

## THE DISCOVERY OF SILANE COUPLING AGENTS

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Discovery of the hydrosilation process led Bailey and others to explore the chemistry of reactive organosilanes. This began with the already available vinyltriethoxysilane. The peroxide-catalyzed polymerization led only to low molecular weight polymers, which did not merit further interest. At this time Bailey's research shifted to the synthesis of other organofunctional silanes and silicones capable of undergoing a variety of organic reactions. Shortly thereafter, commercial developments outside of Linde Silicones would soon greatly accelerate this work.

In the late 1940's, reinforced polymers had attracted considerable interest by the military because of their potential use in military aircraft. Glass fabric reinforced polyester laminates, in particular, were being evaluated as spacers for self-sealing gasoline tanks and as non-shattering structural components such as wings. These laminates were based on unsaturated polyesters and approximated the flexural strength of equivalent weights of structural steel. They were also lighter and stronger than equivalent thicknesses of structural aluminum alloys.

The critical deficiency of these laminates, which effectively prevented their commercial use, was the great loss in physical strength they exhibited on extended exposure to water vapor or liquid water. The loss in strength typically amounted to a catastrophic 60%! This was true whether one used desized glass or starch-oil sized glass, which was all that was available at the time. Some modest improvement was noted when a novel sizing agent, chromium methacrylate chloride, was used. The initial flexural strength was slightly increased and the loss on humid aging was decreased modestly to around 40%. This loss in physical strength was still unacceptably high for the use of these laminates in aircraft.

In an attempt to solve this problem, the Air Force granted a contract to the Bjorksten Research Laboratory in Madison, Wisconsin in late 1949 or early 1950 to develop a superior sizing agent for glass cloth polyester laminates. Success was achieved shortly thereafter.

The breakthrough results achieved by the Bjorksten Labs was reported in a paper presented at the Spring Meeting of the Reinforced Plastics Division of the SPI at Chicago in late February-March, 1951. They reported that vinyltrichlorosilane or its admixture with an allyl alcohol derivative not only raised the initial strength of the laminate by 15 to 25%, it also dramatically reduced the loss on humid aging to from 0 to 10%. The resulting laminates were now stronger after humid aging than dry chromium methacrylate chloride sized laminates. These striking results attracted great attention and resulted in a special meeting organized by the Materials Laboratory of the Wright Air Development Center held later in March of the same year.

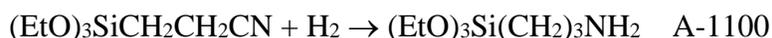
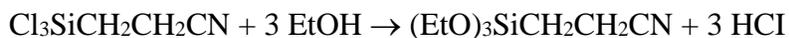
Following a presentation by Dr. Bjorksten of the results at his laboratory, Dr. Robert Steinman of the Garan Chemical Co., of Los Angeles, reported virtually the same results using an undisclosed chemical in aqueous solution which was later identified as vinyltriethoxysilane. This was clearly superior to the use of vinyltrichlorosilane as it avoided HCl formation. At the same time, the Owens-Corning fiberglass representatives present at the meeting indicated that they also had a promising laboratory process for this same purpose. Further, plant trials were expected very shortly that they anticipated would be competitive with the Bjorksten and Garan processes. Some months later it was learned that the new Owens-Corning treatment, called Finish 136, was based on a product supplied by the Cowles Chemical Company. The product was made from vinyltrichlorosilane, which was converted to a water soluble sodium salt which could be directly applied to glass from aqueous solution.

Thus, the discovery which was the basis for the coupling agent, or, as it was later known as the organofunctional silane business, was made almost simultaneously in 3 different labs. It appears that the Bjorksten labs were first, closely followed by Garan and Owens-Corning. It also appears that all three treatment processes were based on samples of vinyltrichlorosilane or its ester obtained from Linde.

Members of Linde Silicones attended both of these meetings and the decision was quickly made to enter this promising field. Based on laboratory work carried out by Murray Jellinek, aided by Dave Braun and Sarah Camiolo, new vinylsilane esters products were introduced to the market by early 1953.

The rapid commercial acceptance of the vinylsilane coupling agents stirred renewed interest in George Wagner's Research group. The vinylsilanes were believed to bond with the silanol bonds on the glass surface and the vinyl functionality would then react chemically with the unsaturation in the polyester. The overall result would be a chemical bond between the glass surface and the polyesters. This made for improved reinforcement or increased laminate strength, while preventing water from degrading this interaction. Wagner believed that the availability of silanes with new types of organic functionality would greatly broaden the commercial utility of silane sizing agents.

To carry out this work, George asked Vic Jex, a recent addition to the Research group to synthesize a silane containing an amine functionality via a new route. Bailey had previously prepared amino functional silanes via the reaction of chloroalkylsilane esters with ammonia. However, this route resulted in extensive salt formation along with some undesirable side reactions. The new process involved the hydrosilation of acrylonitrile with trichlorosilane, followed by esterification and hydrogenation:



Unfortunately, the first step, which involved platinum catalysis, could not be made to go. This was one of the very few cases of hydrosilation for which platinum catalysis was ineffective. Perhaps fortuitously, Dr. Jex, as part of his graduate thesis, had investigated the base-catalyzed cyanoethylation of sugar molecules. As it turned out, the tertiary amine catalyzed cyanoethylation of trichlorosilane was the critical step in the synthesis of the amino functional silane. The product, gamma-aminopropyltriethoxysilane, received the commercial designation of A-1100.

Not too long afterwards, an Owens-Corning representative was brought to Dr. Wagner's office by Dr. Jellinek. There, he inquired whether a sizing agent suitable for use with epoxy resins might be available. He was promptly given the A-1100 sample that had been prepared by Vic Jex. Subsequent tests at Owens-Corning proved the effectiveness of A-1100 for epoxy resins. With the rapid industrial acceptance of the Linde Silicones vinyl- and aminoalkylsilane coupling agents in the 1950's, Linde became the leading supplier of silane coupling agents, a position that UCC Silicones and its successors have maintained until the present time.

As a postscript, for his "...pioneering contributions to the technology of organosilicon monomers and of polyalkylene oxide lubricantst" George Wagner was to receive the Schoelkopf Award from the Western New York Chapter of the ACS on May 19, 1960. Several years before that, Dr. Wagner had left Linde Silicones to assume greater responsibilities, initially within Linde, and subsequently for other Divisions within UCC.