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-

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[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 $= 10^6$ kg.

rial 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.
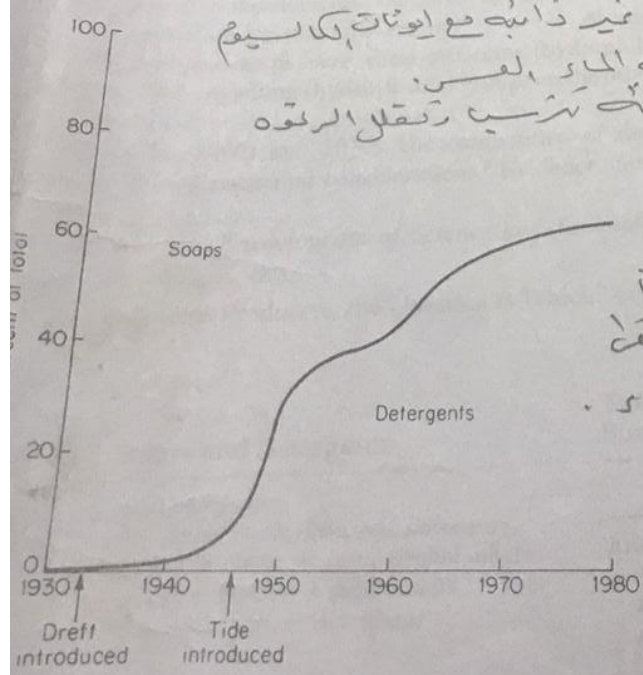
DETERGENTS[2]

٭ الفرق بين الصابون ملتقات

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

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[2]Scientifically, 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.

٭ الصابون يكون مركبات غير ذائبه مع ايونات الكالسيوم
والمغنيسيوم الموجوده في الماء العسر.
- هذه المركبات الغير ذائبه ترسب وتقلل الرغوه
تعمل التنظيف.

٭ المنظفات تعمل مع
ايونات الماء العسر ولكن
الناتج اما ان يكون ذائب او يبقى
للغرويات منتشره في الماء.

9.1. Relative production of detergents and soap.

2

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	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-

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

[4] For 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	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 alkyl-benzene 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 sulfo-nates."[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 (detergentcy). 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., $-OSO_4^-$ or SO_3^{2-}; cationic, e.g., $-N(CH_3)_3^+$ or $C_5H_5N^+$; or nonionic, e.g., $-(OCH_2CH_2)_nOH$.

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. 29.2). Soap is

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[5]Abbreviation for surface-active agents.

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

Table 29-4 Tabular Comparison of the Various Fat-Splitting Processes

	Twitchell	Batch autoclave		Continuous Countercurrent[*]
Temperature, °C	100–105	150–175	240	250 4.1–4.9
Pressure, MPag		5.2–10.0	2.9–3.1	
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.
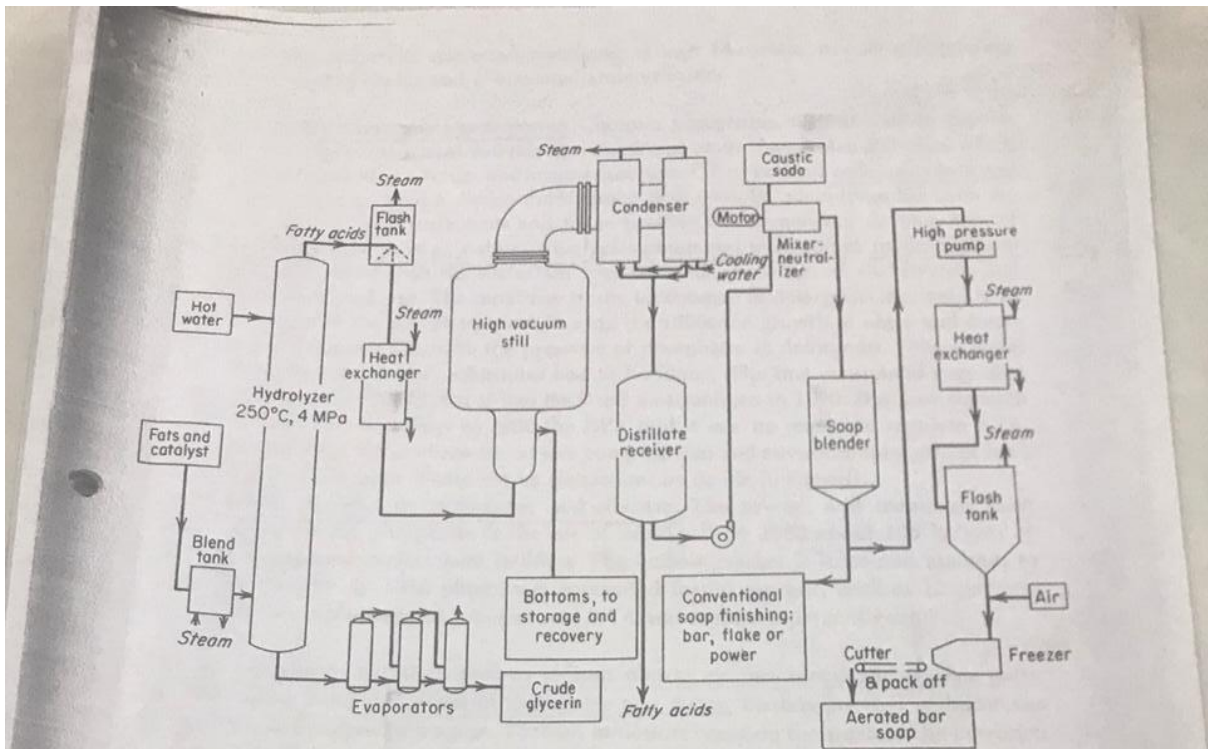*See Fig. 29.8.

Fig. 29.3. Continuous process for the production of fatty acids and soap. (*Procter & Gamble Co.*)
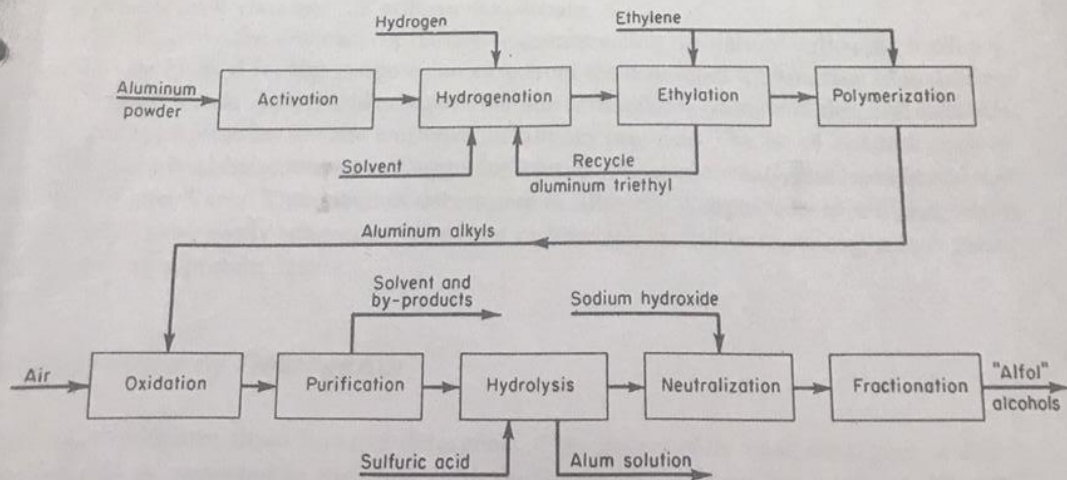

Fig. 29.4. The alfol process. Fatty alcohols made by means of the organometallic route have carbon chain lengths ranging from 6 to 20 carbons. The alfol process used by Conoco commences by reacting aluminum metal, hydrogen, and ethylene, all under high pressure, to produce *aluminum triethyl*. This compound is then polymerized with ethylene to form aluminum alkyls. These are oxidized with air to form aluminum alkoxides. Following purification, the alkoxides are hydrolyzed with 23 to 26% sulfuric acid to produce crude, primary, straight-chain alcohols. These are neutralized with caustic, washed with water, and separated by fractionation. Basic patents covering the process have been licensed. (*DuPont-Conoco.*)

amides, aliphatic carboxylic acid esters containing at least 18 carbons in one or preferably both acid and alcohol chains, and N-alkylated aminotriazines.

BUILDERS. Builders boost detergent power. Complex phosphates, such as sodium tripolyphosphate, have been used most extensively. These are more than water softeners which sequester water-hardening calcium and magnesium ions. They prevent redeposition of soil from the wash water on fabrics. Proper formulation with complex phosphates has been the key to good cleaning with surfactants and made possible the tremendous development of detergents. Polyphosphates (e.g., sodium tripolyphosphate and tetrasodium pyrophosphate) have a synergistic action with the surfactant together with an enhanced effectiveness and hence reduce the overall cost. The rapid rise in the acceptance of detergents stemmed from the building action of the polyphosphates. During the 1960s the growth of algae and eutrophication in lakes became linked to the presence of phosphates in detergents. Several states restricted phosphate use so that substitutes had to be found. The first compound suggested was nitrilotriacetic acid (NTA), but it was declared a carcinogen in 1970. But new research results have vindicated its safety; in 1980 the EPA said it saw no reason to regulate NTA. This has not freed NTA for use because various congressional and environmental groups have challenged the EPA decision. There are no restrictions on its use in Canada.

Other builders are citrates, carbonates, and silicates. The newest, and seemingly most promising, substitute for phosphates is the use of zeolites.[14] By 1982 about 136 kt/year of zeolites were being used as detergent builders. The builder market is large and amounts to over 1000 kt annually. In 1980 phosphates accounted for 50 percent, zeolites 12 percent, silicates 13 percent, carbonates 12 percent, and NTA and citrates 2 percent each.

ADDITIVES. *Corrosion* inhibitors, such as sodium silicate, protect metal and washer parts, utensils, and dishes from the action of detergents and water. Carboxymethyl cellulose has been used as an *antiredeposition* agent. *Tarnish inhibitors* carry on the work of the corrosion inhibitor and extend protection to metals such as German silver. Benzotriazole has been used for this purpose. *Fabric brighteners* are fluorescent dyes which make fabrics look brighter because of their ability to convert ultraviolet light to visible light. Two dyes thus used are 4(2H-naphtho[1,2-d]triazol-2-yl)stilbene-2-sulfonate and disodium 4,4′-bis(4-anilino-6-morpholino-S-triazin-2-ylamino)-2,2′-stilbene disulfonate.

Bluings improve the whiteness of fabrics by counteracting the natural yellowing tendency. The ingredients used for this purpose can vary from the long-used ultramarine blue (bluing) to new dye materials. *Antimicrobial* agents include carbanilides, salicylanilides, and cationics. Peroxygen-type *bleaches* are also employed in laundry products. The use of *enzyme*-containing detergents has been common in Europe for several years and recently has been introduced into the United States. The enzymes decompose or alter the composition of soil and render the particles more easily removable. They are particularly useful in removing stains, particularly those of a protein nature.

Manufacture of Detergents

Table 29.5 compares three types of detergents. The most widely used detergent, a heavy-duty granule, is presented in Fig. 29.6, with the quantities of materials required. The reactions are:

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[14]Layman, Detergents Shift Focus of Zeolites Market, *Chem. Eng. News* **60** (39) 10 (1982).
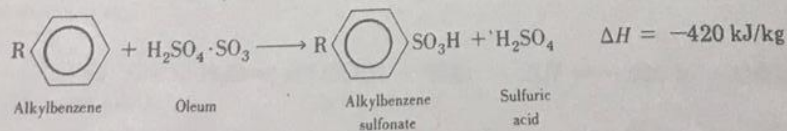
Table 29.5 Basic Composition of Three Types of Dry Phosphate-Based Detergents (Granules)

Ingredient	Function	Ingredient on Dry-Solids Basis, wt %		
		Light-Duty High Sudsers	Heavy-Duty Controlled Sudsers	Heavy-Duty High Sudsers
Surfactants				
Organic active, with suds regulators	Removal of oily soil, cleaning	25–40	8–20	20–35
Builders				
Sodium tripolyphosphate and/or tetrasodium pyrophosphate	Removal of inorganic soil, detergent-building	2–30	30–50	30–50
Sodium sulfate	Filler with building action in soft water	30–70	0–30	10–20
Soda ash	Filler with some building action	0	0–20	0–5
Additives				
Sodium silicate having 2.0 ≤ SiO₂/Na₂0 ≤ 3.2	Corrosion inhibitor with slight building action	0–4	6–9	4–8
Carboxymethyl cellulose	Antiredeposition of soil	0–0.5	0.5–1.3	0.5–1.3
Fluorescent dye	Optical brightening	0–0.05	0.05–0.1	~0.1
Tarnish inhibitors	Prevention of silverware tarnish	0	0–0.02	0–0.02
Perfume and sometimes dye or pigment	Aesthetic, improved product characteristics	0.1	0.1	0.1
Water	Filler and binder	1–5	2–10	3–10

SOURCE: Van Wazer, *Phosphorus and Its Compounds*, vol. 2, Interscience, New York, 1961, p. 1760.

LINEAR ALKYLBENZENE SULFONATION

1. Main reaction:

$$R\langle\bigcirc\rangle + H_2SO_4 \cdot SO_3 \longrightarrow R\langle\bigcirc\rangle SO_3H + {}'H_2SO_4 \qquad \Delta H = -420 \text{ kJ/kg}$$

Alkylbenzene   Oleum   Alkylbenzene sulfonate   Sulfuric acid

2. Secondary reactions:

$$R\langle\bigcirc\rangle SO_3H + H_2SO_4 \cdot SO_3 \longrightarrow R\langle\bigcirc\rangle \overset{SO_3H}{SO_3H} + H_2SO_4$$

Alkylbenzene sulfonate   Oleum   Disulfonate   Sulfuric acid

$$R\langle\bigcirc\rangle SO_3H + R^1\langle\bigcirc\rangle \longrightarrow R\langle\bigcirc\rangle - SO_2 - \langle\bigcirc\rangle R^1 + H_2O$$

Alkylbenzene   Alkylbenzene   Sulfone 1%   Water
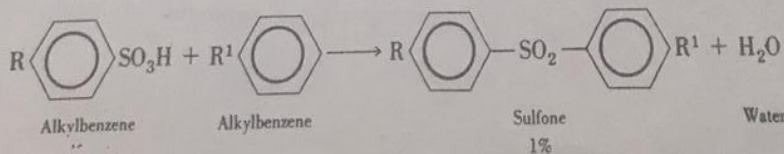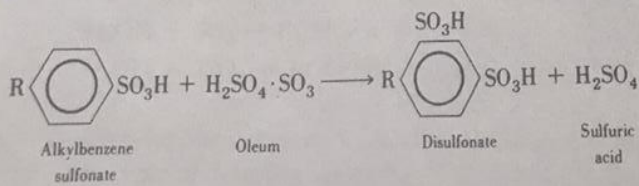
In order to produce 1 t of finished product, the following materials (in kilograms) are required:

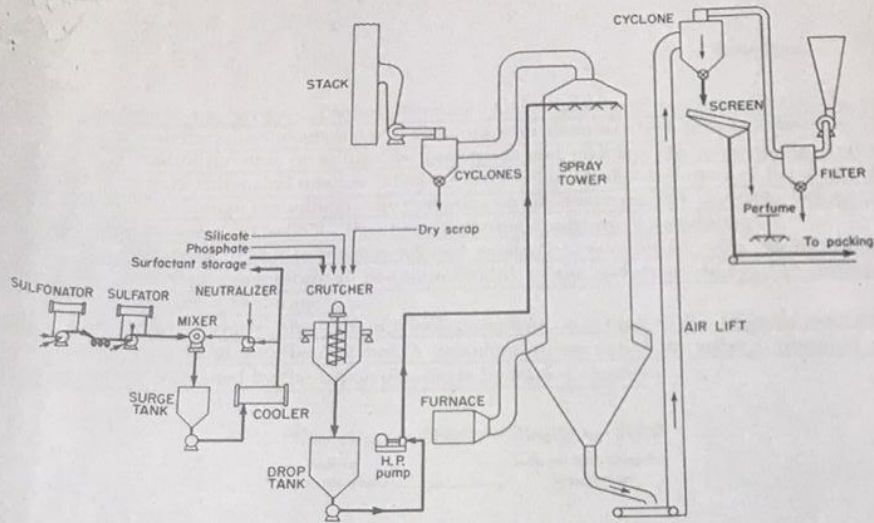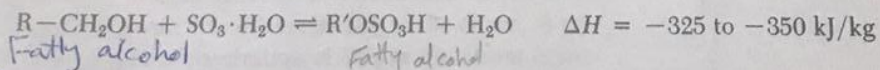|			
① Surfactant Materials		② Corrosion Inhibitor	
Alkylbenzene (petrochemical)	75	Sodium silicate	125
Fatty alcohol (from tallow)	75	③ Builder	
Oleum	150	Sodium tripolyphosphate	500
NaOH solution	200	④ Miscellaneous additives	30
		⑤ Water	500

Fig. 29.6. Simplified continuous flowchart for the production of heavy-duty detergent granules. (*Procter & Gamble Co.*)

FATTY ALCOHOL SULFATION

① Main reaction:

$$R-CH_2OH + SO_3 \cdot H_2O \rightleftharpoons R'OSO_3H + H_2O \qquad \Delta H = -325 \text{ to } -350 \text{ kJ/kg}$$

Fatty alcohol   Fatty alcohol sulfate

② Secondary reactions:

$$R-CH_2OH + R'-CH_2-OSO_3H \rightarrow R-CH_2-O-CH_2-R' + H_2SO_4 \qquad أثير$$
$$R'-CH_2-CH_2OH + SO_3 \rightarrow R'-CH=CH_2 + H_2SO_4 \qquad الكين$$
$$R-CH_2OH + SO_3 \rightarrow RCHO + H_2O + SO_2 \qquad الديهيد$$
$$R-CH_2OH + 2SO_3 \rightarrow RCOOH + H_2O + 2SO_2$$
$$حامض$$
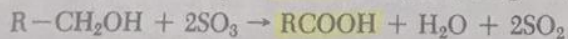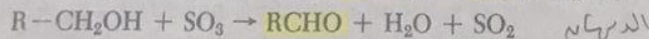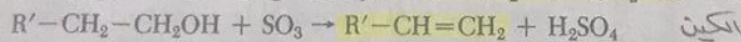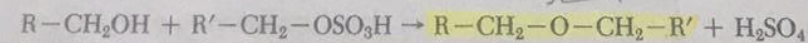
This presentation is supplemented by Table 29.5, which gives the basic constituents in more detail for the three types of detergent granules. The continuous flowchart in Fig. 29.6 can be broken down into the following coordinated sequences:

⑨

Sulfonation-sulfation. The alkylbenzene (AB) is introduced continuously into the sulfonator with the requisite amount of oleum, using the dominant bath principle shown in Fig. 29.8 to control the heat of sulfonation conversion and maintain the temperature at about 55°C. Into the sulfonated mixture is fed the fatty tallow alcohol and more of the oleum. All are pumped through the sulfater, also operating on the dominant bath principle, to maintain the temperature at 50 to 55°C, thus manufacturing a mixture of surfactants.

Neutralization. The sulfonated-sulfated product is neutralized with NaOH solution under controlled temperature to maintain fluidity of the surfactant slurry. The surfactant slurry is conducted to storage.

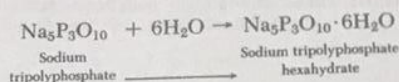The surfactant slurry, the sodium tripolyphosphate, and most of the miscellaneous additives are introduced into the crutcher. A considerable amount of the water is removed, and the paste is thickened by the tripolyphosphate hydration reaction:

$$Na_5P_3O_{10} + 6H_2O \rightarrow Na_5P_3O_{10} \cdot 6H_2O$$

Sodium tripolyphosphate ⟶ Sodium tripolyphosphate hexahydrate

This mixture is pumped to an upper story, where it is *sprayed* under high pressure into the 24-m-high spray tower, counter to hot air from the furnace. Dried granules of acceptable shape and size and suitable density are formed. The dried granules are transferred to an upper story again by an air lift which cools them from 115°C and stabilizes the granules. The granules are separated in a cyclone, screened, perfumed, and packed.

The sulfonation conversion is shown in Fig. 29.7 to be extremely fast. The reactions also need to have the high heats of reaction kept under control, as shown in more detail in Fig. 29.8, depicting the circulating heat exchanger, or dominant baths, for both these chemical conversions and for neutralization. The use of oleum in both cases reduces the sodium sulfate in the finished product. However, the oleum increases the importance of control to prevent oversulfonation. In particular, alkylbenzene sulfonation is irreversible and results in about 96 percent conversion in less than a minute when run at 55°C with 1 to 4% excess SO_3 in the oleum. A certain minimum concentration of SO_3 in the oleum is necessary before the sulfonation reaction will start, which in this case is about 78.5% SO_3 (equivalent to 96% sulfuric acid). As both these reactions are highly exothermic and rapid, efficient heat removal is required to prevent oversulfonation and darkening. Agitation is provided by a centrifugal pump, to which the oleum is admitted. The recirculation ratio (volume of recirculating material divided by the volume of throughput) is at least 20:1 to give a favorable system. To provide the sulfonation time to reach the desired high conversion, more time is allowed by conducting the mixture through a coil, where time is given for the sulfonation reaction to go to completion.

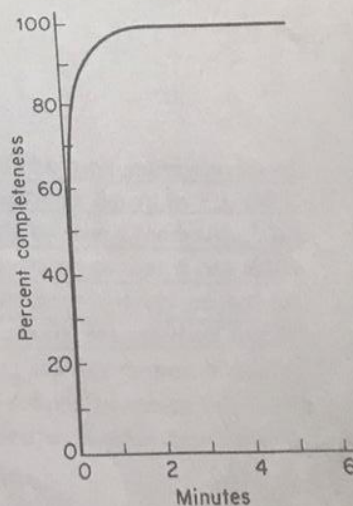Neutralization of the acid slurry releases six to eight times as much heat as the sulfonation reaction. Here a

Fig. 29.7. Alkylbenzene sulfonation completeness versus time at 55°C. (*Procter & Gamble Co.*)
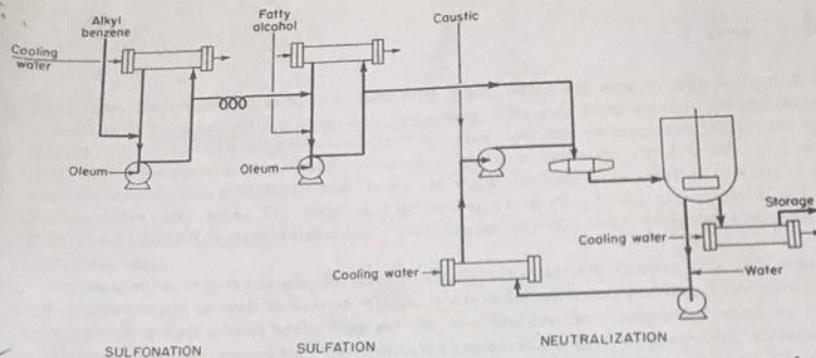
Fig. 29.8. Continuous series sulfonation-sulfation, ending with neutralization, in the circulating heat-exchanging dominant bath to control heat. (*Procter & Gamble Co.*)

dominant bath (Fig. 29.8) is employed which quickly effects the neutralization, since a partly neutralized acid mix is very viscous.

SOAP

Soap comprises the sodium or potassium salts of various fatty acids, but chiefly of oleic, stearic, palmitic, lauric, and myristic acids. For generations its use has increased until its manufacture has become an industry essential to the comfort and health of civilized human beings. The relative and overall production of soap and detergents is shown by the curve in Fig. 29.1. History and industrial statistics are discussed in the first part of this chapter (Table 29.1).

Raw Materials

Tallow is the principal fatty material in soapmaking; the quantities used represent about three-fourths of the total oils and fats consumed by the soap industry, as shown in Fig. 29.1. It contains the mixed glycerides obtained from the solid fat of cattle by steam rendering. This solid fat is digested with steam; the tallow forms a layer above the water, so that it can easily be removed. Tallow is usually mixed with coconut oil in the soap kettle or hydrolyzer in order to increase the solubility of the soap. Greases (about 20 percent) are the second most important raw material in soapmaking. They are obtained from hogs and smaller domestic animals and are an important source of glycerides of fatty acids. They are refined by steam rendering or by solvent extraction and are seldom used without being blended with other fats. In some

cases, they are treated so as to free their fatty acids, which are used in soap instead of the grease itself. Coconut oil has long been important. The soap from coconut oil is firm and lathers well. It contains large proportions of the very desirable glycerides of lauric and myristic acids. Free fatty acids are utilized in soap, detergent, cosmetic, paint, textile, and many other industries. The acidification of "foots," or stock resulting from alkaline refining of oils, also produces fatty acids. The important general methods of splitting are outlined in Table 29.4. The Twitchell process is the oldest.[15] Continuous countercurrent processes are now most commonly used.
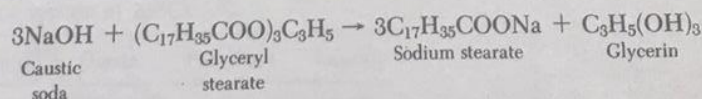
The soapmaker is also a large consumer of chemicals, especially caustic soda, salt, soda ash, and caustic potash, as well as sodium silicate, sodium bicarbonate, and trisodium phosphate. Inorganic chemicals added to the soap are the so-called builders. Important work by Harris of Monsanto and his coworkers[16] demonstrated conclusively that, in particular, tetrasodium pyrophosphate and sodium tripolyphosphate were unusually effective synergistic soap builders. Of considerable economic importance was the demonstration that combinations of inexpensive builders, such as soda ash, with the more effective (and expensive) tetrasodium pyrophosphate or sodium tripolyphosphate, were sometimes superior to the phosphate used alone. It was further shown that less soap could be used in these mixtures to attain the same or more effective soil removal.

Manufacture

The manufacture of soap is presented in Fig. 29.3. The long-established kettle[17] process, however, is mainly used by smaller factories or for special and limited production. As soap technology changed, continuous alkaline saponification was introduced. Computer control allows an automated plant for continuous saponification by NaOH of oils and fats to produce in 2 h the same amount of soap (more than 300 t/day) made in 2 to 5 days by traditional batch methods.

The present procedure involves continuous splitting, or hydrolysis, as outlined in Table 29.2 and detailed in Fig. 29.3. After separation of the glycerin, the fatty acids are neutralized to soap.

The basic chemical reaction in the making of soap is saponification.[18]

$$3NaOH + (C_{17}H_{35}COO)_3C_3H_5 \rightarrow 3C_{17}H_{35}COONa + C_3H_5(OH)_3$$

| Caustic soda | Glyceryl stearate | Sodium stearate | Glycerin |

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[15]This process is described in more detail in CPI 2, p. 619.

[16]*Oil Soap* 19 3 (1942); Cobbs et al., *Oil Soap* 17 4 (1940); Wan Wazer, "Phosphorus and Its Compounds," chap. 27, in *Detergent Building*, Interscience, New York, 1958.

[17]Full descriptions with flowcharts for the kettle process full-boiled (several days), semi-boiled, and cold are available on pp. 623–625 of CPI 2.

[18]Although stearic acid is written in these reactions, oleic, lauric, or other constituent acids of the fats could be substituted. See Table 28.1 for fatty acid composition of various fats and oils.

(12)

The procedure is to split, or hydrolyze, the fat, and then, after separation from the valuable glycerin, to neutralize the fatty acids with a caustic soda solution:

$$(C_{17}H_{35}COO)_3C_3H_5 + 3H_2O \rightarrow 3C_{17}H_{35}COOH + C_3H_5(OH)_3$$

Glyceryl stearate   Stearic acid   Glycerin

$$C_{17}H_{35}COOH + NaOH \rightarrow C_{17}H_{35}COONa + H_2O$$

Stearic acid   Caustic soda   Sodium stearate
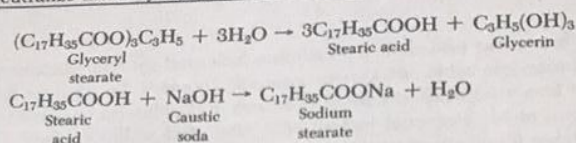
The usual fats and oils of commerce are not composed of the glyceride of any one fatty acid, but of a mixture. However, some individual fatty acids of 90% purity or better are available from special processing. Since the solubility and hardness of the sodium salts (Table 29.6) of the various fatty acids differ considerably, the soapmaker chooses the raw material according to the properties desired, with due consideration of the market price.

In continuous, countercurrent splitting the fatty oil is deaerated under a vacuum to prevent darkening by oxidation during processing. It is charged at a controlled rate to the bottom of the hydrolyzing tower through a sparge ring, which breaks the fat into droplets. These towers, about 20 m high and 60 cm in diameter, are built of Type 316 stainless steel (see Fig. 29.5). The oil in the bottom contacting section rises because of its lower density and extracts the small amount of fatty material dissolved in the aqueous glycerin phase. At the same time daerated, demineralized water is fed to the top contacting section, where it extracts the glycerin dissolved in the fatty phase. After leaving the contacting sections, the two streams enter the reaction zone.[19] Here they are brought to reaction temperature by the direct injection of high-pressure steam, and then the final phases of splitting occur. The fatty acids are discharged from the top of the splitter or hydrolyzer to a decanter, where the entrained water is separated or flashed off. The glycerin-water solution is then discharged from the bottom of an automatic interface controller to a settling tank. See Fig. 29.10 for glycerin processing.

Although the crude mixtures of fatty acids resulting from any of the above methods may be used as such, usually a separation into more useful components is made. The composition of the fatty acids from the splitter depends upon the fat or oil from which they were derived.

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[19]Allen et al., Continuous Hydrolysis of Fats, *Chem. Eng. Prog.*, 43 459 (1947); Fatty Acids, *Chem. Eng.* 57 (11), 118 (1950); Ladyn, Fat Splitting, *Chem. Eng.* 71 (17) 106 (1964) (continuous flowcharts).

Table 29.6 Solubilities of Various Pure Soaps (in grams per 100 g of water at 25°C)

	Stearate	Oleate	Palmitate	Laurate
Sodium	0.1°	18.1	0.8°	2.75
Potassium	—	25.0	—	70.0°
Calcium	0.004†	0.04	0.003	0.004†
Magnesium	0.004	0.024	0.008	0.007
Aluminum	i	i	d	

° Approximate.
† Solubility given at 15°C only.
NOTE: i indicates that the compound is insoluble; d indicates decomposition.

Those most commonly used for fatty acid production include beef tallow and coconut, palm, cottonseed, and soybean oil. Probably the most used of the older processes is panning and pressing. This fractional crystallization process is limited to those fatty acid mixtures which solidify readily, such as tallow fatty acid. The molten fatty acid is run into pans, chilled, wrapped in burlap bags, and pressed. This expression extracts the liquid red oil (mainly oleic acid), leaving the solid stearic acid. The total number of pressings indicates the purity of the product. To separate fatty acids of different chain lengths, distillation[20] is employed, vacuum distillation being the most widely used. Three fractionating towers of the conventional tray type are operated under a vacuum. Preheated, crude fatty acid stock is charged to the top of a stripping tower. While it is flowing downward, the air, moisture, and low-boiling fatty acids are swept out of the top of the tank. The condensate, with part of it redrawn as a reflux, passes into the main fractionating tower, where a high vacuum is maintained at the top. A liquid side stream, also near the top, removes the main cut (low-boiling acids), while overheads and noncondensables are withdrawn. The liquid condensate (high-boiling acids) is pumped to a final flash tower, where the overhead distillate is condensed and represents the second fatty acid fraction. The bottoms are returned to the stripping tower, reworked, and removed as pitch. The fatty acids may be sold as such or converted into many new chemicals.

The energy requirements that enter into the cost of producing soap are relatively unimportant in comparison with the cost of raw materials, packaging, and distribution. The energy required to transport some fats and oils to the soap factory is occasionally considerable. The reaction that goes on in the soap reactor is exothermic.

The following are the principal sequences into which the making of bar soap by water splitting and neutralization can be divided, as shown by the flowchart in Fig. 29.3.

1. Transportation of fats and oils.
2. Transportation and manufacture of caustic soda.
3. Blending of the catalyst, zinc oxide, with melted fats and heating with steam takes place in the blend tank.
4. Hot melted fats and catalysts are introduced into the bottom of the hydrolyzer.
5. Splitting of fats takes place countercurrently in the hydrolyzer at 250°C and 4.1 MPa, continuously, the fat globules rising against a descending aqueous phase.
6. The aqueous phase, having dissolved the split glycerin (about 12%), falls and is separated.
7. The glycerin water phase is evaporated and purified. See Glycerin.
8. The fatty acids phase at the top of the hydrolyzer is dried by flashing off the water and further heated.
9. In a high-vacuum still the fatty acids are distilled from the bottoms and rectified.
10. The soap is formed by continuous neutralization with 50% caustic soda in high-speed mixer-neutralizer.
11. The neat soap is discharged at 93°C into a slowly agitated blending tank to even out any inequalities of neutralization. At this point the neat soap analyzes: 0.002 to 0.10% NaOH, 0.3 to 0.6% NaCl, and approximately 30% H_2O. This neat soap may be extruded, milled, flaked, or spray-dried, depending upon the product desired. The flowchart in Fig. 29.3 depicts the finishing operations for floating bar soap.

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[20]Fatty Acid Distillation, *Chem. Eng.* 55 146 (1948). Pictured flowcharts of both straight and fractional distillation; Marsel and Allen, Fatty Acid Processing, *Chem. Eng.* 54 (6) 104 (1947); ECT, 3d ed., vol. 4, 1978, p. 839.

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 alkyl-benzene 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 sulfo-nates."[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 (detergentcy). 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., $-OSO_4^-$ or SO_3^{2-}; cationic, e.g., $-N(CH_3)_3^+$ or $C_5H_5N^+$; or nonionic, e.g., $-(OCH_2CH_2)_nOH$.

In the anionic class one finds the most used compounds, namely linear alkylbenzene sul-fonates from petroleum and alkyl sulfates from animal and vegetable fats (Fig. 29.2). Soap is

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[5]Abbreviation for surface-active agents.

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