with the anionic though some technicians prefer to use a known aliquot of standard anionic solution with a solution of the unknown quaternary. Those who prefer titration with the quaternary claim better end-points though this may be merely a question of habit.

In the section dealing with methylene blue a procedure was referred to (4) which contains a method for determining quaternary halides. This method (28, 40) consists of adding mercuric acetate, which complexes the halide ion forming the quaternary ammonium acetate. The latter compound can be titrated as a base in the solvent system used. The method has a relatively high accuracy, and precision has been successfully applied by the author to the determination of quaternary cationics.

Flanagan *et al.* (13) determined quaternaries by the formation and measurement of a turbidity formed on reaction with a condensed aryl sodium sulfonate (Tamol N). The turbidity is compared against knowns.

Another type of cationic is the amine type. This variety of cationic is best determined by the procedures used for amines in general. Siggia (38) describes a number of methods for determining a variety of amines. The preferred method is the direct titration of the amine as a base or titration of the amine salt as an acid. This can be done in aqueous media, but it is preferable to use the nonaqueous media described by Siggia and Stolten (46) because of the greater accuracy and precision attainable. Mixtures of free amine and amine salts can be determined by titrating one sample with standard acid to obtain the free amine and then by titrating a second sample with standard base to obtain the amine salt.

Some alkylated or ethoxylated amines consist of mixtures of primary, secondary, and tertiary amine mixtures. Such mixtures can be analyzed for their individual amine components by using a scheme of volumetric analysis described by Siggia (39, 42).

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Economics of Syndets and Soap[1]

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THIS IS OPEN to several treatments, one of which is the comparison of the "plant" costs of syndets and soaps. Before data on these costs are discussed, I believe that it might be of interest to review a tabulation of estimated sales of syndets and soaps for the years 1947–1957 inclusive. These data have been compiled with the assistance of the staff of the association of American Soap and Glycerine Producers Inc. ("Soap Association"). They represent an attempt to estimate the United States totals and do not bear a constant relationship to the published data released by the Soap Association. This variation arises from the fact that data released are compiled from reports received from the membership. Membership is not all-inclusive and moreover fluctuates. The sharp change in the ratio of syndet to soap tonnage in the past decade should be noted. Syndets now outsell soaps about 2.5 to 1!

[1] Dinner lecture.

Next to be examined is the price trend for basic raw materials, especially detergent alkylate and prime tallow. The prices shown represent the average cost to large buyers, delivered to the factory.

Noted will be the characteristically erratic behavior of prime tallow, which compares unfavorably with the almost classic price curve for detergent alkylate: the alkylate price curve drops steadily, finally becoming an asymptote as the rate of expansion of sales volume approaches zero. The U. S. production of polypropyl benzene alkylate (so-called dodecyl benzoate or DDB) was only a few hundred thousand pounds in 1946. In 1957 it is estimated to have been about 455,000,000 pounds! Of this volume about 105,000,000 pounds were exported.

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The factors listed in Tables I and II have had a dramatic effect on manufacturing costs. The operations of major plants are no longer directed toward the production of soap. In fact, there are major installations at which no soap is made. Large installations for the continuous production of syndets are the order of the day. Fat-based soap volume, on the other hand, is shrinking rapidly. Declining production has resulted in increased "plant" costs because of the inefficient operation of high-capacity equipment under reduced load. Moreover even industrial customers are demanding white or relatively pale soaps. This limits the use of the darker fatty acids and ''foots'' which are by-products of tallow refining and, by lowering their value, increases the cost of the paler fatty acids used in soap manufacture. Last, but not least, old-line, well-established cosmetic soaps are coming under increased pressure from new syndet or syndet/soap-based bars. These products lather well in hard water and leave little or no ''bathtub ring.'' Because of the nature of their lather and the fact that most of them leave substantially no film on the skin, it is expected that they will make heavy inroads into the toilet bar sales.

ANOTHER IMPORTANT FACTOR is the value of by-product glycerine. Before the advent of synthetic glycerine in large tonnage, the value of by-product glycerine used to fluctuate. Even so, it was generally high and provided a substantial credit against raw material costs. Today the market has been pre-empted by synthetic glycerine produced by the petrochemical industry. The delivered price of soap lye 80% grade glycerine in tank cars dropped from an average of 26.5¢ a pound in 1948 to 15.5¢ a pound in 1957. It is now (5/58) 15.0¢.

To enable one to appreciate the effect of these various factors on ''plant costs, a tabulation covering the last nine full years' operations has been prepared. These ''plant'' costs are for the production of tallow soap, a standard industrial item, and an alkyl aryl sulphonate slurry of orthodox composition. To give continuity the actual formula considered had an active ingredient content, dry basis, of about 40%. Variants of this base are employed in the manufacture of various synthetic detergents, especially those for household use. The costs reported were adjusted to 100% dry basis to eliminate the effect of variations in water content. Since the ''diluent'' was almost entirely sodium sulphate (actually 58% on a dry basis), the data reported are considered to be reasonably valid for slurries of the type in general use for the production of heavy-duty detergents which contain 45% active ingredient (90/10 dry basis). ''Plant'' costs and glycerine credit are expressed in terms of 1949 average = 100%. This year was chosen because it was the earliest one for which reliable cost data for syndets were available to the writer.

The changes in ''plant'' costs are notable: the 10 year trend in syndet base cost has been generally downward, even in the face of rising costs for labor and other items. It is now estimated to be about 12% *below* the 1949 base. On the other hand, the 10-year trend in tallow soap ''plant'' cost has been upward, and sharply so. The years 1952 and 1953, when tallow was abnormally cheap, are exceptions. The current level is estimated to be 80% *above* the 1949 costs.

The comparison presented is, of course, solely on the basis of ''plant'' costs. It does not make any allowance for the over-all savings in working capital and personnel that have resulted from the widespread

TABLE I
Total U. S. Sales, Soaps, and Syndets, Million-pound Units

Year	Soap	Syndets	Syndets/Soap
1947	3,562	408[a]	0.114
1948	3,141	636	0.202
1949	3,101	864	0.279
1950	2,973	1,443	0.485
1951	2,525	1,565	0.619
1952	2,302	1,856	0.806
1953	2,003	2,118	1.057
1954	1,763	2,468	1.400
1955	1,650	2,704	1.639
1956	1,573	3,068	1.950
1957	1,428	3,507	2.455

[a] Soap Association not available. Data obtained from "Census of Manufacturers."

TABLE II
Average Delivered Prices, Prime Tallow and Alkylate

Year	Tallow/100 lbs.	Alkylate/100 lbs.
1947	$17.75	$26.34
1948	17.50	21.00
1949	6.50	17.00
1950	12.25	14.25
1951	8.75	13.67
1952	4.75	13.10
1953	4.50	13.10
1954	7.00	12.55
1955	8.00	12.05
1956	7.25	12.00
1957	8.00	12.50

TABLE III
Plant Cost Trends, Syndets, and Tallow Soap

Year	Plant cost per 100# detergent	Plant cost per 100# tallow soap	Glycerine value per 100# tallow	Alkane price/100#	Tallow price/100#
1949	100%	100%	100%	$17.00	$ 6.50
1950	93	150	102	14.25	12.25
1951	93	112	50	13.67	8.75
1952	93	90	46	13.10	4.75
1953	94	89	33	13.10	4.50
1954	94	142	35	12.55	7.00
1955	90	154	30	12.05	8.00
1956	91	150	29	12.00	7.25
1957	93	169	25	12.50	8.00
1958 (4 mos)	88	180	20	12.00	8.25

adoption of petrochemical-based active ingredients. At one time it was necessary to tie up vast sums in inventories of oils and fats if one were to avoid shortages and price squeezes. An active and alert staff was required to follow the ever-changing markets. Many an ulcer was born in this strained atmosphere!

One last thought: the United States now exports about 1.5 billion pounds a year of tallow and grease. If the soap industry were still tallow-based, this amount of fats would not replace the 3.5 billion pounds of syndets sold in 1957. This can mean one thing only, prime tallow would be even higher than the currently (5/58) quoted price of 8¢ a pound. It might well be 12¢ a pound.

Textile Uses of Syndets and Soap

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THE TEXTILE INDUSTRY is an important market for soaps and synthetic detergents. One estimate of this market is 50 to 100 million lbs. per year (1) whereas another is 64 million dollars (2). For many years this industry has served as a proving ground for synthetic detergents. The initial commercial use of most important syndets can be traced to one or more textile applications.

G. M. Gantz

The textile industry uses a great variety of chemicals which can be considered as surface-active agents. By considering only those products which have no effect on performance of yarn or fabric, one can eliminate softeners, lubricants, water repellents, and antistatic agents. The remaining surface-active agents can be classified into four functional categories: detergents, wetting agents, emulsifiers, and dyeing assistants. By way of reference, Table I lists several types of surfactants and their functional uses in textile processing.

This discussion will cover only soaps and synthetic products that exhibit detergent properties. Important processing operations involving detergency will be considered successively for cotton, wool, and man-made fibers. Several recent references may be cited (1–4). Special mention must be made of the second edition of Speel's "Textile Chemicals and Auxiliaries" (5) and Vol. II, "Surface-Active Agents" by Schwartz, Perry, and Berch (6).

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TABLE I
Important Surfactant Types and Their Functional Uses in Textile Processing

	Detergency	Wetting	Emulsification	Dyeing
Soap	x		x	
Ethoxylated alkylphenols	x	x	x	x
Alkyl benzensulfonates	x	x		x
Alkyl sulfates	x	x		x
Sulfonated amides	x	x		x
Sulfonated esters		x		
Ethoxylated alcohols and acids		x	x	x
Alkyl napthalene sulfonates		x		x
Sulfated oils and fats			x	x
Petroleum sulfonates			x	
Alkylol amides	x		x	
Ethoxylated amines				x
Quaternary ammonium salts				x

Cotton

Mature cotton fibers contain a variety of materials other than cellulose as shown below (7):

Constituent	*%, Dry Weight*
Cellulose	94.0
Protein (N × 6.25)	1.3
Pectic substances	1.2
Ash	1.2
Wax	0.6
Total sugars	0.3
Pigments	Trace
Other	1.4

Yarns and fabrics may contain also "trash" comprising bits of leaves, stems, seed-coat fragments, and aborted seeds. In the course of spinning, weaving, or knitting, yarns and fabrics may pick up dirt, rust, and grease. Warp yarns of fabrics usually contain a size, applied to add abrasion resistance and strength. The detergent problem, in the case of cotton, is to remove natural impurities in the fiber, incidental contaminants from harvesting, spinning, or weaving, and deliberately applied sizing material.

Cotton fabrics are normally subjected to an enzyme desizing treatment, a hot alkali treatment, bleaching with hypochlorite or peroxide, and mercerization. After these treatments the fabric may be dyed, printed, or finished as white goods.

Enzymes convert starch into sugars, and the desizing treatment removes sizing material as well as water-soluble contaminants from the cotton. The hot alkali treatment removes most of the naturally occurring pectins and waxes as well as pigments, protein residues, seed coat fragments, and ash. Bleaching removes very little from the cotton except color. Detergency is involved in the alkaline steeping or boiling operation.

In kier boiling, which is becoming obsolete, thousands of yards of cloth in rope form are piled into an iron vessel which is then purged of air, sealed, and heated with steam. Liquor is circulated continuously from the bottom through a heated side arm and sprayed onto the goods from the top. A typical solution would contain 1–2% sodium hydroxide, ½% sodium silicate, and ¼ to ½% soap or syndet.

A great variety of soaps, syndets, and solvents have been used in kier boil formulas. Potash soaps, sulfated oils, alkanol sulfates, sulfonated amides, and