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G.C. BERRY

A CASE HISTORY

OF

THE DEVELOPMENT OF SILICONES

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Preface

The following survey is a brief history of the development of silicone materials. Almost from the awakening of interest in the element silicon, its organic chemistry has been a focus of attention. Therefore, the survey necessarily must include some account of this early work. Even though we must necessarily rely on earlier judgments for our knowledge of early research workers, we can still hope to attain insight into their personalities and motivations.

The material for the recent history (1930 to present) was obtained through conversations with Dr. E. L. Warrick and Dr. John Speier, whose cooperation and that of the Dow Corning Corporation is gratefully acknowledged. Dr. R. R McGregor, who for many years served as Head of the Dow Corning Fellowship at Mellon Institute, died on April 8, 1965. His book, Silicones and Their Uses,(1) was most helpful in the preparation of this case history.

The limitations of our treatment, which will be apparent to the reader, are cited explicitly in the last section, the Summary Analysis. The limitations must be attributed to the authors, inexperienced in documentary histories and limited in time to devote to this assignment, rather than to the members of the Dow Corning Corporation, who gave generously of their time in recalling the exciting events covering nearly thirty years of time.

Case History of the Development of Silicones

Narrative

Introduction

Liberally dispersed throughout the history of science one finds conjunctions of persons and events, that by chance, or by some logical consequence, sput outstanding discoveries. A careful chronological study of the discovery and subsequent practical application of a particular product may well yield valuable information regarding the factors contributing to its development and one might hope thereby to discern the outlines of some features common to all creative advances. The history of the development of silicones is an excellent example of such a product. The use of silicone products is commonplace in everyday life; yet silicones -- the generic name for high molecular weight organosilicon compounds -- do not exist in nature. The specific molecular structures and products are the rewards of much painstaking thought and investigation, by scientists and technologists who possessed in common at least one outstanding quality -- insatiable curiosity.

Discovery of Silicon and Its Relation to Silicone Technology Prior to 1900

The history of silicones is intimately related to the discovery and subsequent investigations on the element silicon, and therefore this survey must begin at that point. Prior to 1800 the constitution of silica, the most abundant compound in the crust of the earth, had not yet been revealed. Many notable chemists of the day, including Sir Humphrey Davy, Scheele, and others, had directed part of their interest to the subject. However, it was Johann Berzelius, described as a "prodigious worker", who, in 1828, successfully separated the element silicon from its potassium fluorosilicate salt. Instead of momentarily slowing up to notify his contemporaries of his momentous discovery, Berzelius continued in his investigations in a mood which has been described as something of a fury. The result of his continued investigation led to the preparation of silicon tetrachloride. This product is prepared today in a way very similar to the method of Berzelius. It is one of the basic materials used in the manufacture of silicones.

Two years later, in 1830, a French chemist, Persoz, reported(2) that he had prepared a white solid product by treating the chloride of silicon with ammonia. Persoz did not view his observation as an important discovery, and therefore very little subsequent effort was directed towards similar investigations. Fifteen years later, however, in 1845, another French chemist, Ebelman, realizing the importance of the observations of Persoz, treated the chloride with ethyl alcohol and, replacing the chlorine atoms, formed ethyl silicate, which today is prepared in exactly the same manner.

In 1857 Friedrich Wöhler, who had spent some time working with Berzelius in Stockholm, noticed the evolution of a gas which exploded in air from an electrolytic bath in which aluminum rods had been immersed. He later found out that the aluminum rods contained silicon and, in further experiments, deduced that the gas contained silicon, hydrogen, and chlorine. Later work proved the gas to be $SiHCl_3$, "silicochloroform." This compound, first observed more than 100 years ago as a scientific curiosity, is today an important commercial product used in the preparation of silicones. It has been noted that if Wöhler had gone just one step further and used an aliphatic chloride in his experiments rather than HCl, he would have anticipated by nearly a century a significant development in silicone chemistry. Dr. R. R. McGregor, in his book, "Silicones and Their Uses," points out, with reference to the work of Wöhler and his contemporaries, "It all looks so simple in retrospect; but it must be remembered that this was a virgin field and only those with keen observation and insatiable curiosity could note the unusual reactions or muster the patience to follow the results to some definite conclusion." He further states, "...work goes slowly when the background of information is small, and men like Berzelius, Ebelman, and Wöhler had little background on which to rely. To build these foundations was a task only for men of the keenest insight and the utmost determination." We shall observe that these statements are none the less true today than they were a century ago.

The work of Charles Friedel, Professor Mineralogy at the Sorbonne, and C. M. Crafts, an American who had come to Paris to study, must be considered as a milestone in the history of silicon chemistry and the first contribution to the chemistry of organosilicon compounds. In a series of papers dating from 1863 to 1866, they greatly enlarged ~~the~~ knowledge in this area of chemistry,and for the first time reported compounds in which an organic radical was attached to silicon. McGregor states, "No such compounds had ever been made before. The union of silicon and carbon is one of the essential points in the constitution of silicones, and for this reason, if for no other, this synthesis by Friedel and Crafts must be considered a most important step in the history of silicone development."

Crafts returned to the United States to become the Head of the Department of Chemistry at Cornell University and later the President of the Massachusetts Institute of Technology. Friedel maintained his interest in silicon, primarily because he was a mineralogist, and he was later joined in his work by the German chemist Ladenburg. Their interests, however, centered on learning more about the chemistry of silicon itself. If the preparation of compounds containing carbon could shed any light on this, they would attempt to prepare them, but otherwise it appears they were not particularly interested. This attitude was indeed unfortunate when one considers that at this point they were on the threshold of a silicone industry. Friedel and Ladenburg, however, did make many significant contributions to silicon chemistry, many of which remain basic to the modern technology. It is interesting to note that their last joint publication was in 1871, a year after the beginning of the Franco-Prussian War. Friedel, the Frenchman, and Ladenburg, the German, held conflicting political and religious views. For these reasons, Ladenburg returned to Germany; and thereafter Friedel maintained little more than a passive interest in organosilicon chemistry. One should observe, however, that in the twelve-year period that Friedel collaborated with both Crafts and Ladenburg, the foundations for modern silicone technology were laid. McGregor concludes "that in the silicon work with both Crafts and Ladenburg, Friedel must have been the activating force, or the catalyst, because of his interest in mineralogy ... While one would guess that Crafts and Ladenburg did most of the actual work on synthesis, neither of them would have continued with such zeal had it not been for the urging and encouragement of Friedel."

Development of Organosilicon Chemistry (1900-1940)

Although the spark of interest had been ignited in organosilicon chemistry during the latter half of the 19th century, neither organic nor inorganic chemists were able to bring to the subject any definite conclusions. Silicon does have many similarities to carbon in that its compounds react in some ways like organic compounds, and yet it affects the chemical stability of organic material with which it is combined. In many instances, it was observed that silicon compounds are more heat resistant than the analogous organic substances; but on the other hand, decomposition can occur on treatment with acids or alkalies. In any case, the 20th Century began with the chemistry of silicon and its organic derivatives in a state of confusion.

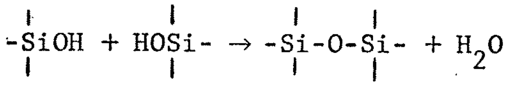
In the period 1900 to 1940 the number of investigators and their interests broadened, although there are only a few whose work can be considered outstanding. One of these, Alfred Stock, at the Kaiser Wilhelm Institute in Breslau, reported in 1912 the preparation of silane SiH_4, which he observed as an impurity in the preparation of the hydrides of boron. McGregor states that "he [Stock] tried to find information about such compounds and was plainly irritated to discover that no one had ever investigated them. There was no alternative but to get the information himself. His study was carried out with great care, and as a result we know much about these rather unstable materials." Stock observed that the longer chains of silicon hydrides were less and less stable, and he found it impossible to isolate any pure compounds higher than Si_4H_{10}. This was rather startling evidence of the fact that the chemistries of carbon and silicon are highly dissimilar, for it is well known that the higher homologues of methane are important constituents of many commercial materials, including very stable lubricating oils. In addition to his work on the silicon hydrides, Stock also prepared several compounds of silicon containing both hydrogen and halogen.

He further proceeded to replace the halogens with methyl groups and, on subsequent treatment with aqueous alkali, obtained an oily product similar to one which Ladenburg had observed many years before, $(C_2H_5)_2Si(OC_2H_5)_2$. Concerning this compound and the work of Stock, McGregor points out, "Again modern silicone preparation had been anticipated, but in such a hazy fashion that only a prophet of the first order could have been expected to see what the future had in store."

In contrast to the inquisitiveness and curiosity of these early experimenters, it should be noted in passing that a team of workers, Schlenk, Renning, and Racky, at the Royal Academy of Science in Munich, in a publication dated 1911,(3) investigated whether it was possible to prepare the triphenylsilane, $(C_6H_5)_3SiH$, which would be analogous to the free radical triphenylmethyl. They answered the question in the negative and then let the whole subject drop without ever asking the obvious question -- why? In addition, in the 1930's several Russian investigators published a number of papers, sensing that there might be some industrial value in the various types of resinous compounds that could be prepared through the use of organosilicon intermediates. Even though they were able to show that several of these compounds were remarkably heat stable, they could convince no one of their value. In view of the very encouraging results, the question arises as to why these workers were not more energetically supported.

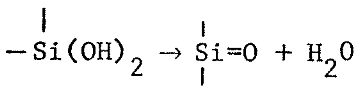
In the period 1900 to 1940, while various investigations on the chemistry of silicon and organosilicon compounds were being carried on there appeared one man who apparently resolved to unravel the properties common to both carbon and silicon. He was Professor F. S. Kipping of the University of Nottingham. McGregor gives a brief description of Kipping as follows: "In the period from 1899 to 1944 he published 54 papers on this subject. As may be surmised from his long period of intensive work, he was one in whom the British tenacity of purpose was evident to a superlative degree. He had one end in view and refused to be diverted from his target. He was confronted with problems which were difficult to resolve, and at times his products transformed themselves into unidentifiable oils and glues which, with typical British understement, he frequently described as 'uninviting'. He was uncomprisingly interested in the chemistry of compounds containing silicon, and even in his later years, when shown some of the first commercial silicones, he could scarcely bring himself to take more than a passive interest in them."

The "uninviting" oils and glues that Kipping observed and later investigated turned out to be some of the forerunners of today's silicone compounds. Kipping demonstrated that many of these products were large molecules formed by the union of a number of small molecules. He showed that the result of the bimolecular reaction



$$-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{OH} + \mathrm{HO}\overset{|}{\underset{|}{\mathrm{Si}}}- \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- + H_2O$$

is elimination of water and formation of a chemical bond uniting two silicone chains and further that the reaction



$$-\overset{|}{\mathrm{Si}}(\mathrm{OH})_2 \rightarrow \overset{|}{\underset{|}{\mathrm{Si}}}=\mathrm{O} + H_2O$$

does not occur. The last observation, showing that no two groups on the same silicon chain react with one another, is basic to organosilicon compounds; but this fact became clear only after long investigation.

The work of Kipping and others paved the way for further studies on the chemistry of organosilicon compounds. It should be noted, however, that apparently no interest or specific effort was directed toward preparing high molecular weight organosilicon materials. As we shall observe, the commercial development of silicones would at least have been severely hampered, and would perhaps have been impossible, without additional knowledge in an entirely distinct field -- that of high polymers.

Development of Polymer Chemistry and the Organic Polymer Industry

Even though a considerable amount of work had been performed in the area of organosilicon chemistry prior to 1940, very little attention had been paid to the "uninviting" oils and glues that Kipping had observed. Fortunately, however, during the long period over which the chemistry of silicon was being investigated, other chemists were studying various other oils, glues, and rubber-like materials. Pickle suggested, in 1910, that rubber was composed of eight-unit rings and termed these structures "polymers." Staudinger,who was studying natural products in Zurich in 1920, conceived the idea of macromolecules, or giant chain molecules held together by the normal covalent bonds long familiar in organic chemistry. He found that the properties of these macromolecules were not simply the summation of the properties of the individual units, but that the macromolecular architecture itself resulted in distinctive physical properties. These new macromolecules were termed "high polymers." While Staudinger was pursuing his work in Switzerland, similar studies were being carried on at the duPont Company laboratories by W. H. Carothers. Carothers, a brilliant experimentalist and penetrating thinker, was studying the principles underlying the preparation of various classes of high polymers. After thirty years, his classic work is still the basis for much of the synthetic aspect of contemporary polymer science and technology.

The work of Staudinger, Carothers and others, established the facts that macromolecular materials could be produced through reactions uniting small molecules into long chains through normal organic chemical procedures employing, generally, bifunctional instead of monofunctional species, and further that the specific important properties of such macromolecular materials as rubbers, fibers, oils, plastics, etc., depend both on the nature of the repeating chemical unit and the length of the molecular chain. These ideas led predictably and directly to the rapid profusion of a host of new synthetic organic polymers and the well known growth of the polymer industry. The period of the thirties and forties was thus an exciting revolutionary time, of rapid development , both of knowledge in polymer science and of the industry born from this new specialized branch of chemistry. Synthetic substitutes for many natural products (nylon for silk, neoprene for rubber, plastics, adhesives and glazing, etc.) with new and tailor-made properties created an era of excitement and progress which continues to our own day.

Sub-Case I: Silicone Polymers for Heat Resistant Resins (Corning Glass Works). Needless to say, the advance of polymer chemistry during the 1920's and 30's set the stage for the inevitable joining of this science with organosilicon chemistry. Glass manufacturers seeing the new organic polymers and realizing their own product to be an inorganic polymer, became interested in the possibility of a hybrid polymer, part organic and part inorganic, combining the rubber-like flexibility of one with the thermal stability of the other. The Director of Research for Corning Glass Works at Corning, N. Y., Dr. E. C Sullivan, engaged Dr. J. F. Hyde, an organic chemist, to investigate this area. In a short time, Hyde was successful in preparing high polymers containing both organic and inorganic constituents. Soon thereafter there occurred a coincidence that determined the future course of activity. McGregor describes it as follows:

> "The Corning Glass Works had just begun the development of glass fibers and was on the lookout for appropriate markets. One of the most promising outlets for this product appeared to be as a woven tape for use in electrical insulation. Cotton, impregnated with a resinous dielectric, had been used; but it would char at elevated temperature. This difficulty could be overcome by the use of glass tape in place of the cotton, but it was found that the resin impregnant would stand only slightly more heat than the cotton would. Thus there was but little advantage in using the glass. To realize the full value of the glass tape there was needed a resinous dielectric that was considerably more heat stable than the organic materials in common use.

> "Hyde was able to point out that the organosilicon compounds he had been developing could be made in resinous form and that certain types were unusually heat stable. The work then turned toward resinous compounds that would be of use as a heat-stable dielectric in tapes made of glass fiber.
>
> "...the [resulting] products were shown to officials of the General Electric Company in the hope that glass-fiber tapes would be recognized as the basis of high-temperature insulation. This approach to high-temperature electrical insulation was recognized as fundamentally correct, and the study of these organosilicon insulating resins was then taken up in the General Electric laboratories, as well, under the capable guidance of Dr. E. G. Rochow and Dr. W. I. Patnode."

Sub-Case II. High Temperature Lubricants and Dielectrics (Mellon Institute and Dow Corning). The Corning Glass Works, realizing the potential which these new organosilicon products held, undertook intensified studies in this area at its Fellowship in Mellon Institute, Pittsburgh, Pa. These studies were aimed not only at the production of insulating resins but also at a general survey of the chemistry of the materials and the engineering required for their production.

Inasmuch as the research at Mellon Institute on organosilicon compounds plays a significant role in the development of this technology, it is desirable at this point to review briefly the history of the Institute and the founding of the Corning Glass Fellowship.

Mellon Institute was founded in 1913 by Andrew W. Mellon and Richard B. Mellon. The Mellon brothers were attracted by the idea of industrially sponsored research fellowships, which had been originated by Dr. Robert Kennedy Duncan of the University of Kansas. It was in 1906, while attending the Sixth International Congress of Applied Chemistry in Rome, that Duncan had formed a conviction that the resources and methods of physical science should be applied to the problems of American industry. In the following year, Duncan succeeded in finding a sponsor for the first Industrial Fellowship at the University of Kansas. In 1911 he was persuaded by the Mellons to come to Pittsburgh and, after a successful trial of his fellowship system at the University of Pittsburgh, Mellon Institute was established under Dr. Duncan's supervision. During the ensuing half century, the Institute has been successful in fulfilling the original goals of Robert Kennedy Duncan.

In the early 1930's one of the industrially sponsored fellowships at the Institute was sponsored by the Macbeth-Evans Glass Company. The personnel consisted of Dr. R. R McGregor and Dr. E L. Warrick, whose interested centered around various glass systems, such as opal glasses, containing crystallites. Typically, the goals and research objectives of the Fellowship under the direction of Dr. H. Blau, Research Director at Macbeth-Evans, were not very specific. According to Warrick, their commission was, "Do anything that looks interesting and which seems likely significant." This general research strategy was continued on the Fellowship after the Macbeth-Evans Company was acquired by Corning Glass Works in the middle 1930's. One of the research problems then under examination was the development of an adhesive for glass blocks. The adhesive used up to that time was an organic material, but it was not satisfactory for this application. In the course of this investigation approximately 100 different organic adhesives were tried -- none successfully. Ethyl silicate was suggested as a possible adhesive by a member of another fellowship, who had been using this material in his studies. After some investigation into the properties of ethyl silicate, it was found that this compound worked rather well, having considerably better adhesion than any of the organic compounds yet tried. With respect to the approach to this particular problem, Dr. Warrick mentions that "The atmosphere at Mellon Institute was such that you could walk into any laboratory and talk freely with other members of the staff, and as a result there was a sense of freedom and a complete dissemination of information."

Even though ethyl silicate was a good adhesive for the glass blocks, it was observed that after a short exposure to the atmosphere, it tended to hydrolyze. Inasmuch as this compound did show promise, however, Warrick decided to investigate other organosilicon compounds as adhesives. Although the interest of Corning Glass Works at that time was primarily in the field of inorganic chemistry, their attitude toward the organosilicon work was very free and the personnel of the Fellowship were permitted to choose any direction for their research. As mentioned earlier, Corning was interested in the intermediate field between plastics and glass and, concurrent with the interest at Mellon Institute in ethyl silicate as an adhesive for glass blocks, Corning had hired Dr. James Hyde who, by 1933, was working on the problem of finding a high temperature resinous material for glass tape. Hyde's work was specifically directed toward investigations on the aromatic organosilicon compounds, while the work generated through the adhesive problem at Mellon Institute was directed toward the aliphatic organosilicon compounds.

A major event in the course of the investigation of the hydrolysis of ethyl silicate was the uncovering by McGregor and Warrick of extensive literature on organosilicon compounds, including especially the work of Kipping. Aided and stimulated by this well of knowledge on organosilicone chemistry and interested in producing new useful materials, they were led to prepare many organosilicon compounds and derivatives of ethyl silicate. Dr. Warrick pointed out that the direction of investigation was at all times internally generated and that Dr. McGregor, who at that time was the Head of the Fellowship, created an atmosphere conducive to good exploratory research. He was willing to talk at any time to the staff about the problems on which they were working, but he <u>never</u> told them what course this research should take. In late 1939 and early 1940, from investigations of the aliphatic silicates, it was noticed that many of the reaction products were high viscosity fluids with temperature-viscosity relations radically different from that of common hydrocarbon lubricating oil. (On heating, the viscosity did not decrease as rapidly as in the hydrocarbon lubricating oil.) In addition, it was noticed that these materials were extremely inert to attack by oxygen. Dr. McGregor, realizing the potential of these materials as oxidation resistant lubricants, mentioned them to a personal friend -- an employee of the Mine Safety Appliances Company -- at a meeting of the Pittsburgh Chemists' Club. By coincidence, Mine Safety Appliances was looking for just such a material for application in oxygen pumping systems. Some of the organosilicon materials were tried, and it was found that they served extremely well in this application. Up to this point, all the work in the area of organosilicon compounds was guided simply by observation and by the basic curiosity of the investigators. After the successful application of the oxidation resistant lubricants, Warrick felt that he ought to pursue some fundamental work on the oxidation stability of these materials.

In 1940, at the encouragement of Dr. McGregor, a pilot plant was established at Mellon Institute to manufacture small quantities of these various silicone fluids. Dr. John Speier, who joined the Fellowship in 1943, points out that Dr. McGregor was "quite a salesman" and that without this element of salesmanship many of the advances which were made during this period could not have been accomplished. It was necessary to "sell" the Corning Glass Works on the possibilities of this new avenue of research.

In the course of studies on the oxidation properties of the silicone fluids, it was noticed that many of the fluids became resinous and rubbery. Feeling that there might be something of interest in these resinous materials, McGregor and his colleagues determined to look further into their preparation and properties. In the meantime (1940-1942), Corning Glass Works had taken an increasing interest in the silicone materials. It was obvious to the company that they did not have people or facilities to explore the area properly. They subsequently made an agreement with the Dow Chemical Company to jointly pursue research in organosilicon chemistry, and in 1943 the Dow~~n~~ Corning Corporation was formed. The investigations into the resinous silicones revealed that they had excellent dielectric properties, and then an additional pilot plant was established at Mellon Institute for limited production of these materials. It is interesting to note that one of the factors leading to organization of the Dow Corning Corporation was the interest of Admiral Hyman Rickover in the silicone dielectrics for use in submarines. During World War II his recommendations enabled the company to secure money to build a complete plant to produce them. Subsequently these silicones were extensively used during World War II as electrical insulating materials in aircraft as well as in submarines. They were the first materials with a product motivation to come out of the Fellowship. Dr. Warrick points out, however, that the decision to investigate these materials was not dictated by Corning, yet the company encouraged continuation of the work whenever interesting properties were uncovered.

Sub-Case III: Silicone Elastomers (Mellon Institute and Dow Corning). While investigating the properties of various methyl silicone polymers in 1944, Dr. Warrick observed that many of them had properties similar to natural gums and rubbers, although they lacked the strength of natural rubber, Warrick again took the opportunity to discuss these rubber-like materials with personnel of another fellowship at Mellon Institute who had been working on natural rubber. They suggested trying benzoyl peroxide to attempt to vulcanize the new silicone compounds since this agent worked very well on natural rubbers. There was no reason to believe that this material would react with methyl silicone compounds as it did with rubber and, as pointed out by Dr. Warrick, the method was simply one of trial and error. But in fact, the silicone material did gain rubber-like characteristics, including considerable strength, through the benzoyl peroxide treatment. As a result of this work, a patent application for the vulcanization of liquid silicone polymers was filed by Dow Corning Corporation in 1944, and eventually issued as U.S. Patent No. 2,460,795.

It was then decided that the work of the Fellowship should be directed toward some fundamental studies of these rubber-like compounds and the chemistry involved in their formation. As an extension of this work, a new research goal was established as the preparation of organosilicon compounds with predetermined functional substituents. Dr. Warrick states, "This fundamental work on functional side groups, begun by Dr. Speier, was extremely successful. Today approximately 30 to 40 per cent of the 800 products marketed by Dow Corning Corporation are the result of these early studies."

The early silicone rubber materials were found to be rather limited in applications by their relatively low strength as compared to natural rubber. Maximum tensile strength was in the order of 500 lbs./in.^{2} and the material had the consistency of "tough cheese" rather similar to the common art gum eraser. Although Dow Corning was able to commercialize some of these rubbers, uses were severely restricted by the poor physical properties.

In the course of the studies on rubber-like materials, it came to be realized that two factors -- the molecular weight of the silicone polymer and the nature of the filler -- were extremely important to the ultimate properties of the rubber. The following is a brief account of how these observations were made.

In the winter of 1949 a significant breakthrough occurred which led ultimately to the high strength silicone rubber in use today. Dr. G. C. Akerlof of the Coal Products Fellowship at Mellon was studying methods for separating oxygen from air. He had heard that certain of the silicone resins were selectively permeable to gases. He discussed his problem with the silicones group, specifically inquiring whether any of the new resins could be made in the form of a thin membrane through which gas might diffuse. In an effort to accommodate Dr. Akerlof, it was decided to attempt to make such a membrane from a certain resin sample that had been on the laboratory shelf for some time. This material, designated as "K-gel", was then thought to be a silicone polymer composed of short chains, and highly crosslinked. A filler of finely divided silica (SiO_2) had shown some success in improving the strength of the rubbers, and this material was chosen for the experiment. Upon vulcanization under high pressure the mixture gave a rubber with remarkable properties. The thin sheet that was formed was extremely elastic and behaved more like natural rubber than any previously prepared. Mr. Silas Braley, Jr., who was a member of the silicones fellowship at the time, and who is now Director of the Dow-Corning Center for Aid to Medical Research, described the amazement at the elastic properties of the material when a piece was stretched across a beaker and he was able to poke his finger almost to the bottom without the film breaking. This was the first time silicone rubber had behaved this way, and actually the sample had a tensile strength of 1000 to 1500 lbs./in.^{2}. Though the film was not useful as a membrane for removing oxygen from air, it did serve to point out a direction for future fellowship research in the field of high strength silicone rubber.

The reasons for the exceptional strength of the membrane film were not at first obvious. It was first thought that the high pressure treatment might have been significant, but the results could not be duplicated by similar treatment of other resins. Further investigation of the "K-gel" revealed that it was not composed of short but highly cross-linked chains, as had been thought previously, but actually had a rather high molecular weight and was only slightly crosslinked. It soon became apparent through experiments with other polymers that high molecular weight was significant in preparing a successful rubber. But it was not the only factor. Before the membrane experiment, fillers such as titanium oxide and diatomaceous earth had been used in rubber preparations; but when preparation of the oxygen-removing membrane was attempted, finely divided silica (SiO_2) was used in the hope of increasing the oxygen removing efficiency. As it turned out, the silica filler affected the strength of the rubber. Upon the recognition of this fact, a considerable effort was undertaken to find appropriate fillers for high molecular weight polymers. Development of a rubber to the product stage form received great impetus from the Dow-Corning research group in Midland, Michigan, who gave all possible support to the group at Mellon and supplied them with various polymers for work on improving strength.

It was not clear in the beginning what properties of the filler were significant and therefore many materials were tried. Through empirical studies, it was learned that small particle size and large surface area were the important features to seek. Any material with small particle size was tried. Finely divided carbon, which is used as a filler in organic rubbers, could not be used because of its reactivity toward the vulcanizing agent. Ultimately, there was found a very finely divided silica (that has since come to be known as "Degussa" silica) manufactured in Germany by Deutsche Gold und Silver Scherdeanstalt.

After these initial observations by the Mellon Institute group, a considerable research and development effort was initiated at the Dow Corning research laboratories on preparation of fillers. It had been observed that on standing the mixture of filler and resin would vulcanize spontaneously. (Soon after the commercial introduction of the high strength rubber -- actually only six months after the first experiments -- many customers were receiving mixed polymer and filler for further use, and to their surprise found a solid mass, which could not be removed from the container.) It was suggested that a surface reaction was occurring with hydroxyl groups on the silica filler. An intensive research program was begun at Dow Corning to find a way to treat the surface of the filler so as to render it unreactive, or at least to slow down the reaction. Finally a method was developed to replace the hydroxyl groups of the silica with methyl groups, and this eliminated the problem of premature vulcanization. A patent application for this procedure was filed in December of 1951 by George Kunkle, Keith Polmanteer, and James McHard, the Dow Corning research men who developed the process. Since the realization that the fillers are the most significant factor in the properties of high strength rubber, the preparation and investigation of various silica fillers has been a major research effort at Dow Corning.

In 1952 work was begun at Mellon Institute in another direction -- on radiation studies of silicone rubber materials. Warrick relates the beginning of this work as follows: "Purely by chance, a professor from the University of Pittsburgh Cyclotron Laboratory came to Mellon Institute and requested various compounds for his irradiation studies. We were happy to give him several of our vulcanized and unvulcanized silicone rubbers just to see what would happen. Much to our surprise, we observed that the unvulcanized material became vulcanized. To confirm our observations, we sent several samples to Stanford Research Institute to investigate the same type of reactions. We found the same results. Because of this we began to intensify our fundamental studies into the effects of radiation on our silicone materials. As a result of this work, radiation resistant rubbers were produced."

One of the fundamental characteristics of silicone polymers and rubbers is a low glass transition temperature. This property accounts for the extremely good low temperature flexibility. However, silicone rubber <u>per se</u> does not have the high tensile strength, and good elongation and tear resistance,of organic rubbers. During the 1950's studies were conducted on the Mellon Fellowship, in cooperation with Dr. L. E. Alexander. It was found that at normal temperatures silicone rubbers are much less prone to crystallize on stretching than natural rubber. Obviously what was needed was a silicone rubber which either would crystallize more readily on stretching or contained some degree of crystallinity in the relaxed state. Subsequently, and with the aid of the Dow Corning Corporation, Dr. R L. Merker developed a series of silicone block copolymers based upon combinations of silphenylene siloxane blocks and dimethylsiloxane blocks. The resulting silicone rubber polymers have tensile strengths in the vicinity of 3000 lbs./in.^{2}

in the unvulcanized state. A patent application for this invention was filed in 1960 and resulted in U.S. Patent No. 3,202,634 in August 1965.

Other fundamental studies were also encouraged in the early 1950's. Dr. Paul Lauterbur who had previously become interested in nuclear magnetic resonance spectroscopy joined the Fellowship. He was able to convince Drs. McGregor and Warrick that Si^{29} NMR spectra had potential for studies of silicon-containing materials. They agreed that this technique might add to the knowledge of silicone technology and encouraged Dow Corning to support the purchase of the NMR equipment. Lauterbur not only studied silicon-containing compounds, but also investigated the newly developing field of C^{13} and P^{31} NMR spectroscopy. It should be pointed out that during the course of his studies Lauterbur, through the Institute policy of encouraging personnel to obtain advanced degrees at the neighboring University of Pittsburgh, was able to complete the work for his doctor of philosophy degree. (The same is true of Warrick and Speier who obtained their Ph.D.'s at Carnegie Institute of Technology and the University of Pittsburgh, respectively, while working at Mellon Institute. Warrick and Speier both mentioned several times during the course of conversations that this educational opportunity was one of the important values of the fellowship system at Mellon Institute.)

<u>Sub-Case IV. Biomedical Applications (Dow Corning)</u>. A notable offshoot from the development of high strength silicone rubber has been the interest of the medical community. Late in the 1950's, after the high strength rubber had been commercialized for some time, Dow Corning began to receive inquiries and requests from surgeons for samples of the material molded in specific shapes and forms. It had been observed in several instances that, when introduced into the human body, silicone rubber did not cause adverse reactions observed with many other materials. Specifically, in several applications, silicone

rubber did not cause the severe blood clotting that has generally been seen with foreign materials used in various prosthetic devices.

Mr. Braley, who transferred from the Mellon fellowship to the Dow-Corning product engineering group in Midland, took an interest in these applications and tried to satisfy each individual request. As experimental prosthetic devices were disseminated throughout the medical circles , publications began to appear lauding the use of silicone rubber. Soon Dow Corning was overwhelmed with requests for the material -- not for large amounts, but for very small quantities molded in specific shapes. The company decided that, even though potential sales of large volumes of silicone rubber for these applications could be not be anticipated, the prospect of practical benefits coming from the research warranted the forming of a group specifically for the study and dissemination of information relating to the use of silicone rubber in medical applications. In 1958, Dow Corning formed its Center for Aid to Medical Research under the direction of Dr. McGregor, the long-time Administrative Fellow in charge of the Mellon Fellowship. Mr. Braley, whose original interest in this work added impetus to the development of these devices, served as McGregor's assistant at the Center. Upon the death of McGregor in 1965, Braley assumed the duties of Director. The Center has continued to grow as new and important medical applications have been found. Silicone rubber has found use in artificial blood vessels, in a drain tube for hydrocephalic children, in heart valves, and in many other substitutes for parts of vital organs. Today the Center publishes a brochure which describes new uses of silicon rubber as they are developed in medical practice.

Retrospect

The names McGregor, Speier, and Warrick figure prominently in this account of the initial work leading directly to the development of organosilocons as useful commercial materials. It is therefore of interest to record some of their thoughts in retrospect concerning the nature of some of the events which produced the successful result.

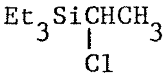
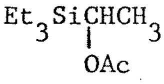
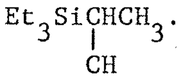
Dr. McGregor's views are recorded in many places including especially his book on "Silicones and Their Uses" published in 1954. We reproduce as Appendix B his section on the "Commercial Development of Silicones". Here we quote from the latter part (pp. 24-26) of the introductory chapter on early studies in Organosilicon Chemistry:

> "The stage was at last set for the appearance of silicones. And it is only right that we should recognize who was responsible for the setting. Long years of earnest work by scientists who were curious about natural phenomena had been rewarded by a wide knowledge of the peculiarities of silicon chemistry. Others who were curious about large molecules, how they were formed naturally and how they could be produced synthetically, had learned fundamental truths about them and had shown principles governing their formation. It was not too much to expect that these two lines of activity should be brought together, that the knowledge of silicon-containing compounds and the knowledge of the principles governing the formation of large molecules should result in the synthesis of large molecules containing silicon. What the properties of such compounds would be one could only guess, but the fact that the two necessary lines of information had been developed assured the appearance of the joint product. Now it was simply a matter of time.
>
> "But it should not be assumed that the beginning of 'applied' research marked the end of 'pure' research. Although the importance of the commercial applications of silicones had become recognized by industry the intriguing nature of their chemistry was being attested by numerous academic publications. Work that had been started as a result of scientific curiosity a century earlier was now bearing fruit that had not been foreseen. It had been assumed originally that results would show silicon to be simply an analogue of carbon. While this proved to be the case in a limited sense, the differences were much more evident than the similarities. What had been started as a search for further knowledge proved to be the groundwork for technological advance that has proved helpful to industry and in so doing has contributed its part to improving our standard of living.

"It would be a mistake to consider this the end of the story from the standpoint of either pure or applied science. While industry is naturally doing a great deal to further its knowledge of these compounds and to develop more economical methods of preparing them, the centers of pure research are doing their share to clarify points in organosilicon chemistry that are still obscure. The number of papers of this latter type appearing between the years 1945 and 1950 have been about 100 times as great as in the century preceding. Industry has recognized the fact that it has eaten up in 10 years the pure research of 100 years. Without this type of research, technology would wither. Thus we see a greater and greater overlapping of the fields of pure and applied research, the only point of distinction between the two being the motivation of the individual who does the work. And who shall say that the mental satisfaction of the one is any less real than the material satisfaction of the other?"

The recollections of Dr. Speier are of special interest:

"In 1943 I came to M.I. with a M.Sc. degree from the University of Florida where I worked on terpenes and other natural products. These I liked. They are highly reactive complex molecules that are forever rearranging and reacting with all kinds of things. The silicones struck me as, in Kipping's term, 'uninviting.' The silicones we were settling down to, all had methyl or phenyl groups attached to silicon. The intermediates all reacted with water and sooner or later ended up as polymers with nothing but methyl or phenyl groups attached to an SiOSi chain or network. These may have been and are great dielectrics, etc. but chemically they are nearly inert and they are useful chiefly for this reason. I couldn't get real excited about making hundreds more like these. Further, rubbers and fluids were never very intriguing to me for some unknowable reason. I wanted to put organically reactive groups on silicon in place of the methyls and phenyls. These I wanted to attach to the Si-C bond to come up with families of silicon-substituted organically functional molecules, which would give the opportunity to study the effect of an atom like silicon upon the chemical properties of organic functional groups.

"The trouble with this idea was that such molecules were practically unknown. Friedel and Crafts had made  $\mathrm{Et_3Si}\underset{\mathrm{Cl}}{\mathrm{C}}\mathrm{HCH_3}$,  $\mathrm{Et_3Si}\underset{\mathrm{OAc}}{\mathrm{C}}\mathrm{HCH_3}$ and  $\mathrm{Et_3Si}\underset{\mathrm{CH}}{\mathrm{C}}\mathrm{HCH_3}$. Kipping had made a few sulfonic acids having groups like , and a few nitro compounds such as $\mathrm{Si(C_6H_4NO_2)_4}$. That was about all there was, and these were not what I wanted. I wanted structures that were functional at the silicon atom, i.e., with groups like $\mathrm{-SiCl_3}$, $\mathrm{-Si(OMe)_3}$, $\mathrm{-SiMeCl_2}$, $\mathrm{SiMe_2OH}$, etc., and also functional on the organic group. I had some ideas of how these might be made in systematic series to given an idea of 'silicon' effect on organic molecules and the effect of other atoms and groups on silicon upon the effect of that silicon.

"I talked to Dr. Bernard Daubert at Pitt about how such molecules might be incorporated into fats, proteins, and other natural products (which hasn't been done yet!) and he agreed to be my faculty advisor on such a project and accept work like this for my Ph.D.

"I talked to Dr. McGregor, and in his usual manner he encouraged the whole thing and said go ahead. I talked to Warrick, he was much interested in making silicone fluids with at least a few organically functional sites in them to serve as means for vulcanization to make rubbers. Also such groups might have led to stronger rubbers which he greatly desired.

"So the three of us talked to Shailer L. Bass, who was Dow Corning's director of research (now president). He said okay; we could try if we wanted to. Daubert insisted that anything we did for a degree had to be published. Bass and the legal department at Dow Corning and at Corning agreed to this with only a few days of discussion (six months would be needed today) and we took off.

"The results of this line of research have been for the most part gratifying. Dow Corning has many patents on such compounds now. I have about 45 myself and the people working with or around me must have about as many more. There has been much unexpected fallout in every area of Dow Corning's present business. The commercial use of such functional is now a new thing. They are now appearing on the market and no one knows really where they will end up. The story may be more, or less interesting in 1975."

Today the Dow Corning Corporation is the largest company in the field of organosilicon products and holds approximately 60% of the total market. Although much of the early work in this area was performed at Mellon Institute, a good deal of the subsequent engineering and fundamental work on silicones was performed at the Dow Corning laboratories. In estimating the value of Mellon Institute to organosilicon chemistry, Dr. Warrick states, "The value of the Institute was pretty high; but, of course, the same information would have been found eventually without the Institute. However, the Fellowship certainly accelerated the science of organosilicon chemistry." When asked what at Mellon Institute contributed to the acceleration, Warrick stated, "The freedom to work on subjects of interest and the proximity and existence of people in other fields were the major contributing factors. Also, the general relaxed climate and pace of work contributed a great deal." Dr. Warrick felt that the single motivating factor for the studies at Mellon Institute was the accumulation of fundamental knowledge in the field of organosilicon chemistry. He added that the very informal channels of communication with the sponsor organization contributed to the general atmosphere of this research effort.

Concerning "the relaxed climate and pace" Dr. Speir added

> "In a way Warrick is right, if he means unregimented. We came and went pretty freely with little supervision or comment by anyone. If we took two hours for lunch, no one objected.
>
> "On the other hand, if we worked till midnight and we did many, many times -- no one said anything either. The pace of work was self-imposed but very fast. Very few of us worked a 40 hour week, and those that did usually left after a bit (by their own choice).
>
> "McGregor could usually be found working on Sundays, Saturdays, anytime at night, even if he might disappear in the middle of the morning when a good organization man would be at his greatest prominence. The same for Warrick. I was trying to work full time and get a Ph.D. as fast as I could. So during 1944-1947 I practically lived in the Institute. After I got the degree, I don't think I slowed down very much except I did quit working on Sunday.

"If there is a moral in all this I guess it has to do with the freedom we enjoyed at Mellon Institute to depart from urgent, obvious needs of a struggling young company, to attack problems that seemed important to a struggling young student. It is not possible that everyone can enjoy this kind of freedom; but somehow it is imperative that some must enjoy it. How any manager can select who should have it and who should not, and when, is a mystery to me. Fellowship 222 at M.I. was a good and profitable one. Was this an accident of history or can similar things be brought about repeatedly by careful design?"

References

(1) R. R. McGregor, "Silicones and Their Uses," McGraw-Hill Book Company, Inc., New York, 1954.

(2) M. Persoz, Ann. chim. et phys. (2), 44, 315 (1983).

(3) W. Schlenk, F. Renning, and G. Racky, Ber. 44, 1178 (1911).

APPENDIX A

Mellon Institute: Organization and Character

"Mellon Institute is an endowed nonprofit corporate body for conducting comprehensive investigations in the natural sciences, for training research workers, and for providing technical information for the benefit of the profession, the public, and industry."

The above brief descriptive paragraph appearing on Mellon Institute literature expresses the purposes motivating all activities at the Institute. Researc activities and the scientists who perform whem fall into two categories, the Fellowships and the Independent Research Groups.

A Fellowship is a group of scientists (one or more) working on fundamental or applied problems of interest to a particular sponsor, either a single firm or an association of companies , which bears all costs, including overhead charges, for the activities of its Fellowship. Although support for Fellowship activities is usually on a year-to-year contract basis, most of the Fellowships have been stable with regard to personnel and sponsor for many years. Three hundred investigators are engaged in Fellowship activities.

As compared to other research institutes, Mellon Institute is unique in several ways.

--Founded over fifty years ago as part of the University of Pittsburgh, it was the first of the institutes to undertake research aimed at the utilization of science for the development of industrial technology. During its early years, it served as a prototype for other institutes and a training ground for industrial research departments that have come to constitute much of the strength of the chemical and petroleum industries. Companies like Union Carbide and Dow Corning trace their early successes, or even origin, to work done under contract at Mellon Institute.

- --Heeding the lessons of academic experience, Mellon Institute, alone among the institutes, requires that contracts involve the effort of at least one research worker for one year, and that the individual researcher normally engages during any given period in work exclusively for a single sponsor. Indeed, in the university tradition, he is designated as a "Fellow" and his project as a "Fellowship" for a given sponsor. There is a requirement that significant results be published, when the sponsor's interests have been protected, and that projects shall have social merit.

- --Thus, Mellon Institute personnel have long been engaged in pioneering applied research based on research competence in chemistry and related areas of physics, much of it for materials producing companies and in continued close contact with their personnel. Advanced development work, better done in industrial plants or requiring more advanced engineering, has not generally been undertaken.

Mellon Institute evolved to provide a transitional stage between the scientific community in the university and the industrial-research community; it has some of the features of each and is closely allied with both.

While evolving from the University, Mellon Institute has retained informal semiautonomous positions for the "research director", the "Fellowship Head," and the "Research Fellow", who are somewhat akin to a Department Head, Professor and senior postdoctoral student, respectively, in a university. Research tends to be deeply rooted in chemical, physical, and biological science, and such that one or two problems occupy an investigator full time for a year or more. The sponsor is, in a sense, in the position of supplying "fellowship support" for progress in a new area. Further, the research fellows regard themselves as temporary, though loyal, members of the Institute, destined to go on to industry or academic posts elsewhere. Freedom of inquiry, lack of administrative detail, and informality, lend the Institute something of the atmosphere of the university instead of the stringently managed atmosphere sometimes necessary in industrial development work.

On the other hand, members of the Fellowships, unlike their university cousins, are generally highly motivated towards pioneering applied research, i.e., to using their creative talents to pioneer new technology. They are aided in this task generally by close contact with personnel from industry, including especially the sponsor but also other members of the institute, visitors from other sponsors, alumni of the Institute and members of industry locally. In addition, travel to the sponsor laboratory or plant, and to scientific and engineering meetings is encouraged. Thus the Fellow at Mellon Institute generally is exposed to a number of sources of knowledge of new science, of new technology and of some of the "open problems" or "needs" in each.

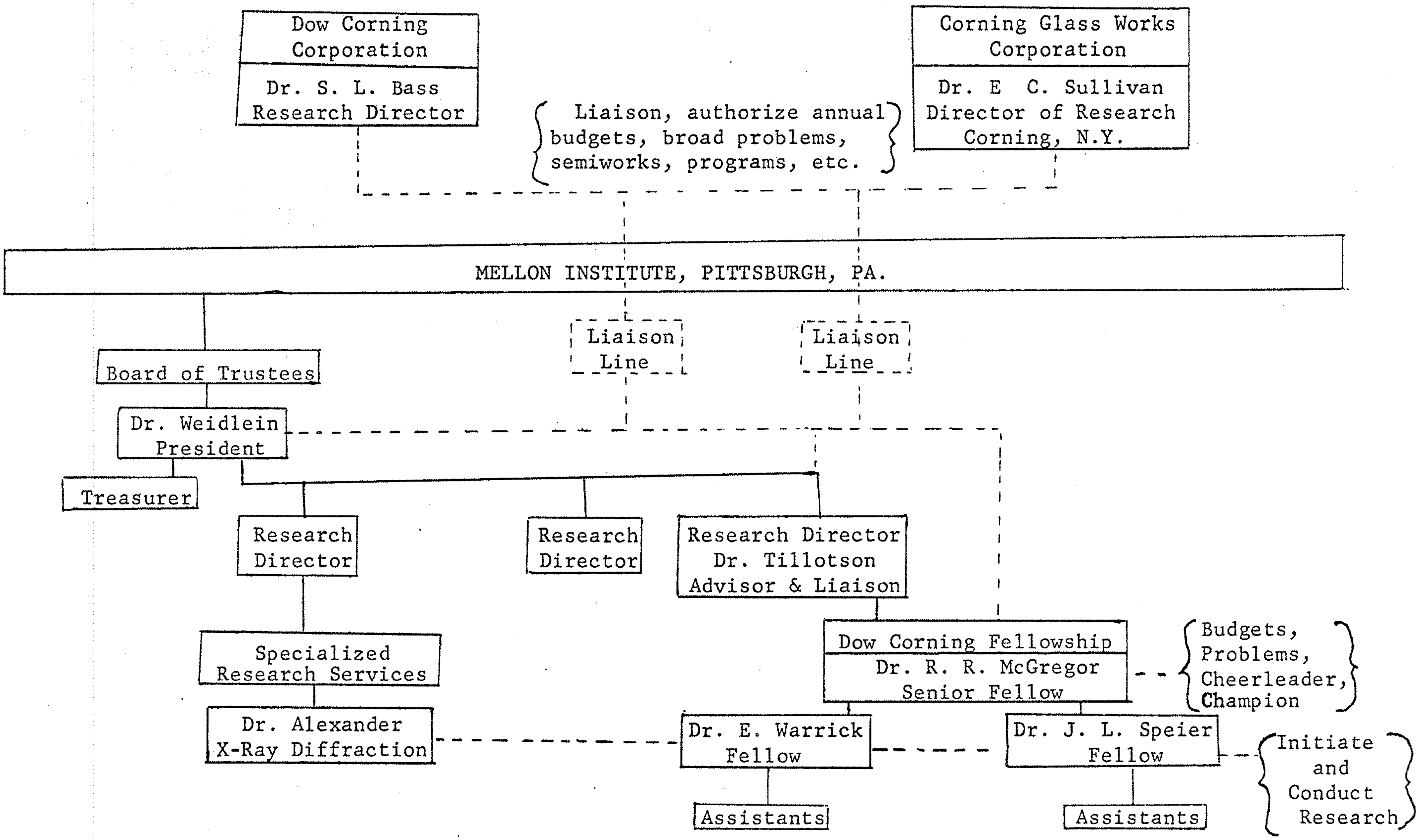
It is pertinent to mention the "alumni" of Mellon Institute. Perhaps uniquely among "mission-oriented" laboratories, the Institute regards it as a basic goal to train personnel and to encourage recruiting of its personnel by the outside world. A great number of the Institute's 3000 alumni today hold responsible positions in the industrial and academic research-oriented community.

The disciplines represented at Mellon Institute over the years include chemistry, and materials especially, together with biochemistry and certain areas of physics and mathematics.

The Independent Research within the Institute is supported by income from a Fundamental Research Trust established in 1957 and by grants and contracts from government agencies. The twin goals are new fundamental scientific knowledge and the development of promising young scientists. Publication of significant findings is mandatory. A total of nearly one hundred and fifty investigators are involved in these fundamental studies -- a permanent staff of about twenty senior fellows and about fifty Fellows on two or three year tenure appointments. Although the Institute has always supported basic science studies, the program of the present scope emerged since 1957 subsequent to most events in this case history. Consequently the Independent Research is not emphasized here.

ORGANIZATION FOR CORNING AND DOW CORRNING SUPPORTED SILICONE RESEARCH AT MELLON INSTITUTE

(As Seen from Mellon Institute Files)



APPENDIX B

"Commercial Development of Silicones," excerpt from Silicones and Their Uses, R. R. McGregor, (McGraw Hill, 1954)

"In view of the wide background of knowledge just described the question may be asked: Why was the commercial development of silicones so long delayed? The previous history provides some of the answers. The classical chemists had long been schooled in investigation methods that called for the separation, by distillation or crystallization, of pure compounds. Large, poorly definable polymeric bodies did not lend themselves to this method of approach. No doubt Kipping expressed the sentiments of many other chemists of his day when he described such products as "uninviting glues.' There was little commercial background at the time to suggest that these 'glues' had any practical significance. Further, those interested in chemical research had few, if any, connections with industry. Without the backing which industry could furnish there was great difficulty and little incentive in embarking on a study of such indefinable products.

The word 'polymer' had been in commun use for years, but it was not until Staudinger voiced his concept of 'macromolecules' in the 1920s that there was a major interest in the study of them. The recognition that these undistillable and non-crystallizable bodies were built up by known chemical reactions and could be considered simply as very large molecules opened up the enormous field of polymer research. This heralded the beginning of the 'plastic age', and high polymers of many types began to appear as commercial products. Some of these products were transparent and could be used, with more or less success, in the place of glass.

The possibility of a hybrid polymer -- a cross between the organic polymers (plastics) and the inorganic polymers (glasses) -- appealed to some glass manufacturers as a desirable possibility. Dr. E. C. Sullivan, then Director of Research for the Corning Glass Works of Corning, N.Y., engaged Dr. J. F. Hyde, an organic chemist, to investigate this matter.

Hyde was acquainted with the literature describing organosilicon research, and he had the advantage of the rapidly accumulating knowledge of large polymers. By using knowledge from both these fields he was able to prepare large polymers containing both organic and inorganic constituents.

At this point there arose one of thos coincidences that often direct a course of action. The Corning Glass Works had just begun the development of glass fibers and was on the lookout for appropriate markets. One of the most promising outlets for this product appeared to be as a woven tape for use in electrical insulation. Cotton, impregnated with a resinous dielectric, had been used but it would char at elevated temperature. This difficulty could be overcome by the use of glass tape in place of the cotton, but it was found that the resin impregnant would stand only slightly more heat than the cotton would. Thus there was but little advantage in using the glass. To realize the full value of the glass tape there was needed a resinous dielectric that was considerably more heat stable than the organic materials in common use.

Hyde was able to point out that the organosilicon polymers he had been developing could be made in resinous form and that certain types were unusually heat stable. The work then turned toward resinous compounds that would be of use as a heat-stable dielectric in tapes made of glass fiber.

Studies and experimental work were then conducted along these lines. When sufficient progress had been made to justify a demonstration, the products were shown to officials of the General Electric Company in the hope that glass-fiber tapes would be recognized as the basis of high-temperature insulation. This approach to high-temperature electrical insulation was recognized as fundamentally correct, and the study of these organosilicon insulating resins was then taken up in the General Electric laboratories as well, under the capable guidance of Dr. E. G. Rochow and Dr. W. I. Patnode. About this time the Corning Glass Works

Fellowship at Mellon Institute, Pittsburgh, under the headship of the author, undertook similar work, aimed not only at the production of insulating resins but also at a general survey of the chemistry of the materials and the engineering required for their production.

The knowledge of this work catalyzed similar investigations by other industrial laboratories, and soon the technical literature showed that ever-increasing attention was being given to organosilicon compounds.

By 1942 work had progressed with the Corning group to the point where commercial production could be considered. As the manufacture of these materials was in the nature of an organic synthesis rather than a glassmaking operation, the Corning Glass Works approached the Dow Chemical Company with a view to obtaining engineering and research assistance. The result was that in 1943 the formation of the Dow Corning Corporation, financed jointly by the Dow Chemical Company and the Corning Glass Works, was announced. The fury of World War II was then at its peak and high priority was granted to Dow Corning for the erection of a factory and procurement of equipment, as Dow Corning was the only source of several organosilicon products demanded by the military forces. While these materials were being produced in commercial quantities, research on their improvement continued and it was inevitable that new and valuable products would be found. With the close of the war it was therefore possible to offer to industry commercial quantities of a wide range of products with properties that had not been known previously.

Meanwhile other companies, though not actually producing, had been conducting vigorous research. In 1946 the General Electric Company announced the opening of its plant for the production of silicones. In 1949 the Plaskon Division of the Libbey-Owens-Ford Glass Company advertised silicone products for sale, directing attention largely to materials useful with alkyd coatings. About this time the Linde Air Products Company, a division of Union Carbide and Carbon Corporation, commenced pilot-plant work in tonawanda, N.Y. At this writing they are planning for full-scale production of a broad line of silicone products.

Although the original aim of the investigations carried out had been to develop electrical insulating resins, the first materials to be made commercially were the silicone fluids.

The limited amounts of fluids that were first available restricted their use to applications such as damping fluids in sensitive instruments used by the Air Force. The stability of the fluids and their small change of viscosity with temperature were the properties that proved the most value here. As production increased the fluids were formulated into a greaselike material that proved to be of great value as an ignition sealing compound for use in the spark-plug wells of military aircraft engines. The resins had by this time reached the point of development where it was possible to use them, in conjunction with glass-fiber tapes, as the insulating medium in motors. Cooperative work with the armed forces helped in their development and appraisal.

The usefulness of the fluids as antifoam agents in petroleum oils had been demonstrated and some military specifications demanded their addition to many types of oils.

In 1945 both the Dow Corning Corporation and the General Electric Company announced the development of a silicone rubber that was useful at temperatures too high for the functioning of organic rubber.

All these products were so necessary for military requirements that little or none of them was available for civilian use. When hostilities concluded in the summer of 1945 the military demands ceased and silicones were left without a market. But the versatility of these materials was such that energy and ingenuity soon showed how they could be adapted to a peacetime economy.

The fluids were found to be excellent mold-release agents in the molding of rubber tires and other rubber goods, as well as of many types of plastics. Polishes and lubricants were developed, and the damping fluids were adapted to peacetime requirements. The resins were improved and developed into high-temperature coatings and laminating materials. The silicone rubber was given improved physical properties and was formulated to maintain its properties at extremely low temperatures while still retaining its high-temperature stability. Application to the waterproofing of textiles was developed.

"Evidence accumulated that the silicones in one form or another could be profitably applied in almost any industry one could name. Demand for peacetime applications soon surpassed the requirements for early military use, and expansion of facilities became necessary for all producers.

"The pattern of growth is familiar, for as production has been increased prices have dropped. This allows application to a greater variety of industries and products; more production is then required and the cycle is repeated. The conclusion of the matter appears to be still far distant, and nobody short of a professional soothsayer is willing to hazard a guess as to the position of silicones in the industries of the future."

ANALYSIS FOR A CASE HISTORY OF THE DEVELOPMENT OF SILICONES

For the purpose of analysis, this case history has been divided into sub-cases as shown below.

Sub-Case	Title
I	Silicone polymers for heat resistant resins (Corning Glass Works)
II	High Temperature Lubricants and Dielectrics (Mellon Institute and Dow Corning Corporation)
III	Polysilicon Elastomers (Mellon Institute and Dow Corning Corporation)
IV	Biomedical Applications (Dow Corning Corporation)

DESCRIPTION OF REIs

Stage*	REI	Description
		Sub-case I. Silicone Polymers for Heat Resistant Resins (Corning Glass Works)
0	a	Development of silicone chemistry and polymer science
1	b	Recognition of possibility of new class of polymers with silicon as part of chains (Sullivan-Hyde)
2	c	Recognition of need for high temperature resin for dielectrics (with glass fiber) and that new silicon resins could do the job (Hyde)
3,4	d	Corning takes result to General Electric
2	e	Recognition at GE of a new class of polymers and assignment of Rochow and Patnode
		Sub-case II. High Temperature Lubricants and Dielectrics (Mellon Institute and Dow Corning)
3	f	Recognition that ethyl silicate may be useful adhesive for glass blocks (McGregor-Warrick)
1	g	Recognition of treasure of literature on organosilicon chemistry and possibility of making useful new materials (McGregor-Warrick-Kipping)
3	h	Recognition of viscosity-temperature properties and oxidation resistance of new aliphatic silicone fluid as possible high-temperature, stable lubricants for oxygen pumping systems (McGregor-Warrick)
5	i	Establishment, in 1940, of a pilot plant at Mellon Institute for the manufacture of small quantities of silicone fluids

* See Page for identification of the stages of development considered here.

0	j	Decision to look at the fundamentals of oxidation stability of silicone fluids (McGregor)
1	k	Recognition that resinous rubbery materials with good dielectric properties could be made by oxidation of silicone fluids (McGregor-Warrick-Speier)
5	l	1940 pilot plant at Mellon Institute for production of dielectric resins
6	m	Formation of Dow Corning with a Government contract for production of dielectric materials for submarines (and lubricants for aircraft)
		Sub-case III. Polysilicon Elastomers (Mellon Institute and Dow Corning)
1	n	Recognition that silicone polymers were elastomeric (McGregor-Warrick-Speier)
2	o	Vulcanization to useful rubber (Warrick)
0	p	Decision to investigate fundamentals of organosilicon chemistry with view to synthesis of polymers of varied structure (various side groups) (McGregor-Warrick-Speier)
0	q	Chance exploratory work on radiation of silicone resins showed possible vulcanization route
1	r	Decision to investigate fundamentals of radiation effects on silicone rubbers led to development of radiation resistant silicone rubbers
1	s	Chance exploratory work on vulcanized silicone resins with SiO_2 filler (as gas preferential diffusion membrane) showed extremely high strength.

2	t	Intensive studies at Mellon Institute and later at Dow Corning led to the development of superior polymer-filler combination
0	u	Recognition by Dr. Alexander, Warrick, et al., that silicones are less prone to crystallize than normal rubber, and acceptance of crystallizable structure as a goal
1,2	v	Development by Merker et al at Mellon Institute of crystallizable block copolymers which behave as high modulus crystallizable (1958-1965)

Sub-case IV. Bio-Medical Applications (Dow Corning)

1	w	Recognition by medical community that silicone rubber had unusual nonthrombogenic tendencies when implanted in the body (prosthetic devices)
2	x	Decision to form a research group for the study and dissemination of information relating to the use of silicone rubber in medical applications (1958). Center for Aid to Medical Research at Dow Corning
3	y	Tests and demonstrations by surgeons of utility in artificial blood vessels, heart valves, etc.

STAGES AT WHICH REIs OCCURRED

Stage No.*	Sub-case I	Sub-case II	Sub-case III	Sub-Case IV
0	a	j	p,q,u	
1	b,e	g,k	n,r,s,v	w
2	c		o,t,v	x
3	d	f,n		y
4				
5		i,l		
6		m		

* Stages were defined by the Committee for purposes of this study, as follows:

STAGES

No.	
0	Scientific finding (knowledge)
1	Recognition of new material (process) possibility
2	Creation of useful material (process) form
3	Feasibility of using the material (process) in hardware
4	Possibility of using the hardware containing the material in a system
5	Production of the system (product)
6	Operation of the system (product)

FREQUENCY OF FACTORS CONSIDERED IN ANALYZING EVENTS OF REIs

From the study of all the cases, the Committee selected a number of the more prominent factors which seemed to be operating with some frequency in the identified REIs and listed them as follows:

List of Factors Considered in Analyzing Events of REIs

1. High educational level (advanced degree) of principal investigator
2. Importance of management
3. Importance of Government-sponsored research
4. Importance of recognized need
5. Requirement of flexibility to change direction during work and local control of funds (easily available resources)
6. Industrial laboratory involvement
7. Basic research in the laboratory (or institution or organization)
8. Communications across organizations
9. Technical problem as the principal obstacle
10. Importance of a "champion"
11. Freedom for individuals
12. Broad spectrum of types of laboratories
13. Geographic proximity
14. Prior experience with innovation
15. Organizational structure (barriers and bonds)

FREQUENCY OF FACTORS FOR REIs

(Statistical Analysis)

	Research-Engineering Interactions																													
	Sub-case I						Sub-case II									Sub-case III										Sub-case IV				Total
Factors	a	b	c	d	e	Total	f	g	h	i	j	k	l	m	Total	n	o	p	q	r	s	t	u	v	Total	w	x	y	Total	Frequency
4		(X)	X	X	X	4/5	X		X	X		X	X	X	6/8	X	X	X		X		X	X	X	7/9	X	X	X	3/3	20/25
5	X	X	X		X	4/5	X	X	X		X	X			5/8	X	X	X	X	X	X	X	X	X	9/9	X	X		2/3	20/25
8			X	X	X	3/5			X	X		X	X	X	5/8	X	X		X		X	X	X	X	7/9	X		X	2/3	18/25
11	X	X	X		X	4/5	X	X	X		X				4/8	X	X	X	X	X	X		X		7/9	X	X		2/3	17/25
1	X	X			X	3/5		X	X		X	X			4/8	X		X		X	X		X	X	6/9	X			1/3	14/25
7	X		X		X	3/5	X	X	X		X	X			5/8	X		X		X		X	X	X	6/9				0/3	14/25
12	X			X	X	3/5	X		X				X	X	4/8	X	X		X		X	X	X	X	7/9				0/3	14/25
15	X	X	X			3/5	X		X					X	3/8		X		X		X	X	X	X	6/9		X		1/3	13/25
2		X		X	X	3/5				X	X		X	X	4/8			X		X		X		X	4/9		X		1/3	12/25
6		X	X	X	X	4/5								X	1/8			X		X		X	X	X	5/9		X	X	2/3	12/25
10	X	X	X			3/5				X	X		X	X	4/8			X				X			2/9		X	X	2/3	11/25
14	X	X	X	X	X	5/5									0/8			X		X			X	X	4/9		X		1/3	10/25
13			X	X	X	3/5	X		X					X	3/8		X		X		X				3/9				0/3	9/25
9						0/5									0/8								X	X	2/9				0/3	2/25
3						0/5								X	1/8										0/9				0/3	1/25
Stage:	0	1	2	3-4	2		3	1	3	5	0	1	5	6		1	2	0	0	1	1	2	0	1-2		1	2	3		

FREQUENCY OF FACTORS FOR REIs

		Total Frequency
4.	Importance of recognized need	20/25
5.	Requirement of flexibility to change direction during work and local control of funds (easily available resources	20/25
8	Communications across organizations	18/25
11	Freedom for individuals	17/25
1	High educational level (advanced degree) of principal investigator	14/25
7	Basic research in the laboratory (or institution or organization)	14/25
12	Broad spectrum of types of laboratories	14/25
15	Organizational structure (barriers and bonds)	13/25
2	Importance of management	12/25
6	Industrial laboratory involvement	12/25
10	Importance of a "champion"	11/25
14	Prior experience with innovation	10/25
13	Geographic proximity	9/25
9	Technical problem as the principal obstacle	2/25
3	Importance of Government-sponsored research	1/25

Summary Analysis

In the editing of this report, nearly a year after the narrative of the case history was completed, limitations of our treatment became apparent:

(1) The developments under review are generally twenty to thirty years old; and, therefore, the participants in the discussions are often unable to recall specific details which are of crucial importance in this kind of analysis.

(2) The participants at Mellon Institute were more immediately involved in stages 0, 1, and 2, and consequently these receive the greatest emphasis. Interactions influencing stages 3, 4, 5, and 6 are generally given little attention. Thus, inadequate attention is given to the contribution and interaction in the research and engineering departments at the Dow Corning Corporation.

(3) The treatment of the four subcases is very uneven, though none is treated in its entirety. For example, the treatment of subcase I is obviously inadequate. Similarly, the role of the Dow Chemical Company and the government in the formation of Dow Corning is not made explicit.

(4) Some of the happenings reported here occurred in a different era, before research in industry (generally) was highly organized; and they involved a new company with research-oriented management at a time before the development of divisional lines, etc. Thus, contact between top-level management and the research chemist was close and the many communication barriers that can exist in a larger and older organization had not appeared.

Any strength in this review lies, perhaps, in the picture it gives of the ways in which highly motivated scientists use basic scientific knowledge, observed behavior, awareness of needs, and tricks of existing technology in various adjoining fields, to find their way to novel applications. To a degree there is little that is systematic in this.

Implicit in the present case was faith on the part of the investigators and their sponsors that there were opportunities to take advantage of the growing understanding of organosilicon chemistry in making new materials with unusual combinations of properties and finding profitable new applications for them. The "formula" for success amounted to this: alert, perceptive, intellectually flexible men motivated by curiosity and the will to succeed, working in an atmosphere that exposed them, perhaps haphazardly, to ideas and needs from many directions. To a degree, this exemplifies the advance of basic science, unpredictable and unprogrammed, yet often swift. The emphasis is necessarily on the individual scientist, on his training and environment. The tremendous importance of the contribution of a few individuals is impressive. The function of communication to management, fulfilled by the champion or "salesman", is illustrated here by instances showing how well it can work when the conditions -- and the men -- are right.

The thesis that new science and new materials will lead to new, perhaps unforeseen, applications has been the guiding philosophy, more often than not, in the development of the organic polymer industry. Perhaps this was the natural result of the circumstance that the synthetic arts were more advanced than the physics of materials. Today, with more severe demands on materials and better physics to guide us, explicit definition of needs and goals becomes commonplace and taken for granted. This may represent, in part, a limitation -- a danger to innovation through hardening of attitudes as to what is and what is not feasible.