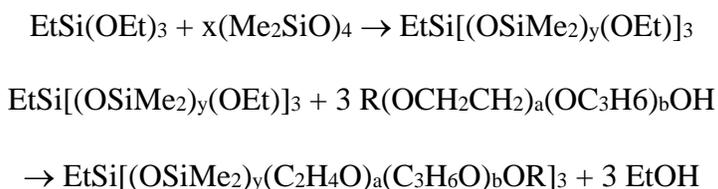


THE DISCOVERY OF SILICONE SURFACTANTS FOR POLYURETHANE FOAM

Bernard Kanner
5 Robin Lane
West Nyack, NY

By 1953, Don Bailey's research interests had shifted to the synthesis of new types of silicone-organic copolymers initially directed to the preparation of silicone fibers. Initially, he sought to introduce chain-stiffening groups into the siloxane backbone. The synthesis routes employed presented considerable difficulties and progress was discouragingly slow. His effort then shifted to the incorporation of polyether blocks. In the course of introducing dipropylene glycol units into the silicone chain, he made the observation that Si-O-C and Si-O-Si bonds reacted equivalently using base-catalyzed equilibration conditions. This led to a convenient synthesis of alkoxy-endblocked silicones. The alkoxy-endblocked silicones were then reacted with a series of hydroxyl terminated polyethers (UCONs), which were Union Carbide products. These included polymers made from ethylene and propylene oxides as well as mixtures of the two oxides.

These were the first known copolymers of silicones with polyethers and had both linear and branched structures:



These, and many other structural and compositional variations, were synthesized by Bailey and F. M. O'Connor (See for example, U.S. Patent 2,834,748, issued May 13, 1958 and U.S. Patent 2,917,480, issued December 15, 1959). These new copolymers, of course, proved to be of no interest as silicone fibers, but the latter objective was quickly shelved when it appeared that these novel copolymers might have many other interesting possibilities.

Tom Welch (later a Director of R&D for Silicones), who came to Linde with a extensive background in rubber technology, was seeking improved tire mold release agents, and was aware of the lubricating properties of UCON fluids. He was the first to use the new copolymers for mold release at Dunlop Tire in Buffalo. Other uses envisioned for these copolymers included antifoams, lubricants, hydraulic fluids, brake fluids and textile treatment. The metal-on-metal lubricating properties of these copolymers were markedly superior to pure polydimethylsiloxanes.

These intriguing early results led to a period of intense examination of the potential utility of these compounds in a number of applications. This effort continued for more than

two years, but did not lead to the successful marketing of any new products. It was recognized early on that a possible drawback of copolymers prepared by the transesterification was their limited hydrolytic stability, especially in the presence of acids or bases.

To overcome this problem, hydrolytically stable copolymers were prepared via the platinum-catalyzed hydrosilation of polydimethylsiloxane polymers containing methylhydrogensiloxane units with allyl-endsblocked polyethers. By this time, interest in silicone-polyether copolymers was beginning to wane, however, as none of the potential new applications had yet proved to be commercially attractive. For this reason, the filing of patents on the new non-hydrolyzable copolymers was not actively pursued. However; other developments were then underway which were soon to change the entire future of silicone-polyether copolymers.

Polyurethanes, the reaction products of isocyanates with diols, had been discovered in Germany during World War II. The commercial exploitation of polyurethanes developed rapidly in the late 1940's, especially for polyurethane foam. Foamed polyurethane elastomers were made via a two step, so-called, prepolymer process. In the first step, an excess of an aromatic diisocyanate, such as toluene diisocyanate, was reacted with a hydroxyl-terminated polyester forming a viscous isocyanate-terminated prepolymer. In the second step, sufficient water was added to react with the excess isocyanate, forming urea, generating carbon dioxide, thus foaming the final polymer. The resulting foamed elastomer was of relatively low density, while retaining attractive physical properties; making it economically attractive for a number of applications.

The polyurethane foam prepared in this was inherently self-stabilizing because of its high viscosity. However, it was found that the addition of a small amount of a low molecular weight polydimethylsilicone oil considerably improved the foam cell uniformity. It was later established that the soluble low molecular weight polydimethylsilicone acted as a surfactant by lowering the surface tension of the reacting urethane mass. As interest in the commercial prospects of polyurethanes grew, efforts were underway in a number of laboratories, including DuPont, Mobay and UCC Chemicals. This took the direction of streamlining the foaming process and employing less expensive intermediates, thereby improving its overall economics. The main avenues of research involved substitution of the cheaper hydroxyl-terminated polyoxypropylenes for the polyester component and simultaneously reacting the isocyanate with the polyol and water all at once (known as the "one-shot" process).

Two problems had to be overcome before this process could be commercialized. The reactions between the isocyanate, polyols and water proved to be unacceptably slow. Effective catalysts had to be found. It was now also necessary to find a more effective foam stabilizer than the silicone oil that worked for the prepolymer process. As the viscosity of the "one-shot" polyurethane foam mixture was far lower than the prepolymer system, it was inherently much less stable and collapsed completely in the absence of an appropriate stabilizer.

At UC Chemicals Co. at South Charleston, West Virginia, the effort to solve these problems was headed by Fritz Hostettler and Eugene F. Cox. They made the important discovery that certain tin compounds, initially organotin compounds and, subsequently, stannous compounds, in combination with a variety of tertiary amines were excellent catalysts for the new process. They also had unexpected synergistic interactions for the "one-shot" process. The remaining problem, stabilization of the reaction mass, proved to be far more difficult of solution. Hostettler and Cox had tried more than 100 surfactant candidates, including many polydimethylsilicones and a wide range of organics without success. It was far from clear that a solution lay ahead. At this point fortune intervened in an unexpected fashion.

At Silicones R&D in Tonawanda, Tony Pater was one of several investigators in the Development group who were trying to develop commercial applications for the silicone polyether copolymers that had been made by Bailey and O'Connor. After more than two years of active investigation, although optimism still remained, a real commercial winner was yet to be identified. Three of the Bailey-O'Connor copolymer candidates had been scaled up in the pilot plant to facilitate these efforts. The three candidates were fairly closely related, differing mainly in the polyether component. These experimental compositions were identified as X-520, X-5:21 and X-522. In X-521 and X-522, the polyethers were based on all oxyethylene and oxypropylene units, respectively. Only in the case of X-520, (Later, L-520), did the polyether block contain both oxyethylene and oxypropylene units (50 % by weight of each component).

As part of an effort to interest other laboratories in evaluating these new compositions, Tony had scheduled a visit to the South Charleston Chemicals laboratories in the latter part of 1956. Before an R&D audience, Tony reviewed the extensive efforts at Linde to synthesize, characterize and commercialize the silicone-polyether copolymers. The South Charleston Chemicals R&D were invited to assist in this effort. Fritz Hostettler happened to be present at this review. Samples of the new copolymers were requested, and when they arrived in the early part of 1957, they were quickly evaluated in the "one-shot" South Charleston, prototype polyurethane system. Within the first few experiments, a new industry was essentially established. It was quickly observed that while X-521 and X-522 did not prevent foam collapse, X-520 was an excellent foam stabilizer for one-shot polyurethane foam.

Chance, as it does in so many important discoveries, had played a vital role. The timing of the development of the "one-shot" polyurethane foam system and the synthesis of the first silicone-polyether block copolymers could hardly have been better orchestrated. The selection of the three copolymer candidate compositions for scale up so as to include X-520 (L-520) which was to be one of the surfactant mainstays for the Polyurethane Industry for the next four decades, was indeed fortuitous. A great many other structural and compositional variations which had also been synthesized had failed to stabilize the one-shot polyurethane foam system.

With these discoveries and their subsequent confirmation in a number of other industrial laboratories, the commercialization of the "one-shot" polyurethane systems was

assured. The development of appropriate foam formulations, foaming equipment and full scale testing required an additional couple of years. Significant sales of L-520 surfactant then began in the late 1950's. Of all the developments and discoveries that made the "one-shot" polyurethane foam process possible, it is generally recognized that the stabilization of the foam by L-520 was the most important. Don Bailey was to become a recipient of the Schoellkopf Award in 1968 for his pioneering work on L-520 and other silicone-polyether copolymers.