

30 min., depending upon the type of system employed. Product is of excellent quality in regard to color and completeness.

Product Storage and Handling

The same general rules apply to the storage and handling of sulfonates as to sulfates, with one notable exception. That is, the sulfonic acid itself can be successfully stored if it is freed of its residual spent acid. Also, since the sulfonates are more stable to hydrolysis, excessive temperature in storage and absence of buffering are not nearly so serious. In materials of construction, requirements are similar except that monel is not advisable in the dilution and layering steps where the acid strength is variable around an average 80%. Finally alkyl benzene, being non-hygroscopic in nature, requires none of the special protection necessary for the handling and storage of lauryl alcohol.

Summary

There are a number of approaches to the prob-

lems involved in technical sulfations and sulfonations. These involve the choice of either batch or continuous processing, depending upon consideration of the projected volume, the variety of products to be manufactured, and the ultimate disposition of these products. Technical considerations of process design involve selection of process equipment, sizing, piping, and plant layout. For the best results, particular attention must be paid to the control of process variables during actual production. These considerations, together with the application of sound chemical and chemical engineering practices in process formulation, are all essential to the production of high quality organic sulfates and sulfonates for detergent use.

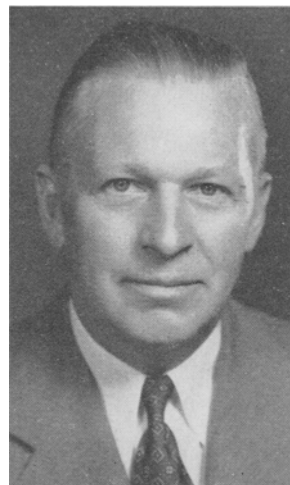
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The Changing Scenes of Syndets and Soaps¹

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THE USE OF SOAP, and I'll use this word to include synthetic detergents, is a measure of a country's development. We will take a look at this in two ways, first historically, and second by countries. We'll find that as a country develops, it uses more soap. It would be a great shock in many ways if we were to



Roy W. Peet

subjected to the comic strip, space-time machine and be whisked back to some location around the Mediterranean about 500 B. C. One of our first exclamations would be, "no soap!" Water and oils were both used for cleanliness before soap was available. Cleanliness was, and still is, closely related to religion. John Wesley, founder of Methodism, probably made the most famous remark about cleanliness when he said about 1750, "cleanliness is indeed next to godliness." Instructions given in the Koran by Mohammed include the following. "All true believers are strictly enjoined to wash their head, their hands as far as the elbows, and their feet as far as the knees, before saying their prayers; and when water is not to be procured, fine sand is to be used as a substitute." Bathing in the Ganges is believed to wash away sins as well as physical ailments. The development of the relationship between cleanliness and health is not clear, but there was some concept of this in early times. The

Egyptians were the chemists of early days, and Egypt was the center of early soap-making. They had precepts or laws involving cleanliness in matters of health, the choice and preparation of foods, and the care of children. The Jewish people likewise had and still have carefully prescribed practices which would seem to be dictated by a sound concept of the relationship between cleanliness and the prevention of disease. Bathing and cleanliness are frequently found definitely associated with periods of deep religious and emotional dedication or action. Where hygiene begins, and where religion or superstition ends, is difficult or impossible to decide.

The rise and fall of the Roman Empire, because of its influence on the political, economic, and cultural world of that day, had much to do with the spread of running water, sanitation, and cleanliness. The Roman aqueducts carrying water to the cities from far-away sources are marvels of conception and execution. Water made possible the big public baths that still remain as tourist sights. The Romans took to bathing in a big way and had hot water, steam rooms, and cold plunges. Prior to the time of soaps they used a kind of skin scraper to remove dirt and perspiration in the process of bathing. These baths were not associated with religion but instead were cultural and aesthetic. I understand that the Pennsylvania Station in New York is a reproduction of the Caracalla Thermae in ancient Rome, which provided simultaneous bathing facilities for about 3,000 people.

The Greeks established bathing as an aesthetic pleasure and practice with no relationship to religion. Marriage was surrounded by a ritual of purification including bathing, but the Greeks valued the bath as a means of creating a feeling of well being, to enhance the beauty of the individual through cleanliness, and to suppress unpleasant body odors. There

¹ Dinner lecture.

are descriptions of public baths and of sanitation in Turkey, in Egypt, among the Moors in Spain, and elsewhere. From Rome soaps and bathing were taken like laws and water systems to many countries. It must be remembered that at the height of the Roman Empire, about 100 years after the birth of Christ, it encompassed all of Europe as we know it, except Germany. It included the North of Africa and Egypt, Mesopotamia, Turkey, Persia, and the edges of the Black Sea.

Lesser known is the fact that the Byzantine Empire, with its capital at Constantinople, which remained Christian until the 15th century, preserved the Grecian and Roman culture—including baths, bathing, and sanitation—long after Rome fell to the barbarians in 467 A.D. After the fall of Rome the force of arms became the most respected law throughout Europe, and the feudal estates developed naturally as economic and mutually protective units. Most requirements were simple, the economy was basically agricultural, and there was little effort to re-establish the culture that had been destroyed. A report by the United States Public Health Service states: "In Europe the fall of Rome marked the beginning of the Long, Dark Ages. Bathing went into an extended eclipse with terrible repercussions. Plague after plague swept over the filthy land in one devastating wave after another, leaving in their wake untold millions of dead." The Black Death swept over Europe and caused a mortality in some places as high as two-thirds of the entire population. Practically the only public health principles transmitted to later generations were those of isolation and quarantine, and, of course, these were inadequately carried out.

NO ONE KNOWS exactly when soap was first discovered or made. It seems fairly clear that other substances, including water, oils, and abrasive materials were used prior to the time soap was available. As nearly as can be determined, soap proper came into limited use about, or shortly after, the time of Christ. There are many stories on the discovery of soap and soap making. Probably all have a foundation of truth because the accidental blending of lye from ashes and fat around sacrificial temples or other places of animal slaughter would be almost inevitable and would produce a kind of crude soap. Gradually, but slowly, concepts of cleanliness and sanitation and of the importance of the bath to the public health began to appear. A more general use of soap by the common people spread from country to country. In the seventh century soap had become sufficiently important to unite the soap makers into craft guilds. A century later Spain had as many soapmakers as Italy. Toward the end of the 12th, or at the beginning of the 13th century, Marseilles in France, which had made soap as early as the ninth century, became the chief center in Western Europe. Venice in Italy, and later Savonne in France, became principal centers of soap manufacture. Soap was made in Bristol, Coventry, and London, England, in the 12th century.

The Crusades from the 11th to the 13th century brought some of the knowledge and practices of the East to Western Europe. Water systems, public baths, sanitation were all subjects of interest and novelty to many of the Crusaders. An awakening interest in knowledge generally began about this time. Commerce and trade flourished. The trade in rich

spices, silks, and ivories brought by caravans from the East further enhanced the desire for knowledge and the awareness of other cultures. Queen Isabella of Spain, who pawned her jewels so that Columbus could make the voyage which resulted in the discovery of America, is said to have boasted that she had had only two baths in her life: one when she was born and one when she was married, but Henry IV of England is said to have instituted the Order of the Bath in 1399 to prevail on his nobles to wash themselves.

The first real manufacture of soap in America began in 1608 in Jamestown, Va. when the second ship from England brought several German and Polish craftsmen with the knowledge of how to make soap from fat and ashes. Of course, soapmaking was largely a household activity until well into the 19th century. Even today, many of us can recall soap being made by our parents or grandparents. The increase in soapmaking and consumption has largely paralleled industrial progress. The development of modern industry was made possible by the development of power to operate the factories. At first, this was water power with great water wheels operating overhead drive shafts, and belts from them, in turn, operating industrial machines. The discovery and development of the steam engine gave a second great impetus to the development of factories and freed them from the necessity of locating along rivers and streams. More recently, the discovery and utilization of electricity, made by generators driven by water, steam, or the compression engine, further increased the number of factories and likewise broadened their geographical location.

The textile industry was among the first industrial pioneers in utilizing water power to make large-scale factory production possible. The mechanization and lower costs of factory-made textiles, particularly cotton, brought need for soap in both processing the textiles in the factory and in laundering the low-cost, washable clothes which resulted. The large-scale factory production and popular acceptance of plumbing equipment made washing and cleanliness easier and far more widespread. The central heating in homes today is of fairly recent adoption and, in turn, led to the convenience of having hot water available at the turn of a tap. The development and growth of factory-produced, home washing-machines has taken much of the drudgery out of keeping things clean. Thus power has permitted the production of those things which have made sanitation and cleanliness easy and at a sufficiently low cost to appeal to people.

The development of factories and factory-made sanitary and plumbing equipment has paralleled the growing realization that cleanliness is desirable from a public health viewpoint. Where originally the rituals of religion and sometimes superstition dictated some cleanliness practices, the growth of scientific knowledge in the detection and recognition of germs in relation to disease has proven that these early practices were sound and that cleanliness pays in terms of health and even of life. The epidemics and scourges of the past are largely understood and eliminated or minimized by today's scientific knowledge. Cleanliness plays a big part in breaking the chain portrayed by the vivid and well-publicized statement, "germs live from hand to mouth!" Henry Sigerist, professor of the history of medicine at Johns Hopkins University, has said: "cleanliness became the chief pos-

tulate of the hygiene movement of the 19th and 20th centuries. It had to overcome many obstacles, notably the resistance of people who claimed that the frequent use of soap was harmful to the skin."

And thus, in what seems like an orderly and almost preordained pattern, the scientific discovery and realization of the need for cleanliness and sanitation came along together with the development of factories producing the necessary equipment to make cleanliness and sanitation practical in the home. And the increasing consumption of soap was, of course, a concurrent consequence.

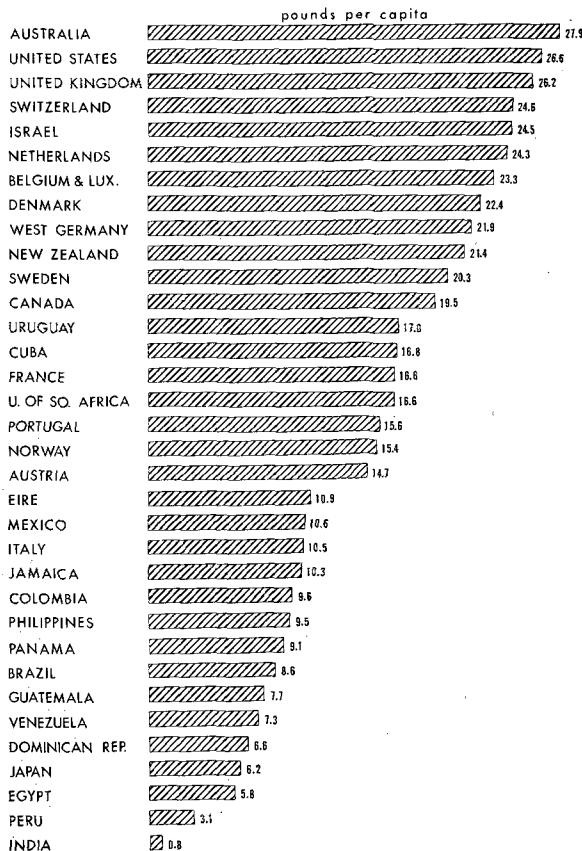


FIG. 1. Soap and synthetic detergents, 1953-54 estimated domestic consumption.

A FEW YEARS AGO the Association made a survey of the consumption of soap and detergents by countries. This was done first for the years 1950-51 and was repeated for the years 1953-54. We found a great spread in the per-capita consumption of soaps and detergents by countries, varying from less than 1 lb. per-capita to a high of 27.9 lbs. per-capita. India was the lowest, Australia the highest. The exact level is not too significant, but if we divide the 33 countries for which figures are available into three groups, those with high consumption of 20 lbs. or over, those in the middle with 10-20 lbs., and those with a low consumption of less than 10 lbs., there are recognizable differences in the countries. The most highly industrialized countries were at the top and those primarily rural at the bottom. Among the high-consumption countries were the United States, United Kingdom, the Netherlands, West Germany, Belgium, and Luxembourg and also, quite interestingly, Israel.

At the other end, in addition to India, were Japan, Peru, Egypt, Dominican Republic, and Brazil. Those in the middle bracket included Italy, Mexico, Cuba, France, Portugal, Norway, and Eire.

In checking soap and detergent consumption per capita with infant mortality, we found what might be expected—infant mortality was highest in those countries having the lowest soap consumption. The use of soap is not the sole reason because usually lower levels of sanitation, of public health rules and regulations, and of sanitation facilities were found in the countries with low per-capita soap and detergent consumption. Diets likewise have a bearing on this problem. We have examined these statistics on per-capita consumption of soaps and detergents by countries for the difference in the ratio of synthetic detergents to the total. Synthetics have grown in three countries to the point that they exceed 50% of the total of soaps and synthetic detergents. These are Austria, West Germany, and the United States. In seven additional countries synthetics have grown to a point where they now equal or exceed 25%. These are Canada, Cuba, Denmark, Israel, Netherlands, Sweden, and Switzerland.

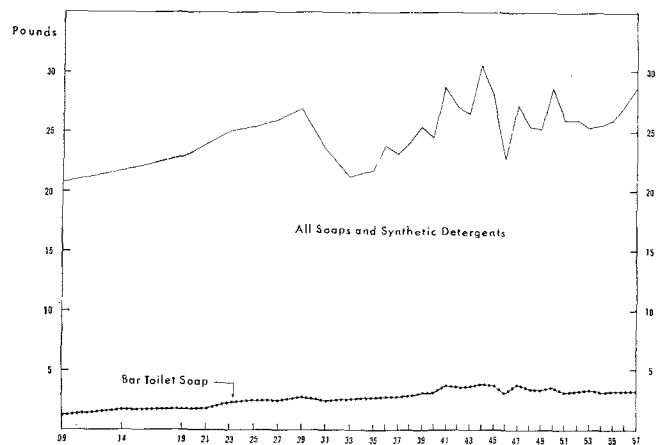


FIG. 2. Per capita soap and synthetic detergent sales, 1909-57.

Confining ourselves to a brief look at trends in the United States, we found our per-capita consumption of soaps had increased from around 20-21 lbs. in 1909 to over 28.5 lbs. per-capita today. This increase does not reflect the full increase in detergency or washing power, however, because today's products are more efficient or give more washing power per pound than the products of 1909. There are some interesting peaks and valleys at the top of Figure 2. The increase in per-capita consumption led up to a peak of around 27 lbs. in 1929, when the great depression broke. Per-capita sales fell sharply to the low level of around 21 lbs. in 1933. Then sales climbed with more or less regularity to the peak of World War II, something more than 30 lbs. per capita. The shortage of fats in World War II had its full effect in 1946, and the per-capita fell below 23 lbs. The sharp peak in 1947 was caused by additional sales to fill the pipe lines of distribution. The peak in 1950 was caused by the Korean scare out of fear that we might be in for another war period and a shortage of soaps.

In the last two years, 1956 and 1957, there has been

an interesting increase in the per-capita consumption of soaps and detergents to 28.5 lbs. This is an all-time, peace-time high. A steady, intelligent campaign of cleanliness promotion by the Association has played a part in this increase but likewise a good part must be attributed to the increasing availability and use of washable materials of all kinds. Men's clothing, women's clothing, upholstery materials, fabrics, the increased use of washable plastics, automobile seat covers, wall and floor coverings and coatings, etc., all invite greater cleanliness and the greater use of soaps and detergents.

The trend on per-capita consumption of bar toilet soaps is shown at the bottom of the chart. Toilet soap rose in per-capita sales from 1.2 lbs. in 1909 rather steadily to 3.0 lbs. in 1940, just prior to World War II. It increased sharply during the war years when toilet soaps were shipped to men in the armed services in many countries to levels of 3.6 to 3.8 lbs. and has held fairly steady after the war years at around 3.1 to 3.3 lbs. per-capita. Toilet soaps have remained essentially the same product today as they were in these earlier years. People's skin is the same, water problems are the same, and the product is the same so that the trends on toilet soaps are different from those in other kinds of soaps. If the new detergent bars replace soaps to a large extent, it is possible that we may see some rather sharp changes in sales on a pound per-capita basis.

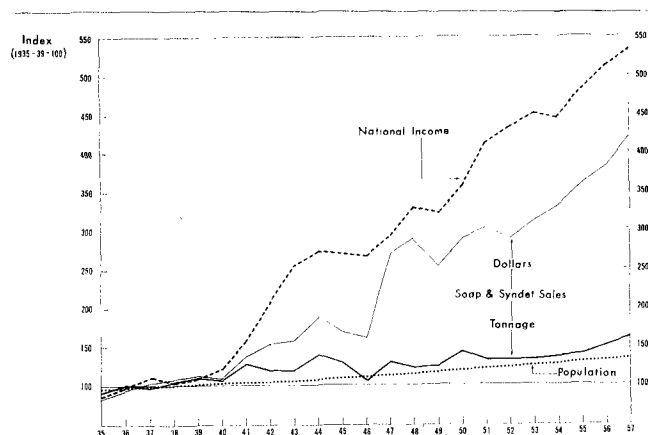


FIG. 3. A growing industry in a growing country; soap and syndet dollars parallel national income, soap and syndet tonnage parallel population.

Figure 3 shows on an index basis the comparison between the dollar sales of soaps and synthetic detergents with national income. The years 1935-1939 have been averaged and represent an index base of 100. As shown, national income has increased more than five times since those base years. The dollar sales of soaps and synthetic detergents have followed a somewhat similar pattern and have increased more than four times. (In talking budgets with the board of directors of our Association, at this point I would have to point out that the Association expenditures on soap have increased only three times in the same period.)

Like the song from the movie, "The Man Who Knew Too Much," "whatever will be, will be; the future's not ours to see." Nevertheless everyone has a great interest in the future and, in some ways, every company must predict to some extent. Many people

can help with predictions on national income, and this would be a rough start toward a prediction on soap and synthetic-detergent dollar sales. At the bottom of the figure, population and tonnage sales of soaps and synthetic detergents are shown on an index basis, using the same base years 1935-1939. Tonnage sales of soaps and syndets roughly parallel population trends and estimates for future years. This provides a basis for predictions on soap and syndet tonnage.

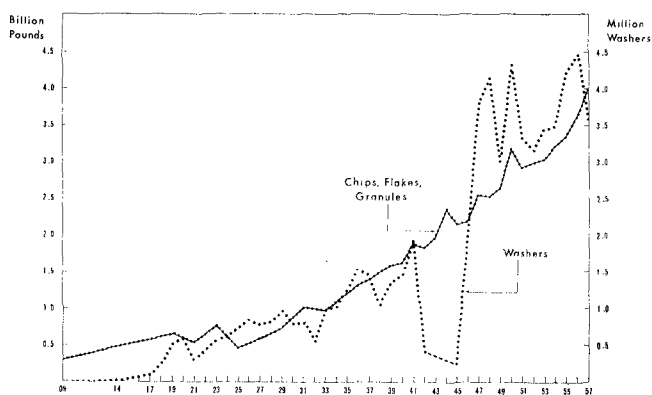


FIG. 4. Sales, washing machines vs. chip, flake, granulated soaps and syndets, 1909-57.

Figure 4 shows the annual sales of washing machines in units from 1909 to 1957. The terrific dip in the early 40's was, of course, caused by the shortage and consequent allocation of metals during World War II. The other line is the total tonnage of chips, flakes, granules, and synthetic detergents, representing largely all soaps other than bar soaps. Since the data on bulk products and on package products were not separated in the early years, these charted tonnage figures represent both bulk and packaged, in other words, both industrial and household.

The soap industry, as can be seen, was much more fortunate in maintaining its volume during World War II than was the washing-machine industry. The sale of electric washers was only 3,000 in the year 1909 but had grown rapidly to 500,000 in 1919. In 10 years, by 1929, the annual sale had nearly doubled to 956,000. By 1940 this was up to nearly 1,500,000. In 1950 the figure was 4,311,000. These are annual sales and not the total home inventory which, of course, increased annually with the sale of new machines.

In figure 5, instead of the annual sales of washing machines, we have charted the home ownership of washers on the basis of units per thousand of population and compared it with pounds per-capita of total chips, flakes, granules, and synthetic detergents and with pounds per-capita of bar laundry soaps. These washing machines required a new type of product. Originally the housewife had to chip up her bar of laundry soap and then get the little chips dissolved in the water to make suds before she could add clothes to the washing machine. For a while a little soap chipper, like a cabbage grater, was a standard household item. Some soap manufacturer realized that this was a real opportunity to serve. He did the chipping in his factory and sold the resultant chips in a carton. The response was immediate. The prod-

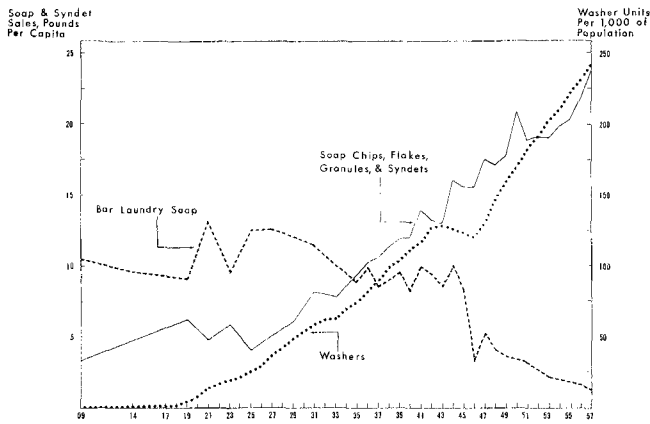


Fig. 5. How developments in one industry affect another. Washing machines change soap type.

uct relieved the housewife of the drudgery of chipping and dissolving the soap. The package chips dissolved readily, and everyone was delighted. The product sold at a higher price per pound, but this was no obstacle for the improved service.

Spray-dried granulated soaps were developed which were even more soluble and lent themselves better to fast production. They stopped the growth of chip soaps and to a great extent replaced them. Washing powders, which were soap granules with a very low soap content, enjoyed a good volume in the early days but fell off in volume rapidly with the more efficient, higher soap-content products. The synthetic detergents made available in volume after the end of World War II were entirely suitable for washing-machine use, having the same advantage of easy solubility that the package soaps had and an additional advantage in not being partially used up in overcoming water hardness.

As shown in Figure 5, the home ownership of washing machines has increased from practically 0 in 1909 to about 240 machines per thousand of population in 1957. Soaps and detergents of the type suitable for home washing-machine use have increased from about 3 lbs. per-capita in 1909 to more than 23 lbs. in 1957. The growth pattern of washing machines and these products is amazingly similar. In 1909 the usual procedure for home laundry was a galvanized washtub, a scrub board, and a cake of bar laundry soap. The cake of soap was rubbed on the fabric and the fabric rubbed on the scrub board in much the same way that in primitive countries today the garments are cleaned on the banks beside running streams. As the home inventory of washing machines increased, the laundry bar no longer served its original, useful purpose, and sales began to fall. They reached a peak in 1925-1927 of over 12 lbs. per-capita and from this level have fallen to less than 1½ lbs. in 1957.

Figure 6 shows the sweeping changes in tonnage of the basic kinds of nonpersonal soaps of the type suitable for clothes-washing use. In 1909 laundry bars were slightly under 1,000,000,000 lbs. and increased to nearly 1,500,000,000 in 1927. They more or less held their own through 1944 during World War II, after which they fell off sharply and are now only slightly more than 200,000,000 lbs. During the war period when bar laundry soaps maintained a fairly constant tonnage of around 1,200,000,000 or

1,300,000,000 lbs., the products suitable for washing machines, chips, flakes, granules, and powders grew rapidly and finally began replacing the volume formerly enjoyed by bar laundry soaps. Synthetic detergents had been sold prior to World War II but in very small volume. During the war they were largely allocated to essential military use, and it was quite difficult to get approval to build additional production capacity. At the end of World War II however plants were built quite rapidly, and the volume of synthetic detergents grew with amazing rapidity.

Their popularity was, of course, caused by the fact that they did not form insoluble soap or curds with the mineral salts of hard water and that all of the product was used for detergency rather than for overcoming the water hardness. Thus, both from the viewpoint of economy as well as of a cleaner wash, particularly in hard water, the synthetic detergents had advantages the housewife wanted. From an estimated volume of only 30,000,000 lbs. in 1940, they had grown rapidly to 1,400,000,000 lbs. in 1950; in 1957 they were 3,507,000,000 lbs., 71% of the industry's total tonnage.

There has been a noticeable recent trend in synthetic detergents with a rapid increase in liquids compared to solids. Association Sales Census data (not expanded to estimated U. S. total figures) show that both have grown, the solids from 1,071,000,000 lbs. in 1950 to 2,537,000,000 in 1957 and liquids from 23,000,000 lbs. in 1950 to 356,000,000 lbs. in 1957. This is a growth from 2% of the synthetic tonnage in 1950 to 12% in 1957. The consumer has quite evidently found these products satisfactory, possibly because of solubility or possibly because of more attractive or more convenient packaging.

THE CHANGE from household soaps to synthetic detergents has affected other industries, particularly the producers of tallow and grease and probably coconut oil. The apparent production of tallow and grease in 1940 was 1,370,000,000 lbs. In 1957 this has more than doubled to 2,968,000,000. Of this total the soap industry used 76% in 1940 but was down to 26% in 1957. The actual decrease in pounds used by the soap industry is only 259 million pounds, but the increased production of tallow and grease gives the country a big surplus, which has found a market in exports. These were only 8,000,000 lbs. in 1940 and have varied between 1,300,000,000 and 1,500,000,000 for the years, 1955, 1956, and 1957.

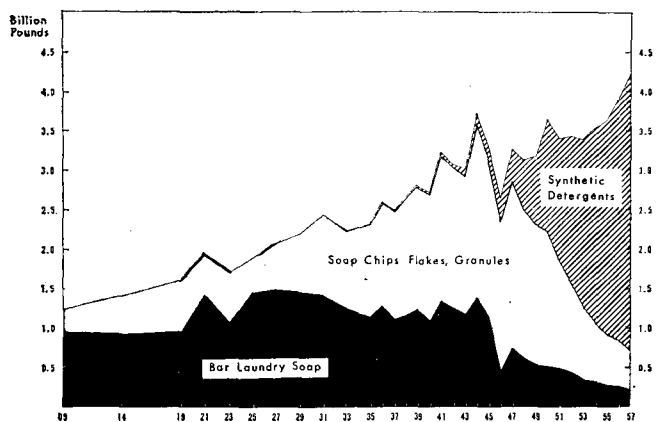


Fig. 6. Sales of laundry soap and synthetic detergents, 1909-57.

We had in our Association office recently a small group of Japanese soap-makers who had formed what was called the All-Japan Soap Association. This organization was at least partially developed and sponsored by the National Renderers Association and the Department of Agriculture of the United States. It is another one of those fine examples of industry-government cooperation of benefit to the people of this country and to others. It is a highly intelligent activity to solve a very serious problem.

The change from soaps to synthetics has also had repercussions in the production of glycerine. The production of glycerine in 1940 totalled 158,000,000 lbs., of which 148,000,000 were produced by the soap industry and 10,000,000 by other sources, none of which included any synthetic glycerine. This production of natural glycerine from soap and other processes has fallen from 158,000,000 lbs. to approximately 140,000,000 lbs. in 1957. Because glycerine is a useful and valuable product, others saw in this drying up of the source of natural glycerine, industrial opportunity, and today at least two companies are producing glycerine from propylene to the extent in 1957 of 100,000,000 lbs. All sources in 1957 gave a total production of 240,000,000, an increase of about 50% from 1940.

A further trend has taken place which, while not a part of the soap industry, has a vital effect on soap-industry marketing. The distribution of soaps has changed along with all other grocery items, and today a very large and vital part of this distribution is

through chain stores and supermarkets where the purchaser takes the package off the shelf and is not served by a grocery clerk. This has emphasized the importance of brand names, of advertising, of shelf display, and of package design.

The soap industry has been a leader of trends in advertising and merchandising. It has used coupons on the wrapper or package, it has had premium packs, house-to-house sampling and couponing, 1¢ sales, contests, comic strips, radio, television, and about every kind of innovation. The most recent was a New York subway ride for soap coupons.

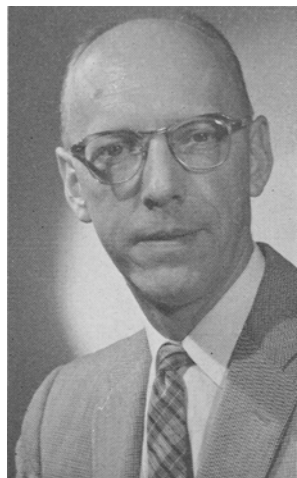
I can recall early days where a premium or an imitation pearl necklace or other gadget for the wife of the independent grocery store owner might be the inducement to make a sale. Not so any longer. I also recall finding a method to sell an excessive amount of soap in stores along a highway from Kansas City to Bonner Springs, Kans. On my next trip I found what the chain store and supermarket know today, the whole problem of successful selling is not putting the product into the store but instead moving it off the shelf into the hands of the consumer.

We can look backward and see so clearly the trends. Unfortunately we cannot see exactly the trends which will come in the future. I cannot help but think about the sage advice given me by an older man, no longer living, who in relation to personnel changes in a company said, "it has been my observation that a young man's opportunity comes in a period of change."

A Review of Ethylene Oxide Condensation with Relation to Surface-Active Agents

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IN THE MANUFACTURE of surface-active agents, ethylene oxide condensation is one of the principal processes employed to introduce hydrophilic functional groups into the molecular structures of organic compounds. The ultimate objective of the process is the production of surface-active agents having the desired hydrophile-lipophile balance (H.L.B.) for such commercial applications as detergency, emulsification, wetting, textile processing, etc. As a means of increasing the hydrophilic properties of organic compounds, ethylene oxide condensation ranks in importance with such processes as saponification, sulfonation, sulfation, quaternization, etc.



R. D. Fine

Surface-active agents produced by these other processes dissociate to some extent in aqueous solutions, forming ions which characterize the compounds as either anionic

or cationic, depending upon the electrical charge exhibited by the lipophilic component. These ions are free to react with other ions which may be present when the products are used. Such reactions can result in the inactivation of the surface-active agent and other undesirable effects. Except for certain organic amine derivatives, such ionic dissociation does not occur with ethylene oxide condensation compounds, and they are considered nonionic. In aqueous media these compounds form colloiddally dispersed micelles. Although visually they may appear to be completely soluble in water, their colloidal character is demonstrated by the presence of the Tyndall effect when a beam of light is passed through an aqueous solution. Some migration of micelles of nonionic compounds may occur in aqueous media in an electrostatic field, but this is believed to result from the presence of charges on the micelles themselves with respect to the solvent rather than to the existence of ions (1). The nonionic character of these compounds greatly increases their range of compatibility with other materials that may be encountered in use. Although high concentrations of sodium ions may salt out such products from solution, most of them exhibit a high tolerance for hard water salts, and some types are stable in the presence of relatively strong acids and bases.

Another characteristic of ethylene oxide condensation compounds that differentiates them from ionic