The birth of the tweens
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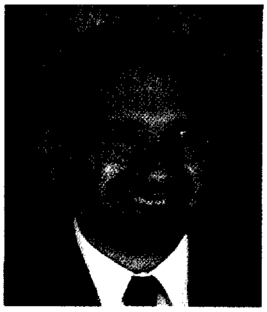

The Birth of the Tweens

For half a century, Hydrophile Lipophile Balance has been the best starting point for emulsion formulation. BY STEVE HERMAN

"...originality consists of the achievement of new combinations, and not of the creation of something out of nothing."
—Richard V. Clemence

Ethoxylated products arose phoenix-like from the ashes of war, propelling surfactant technology.

ETHOXYLATION SEEMS to have been with us forever. In truth, ethoxylated products arose phoenix-like from the ashes of war, propelling surfactant technology into the modern era. There is much talk today about technology transfer: A great example—and a fascinating story—can be found in the birth of Tween 20.

In the era before INCI names, trade names were common parlance. In that far off world, Tween 20 reigned as a great surfactant, legally protected by patent as an Atlas (and later an ICI) product. There was no CTFA Dictionary to depersonalize it to Polysorbate 20, and no other manufacturers with their clones. ICI (now Uniqema) acquired the Tweens around 1970 from Atlas Chemical Company. The Atlas explosives plant in Tamaqua, PA, is where our tale begins in the mid-1940s.

Atlas Powder Company manufactured blasting caps, essentially a copper tube filled with fulminate of mercury. Mercury fulminate is perhaps the oldest known initiating compound. It can be detonated by either heat or shock. Even the action of dropping a crystal of the fulminate causes it to explode. The cap was used to detonate dynamite. A safer device was obviously desirable due to the sensitivity of the fulminate. A Swarthmore professor found that safer product, mannitol hexanitrate. Atlas used the information to produce a safer blasting cap, necessitating the procurement of a large quantity of mannitol.

The method used to produce mannitol by Atlas made, as a byproduct, four pounds of sorbitol for every pound of mannitol. Atlas now needed a use for all the sorbitol. As a polyhydric alcohol, sorbitol first found use as a humectant to replace glycerine in certain applications, and it now is used in oral-care products.

To find use as an emulsifier, the sorbitol was esterified to compete with glycerol monostearate. Unfortunately, most of the hydroxy groups were lost during the process, resulting in sorbitan monostearate rather than sorbitol monostearate. The resulting products were only useful in stabilizing w/o emulsions. We now have arrived at the Spans, and the closing days of World War II.

Some World War battles were fought in the chemical laboratories, sometimes ending in success, sometimes in failure. In the first war, Germany was cut off from its rubber supply. Attempts to produce a good replacement product that could be manufactured in sufficient quantities failed, creating shortages in boots and tires. In the second war, Japan cut off 90 percent of America's rubber, putting us in the same position Germany had been in 20 years earlier. This time, attempts to create synthetic rubber succeeded. America also found a method of making high-octane fuel from low-grade petroleum, allowing better performance from Allied planes.

When the war ended in Europe, German rocket scientists came to the U.S. to establish the American space program. Many Allied organizations went to Germany to copy governmental and industrial documents, including: the Commerce Department Office of Technical Services, FIAT (War Department Field Information Agency Technical), CIOS (Combined Intelligence Objectives Subcommittee), and BIOS (British Intelligence Objectives Subcommittee). Extensive information on the chemical industry came from the I.G.Farben investigation.

Included in the team of scientists from the U.S. sent to Germany to study the chemical industry was Dr. Rudolph Goepp of Atlas Powder Company. In

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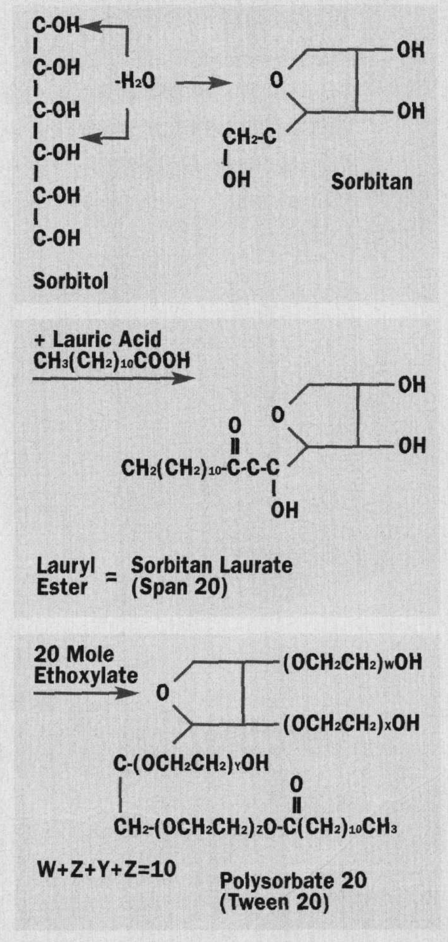
Germany, Dr. Goepp observed the use of alkylene oxides to convert hydrophobic organic molecules into water-soluble form. Especially useful for this purpose was ethylene oxide.

The only common surface active agents in personal care before the mid-1930s were soaps, which are anionic surfactants. Alcohol sulfates for shampoos and detergents were the first challengers to soap in 2,000 years, followed by the first wave of nonionics. The discovery of ethoxylation revolutionized the world of surfactants.

FIGURE 1: SORBITOL TO POLYSORBATE 20



Back home, Dr. Goepp's newfound wisdom was applied to the Spans, and the Tweens were born. Tragically, on a return trip to Germany, Dr. Goepp's plane went down over Greenland, and he never saw the fruits of his technology transfer. A talented team led by William Griffin continued the work on nonionics.

The new surfactants were water soluble, and formed o/w emulsions. Figure 1 shows the path from sorbitol to Tween 20. The new surfactants weren't known as Tweens at first: Tween 20 was born as G-7596T. T is the 20th letter of the alphabet, and denoted 20 moles EO.

As Bill Griffin carried on the investigations at Atlas, he observed how blends of the ethoxylates created a flexible series of surfactants.

The HLB (Hydrophile Lipophile Balance) was developed, and initially used only for internal product development at Atlas. Atlas recognized the theory would only be useful if it were disclosed to the whole industry. As presented in the first paper[1] in 1949, a large number of surfactants, including anionics, were evaluated using a laborious experimental procedure. Ethoxylation was not even mentioned in the early paper, and no chemical structure for the Tweens was disclosed. Still, the first paper contained a surprising number of concepts that have survived to the present, such as the HLB Computagraph. The Atlas patents for ethoxylated surfactants were not yet in effect, so there was cause for discretion.

There was no easy-to-use HLB theory available until five years later.[2] In Griffin's 1954 paper, Tween 20 was identified as "polyoxyethylene sorbitan mono laurate," and the emphasis of HLB theory was placed firmly on the nonionics. A simple formula for molecules where the only hydrophilic portion was ethylene oxide was introduced, HLB=E/5, where E is the weight percent of EO. This paper codified HLB theory into the form used today.

For half a century, HLB has been the best starting point for emulsion formulation. Bill Griffin has been much honored for his contributions to our industry, most recently as recipient of the Maison G. deNavarre Medal of the Society of Cosmetic Chemists in 1999. It was a long way from blasting caps to the award dinner at the New York Hilton for Bill Griffin, a path that has helped create a real science of cosmetic chemistry. GCI

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References

Bill Griffin provided much information through e-mail and phone interviews. Dr. Jeffrey Johnson of the Department of History, Villanova University, supplied background on technology transfer from Germany after World War II.

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2. Griffin, William C., "Calculation of HLB Values of Nonionic Surfactants," *JSCC*, 5, 249-256 (1954).