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Synthetic Detergents. Development and Use in Domestic Washing-Products

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IN ANY HISTORY of the development of the newer detergents it seems fitting to recall that the first detergent, soap, was known to the ancient Romans (1). Its first recorded method of manufacture, from goat's tallow and wood-ash extract, was ascribed to the Gauls of northern Italy. Over the centuries the manufacture and use of soap expanded very slowly in Europe, perhaps partly as a household art but notably as a manufacturing enterprise in Marseilles, where it was controlled by a Gaulist community in about the seventh or eighth century. Both manufacture and use spread to the rest of France, Germany, Belgium and, finally, to England by the 16th century. The product of the early soap-makers was a luxury item, subject, particularly in England, to heavy taxes. It was late in the 19th century that this basic situation changed. Then the rapid expansion of centralized manufacture and skilled selling in many nations made soap a low-priced necessity in the great majority of homes.

In addition to its household use, soap was employed over the years in many industries as a detergent and wetting agent. The textile industry has always been the largest such consumer requiring detergents for washing, scouring, and desizing operations, and wetting agents for dye leveling, mercerizing, and bleaching. These needs were met for years by the skillful blending of soaps made from various oils and fats combined with soda or potash, taking advantage of the differences in detergency and wetting power that depend on the length of the carbon chains of the individual fatty acids and on their degree of saturation. Although soaps perform well in warm, soft water, they are not ideal for the textile manufacturer's use. All of them suffer from the drawback that the calcium and magnesium salts are very insoluble, lack detersive properties, and, when precipitated on the fibers, impede penetration of solutions resulting in an unevenness in the finishing of fabrics. Such considerations made the textile industry ready to test and accept products that promised to overcome the deficiencies.

In 1831 Fremy observed that unsaturated oils, notably olive oil, would react with concentrated sulfuric acid. Three years later Runge neutralized a product of this type to obtain a wetting agent that greatly aided the dyeing of cotton textiles with certain red colors (2). These Turkey Red oils, as they became known, were the first improvements on soap, but unfortunately they were not good detergents.

The next improvement over soap came with the discovery that the sulfate esters of the fatty alcohols from spermaceti oil had a high tolerance for the calcium and magnesium ions present in hard water and that their solutions would rapidly wet-out fabrics. Although Dumas and Peligot (3) prepared the first sperm-alcohol sulfates in 1836, it was not until the end of the 19th century that these substances began to be used in the textile industry as dyeing assistants, as wetting agents, and as detergents to replace soap in special applications. Although the supply of these natural fatty alcohols was enough to make available a high-cost specialty product, its manufacture and use were of no interest to the soap-makers, who at that time had other more pressing technical and business problems.

Under the pressure of the fat shortage during World War I German scientists examined the possibilities of many synthetic washing-compounds. Lower alkylated naphthalene sulfonates, whose sodium salts were good wetting agents but poor detergents, were first developed. From this start there were great advances during the next 15 years. As a first step during the 1920's the preparation of fatty alcohols from fatty acids and their esters by both high pressure hydrogenation and sodium reduction processes grew to a highly developed technology (4). Sodium fatty alcohol sulfates became important in Germany before 1930 as detergents as well as textile finishing aids.

THE FIRST AMERICAN synthetic detergent packaged for household use, Dreft, reached grocers' shelves in 1932. This was a free-flowing powder, which comprised about 40% sodium lauryl sulfate (from coconut oil) with sodium sulfate and moisture as the remainder of the formulation. It was manufactured under patents issued to Bertsch (5) and licensed to American Hyalsol Corporation, a venture jointly owned by the Procter and Gamble and du Pont companies. Because of its acceptable detergency in washing lightly-soiled, fine-fabric garments and in dishwashing, this new detergent enjoyed a small and slowly increasing sale until recent years. Acceptance in this "light-duty" cleaning field, created earlier by the makers of ultra-thin soap flakes and soap beads, was possible in part because certain package weights and premium prices were already established at levels that could be met economically by the new product.

Improvements in the performance of this fatty alcohol sulfate detergent were accomplished during the period 1932 to 1946. A slight increase in detergency and a considerable increase in foam stability were obtained by the deliberate addition of unsulfated fatty alcohol, besides that remaining after the sulfation reaction. For example, inclusion of about 2% lauryl alcohol made possible a decrease of nearly a third in the organic surfactant, a major economic gain. Other foam stabilizing compounds, covered in patents issued to members of the Procter and Gamble research group, included fatty amides, fatty ethanolamides, and morpholides (6).

Another anionic detergent, Vel, marketed by Colgate-Palmolive, also appeared before World War II. In this the sodium salt of coconut oil monoglyceride monosulfate (7) was the organic detergent, again with sodium sulfate as the builder. During this period light-duty products containing fatty acid methyl taurates were extensively investigated but never reached the market in the United States although such a composition was sold in the household trade by the Unilever company in Germany under the name of Fex.

Perhaps a short digression can be permitted here to examine the rather exacting requirements that a household product must satisfy. Although preferences exist, industrial users can usually deal with a compound in any physical form in which it may be offered; solution, paste, dry or sticky solid, and unfavorable properties, such as high hygroscopicity or viscosity, can be permitted. The homemaker, on the other hand, demands her detergent in a convenient physical form. She expects it to dissolve rapidly in hot or cold water and quickly to produce suds that remain throughout the washing operation but disappear easily during rinsing. She has long purchased in paper containers such fabric-cleaning agents in the form of dry, free-flowing, particulate powders of good color and odor. Absorption of atmospheric moisture by a product to the extent that it becomes pasty, sticky, or cakes is intolerable in such containers. In all cases a specific detergent efficiency must exist; the product must be safe for fabrics and skin, and the price must be acceptable. From the number of synthetic detergents available in comparison with those that have been sold successfully in the household trade, it might be concluded that it is easier by a factor of a thousand or so to synthesize a new compound having detergent qualities than it is to select, formulate, package, and sell successfully a product of this kind.

Up to 1946 the price comparison between heavy-duty soaps and the formulated newer detergents was about one to two. Further use of the synthetic detergents in "heavy-duty" application, that is, in the washing of the family laundry, required a price reduction and an increase in the detergent efficiency. Replacement of a large part of the sodium sulfate in the fatty alcohol-sulfate mixtures by one of the alkaline polyphosphates was found (8) to build the formulation effectively to the point where detergency approaching that of soap was attained. Also, in the presence of the polyphosphates, smaller amounts of the organic surfactant (down to 20% of the composition) could be utilized without sacrifice of the foaming and soil-removal properties. Prevention of the redeposition of the soil once removed, a prime necessity in laundering cottons, was accomplished by the inclusion of less than 1% of sodium carboxymethylcellulose in the formulation, applying a discovery made in Germany during World War II (9). Tide, the first of the all-purpose laundry, synthetic detergents, successfully combined all of these features and, when launched by Procter and Gamble early in 1947, started the dramatic replacement of soap as the general household laundry detergent.

Also, at about this time, tetrapropyl benzene was made available in large quantities from petroleum sources (10). The sodium sulfonate of this alkylated benzene is deficient in detergent properties but, built by the addition of one of the polyphosphates and with carboxymethylcellulose and fluorescent dye added, gives satisfactory detergents. Competitors of Tide were soon on the market, using the alkylaryl sulfonate surfactant. Improvements in these anionic detergents have been made in recent years by the addition of small amounts of materials ordinarily classified as oil-soluble emulsifying agents. These organic builders increase foam stability, improve detergency, and make possible a lower total content of organic surfactant in the product.

These organic builders are insoluble, nonionic surface-active agents and, although extremely important in modern anionic detergent formulations, have little or no detersive action alone. The true class of nonionic detergents is ordinarily limited to other more strongly hydrophilic compounds. The best known types of these materials consist of a hydrophobic portion, usually a fatty acid, fatty alcohol, or alkylated phenol, combined with a polyoxyethylene $[-O(CH_2\ CH_2O)_xCH_2\ CH_2OH]$ hydrophylic structure. The polyoxyethylene chain can be almost any desired length with each additional alkylene oxide group modifying the solubility and other properties of the resultant synthetic detergent.

Again in about 1930 German scientists were the originators of this new kind of detergent (11), and again it was the textile industry that served as the testing ground (12). For example, although mineral oil had been long known in woolen mills to be an excellent yarn lubricant, it had not been employed because once applied to the fibers it was very difficult to remove. Certain of the oxyethylated surfactants were found to have excellent detergency in this appli-

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cation and were not substantive to wool so that the detergent baths were not rapidly depleted as would be the case with an anionic.

The nonionics are good solubilizers for oily soils, good dispersing agents for lime soaps, and are better detergents unbuilt than are most anionic detergents without builders. However, when combined with the best alkaline builders, such as the polyphosphates, they deterge soiled cottons and other fabrics as well as but not better than do the similar, built anionic formulations. They are, in general, poor-to-fair foam producers although there are some exceptions to this.

THE CHIEF USE of nonionic detergents in household washing products is a direct result of the relatively low volume of foam generated even with vigorous surface agitation of their solutions. In rotary-drum, domestic washing-machines the mechanical work necessary for good cleaning comes from elevating the clothes above the water surface and dropping them back into the washing solution. A large volume of stable suds so cushions the mechanical shock that poor cleaning results, and a small volume of relatively fragile suds is desirable. Using a nonionic detergent derived from tall oil condensed with ethylene oxide, and including the usual builders and soil-suspending agents, the Monsanto Chemical Company produced such a product, All. This low sudsing product has been available in the U. S. market nearly as long as have the more widely used, high-foaming products containing anionic detergents.

Most of the nonionic surfactants are liquids but can be mixed with the builders to form dry, free-flowing powders because relatively small amounts are ordinarily used. The liquid state does suggest however that if a satisfactory combination of properties exists in such a surfactant, a concentrated product would be available to the consumer in convenient form. Shelton (13) has reported that in 1945 one of the General Aniline and Film Company's liquid nonionics was found to be superior to other available compounds for washing hard surfaces, especially dishes and glassware. After considerable market research the maker decided to sell this detergent as a consumer product named Glim. This first nonsoap, liquid detergent with its otherwise attractive properties lacked foaming power and foam stability, a real deficiency in the eyes of the housewife. Other manufacturers have since developed light-duty, liquid detergents that produce copious foam, while rinsing easily to impart a clean sparkle to the dishes. The fatty acid mono- and dialkylolamides, particularly the lauric acid derivatives, have been used extensively as foam stabilizers (14) with various anionics in the newer products.

Liquid detergents, of course, pose an entirely different set of packaging problems from the granulated detergents. The early, light-duty liquids were sold in glass bottles which regrettably would occasionally slip from the housewife's wet hands with unfortunate results. After many formulation changes and an intensive cooperative investigation with the can-makers, the corrosion of metal containers was prevented, and in 1953 Lux Liquid in a can was marketed. Three years later this lead had been followed by all of the manufacturers of the better known, light-duty liquids, and a new upsurge in consumer sales to approximately three times 1952 levels was reported for this product class (15).

With the success of light-duty liquids in mind one is immediately led to inquire about the possibility of preparing a liquid detergent for family laundry use. Synthetic detergents for such use require builders to develop the requisite cleaning power; and the most satisfactory builders, the alkaline polyphosphates and silicates, at useful concentrations tend to salt out of solution both the anionic and nonionic surfactants. Also, for completely satisfactory cleaning, a soil-suspending agent is needed in the formulation. All such materials known to be useful with synthetic detergents are easily precipitated in ordinary solutions of inorganic salts. In spite of these formidable problems and those involved in packaging such a product, a heavy-duty, liquid detergent, Wisk, having good foaming power and efficient detergency, was marketed early in 1956. In this, anionic and nonionic surfactants are combined with builders, soil-suspending agent, optical brightener, etc., to form the first complete product of its class. Recently a companion low-sudsing liquid, Hum, for automatic washers, was also introduced by Lever Brothers Company.

In recent years we have seen soap, the earliest detergent, replaced by granulated synthetic detergents in what amounted to a revolution in the usage of domestic washing-agents. Now with the impressive gains by the liquid detergents, we may be at the beginning of a second revolution in this field.

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