 (1982).

Being generally weak in detergent power, although they have good lubricating, antistatic, and germicidal properties, they are not usually used as household detergents. Anionics and cationics are not compatible with soap.

Ethylene oxide condensates of fatty alcohols illustrate the molecular structure of nonionic surfactants. There are many excellent soil-removing types that are low sudsers and hence are useful in drum-type automatic clothes washers. Nonionics are more effective than anionics in removing soil at the lower temperatures necessary for laundering synthetic fibers. They are also more effective at removing body oils.

Biodegradability.⁸ In view of the attention being given to water pollution control and abatement, product-development chemists and chemical engineers have realized that surfactants being developed for use in household and industrial detergents that go down the drain to the sewer must be readily decomposable to inorganic compounds by the microbial action of sewage treatment and in surface streams. This new parameter has been added to the performance, efficiency, and cost factors the detergent industry must consider in developing new products. Some surfactants, like tetrapropylene-derived alkylbenzene sulfonate, degrade slowly, leaving a persistent residue. Others are more readily decomposable by microorganisms and leave practically no persistent residues. The ease with which a surfactant is decomposed by microbial action has been defined as its biodegradability. Tests are being developed and standards are being established for biodegradability. To have broad application, such standards must recognize the breadth of variation in environmental conditions. Materials which may be only partly degraded in inefficient treatment processes can be completely decomposed by more sophisticated biological treatment systems. Methods of testing radiolabeled surfactants of anionic, cationic, and nonionic types and builders have been developed to determine the rate of biodegradation in parts per billion in natural waters and also to determine if threshold concentrations, below which degradation is not observed, exist.⁹

STRAIGHT-CHAIN ALKYL BENZENES. Biodegradable detergents are made primarily from phenyl-substituted *n*-alkanes of 11 to 14 carbon atoms. The straight-chain paraffins or olefins needed are produced from petroleum as shown in Fig. 3.2. In 1981, 233 kt were produced in the United States.

n-Alkanes are separated from kerosene by adsorption using molecular sieves. Branched chain and cyclic alkanes have larger cross-sectional diameters than do the linear molecules, thus making sieve separation possible. The other common method of separation of the normal paraffin compounds from the branched and cyclic ones is by reaction with urea or thiourea. Urea will react with linear chain hydrocarbons having at least seven carbon atoms to give a crystalline adduct which is separable by filtration. No such adduct is formed with the branched chain or cyclic compounds. The adduct can then be decomposed by heating with hot water at 80 to 90°C. Conversely, thiourea will react with the branched chain hydrocarbons but will not form adducts with straight-chain or aromatic ones. The separated *n*-paraffins are converted to benzene alkylates or are cracked to yield α -olefins.

Linear olefins are prepared by dehydrogenation of paraffins, by polymerization of ethylene to α -olefins using an aluminum triethyl catalyst (Ziegler-type catalyst), by cracking paraffin wax, or by dehydrohalogenation of alkyl halides.

⁸Larson, "Role of Biodegradation Kinetics in Predicting Environmental Fate," in Maki, Dickson, and Cairns (ed.), *Biotransformation and Fate of Chemicals in the Aquatic Environment*, Am. Soc. for Microbiol. Publ., Washington, D.C., 1980.

⁹Larson and Wentler, Biodegradation of Detergent Materials, *Soap Cosmet. Chem. Spec.* 58 (5) 53 (1982).

α -Olefins or alkane halides can be used to alkylate benzene through the Friedel-Crafts reaction, employing hydrofluoric acid or aluminum fluoride as a catalyst.

FATTY ACIDS AND FATTY ALCOHOLS

Economics. Fatty alcohols and fatty acids are mainly consumed in the manufacture of detergents and soaps. Fatty acids, both saturated (e.g., stearic acid) and unsaturated (e.g., oleic), have long been employed in many industries as both free acids, and, more frequently, as salts. Examples are:

Magnesium stearates in face powders.

Calcium or aluminum soaps (insoluble) employed as water repellents in waterproofing textiles and walls.

Triethanolamine oleate in dry cleaning and cosmetics.

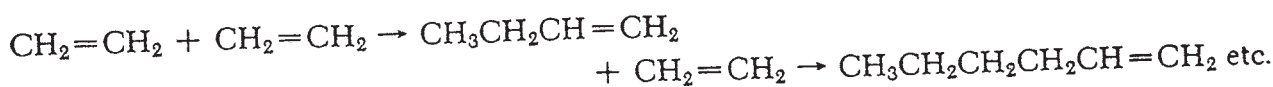
Lithium stearate as a component of greases.

Rosin soap consumed as a sizing for paper.

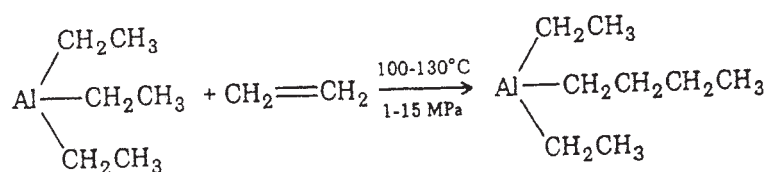
Manufacture of Fatty Acids.¹⁰ Basic raw materials, such as oils and fats, which have been used for a long time (Chap. 2), have, since about 1955, been very extensively supplemented by improved chemical processing and by synthetic petrochemicals. A selection from these processes is given here. Table 3.4 compares three processes for splitting fats that have been used for many years. Figure 3.3 illustrates the high-pressure hydrolysis, catalyzed by zinc oxide, which is used in the soap industry. Fatty acids are drawn off from the distillate receiver for sale or for further conversion to fatty acid salts (calcium, magnesium, zinc, etc.). Several older and less used separation methods for purifying fatty acids are panning and pressing, fractional distillation, and solvent crystallization.

Manufacture of Fatty Alcohols. The Ziegler catalytic procedure for converting α -olefins to fatty alcohols and the methyl ester hydrogenation process are the important methods for preparing fatty alcohols. See also the flowchart in Fig. 3.4 and the text presented under soap for the continuous hydrolysis of fats to furnish fatty acids which may be hydrogenated to fatty alcohols.

The Ziegler¹¹ procedure is an important one for manufacturing C_{12} to C_{18} α -olefins and fatty even-numbered straight-chain alcohols for detergents. See Fig. 3.4. Gaseous ethylene is converted to higher, linear aluminum trialkyls and α -olefins by the action of aluminum triethyl which takes part in the reactions.



CHAIN GROWTH REACTION



¹⁰ECT, 3d ed., vol. 4, 1978, p. 837.

¹¹Sittig, *Detergent Manufacturing*, Noyes, Park Ridge, N.J., 1979; ECT, 3d ed., vol. 1, 1978, p. 740.

Table 3-4 Tabular Comparison of the Various Fat-Splitting Processes

	Twitchell	Batch autoclave		Continuous Countercurrent*
Temperature, °C	100–105	150–175	240	250
Pressure, MPag		5.2–10.0	2.9–3.1	4.1–4.9
Catalyst	Alkyl-aryl sulfonic acids or cycloaliphatic sulfonic acids, both used with sulfuric acid 0.75–1.25% of the charge	Zinc, calcium, or magnesium oxides, 1–2%	No catalyst	Optional
Time, h	12–48	5–10	2–4	2–3
Operation	Batch	Batch		Continuous
Equipment	Lead-lined, copper-lined, Monel-lined, or wooden tanks	Copper or stainless-steel autoclave		Type 316 stainless tower
Hydrolyzed	85–98% hydrolyzed 5–15% glycerol solution obtained, depending on number of stages and type of fat	85–98% hydrolyzed 10–15% glycerol, depending on number of stages and type of fat		97–99% 10–25% glycerol, dependent on type of fat
Advantages	Low temperature and pressure; adaptable to small scale; low first cost because of relatively simple and inexpensive equipment	Adaptable to small scale; lower first cost for small scale than continuous process; faster than Twitchell		Small floor space; uniform product quality; high yield of acids; high glycerin concentration; low labor cost; more accurate and automatic control; lower annual costs
Disadvantages	Catalyst handling; long reaction time; fat stocks of poor quality must often be acid-refined to avoid catalyst poisoning; high steam consumption; tendency to form dark-colored acids; need more than one stage for good yield and high glycerin concentration; not adaptable to automatic control; high labor cost	High first cost; catalyst handling; longer reaction time than continuous processes; not so adaptable to automatic control as continuous; high labor cost; need more than one stage for good yield and high glycerin concentration		High first cost; high temperature and pressure; greater operating skill

SOURCE: Mostly from Marsel and Allen, Fatty Acid Processing, *Chem. Eng.* 54 (6) 104 (1947). Modified in 1982.

*See Fig. 29.8.