Reference # 4 Section 5.15 Soaps &
Detergents (August 1992)
1 Copy

third edition

CHEMICAL PROCESS INDUSTRIES

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McGRAW-HILL BOOK COMPANY
NEW YORK ST. LOUIS SAN FRANCISCO
TORONTO LONDON SYDNEY

TABLE 29.1 ***Production and Sales of Soaps and Detergents***

	Soap					Detergent			[illegible]
Year	*Toilet bars*	*Granulated and chips*	*Laundry bars*	*Other*	*Total soap*	*Granulated and paste*	*Liquid*	*Total detergents*	[illegible]
1940	342	1,179	897	243	2,663	....	...	26	[illegible]
1945	433	1,508	677	286	2,906	....	...	130	[illegible]
1950	489	1,430	386	178	2,484	1,070	22	1,093	[illegible]
1955	494	508	221	120	1,350	2,164	153	2,317	[illegible]
1960	577	248	155	74	1,056	2,665	645	3,310	[illegible]
1962	...	....	...	...	1,041	....	...	3,752	[illegible]
1963	...	....	...	...	1,026	....	...	3,863	[illegible]
1964	...	....	...	...	986	....	...	4,040	[illegible]

Source: Stanford Research Institute Chemical Economics Handbook, and Facts and Figures, *C&EN*.
See Fig. 29.1 for curve of relative production of detergents and soaps.

process jointly developed by Sharples and Lever Brothers and first installed at the latter's plant in Baltimore in 1945. Since then, there have been many installations of both types. These continuous soap processes, although extremely important technological developments, have been partially eclipsed by synthetic detergents.

USES AND ECONOMICS The detergent sales in 1964 amounted to $1 billion and 4,040 million lb, up 3.3% in value and 4.6% in volume from 1963. Soap sales were lower for 1964, amounting to $319 million and 986 million lb (Table 29.1).

DETERGENTS[1]

By reason of the much larger proportion of the washing markets now supplied by detergents, these much more complex synthetic products are presented before soaps (Fig. 29.1). The parallel comparison as shown by Table 29.2 indicates the significant *difference* in the processes used to manufacture detergents and soaps and also the *difference* in chemical composition, with resultant *difference* in action. The soaps give precipitates, and hence are not efficient in hard or acid waters, whereas the detergents are. Furthermore, although

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[1] Scientifically, the term detergent covers both soap and the "synthetic detergents," or "syndets," but widespread usage applies the term *detergent* to the synthetic cleaning compounds as distinguished from soaps, will be so used in this book. The U.S. Tariff Commission reports on detergents under the name surface-active agents, under the broader class of synthetic organic chemicals.

TABLE 29.2 ***General Difference between Composition and Continuous Manufacture of Soaps and Detergents***

To make synthetic detergents (continuous process):	*To make soap (continuous process):*
TALLOW + hydrolysis (splitting fats) ⟶	TALLOW + hydrolysis (splitting fats) ⟶
TALLOW FATTY ACIDS; + high-pressure hydrogenation ⟶	TALLOW FATTY ACID; + NaOH ⟶
TALLOW FATTY ALCOHOL; + sulfation ⟶	SALT OF FATTY ACID; + builders, etc. ⟶
SULFATED TALLOW FATTY ALCOHOL; + NaOH ⟶	SOAPS
SODIUM SALT OF SULFATED TALLOW FATTY ACID; + builders, etc. ⟶	
DETERGENTS	

TABLE **29.3** ***Basic Composition of Three Types of Dry 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 $\leq SiO_2/Na_2O \leq$ 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	*ca.* 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, p. 1760, Interscience, 1961. *Approximate.

ordinary soaps do vary somewhat in chemical composition, they are essentially and simply the sodium or potassium salts of various fatty acids. On the other hand, detergents are very complex mixtures of many substances, all chosen to impart a *particular action in cleaning.* The modern concept of surface-active agents, or surfactants, includes soaps, detergents, emulsifiers, wetting agents, and penetrants. These all owe their activity to a modification of the properties of the surface layer between two phases in contact with another. Most of the surface-active agents are a combination of water-attracting, or hydrophilic, groups on one end of the molecule, with water-repelling, or hydrophobic, groups on the other. The detergents excel in possessing these special properties to effect soil removal. There are light- and heavy-duty detergents, and Table 29.3 differentiates between these in composition.

DETERGENT RAW MATERIALS

The large volume of active organic compounds, or surfactants,[1] for both detergents and soap are manufactured in final form by the soap and detergent companies. Examples are alkyl-benzene sulfonate (ABS) and fatty alcohol sulfates, which these companies manufacture in the billions of pounds. The same is true for fatty acids, the basic materials for soaps. Most of the inorganic materials are purchased, such as oleum, caustic soda, various

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[1] Abbreviation for surface-active agents.

sodium phosphates, and the large number of additives, the latter amounting to 3% or more of the total product weight.

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."[1] 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 tensions. 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 (detergents). In wash water, soaps or detergents increase the wetting ability of the water so that it can more easily penetrate the fabrics and get to the location of the soil. Then soil removal begins. Each molecule of the cleaning solution may be considered as 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 are pulling 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 OF SURFACTANTS 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 an anionic, e.g., $-OSO_3^{\ominus}$ or $-SO_3^{\ominus}$; cationic, e.g., $-N(CH_3)_3^{\oplus}$ or $C_5H_5N^{\oplus}$; zwitterionic, e.g., $-N^{\oplus}(CH_3)_2(CH_2)_2COO^{\ominus}$; semipolar, e.g., $-N(CH_3)_2 \longrightarrow O$; or nonionic group, e.g., $-(OCH_2CH_2)_nOH$. In the *anionic* class one finds the most used, namely, the alkylbenzene sulfonates (ABS), from petroleum, and the alkyl sulfates, from animal and vegetable fats (Fig. 29.2). Other examples are alkylbenzene-ether sulfonate, alkylphenol-ethylene oxide sulfonate, alkylglycerol-ether sulfonate, alkyl esters of isothionate, and methylalkyl laurates.[2] These latter are generally employed in newer applications, such as liquids and bars, where special properties are needed and where a premium price will be paid. Soap is also anionic in character. The quaternary trimethylalkylammonium halides, of which cetyltrimethylammonium bromide is an example, are the most common *cationic* surfactants. Dialkyl-dimethylammonium chloride is a cationic fabric softener. Being generally weak in detergent power, although they have good lubricating, antistatic, and germicidal properties, they are not used as household detergents. Anionics and cationics are not compatible since they combine into an insoluble precipitate. For this same reason cationics are not compatible with soap. The alkyl betains are representatives of the *zwitterionics;* dimethylalkylamine oxides are *semipolar;* and the ethylene oxide condensates of alkylphenol illustrate the molecular structure of truly *nonionic* surfactants, of which there are many excellent soil-removing types and which are chiefly emulsifying agents but low sudsers, and hence useful in drum-type automatic clothes and dish washers. Examples

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

[2] Kastens and Ayo, *I&EC*, **42,** 1626 (1950); U.S. Pat. 1,932,180.

are chains of a lower alkyl oxide combined with longer alkyl chains or alkylphenols, for example, nonylphenol-ethylene oxide condensate.[1] Here the side chain of polyethylene oxide imparts hydrophilic properties, the hydrophobic action coming from alkylbenzene or fatty acids or amines. In general, the hydrophilic nature of these functional groups decreases from ionic to nonionic groups. Much of the organic detergent chemical research carried out in recent years deals with the synthesis of new surfactant molecules as an extension of the reactions

Anionic, giving, in solution, surface-active ions bearing a negative charge:

$$C_{12}H_{25}OH + SO_3 \longrightarrow C_{12}H_{25}OSO_3H \xrightarrow{NaOH} C_{12}H_{25}OSO_3^{\ominus}Na^{\oplus} \qquad \text{(for detergent)}$$

$$\text{Fat} + H_2O \longrightarrow C_{17}H_{35}COOH \xrightarrow{NaOH} C_{17}H_{35}COO^{\ominus}Na^{\oplus} \qquad \text{(soap)}$$

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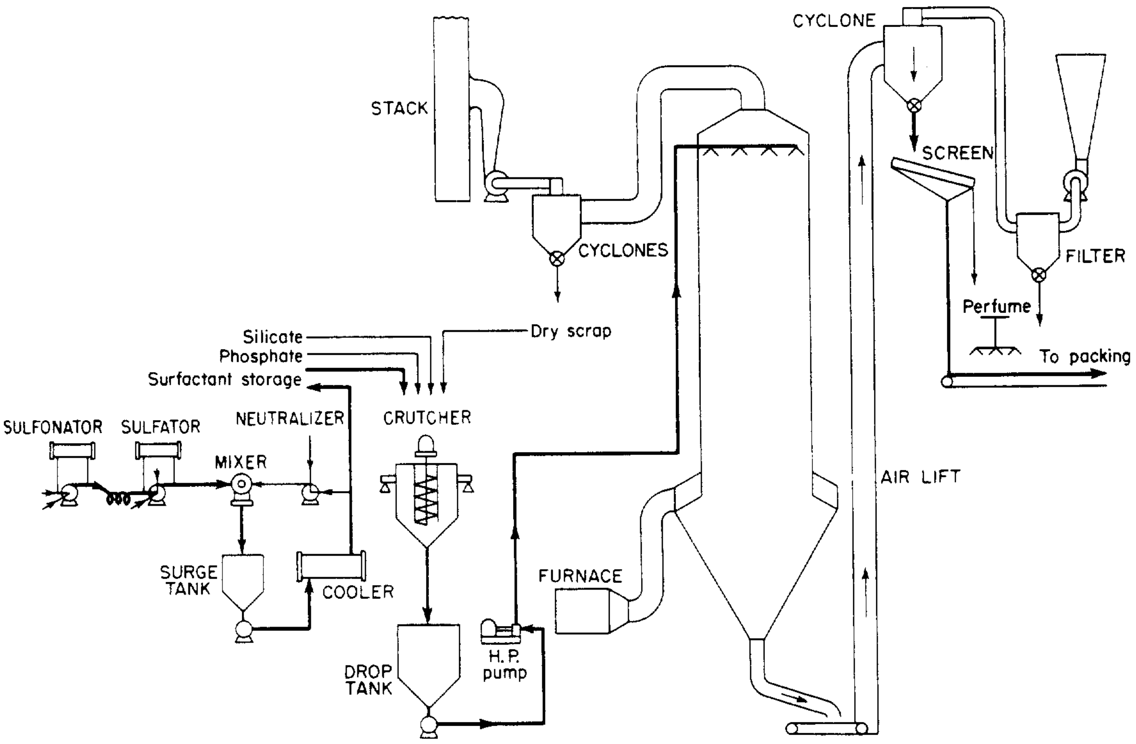
[1] Jelinek and Mayhew, *I&EC*, **46**, 1930 (1954); Nonionic Surfactants Pick Up Speed, *CE*, **70** (7), 34 (1963).



RAW MATERIALS FOR SYNTHETIC DETERGENT GRANULES
Basis: 1,000 lb. finished product

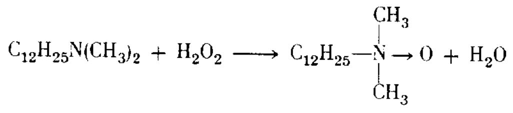
Surfactant materials		Corrosive inhibitor	
Alkylbenzene (petrochemical)	75 lb.	Sodium silicate	125 lb.
Fatty alcohol (from tallow)	75 lb.	Builder	
Oleum	150 lb.	Sodium tripolyphosphate	500 lb.
NaOH solution	200 lb.	Miscellaneous additives	30 lb.
		Water	500 lb.

Fig. 29.2 Simplified continuous flowchart for heavy-duty detergent granules. (*Procter & Gamble Co.*)

Cationic, yielding, in solution, surface-active ions positively charged:

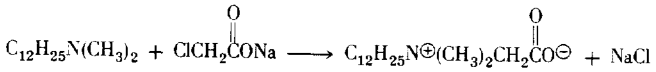
$C_{12}H_{25}Cl + N(CH_3)_3 \longrightarrow C_{12}H_{25}N(CH_3)_3^{\oplus}Cl^{\ominus}$

Semipolar:

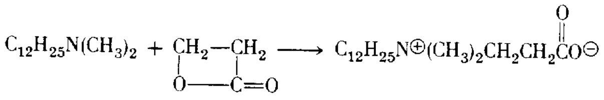


$$C_{12}H_{25}N(CH_3)_2 + H_2O_2 \longrightarrow C_{12}H_{25}-\overset{CH_3}{\underset{CH_3}{N}}\rightarrow O + H_2O$$

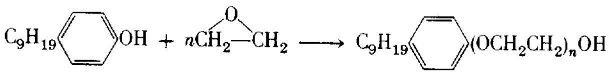
Zwitterionic:



$$C_{12}H_{25}N(CH_3)_2 + ClCH_2\overset{O}{\overset{\|}{C}}ONa \longrightarrow C_{12}H_{25}N^{\oplus}(CH_3)_2CH_2\overset{O}{\overset{\|}{C}}O^{\ominus} + NaCl$$



Nonionic:



SUDS REGULATORS An ingredient often used with a surfactant is a suds regulator, either a stabilizer or suppressor. These materials have no common chemical relationship and are often specific for certain surfactants. Examples of stabilizer surfactant systems are lauric ethanolamide-alkyl-benzene sulfonate and lauryl alcohol-alkyl sulfate. Suds suppressors are generally hydrophobic materials, some examples of which are long-chain fatty acids, silicones, and hydrophobic nonionic surfactants.

BUILDERS[1] Builders boost detergent power and are almost exclusively complex phosphates, such as sodium tripolyphosphate. These are more than water softeners which sequester the water-hardening Ca and Mg ions. They prevent the redeposition on fabrics of the soil from the wash water. Proper formulation with *complex phosphates* is the key to good cleaning and a full partner with the surfactants in making possible the tremendous development of detergents. The polyphosphates (e.g., sodium tripolyphosphate and tetrasodium pyrophosphate) have a synergistic action between moderate amounts of these inexpensive inorganic salts and the relatively low percentage of the surfactant, and hence reduce the overall cost, together with an enhanced effectiveness. The rapid rise in the acceptance of detergents stemmed from the building action of the polyphosphates. Surfactants, suds regulators, and detergency builders make up the basic surfactant detergent formulation; however, small amounts of additives are necessary (3% or less).

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 is an ingredient used for this purpose. *Fabric brightener* is the name applied to fluorescent dyes, which make fabrics look brighter because of their ability to convert ultraviolet light to visible light. The structural formulas for such dyes are

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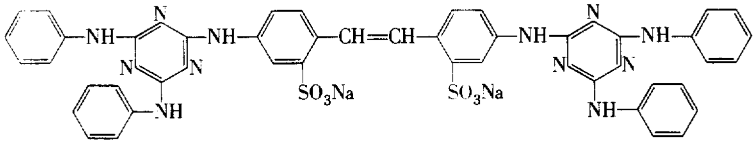
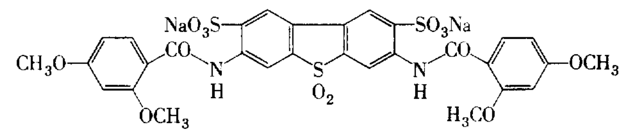
[1] Van Wazer, Phosphorus and Its Compounds, chap. 27, Detergent Building: Theory and Practice, Interscience, 1961. Very important study.



Disodium 4,4′-*bis*[(4,6-dianilino-1,3,5-triazin-2-yl)amino]-2,2′-stilbenedisulfonate
(CI fluorescent brightening agent 8)



Disodium 3,7-*bis*(2,4-dimethoxybenzamido)dibenzothiophenedioxide-2,8-disulfonate
(CI fluorescent brightening agent 9)

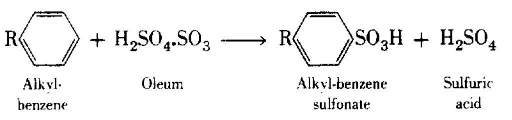
Bluings improve the whiteness appearance of fabrics by counteracting the natural yellowing tendency. The ingredients used for this purpose can vary from the long-used ultramarine blue to new dye materials. *Antimicrobial* agents are ingredients which are not now in general use in household products; there are several, including carbanilides, salicylanilides, and cationics. Peroxygen-type *bleaches* can also be employed in laundry products, but, their use in this country has been limited. Peroxygen-bleach-containing detergents are common in Europe, where hypochlorite bleaches are uncommon, because of the greater effectiveness of these peroxygen bleaches under high-temperature European washing conditions. *Perfume* has become an accepted ingredient, and here the compositions and fragrances vary widely. However, the soap and detergent industries are the largest consumers of perfumes among the industries of the United States. *Coloring* is a means of emphasizing certain properties of a product and of obtaining distinctiveness.

MANUFACTURE OF DETERGENTS

The most widely used detergent, a heavy-duty granule, is presented in Fig. 29.2, with the quantities of materials required. The reactions are

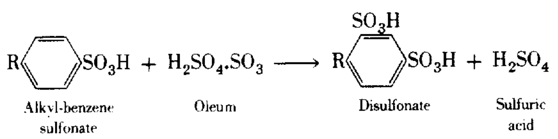
Alkyl-benzene sulfonation:

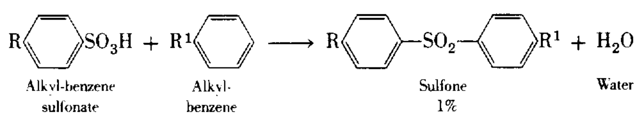
1. Main reaction



$\Delta H = -180$ Btu/lb of alkyl-benzene

2. Secondary reactions





Fatty alcohol sulfation:

1. Main reaction

$$R{-}CH_2OH + SO_3.H_2O \rightleftharpoons R'OSO_3H + H_2O \qquad \Delta H = -140 \text{ to } -150 \text{ Btu/lb fatty alcohol}$$

2. Secondary reactions

$$R{-}CH_2OH + R'{-}CH_2{-}OSO_3H \longrightarrow R{-}CH_2{-}O{-}CH_2{-}R' + H_2SO_4$$

$$R'{-}CH_2{-}CH_2OH + SO_3 \longrightarrow R'{-}CH{=}CH_2 + H_2SO_4$$

$$R{-}CH_2OH + SO_3 \longrightarrow RCHO + H_2O + SO_2$$

$$R{-}CH_2OH + 2SO_3 \longrightarrow RCOOH + H_2O + 2SO_2$$

This presentation is supplemented by Table 29.3, which gives the basic constituents in more detail for three types of detergent granules. The continuous flowchart of Fig. 29.2[1] can be broken down into the following coordinated sequences:

Sulfonation-sulfation. The alkyl-benzene (AB) is introduced continuously[2] into the sulfonator with the requisite amount of oleum, using the dominant bath principle shown in Fig. 29.4 to control heat of *sulfonation* conversion and maintain the temperature at around 130 F (Ch and Op). 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 temperature at *120 to 130 F* (Ch and Op), 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 (Ch and Op). The surfactant slurry is conducted to storage (Op).

Into the *crutcher* is introduced the surfactant slurry, the sodium tripolyphosphate and most of the miscellaneous additives (Ch and Op). A considerable amount of the water is removed, and the paste is thickened by the tripolyphosphate hydration reaction:

$$\underset{\substack{\text{Sodium}\\\text{tripolyphosphate}}}{Na_5P_3O_{10}} + 6H_2O \xrightarrow{\quad} \underset{\substack{\text{Sodium tripolyphosphate}\\\text{hexahydrate}}}{Na_5P_3O_{10}.6H_2O}$$

This mixture is pumped up to an upper story, where it is *sprayed* under high pressure into the 80-ft-high spray tower, counter to hot air from the furnace (Op). Here are formed the dried acceptable shaped and sized granules with the suitable density. The dried granules are transferred to an upper story again by an air lift which cools from 240 F and stabilizes the granules (Op). The granules are separated in a cyclone, screened, perfumed, and packed (Op).

The sulfonation conversion is shown by Fig. 29.3 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. 29.4, 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, the alkyl-benzene sulfonation is irreversible and reacts to about 96% conversion in less than a minute when run at 130 F

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[1] Fedor *et al.*, Detergents Continuously, *I&EC*, **51** (1), 13 (1959) (detailed flowcharts and reference); Gushee and Scheer, Speciality Surfactants, *I&EC*, **51** (7), 798 (1959) (excellent presentation).

[2] New Process Tames Sulfur Trioxide Sulfonation, *CE*, **69** (5), 70 (1962), flowchart; Gilbert, Sulfonation, Interscience, 1965.

with 1 to 4% of excess SO_3 in the oleum (Fig. 29.3). A certain minimum concentration of SO_3 is in the oleum. The π value is necessary before the sulfonation will start, which in this case is about 78.5% of 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. The 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 (Fig. 29.4), where time is given for the sulfonation reaction to go to completion.

The *neutralization* of the acid slurry releases six to eight times as much heat as in the sulfonation reaction. Here a dominant bath (Fig. 29.4) is employed which *quickly* effects the neutralization since a partly neutralized acid mix is very viscous.

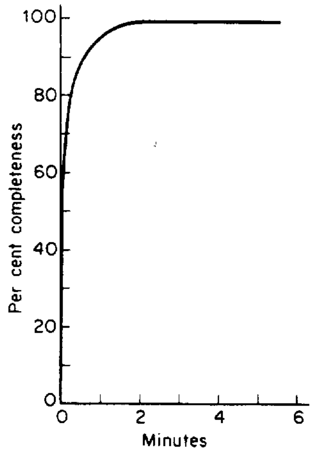

Fig. 29.3 Alkyl-benzene sulfonation completeness versus time at 130 F. (*Procter & Gamble Co.*)

Much more than half of the detergents sold are represented by the heavy-duty granules described, the aryl-sulfonate being, in 1963, a branched-chain dodecyl-benzene sulfonate. The next section will discuss variations to improve the biodegradability. Other surfactants (Table 29.4) are being used in increasing amounts, especially for types of detergents such as liquids, tablets, and bars. Many of these are more rapidly biodegradable, for instance, than those which are branched-chain benzene-sulfonates.

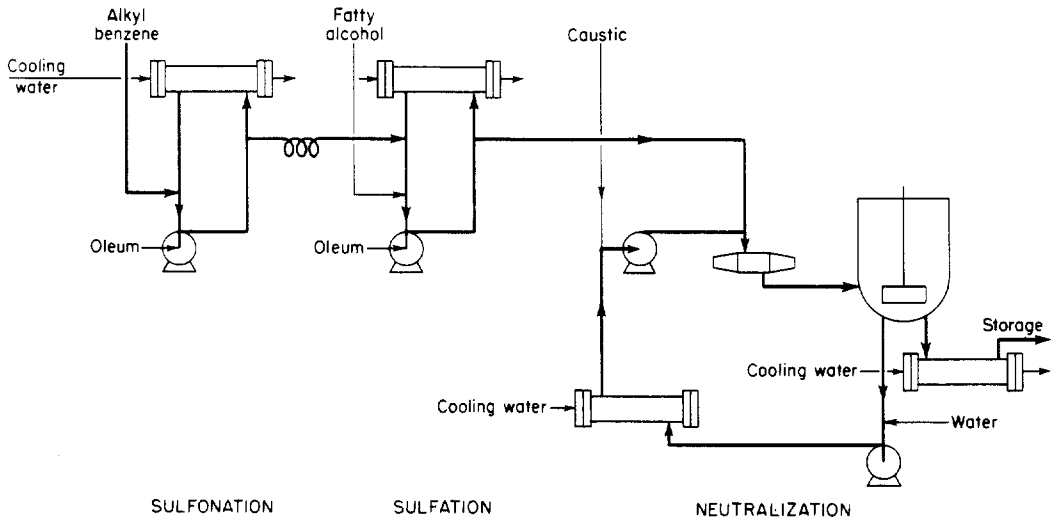

Fig. 29.4 Continuous series sulfonation-sulfation, ending with neutralization, in the circulating heat-exchanging dominant bath to control heat. (*Procter & Gamble Co.*)

TABLE 29.4 ***Synthetic Surface-active Agents, U.S. Production and Sales, 1964***

Chemical	*Production** *1,000 lb*	*Unit sales value†* *per lb*
Grand total	2,118,688	$0.18
Amphoteric	4,562	0.61
Anionic	1,434,399	0.14
Cationic	98,348	0.45
Nonionic	581,379	0.25
Benzenoid surface-active agents, total	1,347,809	0.13
Not sulfated or sulfonated, total	273,786	0.22
Amides, amines, and quaternary ammonium salts, total	8,018	0.95
Carboxylic acid esters and ethers, total	263,545	0.19
Phosphoric and polyphosphoric acid esters and salts, total	2,223	0.37
Sulfated and sulfonated, total	1,074,023	0.11
Alkylphenols, ethoxylated and sulfated, total	40,579	
Benzenesulfonates, total (76% branched-chain dodecyl and tridecyl)	590,670	0.16
Lignosulfonates, total	426,788	0.04
Naphthalenesulfonates, total	9,634	0.41
Nonbenzenoid surface-active agents, total	770,879	0.28
Not sulfated or sulfonated, total	461,149	0.33
Amides, amines, and quaternary ammonium salts, total	162,816	0.40
Carboxylic acid esters, total	132,281	0.33
Ethers, total	119,474	0.25
Tall oil acids, potassium salt	6,379	0.17
Phosphoric and polyphosphoric acid esters, total	4,890	0.68
Other nonbenzenoid surface actives	30,499	0.16
Sulfated and sulfonated (misc.), total	309,730	0.22

Source: Synthetic Organic Chemicals, U.S. Production and Sales of Surface-active Agents, U.S. Tariff Commission, 1964. More details in original reference. *All quantities are given in terms of 100% synthetic organic surface-active ingredient. †Calculated from rounded figures.

BIODEGRADABILITY OF SURFACTANTS

In view of greater attention being given to water-pollution control and abatement, product-development chemists and chemical engineers in recent years have realized that surfactants being developed for use in household and industrial detergents which go down the drain to the sewer must be as readily decomposable by the microbial action (1) of sewage treatment and (2) of surface streams as ordinary constituents of household wastes. This new parameter has been added to the performance, efficiency, and cost factors which the detergent industry must consider in developing new products. Some surfactants, like tetrapropylene-derived alkyl-benzene sulfonate, degrade *slowly* with 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*. Attempts are being made to develop tests and set standards for biodegradability.[1] Such standards will have limited application because biodegradability depends on environmental conditions. Materials which are "completely biodegradable" when microbes are present do not degrade in potable water. On the other hand, materials

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[1] Biodegradability of Detergents, *C&EN*, Mar. 18, 1963, pp. 102–112: "Maximum of 10% of the total organic residue from sewerage treatment plant is TPBS"; Variable Pattern Sums Up Organics, *CE*, **70** (2), 97 (1963) (biodegradability).

which may be "nondegradable" in inefficient treatment processes can be completely decomposed by more sophisticated biological treatment systems. Tests that measure die-away in a river water, or which stimulate the biological processes employed in sewage-treatment plants, are being used for biodegradability measurements.

Based on research which had been under way for several years, the detergent industry set a Dec. 31, 1965, target date for more readily degradable detergents. Although complete conversion is the overall objective, the most important step is a substitution for tetrapropylene-benzene sulfonate (TPBS). See Table 29.4, benzene sulfonates, branched chain. This one detergent raw material has been the workhorse of the detergent industry. By 1962 it had earned for itself a 70% share by weight of the market for surfactants used in household dish-washing and laundry products, and is consumed in amounts in the neighborhood of 500 million lb. TPBS is produced by alkylating benzene with propylene tetramer, followed by sulfonation of the benzene ring. The propylene tetramer consists of a multitude of *branched* isomers, with little, if any, straight-chain alkyl groups. The research on a more readily degradable surfactant has developed a straight-chain hydrocarbon to make the alkyl-benzene. The straight-chain material gives more readily degradable detergents, and will fit easily into the detergent formulations in which it will replace TPBS.

STRAIGHT-CHAIN ALKYL-BENZENE

With the endeavor to improve the biodegradability[1] of detergents, chemical and engineering efforts are being made to supplant the half billion pounds of various branched-chain alkyl-benzenes, of which the chief is tetrapropyl-benzene sulfonate (TPBS), by *straight-chain alkyl products* along the following lines, as illustrated by Fig. 29.5. These are to

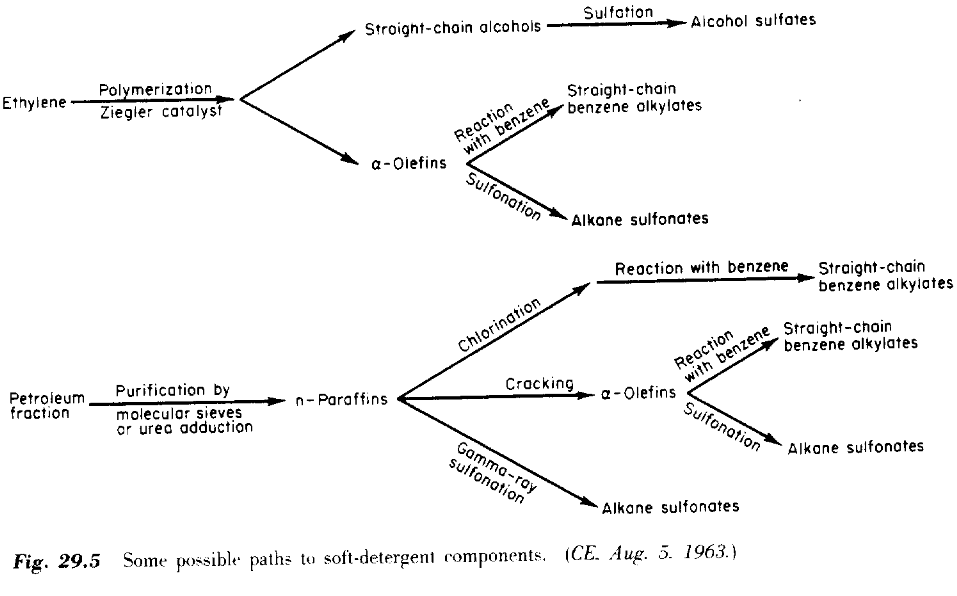

Fig. 29.5 Some possible paths to soft-detergent components. (*CE*. *Aug. 5. 1963.*)

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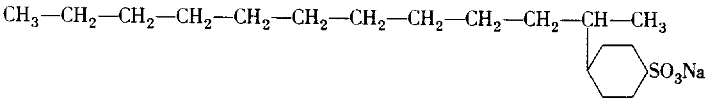
[1] Schwartz and Reid, Surface Active Agents. *I&EC*, **56** (9), 20 (1964) (theoretical and empirical); Biodegradability of Detergents, *C&EN*, Mar. 18, 1963, p. 102; Winton, Detergent Revolution, *CW*, May 30, 1964, p. 111; Rubinfeld *et al*., Straight-chain Alkylbenzenes, *I&EC*, **56** (11), 97 (1964).

be sulfonated after being made into normal, or straight-chain, alkyl-benzenes (LAS).[1] The straight-chain α-olefins (preferably C_{12}) are made

1. By polymerizing ethylene to α-olefins, using Ziegler-type and other polymerizations, e.g., Alfol process (Fig. 29.6), furnishing high-purity, but not cheap, products.
2. By molecular sieve[2] and other means to extract straight-chain paraffins from kerosine (low-priced).
3. By cracking paraffins such as wax (cheap α-olefins).
4. By obtaining fatty alcohols by an improved hydrogenation of natural fats, namely, from the methyl ester of fatty acids (Fig. 29.7).

The α-olefins, or paraffin halides, can be used to alkylate benzene through the Friedel-Crafts reaction, employing hydrofluoric acid or aluminum fluoride as catalyst. The fatty alcohols can be sulfated for detergents as outlined in Fig. 29.2. An example of a biodegradable linear (C_{12}) alkyl-benzene sulfonate is



$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\underset{\displaystyle C_6H_4SO_3Na}{CH}-CH_3$$

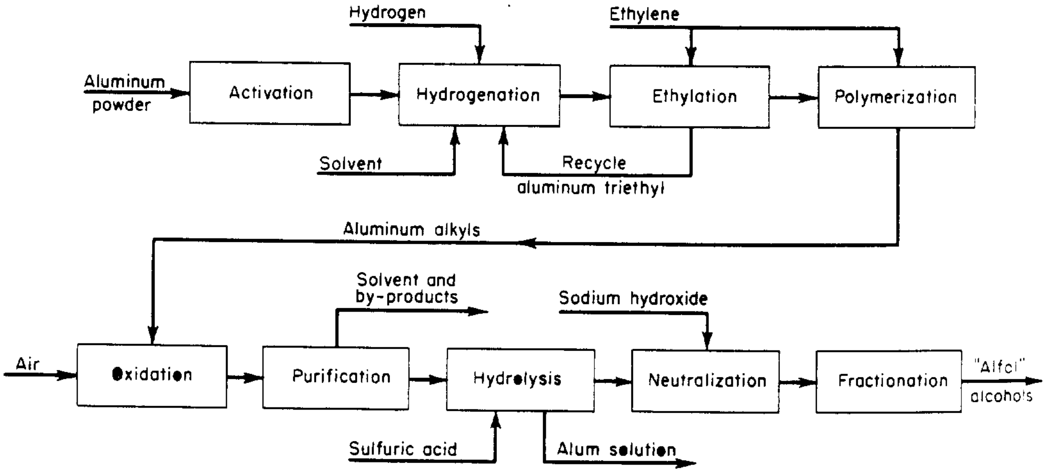


Fig. 29.6 Alfol process—schematic flow diagram. Fatty alcohols made by means of the organometallic route have carbon-chain lengths ranging from 6 to 20. The alfol process used by Conoco commences by reacting aluminum metal, hydrogen, and ethylene, all under high pressure, to produce *aluminum triethyl*. 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. (*Continental Oil Co.*)

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[1] Swisher, LAS, Linear Alkylate Sulfonate: Major Development in Detergents, *CEP*, **60** (12), 41 (1964): "LAS can be completely degraded by bacterial action"; Justice and Lamberti, Revolution in Detergents, *ibid.*, **60** (12), 35 (1964) (chemical structure, performance, and biodegradability); Field Tests for LAS Biodegradability, 36 pp., Soap & Detergent Assoc., 295 Madison Ave., New York, N.Y. 10017.

[2] Danatos, Unusual Separations, *CE*, **71** (25), 155 (1964).

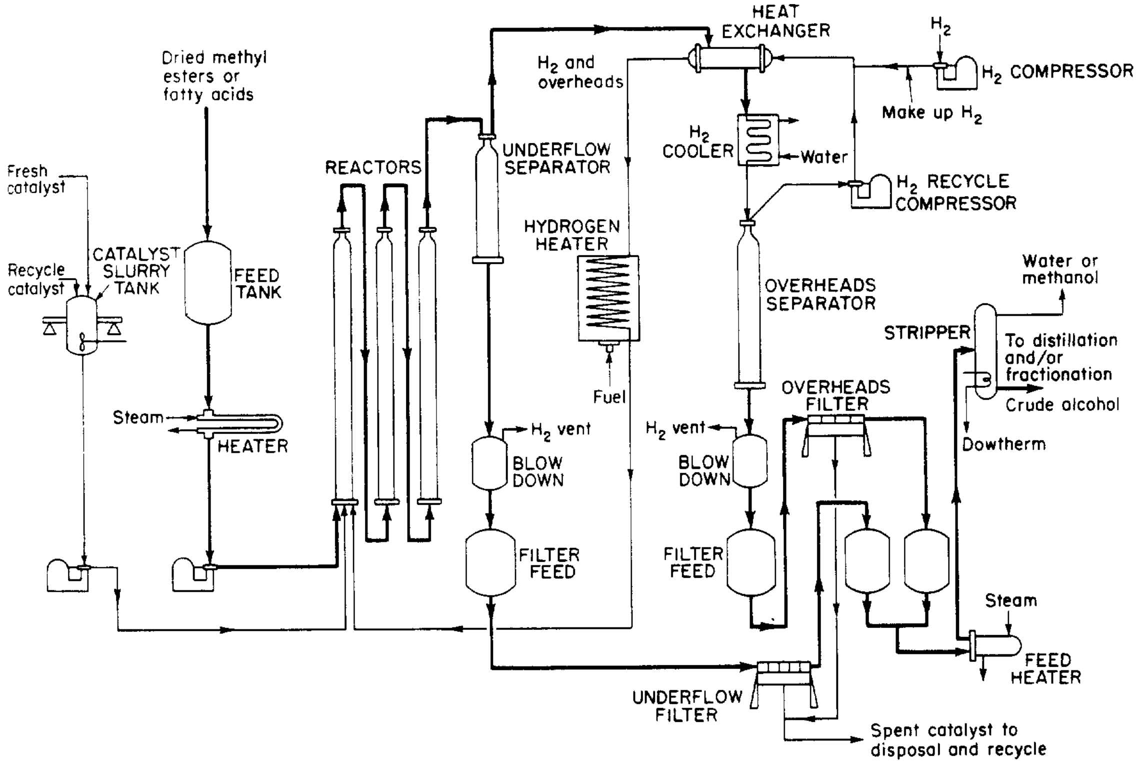

Fig. 29.7 Flowchart for hydrogenolysis of methyl esters to obtain fatty alcohols and glycerin from natural fats. (*ECT. 2d ed., vol. 1, p. 550, 1963.*)

FATTY ACIDS AND FATTY ALCOHOLS, FOR MANUFACTURE OF DETERGENTS AND SOAPS

ECONOMICS The fatty alcohols and fatty acids have their chief consumption areas supplied by detergents and soaps, as presented in this chapter. However, fatty acids, both saturated as stearic acid and unsaturated as oleic, and others, have long been employed in many industries as both free acids and, more frequently, as salts. Examples are

Zn or Mg stearates in face powders.
Ca or Al soaps (insoluble) employed as water repellents in waterproofing textiles and walls.
Triethanolamine oleate in dry cleaning and cosmetics.
Rosin soap consumed as a sizing for paper.

MANUFACTURE OF FATTY ACIDS[1] The long-consumed basic raw materials such as oils and fats (Chap. 28) have, since about 1955, been very extensively supplemented by improved chemical processing and by synthetic petrochemicals. A selection from these processes is mentioned here, with the general procedures depicted by the references, tables, figures, and accompanying text. Table 29.5 compares three processes long used for

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[1] ECT. 2 ed., vol. 1, p. 542, 1962.

TABLE 29.5 ***Tabular Comparison of the Various Fat-splitting Processes***

	Twitchell	*Batch autoclave*		*Continuous countercurrent**
Temperature, F	212–220	300–350	450	485 approx.
Pressure, psig	0	75–150	425–450	600–700
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, hr	12–48	5–10		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; constant utility load
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: Marsel and Allen, Fatty Acid Processing, *CE*, **54** (6), 104 (1947). *See Fig. 29.8.

splitting fats. Figure 29.8 illustrates the high-pressure hydrolysis mostly used in the soap industry, which is catalyzed by zinc oxide. Fatty acids are drawn off from the distillate receiver for sale or further manufacture to fatty acid salts (Ca, Mg, Zn, etc.) or for hydrogenation to fatty alcohols. Several of the older and less used separation methods[1] for purifying fatty acids were the panning and pressing procedures, fractional distillation, and solvent crystallization.

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[1] Muckerheide, Production of Fatty Acids: Separation Methods, *J. Am. Oil Chemists' Soc.*, **31** (11), 544 (1955).

MANUFACTURE OF FATTY ALCOHOLS[1] The U.S. production of higher alcohols above C_{10} is about 300 million lb annually, of which more than two-thirds is consumed in the manufacture of surfactants. The *Ziegler* catalytic procedure for α-olefins to fatty alcohols and the methyl ester hydrogenation process are outlined below. See also the flowchart of Fig. 29.8 and accompanying text presented under soap for the modern continuous hydrolysis of fats to furnish fatty acids which may be hydrogenated to the fatty alcohols.

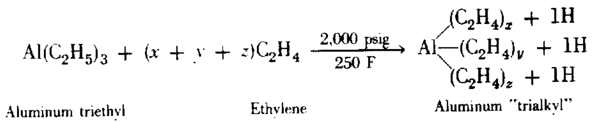
The Ziegler procedure is an important one for manufacturing C_{12}—C_{18} α-olefins and fatty even-numbered straight-chain alcohols for detergents. To summarize, the Ziegler reactions are

Aluminum triethyl preparation:

$$Al + \tfrac{3}{2}H_2 + 2Al(C_2H_5)_3 \longrightarrow 3Al(C_2H_5)_2H$$

$$3Al(C_2H_5)_2H + 3C_2H_4 \longrightarrow 3Al(C_2H_5)_3$$

Build-up reaction (random or Poisson distribution of chain lengths):



$$\underset{\text{Aluminum triethyl}}{Al(C_2H_5)_3} + \underset{\text{Ethylene}}{(x + y + z)C_2H_4} \xrightarrow[250\ F]{2{,}000\ psig} \underset{\text{Aluminum "trialkyl"}}{Al\begin{cases}(C_2H_4)_x + 1H\\(C_2H_4)_y + 1H\\(C_2H_4)_z + 1H\end{cases}}$$

ΔH is exothermic, liberating approximately 1000 Btu/lb of ethylene reacted. The "1H" is for the terminal alkyl (C_2H_5) of the chain.

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[1] ECT. 2d ed., vol. 1, p. 542, 1962. Excellent article with flowcharts.

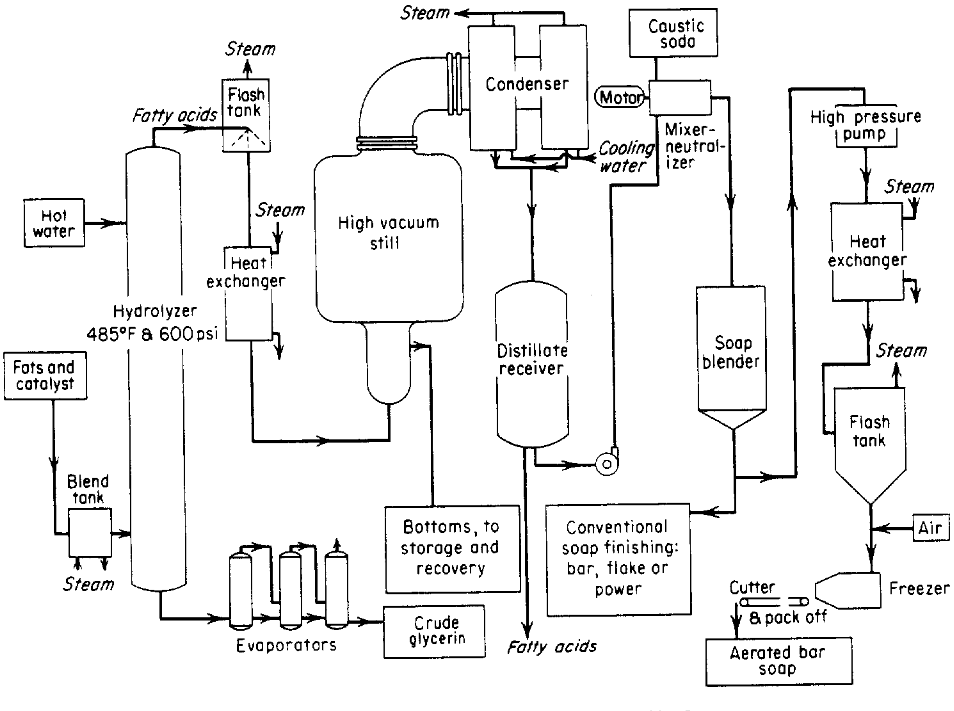
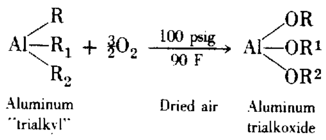


Fig. 29.8 Continuous process for fatty acids and soap. (*Procter & Gamble Co.*)

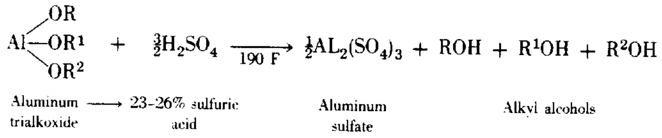
Oxidation reaction:



$$Al(R)(R_1)(R_2) + \tfrac{3}{2}O_2 \xrightarrow[90\ F]{100\ psig} Al(OR)(OR^1)(OR^2)$$

ΔH is exothermic, liberating about 1100 Btu/lb of alkyl oxidized. Its conversion is 98% at 90 F in about 2 hr.

Acidolysis (hydrolysis)



$$Al(OR)(OR^1)(OR^2) + \tfrac{3}{2}H_2SO_4 \xrightarrow[190\ F]{} \tfrac{1}{2}AL_2(SO_4)_3 + ROH + R^1OH + R^2OH$$

Neutralization of slight excess sulfuric

$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$

These reactions furnish a substitute for the C_{12-14} chain length and for the fatty acids in imported coconut oil or copra. Such reactions are run noncatalytically under 2,000 psig and 250 F and in inert hydrocarbon solvent such as heptane or benzene. In these solvents aluminum "trialkyl" is no longer pyrophoric at less than 40% concentration. At the above conditions, it takes approximately 140 min to build up to a C_{12} average chain length, that is, when reacting 5 moles of ethylene for each $\frac{1}{3}$ mole of aluminum triethyl. The main side reaction is a thermal displacement between aluminum alkyl and ethylene to produce α-olefins. The α-olefin can react with either aluminum triethyl or aluminum alkyls in a build-up-type reaction to form straight-chain alkyls or, to lesser extent, somewhat unstable branched alkyls.

The aluminum alkyl is *oxidized* by dried air at moderate temperatures of 60 to 120 F and moderate pressures in presence of a solvent to aluminum alkoxide. This oxidation apparently proceeds by addition of a molecule of oxygen to form a peroxide, which then rearranges to the alkoxide either internally or with another molecule of alkyl. The solvent and any olefins are distilled off from the aluminum alkoxides. *Acidolysis* completes the conversion of the aluminum alkoxide to the fatty alcohols. Water gives a bad gel, but a dilute H_2SO_4 forms the soluble aluminum sulfate, which is readily marketable if kept iron-free. *Neutralization* with dilute caustic prepares the product for final steps of dehydration, recovery of small amount of C_2H_5OH and C_4H_9OH, and fractionation first under atomospheric conditions, then under vacuum, to separate and obtain the fatty alcohols. The Continental Oil Co. has published[1] the *flow diagram* of its 100 million lb/yr plant near Lake Charles, La., and this is reproduced in Fig. 29.6. It is based on the Ziegler reactions.

FATTY ALCOHOLS FROM METHYL ESTERS Fats have long been basic raw materials for soaps and detergents. Such fats as are available are glyceryl esters of fatty acids (C_{12} and C_{16}), and have been hydrolyzed to the acids for soaps and reduced to the alcohols by catalytic hydrogenation for detergent. However, it was found that the methyl

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[1] Lobo *et al.*, The Alfol Alcohol Process, *CEP*, **58** (5), 85 (1962); Starks *et al.*, Synthesis of Higher Aluminum Alkyls, *I&EC*, December, 1963, p. 89 M.363-318; Continental Oil Puts First "Alfol" Alcohol Process on Stream, *CE*, **70** (24), 14 (1963).

esters, also of fatty acids,[1] have been hydrogenated to the fatty alcohols. These methyl esters are prepared by reacting methanol with coconut or tallow triglyceride catalyzed by a small amount of sodium. Previously, the refined oil will have been dried by flashing at 300 F under a vacuum of 25 in. or it will consume relatively expensive sodium and also form soap. The methyl exchange esterification takes place in about an hour, when the reaction mix is settled and separated into an upper layer rich in ester and methanol and the lower layer rich in glycerin and methanol. The ester layer is washed countercurrently and in a continuous manner to remove excess methanol, to recover glycerin, and to remove the catalyst, which would be a poison in hydrogenation. Yields are 90 to 95% of the fatty alcohols.

The hydrogenation of the methyl ester takes place using an Atkins type of catalyst (from copper nitrate, chromic oxide, and ammonia, with final roasting). The hydrogenation is carried out at approximately 3,000 psig and 550 to 600 F. The continuous equipment used is outlined in Fig. 29.7, and consists of three vertical reactors 40 ft high using 30 moles of heated hydrogen per mole of ester, the hydrogen serving not only for reducing but for heating and agitation. The crude alcohols are fractionated to specified chain length.[2]

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 man. We may well gage the advance of modern civilization by the per capita consumption of soap and detergents. The relative and overall production of soap and detergents is shown by the curve of Fig. 29.1. The *history* and *industrial statistics* are in the first part of this chapter (Table 29.1).

SOAP MANUFACTURE is presented in Fig. 29.8. The old and long-established kettle[3] process, however, is mainly used by the smaller factories or for special and limited production. As the soap technology changed, *continuous* alkaline saponification was introduced. Even now computer control[4] enables an automated plant for continuous saponification by NaOH of oils and fats to produce in 2 hr the same amount of soap (more than 300 tons/day) that was made in 2 to 5 days by traditional batch methods.

The present controlling procedure is *continuous splitting*, or *hydrolysis*, as outlined in Table 29.2 and detailed in Fig. 29.8. After the separation of the glycerin, the fatty acids are neutralized to soap.

The basic chemical reaction in the making of soap may be expressed as *saponification:*[5]

$$\underset{\substack{\text{Caustic}\\\text{soda}}}{3\text{NaOH}} + \underset{\substack{\text{Glyceryl}\\\text{stearate}}}{(\text{C}_{17}\text{H}_{35}\text{COO})_3\text{C}_3\text{H}_5} \longrightarrow \underset{\text{Sodium stearate}}{3\text{C}_{17}\text{H}_{35}\text{COONa}} + \underset{\text{Glycerin}}{\text{C}_3\text{H}_5(\text{OH})_3}$$

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[1] ECT, 2d ed., vol. 1, p. 548, 1962. Details with comparisons.

[2] By use of computers working on new data for heat capacitors on heat balances, the throughput and quality have been improved. Cf. Chow and Bright, *CEP*, **49**, 175 (1953); Watson, *I&EC*, **35**, 398 (1943).

[3] Full descriptions with flowcharts for the kettle process full-boiled (several days), semiboiled, and cold are available on pp. 623–625 of CPI 2 and in ECT, vol. 12, pp. 579–585, 1954.

[4] Flowchart for Crosfield Plant with Elliott 405 Computer, *CE*, **69** (21), 152 (1962).

[5] 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.

The controlling chemical reaction is to split, or *hydrolyze*, the fat, and then, after separation from the valuable glycerin, to *neutralize* the fatty acids with caustic soda solution.

$$\underset{\text{Glyceryl stearate}}{(C_{17}H_{35}COO)_3C_3H_5} + 3H_2O \longrightarrow \underset{\text{Stearic acid}}{3C_{17}H_{35}COOH} + \underset{\text{Glycerin}}{C_3H_5(OH)_3}$$

$$\underset{\text{Stearic acid}}{C_{17}H_{35}COOH} + \underset{\text{Caustic soda}}{NaOH} \longrightarrow \underset{\text{Sodium stearate}}{C_{17}H_{35}COONa} + H_2O$$

It should be pointed out that 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 by special processing. Since the solubility and hardness of the sodium salts (Table 29.6) of the various fatty acids differ considerably, the soapmaker chooses his raw material according to the properties desired, with due consideration to the market price.

RAW MATERIALS *Tallow* is the principal fatty material in soapmaking, the quantities used representing about three-fourths of the total oils and fats consumed by the soap industry, as shown by Fig. 28.1. It contains the mixed glycerides obtained from the solid fat of cattle by steam rendering. This solid fat is digested with steam, the tallow forming a layer above the water, where 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%) are the second most important raw material in soapmaking. They are obtained from hogs and the smaller domestic animals and are an important source of glycerides of fatty acids. They are refined by steam rendering or by solvent extraction and seldom used without blending 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 the soap, detergent, cosmetic, paint, textile, and many other industries. 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 29.5. The Twitchell process is the oldest.[1] 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

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[1] This process was described in more detail in CPI 2, p. 619, and in ECT, vol. 12, pp. 579–585, 1954.

TABLE 29.6 ***Solubilities of Various Pure Soaps (At 25 C grams per 100 g of water)***

	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.

phosphate. The inorganic chemicals added to the soap are the so-called *builders*. Important work by Harris of Monsanto and his coworkers[1] demonstrated conclusively that, in particular, tetrasodium pyrophosphate and sodium tripolyphosphate were unusually effective synergistic soap *builders*. Of considerable economic importance was the showing that combinations of inexpensive builders such as soda ash, with the more effective (and expensive) tetrasodium pyrophosphate or sodium tripolyphosphate, were superior sometimes 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.

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 65 ft high and 2 ft in diameter, are built of stainless-steel Type 316 (see Fig. 29.8). 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 deaerated and 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.[2] Here they are brought to reaction temperature by direct injection of high-pressure steam, and 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 discharged from the bottom of an automatic interface controller to a settling tank. See Fig. 29.12 for glycerin processing.

PURIFICATION OF FATTY ACIDS[3] Although the crude mixtures of fatty acids resulting from any of the above methods may be used as such, usually a separation into the 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. 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[4] is employed, with vacuum distillation 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 withdrawn 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

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[1] & *Soap*, **19**, 3 (1942); Cobbs *et al.*, *ibid.*, **17**, 4 (1940); Van Wazer, Phosphorus and Its Compounds, 27, detergent building, Interscience, 1958; cf. Sodium Phosphates, Chap. 16.

[2] *et al.*, Continuous Hydrolysis of Fats, *CEP*, **43**, 459 (1947); Fatty Acids, *CE*, **57** (11), 118 (1950); Fat Splitting, *ibid.*, **71** (17), 106 (1964) (continuous flowcharts).

[3] See this chapter under Fatty Acids and Fatty Alcohols.

[4] Acid Distillation, *CE*, **55** (2), 146 (1948) (pictured flowcharts of both straight and fractional distillation); Marsel and Allen, Fatty Acid Processing, *ibid.*, **54** (6), 104 (1947); ECT, vol. 8, p. 828, 1965; Kenyon Chemicals from Fats, *I&EC*, **42**, 202 (1950).

(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.[1]

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 move some of the fats and oils to the soap factory is occasionally considerable. The reaction that goes on in the soap reactor is exothermic. See Fig. 29.8 for electricity and steam required in the *neutralization process.*

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 of Fig. 29.8:

Transportation of fats and oils (Op).

Transportation or manufacture of caustic soda (Op or Ch).

The blending of the catalyst, zinc oxide, with melted fats and heating with steam takes place in the blend tank (Op).

Hot melted fats and catalysts are introduced into the bottom of the hydrolyzer (Op).

Splitting of fats takes place countercurrently in hydrolyzer at 485 F and 600 psi, continuously, the fat globules rising against descending aqueous phase (Ch and Op).

The aqueous phase having dissolved the split glycerin (about 12%), falls and is separated (Op).

The glycerin water phase is evaporated and purified (Op). See *glycerin.*

The fatty acids phase at the top of the hydrolyzer is dried by flashing off the water (Op) and further heated.

In a high-vacuum still the fatty acids are distilled from the "bottoms" and rectified (Op).

Continuously in high-speed mixer-neutralizer, the soap is formed by neutralization with 50% caustic soda (Ch).

The neat soap is discharged at 200 F into a slowly agitated blending tank to even out any inequalities of neutralization (Op). 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 of Fig. 29.8 depicts the finishing operations of a floating bar soap.

These finishing operations may be detailed: the pressure on the neat soap is raised to 500 psi, and the soap is heated to about 400 F in a high-pressure steam exchanger. This heated soap is released to a flash tank at atmospheric pressure, where a partial drying (to about 20%) takes place because the soap is well above its boiling point at atmospheric pressure. This viscous, pasty soap is mixed with the desired amount of air in a mechanical scraped-wall heat exchanger, where the soap is also cooled by brine circulation in the outer shell from 220 to about 150 F. At this temperature the soap is continuously extruded in strip form and is cut into bar lengths. Further cooling, stamping, and wrapping complete the operation. This entire procedure requires only 6 hr, as compared with over a week for the kettle process. The main advantages of soap manufactured by this process as compared with the kettle process are[2] (1) improved soap color from a crude fat without extensive pretreatment, (2) improved glycerin recovery, (3) flexibility in control, and (4) less space and manpower. Intimate molecular control is the key to the success of this continuous process, as, for example, in the hydrolyzer, where the desired mutual solubility of the different phases is attained by appropriate process conditions.

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[1] Kenyon, *op. cit.;* Potts and McBride, Armour's Star, *CE,* **57** (2), 124 (1950) (pictured flowchart, p. 172); Williams, Versatility in Fatty Acids, *ibid.,* **56** (7), 92 (1949) (pictured flowchart, p. 128).

[2] McBride, Continuous Process for Soap, *CE,* **54** (4), 94 (1947) (pictured flowchart).

TYPICAL SOAPS Main classes of soap are toilet soaps and industrial soaps. These different soaps can frequently be made by one or more of the procedures described. Detergents have replaced about 80% of soaps. Except for the purest of toilet soaps, various chemicals are added as "builders," economically, to improve their overall cleansing quality. Practically all soap as merchandised contains from 10 to about 30% of water. If soap were anhydrous, it would be too hard to dissolve easily. Almost all soaps contain perfume, even though it is not apparent, serving merely to disguise the original soapy odor. Toilet soaps are made from selected materials and usually contain only 10 to 15% moisture, with very little added material, except for the perfume, and perhaps a fraction of a percent of titanium dioxide as a whitening agent. *Shaving* soaps contain a considerable proportion of potassium soap with an excess of stearic acid, the combination giving a slower-drying lather. The "brushless" shaving creams contain stearic acid and fats with much less soap.

Another type of bar soap (in comparison with the floating type of Fig. 29.8) is the *milled toilet soap.* The word milled refers to the fact that, during processing, the soap goes through several sets of heavy rolls, or mills, which mix and knead it. Because of the milling operation, the finished soap lathers better and has generally improved performance, especially in cool water. The milling operation is also the way in which fragrant perfumes are incorporated into the cold soap. If perfume were mixed into warm soap, many of the volatile scents would evaporate. After the milling operation, the soap is pressed into a smooth cylinder and is extruded continuously. The soap is cut into bar sizes, stamped, and wrapped as depicted in Fig. 29.9.

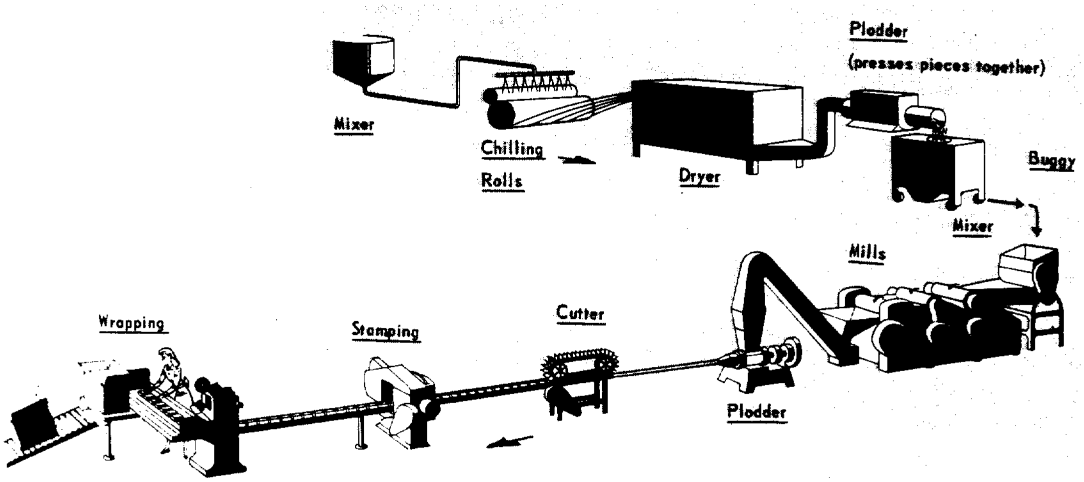

Fig. 29.9 Making soap in milled bars. Another type of bar soap (in comparison with the floating type of Fig. 29.8) is the milled toilet soap. The word "milled" refers to the fact that, during processing, the soap goes through several sets of heavy rolls, or mills, which mix and knead it. The continuous process, as illustrated in the above isometric drawing, illustrates the application of modern chemical engineering to a process industry such as the manufacture of soap. A much more uniform product is obtained and much direct labor is saved. What labor is required is largely for supervision and maintenance. With proper and modern design, there are very few interruptions of continuous operation, and, consequently, there is low maintenance.

Crystal phases in bar soaps[1] The physical properties of bar soap are dependent upon the crystalline soap phases present and the condition of these phases. Any of three or more phases may exist in sodium soaps, depending upon the fat used, the moisture and electrolyte composition of the system, and the *processing* conditions. Milled toilet soaps are mechanically worked to transform omega phase at least partially to translucent beta, producing a harder, more readily soluble bar. Extruded floating soaps contain both crystals formed in the freezer and crystals that grow from the melt after it leaves the freezer. Processing conditions are adjusted for an optimum proportion of the crystallized matrix, which adds strength and rigidity to the bar. If necessary, the bar may be tempered by reheating to strengthen it.

GLYCERIN

HISTORICAL Glycerin[2] is a clear, nearly colorless liquid, having a sweet taste but no odor. K. W. Scheele first prepared glycerin in 1779 by heating a mixture of olive oil and litharge. On washing with water, a sweet solution was obtained, giving, on evaporation of the water, a viscous heavy liquid, which the discoverer called "the sweet principle of fats." In 1846 Sobrero produced the explosive nitroglycerin for the first time, and in 1868 Nobel, by absorbing it in kieselguhr, made it safe to handle as dynamite. These discoveries increased the demand for glycerin. This was in part satisfied by the development in 1870 of a method for recovering glycerin and salt from spent soap lyes. Since about 1948, glycerol has been produced from petrochemical raw materials by synthetic processes.

USES AND ECONOMICS In 1962 the production of crude glycerin was approximately 249 million lb. Synthetic glycerin furnishes 118 million lb (basis 100% glycerol), 47% of the market. Glycerin is supplied in several grades. USP, or CP, ~~grade~~ is chemically

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[1] Ferguson *et al.*, Solid Soap Phases, *I&EC*, **35**, 1005 (1943); Diffractometers for Determining Crystal Structures, *Norelco Reporter*, August, 1958, Phillips Electronics, Mt. Vernon, N.Y.

[2] The term *glycerin* is chosen for the technical product containing the pure trihydroxy alcohol *glycerol*. The spelling of glycerin is that employed by the United States Pharmacopeia.

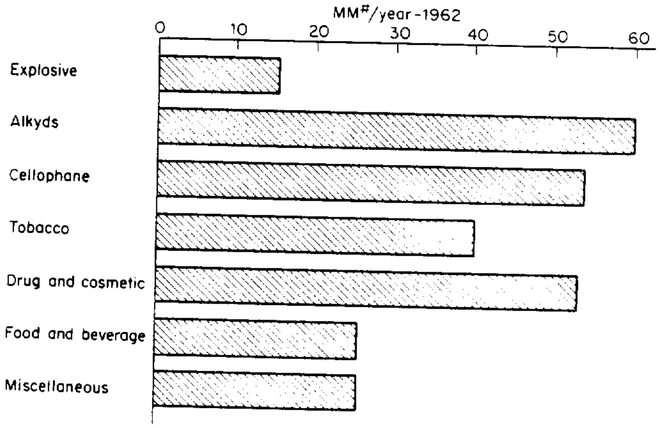

Fig. 29.10 Glycerin consumption by industry.