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PREFACE

The following history of UCC Silicones was written by Dr. Bernard Kanner mainly in the decade after his retirement from UCC Silicones in 1985. It is a "labor of love" by one of the few remaining people who were both an integral part of UCC Silicones for most of its history, and who knew many of the large group of earlier and later members of that organization. Bernie was an active consultant in organosilicon chemistry for UCC Silicones and its successors for many years following retirement.

Bernard Kanner received his Ph. D. in organic chemistry from Purdue University in 1953 under the guidance of Professor H. C. Brown. Following three years with Ethyl Corporation, he joined Union Carbide Corporation at the Tonawanda laboratories in 1955. His tenure has included broad involvement in exploratory and fundamental research in all areas of silicon chemistry, as well as in product and process research in silicone surfactants for urethane foam. His name appears on over one hundred technical publications and patents, primarily in the field of organosilicon chemistry. At the time of his retirement, he had attained the well-deserved rank of Corporate Research Fellow.

In addition to the many contributors acknowledged within, the particular efforts of Dianna Lawrence are greatly appreciated for the assembly of this document in its corrected and final electronic and printed forms.

A HISTORY OF UCC SILICONES

FROM 1942 TO 1957

THE FORMATIVE YEARS

July 1996   Bernard Kanner

INTRODUCTION

The history of the Union Carbide Corporation involvement in the Silicones Industry began with the first few experiments in 1942 and ended with the divestment of a more than $300 million annual sales silicones business in 1993. During the first third of that half century, the financial returns from silicones in terms of sales and profitability were virtually nonexistent. UCC's continuing commitment to silicones in the face of such meager rewards can best be viewed in the context of the times. The first couple of decades following World War II was a period of great optimism and rapid industrial expansion for the chemicals industry in the US. The rest of the world was still recovering from the effects of the war. This atmosphere has changed drastically as the chemicals industry in the West has matured and is now subject to great international competition.

This is the story of the early years of Silicones R&D (with most of the emphasis on the R or research) at the Linde Tonawanda laboratories during which it established a unique identity and before it became a significant business in terms of sales or profitability. The period of time examined is from 1938 until the mid 1950's, the latter coinciding with the point in time when silicones sales first began to expand at a remarkable rate. R&D in silicones actually made its first appearance in 1942 at the Linde laboratories in Tonawanda, NY. The Linde company, whose main business was and continues to be industrial gases (now under the name of Praxair), proved to be a highly successful incubator of new business activities for many years. The earliest effort along these lines was the attempted development of synthetic diamonds. Although these efforts ultimately proved to be unsuccessful, they led serendipitously to the high pressure process for polyethylene, which proved essential for Radar gear during World War II and contributed importantly to its later production worldwide. It was about this same time that the first efforts in organosilicon chemistry began.

The success of silicones at Union Carbide was the result of the contributions of many people in Research, Product Development, Sales, Management, Process Development, Production and other functions. However, during its formative years, R&D was clearly the first among equals in laying the technical groundwork for its future commercial success. As will also be seen, commercial success was also helped by a certain measure of good fortune. Among the many who made important contributions to the success of silicones R&D at Union Carbide, there were three who especially stand out. They are C. O. Strother, G. H. Wagner and D. L. Bailey. It is to this trio of talented and creative researchers that this history is dedicated. Their contributions to basic silicon chemistry made possible Union Carbide's dominance of the coupling agent and polyurethane foam surfactant businesses which continued until the silicones business was sold in 1993 and is easily traced to many segments of today's richly diverse silicones specialty business. All three were to receive the Schoelkopf award in recognition of their efforts. Strother and Wagner are virtually unknown to today's industrial and academic practitioners of silicones technology (outside of Union Carbide). Strother's work on high pressure polyethylene led to early promotion to other responsibilities outside of silicones

before there were any significant sales. Neil Strother retired in 1971 and died in 1983.

Dr. Wagner also left silicones by the mid 1950's, assuming other, larger responsibilities at Linde and then later as vice president of technology for the Mining and Metals and Ferroalloys Divisions of Union Carbide. Wagner also retired in 1971. Today (2001) Dr. Wagner is still quite active as an avid golfer and outdoorsman while continuing his interest in science as an adjunct professor of geology at the University of Arkansas where he has published some 26 papers since his retirement.

Of the three, only Don Bailey remained with the Silicones Division throughout his career where he served as Research Manager and Associate Director of Process R&D. His work led to more than 90 U.S. patents covering the whole range of silicones technology. Dr. Bailey retired in 1978 and continued to consult for Union Carbide for more than 10 years. Bailey was also a dedicated golfer, hunter and fisherman, prior to his death in 1996.

The origins and development of Silicones technology and business at the General Electric Corporation has been described in an excellent book by Herman Liebhafsky. More recently Earl Warrick has written of the major contributions made by the Dow-Coming Corporation, by far the world's leading manufacturer of Silicones. It is therefore timely that the role of Union Carbide Corporation, which became the third major U.S. entrant to the silicones industry some years later, be recorded.

This is by no means a complete record of the early days in silicones R&D. The written records are unfortunately incomplete. Some of the pioneers such as L.I. Dana, Murray Jellinek, Neil Strother and others, who could have helped fill in some of the blanks, are no longer with us. Additionally, I have selected from the information available those portions that I felt to be the most interesting and which had the greatest overall long-term impact. In reconstructing these events, I was helped by a great many individuals and given access to many early documents. In particular I would like to acknowledge the help of George Wagner, Don Bailey, Paul Shafer, Fred Smith, Tom Welch, Tom Hart, Ron Wishart, Vic Jex, Ron Pike, Sam Sterman, Al Cozzi and Fritz Hostettler, who consented to recorded interviews and, in some cases, also provided written recollections of their involvement at UCC. Susanne Strother gave me generous access to a variety of records and memorabilia of Neil's career at UCC. Ron Wishart sent me copies of contributions by Eric Schwarz, Milt Dunham, John Duane, Timmy Coleman and Jim Lorenz. I was given access to some early records at the UCC Vermont Record Center. Larry Jarrett and Jim Ritscher also generously made available to me early UCC silicones records. George Wagner and Don Bailey kindly reviewed this writeup and gave me their comments. My thanks to Jim Ritscher and Curt Schilling for proofreading and updating this document. Any remaining errors are my own.

A. Prelude to Silicones

Despite the economically depressed years of the 1930's, Union Carbide opened new research and development laboratories in both Niagara Falls (1935) and Tonawanda (1938). At the new Niagara Falls Electrometallurgical lab, one of the earliest projects was to develop a process for synthetic diamonds. It was started and personally funded by B. Morehead (a circumstance that would be difficult to imagine today), whose family helped found the Union Carbide Corporation. The research effort was under the direction of B. Bagley and included Dr. William (Bill) Hawes, assisted by Jack Hamilton, a gifted young engineer who designed and set up a high pressure laboratory and by Paul Shafer. After several years of discouraging progress and uncertainties, due in large part by the lack of adequate analytical capabilities, it was decided to close this effort down. The then Linde Air Products Division of Union Carbide was persuaded to continue the project at its newly opened Tonawanda lab.

At Tonawanda, Dr. Leo I. Dana was responsible for Linde Engineering and Chemical Research. Included in the Linde Tonawanda laboratory hierarchy were the Eversole brothers, Jim was Laboratory Director and Bill was a Department Head. Among Bill Eversole's most important contributions was the development of star sapphires for jewel bearings around 1941-2. Other R&D supervisors included John Gaines and Leon Jehle. R&D at Linde followed two distinctly different paths. Those projects directly supporting Linde business interests were funded out of the Linde budget. Projects seeking new ventures of broad corporate interest but unrelated to Linde's specific businesses, and usually of a more exploratory nature, were funded out of a central budget referred to as Corporate Funding or Corporate R&D. This form of support was available to all Divisions. In the late 1930's, organometallic chemistry was regarded as a promising area for Corporate Research by the Research Committee of UCC. The committee was made up of the vice presidents of research of the various divisions. Linde was given the research charter of organometallic chemistry. The committee visualized an industry centering between inorganic and organic chemistry. Thus began a series of diverse and highly successful research programs at Linde which became one of the most productive periods in Union Carbide's R&D history. In a little over a decade, its more notable successes at the Tonawanda Laboratories included synthetic gems (other than diamonds), polyethylene, silicones and molecular sieves.

A physical chemistry section at Linde was organized in late 1938 and shortly thereafter became the responsibility of Dr. Corneille O. Strother. Linde had made efforts in many directions involving many elements of the Periodic Table. Dr. Strother believed that the effort was too broadly scattered and argued for a specific focus on silicon chemistry. This may have been his most important and enduring contribution (G. H. Wagner). Strother was to carry out the first experimental work on organosilicon chemistry and was to continue as a major influence on the overall direction of Silicones at UCC until the early 1950's.

(4)

Picture Here

Neil Strother had joined Union Carbide in 1935 at the corporation's chemical plant in South Charleston, West Va. He had obtained a Ph. D. in physical chemistry under Prof. Hugh Taylor at Princeton in 1933. This was followed by post-doctoral experience in 1934 at the University of Munich and an additional year at Princeton. At South Charleston, he participated in a study of vinyl resins as their use in lacquers was in full swing at that time. Dr. Strother continued his work on vinyl resins at the Mellon Institute in Pittsburgh starting in 1937, before joining Linde in 1939.

Assigned to work with Dr. Strother in the physical chemistry section over the next several years were Paul Shafer and Jack Hamilton who came from the Niagara Falls lab, E. W. Beers, G. M Skinner, Timmy Coleman, Walt Sesny, H. R. Collins and F. F. Denville. An early objective, which was a carryover from Niagara Falls, was the synthetic diamond project.

To carry out this project, an advanced high pressure laboratory was set up in Building 11 at the Tonawanda site. This was largely the accomplishment of Jack Hamilton. Neil Strother later gave Jack Hamilton much credit for his expertise in high pressure technology in avoiding any serious engineering difficulties during the early scale up of the high pressure polyethylene process at Tonawanda.

The advanced high pressure laboratory under the direction of Dr. Strother had the capability of pumping liquids and gases continuously at pressures up to 100,000 psi and pressures up to 500,000 psi in static experiments. Professor Percy Bridgman, a Nobel Laureate for his ultra-high pressure work, stated in later years, following a personal visit to the Tonawanda labs, that some of the techniques used in the Strother facility were quite unique and new to him. The availability of this sophisticated facility was not only particularly suitable for the attempted synthesis of diamonds, it also fortuitously proved to be appropriate for a variety of other, unrelated synthesis projects.

The preparation of synthetic diamonds was sought by the thermolysis of a great many potential intermediates. Some of the more imaginative intermediates included iron carbonyls, carbon suboxide and diiodoacetylene. Experiments were carried out at 25,000 to 100,000 psi and temperatures ranging up to 350°C. The lack of suitable analytical methods greatly complicated identification of the many poorly defined products being collected. Hampered by uncertain identification, any real progress was difficult and the synthesis of diamonds remained elusive. Thus, in spite of a great deal of effort over a number of years, synthetic diamonds were never produced.

B. From "Diamonds" to Polyethylene

During the course of these unpromising experiments, Dr. Strother had become aware of reports that ICI in England had succeeded in polymerizing ethylene to form the new synthetic

polymer, polyethylene. Strother was also aware of a 1929 patent by James Conant and Percy Bridgman of Harvard covering the use of high pressure to polymerize monomers including ethylene. Neil decided to find out whether ethylene could be polymerized using the high temperature-high pressure diamond facilities. It was in December 1940 that Strother directed Ed Beers, Jack Hamilton, Paul Shafer and Fred Smith to subject ethylene to a range of high temperatures and pressures in the diamond project equipment with the occasional use of peroxide catalysis. Shown some of the resulting product by Fred Smith, Strother delightedly concluded that it was most likely polyethylene. Analysis confirmed its composition.

As polyethylene had no clear commercial usefulness at that time, it appeared to be only of modest interest. Nevertheless, Strother decided to optimize the synthesis of polyethylene. The polymerization of ethylene was examined over a broad range of temperatures and pressures to determine the optimum polymerization conditions. However, it was some time before it was realized that traces of oxygen which were inadvertently admitted to the equipment, were critical for ethylene polymerization.

Shown an early sample of polyethylene, Dr. Dana predicted in rather earthy terms that the material had no future and urged Dr. Strother to concentrate further on synthetic diamond studies. The history of major advances in many fields is, of course, strewn by such forecasts. By mid 1941, sufficient experience had been gained in making polyethylene in pound quantities to warrant a detailed examination of its more important physical properties and its commercial potential. The invention of Radar by Great Britain and the involvement of the United States in World War II would shortly provide a dramatic new opportunity for polyethylene.

The Bakelite laboratories in Bloomfield, New Jersey, represented then the major center of Union Carbide's expertise in plastics and testing. Two pounds of polyethylene were brought to the Bakelite development laboratories for a broad evaluation by a group of their polymer chemists. Bakelite had also previously acquired a sample of the ICI polyethylene. It was the middle of the summer of 1941 when Strother visited the Bakelite labs for a review of their results. The overall judgement was highly favorable. A memorandum written by Neil Strother to Jim Eversole in August of 1941, summarizing these results is reproduced on the pages that follow. The UCC polyethylene was clearly superior to the ICI product. Dr. Hanson requested an additional five pounds as soon as possible for extensive wire extrusion studies. It took Fred Smith and Paul Shafer about six months to provide the five pound sample needed for further testing by Bakelite. More comprehensive testing demonstrated Linde's polyethylene's clear superiority to the ICI product. It had better dielectric properties and a melting point that was 35°C higher. It was more flexible at low temperatures without the addition of a plasticizer. Superior heat stability, ease of handling and electrical properties also suggested broad possibilities for wire and cable insulation as well as molding and coating applications.

RESEARCH NOTES NO. 147

MEMORANDUM TO DR. J. F. EVERSOLE

SUBJECT: Examination of Polyethylene Polymer at the Bakelite Corporation,
          Bloomfield, New Jersey.

On the 28th and 29th of July the author visited the Research and Development Laboratory of the Bakelite Corporation to obtain information concerning a polyethylene resin prepared at Tonawanda. In addition to Messrs. Weith, Meharg, Hanson, Turkington, and Skow, a number of the other members of the staff expressed interest in the material. The judgment of all, based on work that could be done with the two pounds of resin supplied, was exceedingly favorable. The electrical properties were good. Also, the resin molded, extruded, and milled well.

There apparently is a definite need for such a material for extrusion upon electrical wires to be used in airplane construction. The materials employed at present do not have the requisite flexibility at the low temperatures prevailing in high altitude flight. The British have been using a combination of polythene and isobutylene for this purpose. However, the small disc of polythene shown the author had very little tensile strength. The molecular weight must have been much lower than the resin under examination.

Plastic flow measurements at 135°C and 1000 lbs. per sq. in. and l50°C and 500 lbs. per sq. in. demonstrated that the polyethylene would have molding characteristics similar to polystyrene.

Three discs were molded at 150°C and 1000 lbs. per sq. in. for electrical measurements. The data obtained follows:

Resistivity at 30°C was at least 10^{15} ohms cms.

Dielectric strength at 28°C was 430 volts per mil.

At	60 Cyc.	10^2 Cyc.	10^6 Cyc.	10^7 Cyc.
Power Factor	0.0003	0.0003	0.0004	0.0005
Dielectric Constant	2.35	2.35	2.3	2.3
Loss Factor	0.0007	0.0007	0.0009	0.001

For comparison, the characteristics of polystyrene are P.F. - 0.0002-0.0004, D.C - 2.5-2.6, L. F. - 0.0005

The polyethylene handled very well on a differential roll mill without sticking at 250°F. Two sheets were milled containing 20% polyisobutylene and 33% polyisobutylene at 300°F. All the sheets were characterized by extreme toughness. However, the higher percentage of polyisobutylene appeared to have exceeded the limits of compatability with a slight decrease in strength. The polyethylene was found to be completely incompatible with polystyrene on melting.

Several pieces were molded for water absorption, exposure and tensile strength tests. The latter test will be done at Bloomfield and the first two are being carried out in this laboratory together with a heat stability test suggested by Mr. Meharg.

Considerable interest was expressed in pressure polymerizations in general. It might prove advantageous to polymerize materials such as styrene under pressure if this would eliminate the use of catalysts. Catalytic substances seem to promote branching chains which contribute undesirable physical properties.

Dr. Hanson requested at least five pounds of the material as soon as possible for an extrusion test on wire. This request presumably is connected with defense work. The heat stability and ease of handling together with the good electrical properties make this the obvious application. Dr. Turkington and Mr. Meharg also wish to experiment with the resin in the coating and molding fields respectively.

C. O. Strother

COStrother:DFK

Tonawanda Laboratory
August 6, 1941

By the time of the outbreak of World War II, the British had demonstrated polyethylene's unique insulation properties for their vital new invention, radar. With the entry of the United States into the war in December of 1941, it assumed responsibility for the further development of Radar.

It was clear that the US would also need substantial quantities of polyethylene for the rapid deployment of radar equipment. At this time ICI decided to license their polyethylene process to E.I. Du Pont de Nemours because of their close association. In the latter part of 1941 the US Navy received samples of wire coated with UCC polyethylene. They were impressed with the excellent physical and electrical properties. Strother was quickly called upon by the Navy to set up a pilot plant at Tonawanda to be in operation by mid-1942. With Jack Hamilton playing a central role in designing the pilot plant, it began operating by July 1942, producing 100 lbs/day. To help prepare suitable coated wire and cable, extruders were supplied by Bakelite.

C. Silanes - The Beginning

Overlapping the setting up of a pilot plant for polyethylene, which was given the highest priority, was the startup of a much more modest project also under the direction of Dr. Strother; the preparation and evaluation of organosilanes. For approximately the next year, the two unrelated projects were carried forward in the same laboratory and by many of the same people.

An ongoing interest in the potential of organosilanes and silicones was widespread in the early 1940's. Although lacking any commercial process for silicone polymer intermediates and with relatively little known about silicone polymer process chemistry or properties, a number of industrial laboratories were keenly interested in exploring the potential of this new family of synthetic polymers. Within Union Carbide, Linde had already been selected as the appropriate site to initiate such a project, to be supported by corporate funding. Because of the nature of Linde's air separation and related interests, it was staffed primarily by physical and inorganic chemists. In contrast, other UCC sites were more highly skilled in organic and polymer chemistry. This point will be returned to later.

Strother initially sought the synthesis of methyl, ethyl, phenyl and benzylchlorosilanes via the Grignard process. These were hydrolyzed to form the corresponding silicone polymers and appeared to have good thermal stability. This and other properties warranted further study, but a more economical process was clearly essential.

The first such explorations involved the attempted reaction of silicon tetrachloride with methane, ethane, ethylene and acetylene at 200 to 1000°C, the reactions of methane and chlorine with silicon and the reaction of trichlorosilane with methyl bromide. Having the sophisticated high pressure, high temperature equipment that was being used to make polyethylene made it convenient to explore these processes. None of these reactions proved successful.

D. The Direct Process - General Electric

During 1941-42, General Electric's success in developing a new reaction of methyl chloride with silicon, later known as the Direct Process, had been widely rumored. It passed from the rumor stage to a virtual certainty as the result of a meeting held at the Union Carbide Metals Division in Niagara Falls. This division was a commercial supplier of silicon metal. The meeting which is described at some length in the following internal memo by H. F. Robertson, is of historic interest in several respects. In the meeting held at Union Carbide Metals Division, certain difficulties were described in reproducibly carrying out the Direct Process for reacting methyl chloride with silicon metal. The problem appeared to be related to the variable behaviour of the copper catalyst. This problem was to remain with the Silicones Industry for the next four decades by which time the role of zinc and especially of tin were finally defined.

The first UCC attempts to react methyl chloride with silicon metal in a hot tube reactor were carried out by Fred Smith, under the direction of Neil Strother in the latter part of 1942. Research on organosilanes and silicones would receive only sporadic attention during the balance of World War II. Much more urgent projects more directly related to the war effort required top priority attention. The scaleup of polyethylene production, extensive support for the development of what came to be known as Ucon fluids, the need for improved processes for synthetic gems to provide jeweled bearings for precision instruments and a variety of classified projects involving uranium refining and other activities in support of the Manhattan project permitted only occasional studies of silicon chemistry.

E.   Silanes on the Back Burner

Polyethylene production, initially at Tonawanda, received the most concentrated attention. In March 1942, with a license from ICI, Du Pont agreed to a Navy contract calling for construction of a 2,000,000 pound plant to be built at the Du Pont site in Belle, West Virginia. The Navy recognized that this would not be sufficient to meet their needs and in December 1942 entered into a similar contract with Union Carbide. So successful was this effort that soon Union Carbide was producing more polyethylene than Du Pont and ICI combined. As related in a Fortune magazine article in February 1954 ... "By spring 1943, it (Union Carbide) was producing polyethylene--months ahead of DuPont's nearby unit at Belle. So well did Carbide do its job that when Du Pont finally started producing satisfactory material, Carbide was already filling the entire demand for the critical ultrahigh frequency (radar) grade. Du Pont's production was shunted off to secondary uses in Signal Corps assault wire and Navy advanced-base underground telephone wire." Through the joint efforts of the Linde, Bakelite and South Charleston laboratories, Union Carbide had developed a high pressure process independent of ICI, enabling it to be the first to produce high-grade polyethylene suitable for radar use.

MEMORANDUM

CC: H. S. McClure   DATE: SEPTEMBER 1, 1942
     J. F. Eversole
     C. N. Smith   SUBJECT: GENERAL ELECTRIC CO.

On August 31ˢᵗ the writer attended a meeting in D. A. B. Kinsel's office at which Mr. Hurley and Mr. Soles of Pittsfield plant of the General Electric Company, Dr. Kinsel and the writer were present.

It appears that the General Electric Company are developing a new insulation material at the request of the Navy Department and they are having some difficulty in getting consistently high yields of the chemical compounds used in making this product. Mr. Hurley is a chemist who is in charge of the chemical end of the unit plant now being operated at Pittsfield and Mr. Soles is a metallurgist who is responsible for producing one of the raw materials used in the process which at the present time is a silicon-copper cinder. Mr. Hurley predicated his remarks with the statement that they would like very much to have any suggestions we could give them as to the cause of the difficulties they are having in making the compounds used in the insulation. However, he said that these compounds were very secret and that he and Mr. Soles would be unable to discuss the process or product except to say that silicon was one of the basic raw materials and that chlorine was involved in the reaction. Further conversation with him brought out the fact that hydrochloric acid, silicon tetrachloride, ferric chloride and aluminum chloride were among the by-products of the reaction. Mr. Hurley also disclosed that two primary products were formed in the reaction which were used to make the final insulation material. This immediately suggested to the writer that the products being made were dimethyl silicon dichloride and methyl silicon trichloride, as those compounds have been described in the March, 1941 Journal of the American Chemical Society by various experimenters at the Schenectady Laboratory of the General Electric Company. This reference was then obtained and showed to Mr. Hurley who agreed that as the two compounds had been mentioned in public print, there was no further need for keeping the identify of the compounds they are making from us.

The difficulty that General Electric have been having has been that the yields of the two compounds mentioned have been variable and that the reaction producing them tends to quickly reach a peak and then drop to a low value. At the present time they are using our regular grade of silicon which contains appreciable amounts of iron and aluminum and these two metals are responsible for the ferric chloride and aluminum chloride by-products. Metallic copper is alloyed with silicon to give a cinder which is the basic raw material. When copper was first used, a bottle of copper powder, which had been around the laboratory for some time and was of unknown origin, was used and this gave high yields of the desired products. After this copper had all been used, subsequent supplies of copper failed to give the uniformly good results of the first batch. This, of course, suggests that the first lot of copper contained a catalyst which promoted the reaction or subsequent batches contained a catalyst which inhibited the reaction. It is possible that the latter consideration is the most likely as once only they were able to produce

good yields of the desired compounds by using silicon alone without any copper being present. However, they have been unable to duplicate this experiment.

They have also had some difficulty in handling and disposing of large volumes of hydrochloric acid formed in the reaction. Once or twice this material has escaped and caused damage to machine tools and other pieces of equipment in the vicinity. For this reason Mr. Hurley proposed to sweep the system out with nitrogen and asked for information regarding the tendency of silicon to form nitrides with this gas. Dr. Kinsel pointed out that atmospheric nitrogen would not react with silicon at the temperature used, which is believed to be about 350°C. However, the nitrogen might react to a limited extent with hydrogen after which the ammonia so formed would react with silicon. It was suggested by Dr. Kinsel that oxygen might be one of the causes of variation in the process. It this is true, Mr. Hurley was urged to pretreat the silicon copper cinder with ammonia in order to reduce any silica on the surface of the cinder and then to flush it thoroughly before carrying out the chlorination reaction. If oxygen was not found to be the cause of the difficulty, it was suggested that they obtain some pure silicon and pure copper and proceed to add various of the impurities found in both of these metals when they are of a commercial grade. Such a procedure, of course, involves a considerable amount of experimental work, however, we were unable to suggest any simpler methods of attack.

Mr. Hurley said that the pilot plant at Pittsfield was operating on a 24 hour basis while there were at least 15 chemists working on the problem in Schenectady where the development originated. The process seems to involve passing an undisclosed source of methyl radical and chlorine over a silicon copper cinder at about 350°C and separating the various liquid products formed in the reaction in a fractionating column. If too high a temperature is used, most of the reaction goes to silicon tetrachloride while the formation of dimethyl silicon dichloride is encouraged if the temperature is reduced. The General Electric Company would like to operate the process at a temperature that would give the correct proportion of the dichloride and trichloride for subsequent hydrolysis and condensation to the final product. Mr. Hurley did not disclose any further details of the process except to confirm the fact that the process did not involve a Grignard reaction as was obvious from the method of manufacture being used. Apparently, ordinary steel equipment rather than special alloy steel is being used and it is anticipated that corrosion difficulties will present a difficult problem as a result.

H. F. Robertson

By the time it had signed the contract with the Navy, UCC had already built a full scale plant in Charleston, West Virginia. With the aid of radar equipment insulated with UCC polyethylene, the Navy decisively defeated the Japanese in the nighttime battle of the Mindanao Straits in the Phillipines. With the end of World War II, peace time uses for polyethylene grew with great rapidity. The high pressure process developed by Union Carbide became one of the principal processes for the worldwide production of polyethylene. The high pressure process remained the only significant process for polyethylene until the introduction of the low pressure process some 30 years later. For his part in directing the Linde polyethylene work, Dr. Strother received a Navy commendation and the 1951 Schoellkopf Award (Niagara Falls).

F. Silanes, Once More

As the polyethylene project moved into commercial production Dr. Strother was able to resume the study of organosilicon chemistry. The first phase of research on silicon chemistry started in March 1942 and continued intermittently until the end of World War II. As the experimental work broadened, Fred Smith was joined by Walt Schreiner and Robert Helstrom. Attempts were made to develop process alternatives to the Grignard process for which the initial results were unsuccessful. The decision had been made that the Linde laboratory would assume responsibility for developing a non-Grignard route to methylchlorosilanes (memorandum of Dr. J. F. Eversole, October 2, 1942). Within days the first work on the reaction of methyl chloride with silicon metal (generally referred to as the Direct Process) began at Linde. Over the next year the reaction of methyl chloride with silicon metal, catalyzed and uncatalyzed, was investigated over a wide range of conditions. Viewed from the perspective of 50 years later, the results were surprisingly unsuccessful.   Typical results are summarized in the following table:

EXPERIMENTS WITH CATALYSTS WHICH PROMOTE THE REACTION BETWEEN METHYL CHLORIDE AND SILICON TO GIVE METHYL SILICON TRICHLORIDE

Reference	Catalyst	Temp, °C	Methyl Cl flow in cc/min.	% $SiCl_4$ in Liquid Product	% CH_3SiCl_3 in Liquid Product	Mole per Cent Conv.	Remarks
1131-20	Cupric Oxide	600	130	60%	30%	15%	
961-33	Cuprous chloride	600	130	63%	8%	2.4%	
961-69	Tin	600	130	---	61%	17.4	No pure $SiCl_4$ separated
961-95	Tin	600	130	29%	52%	13.2%	
961-99	Tin	600	130	22%	60%	15.3%	
1131-24	Tin	600	130	31%	59%	18.0%	
1131-21	Tin	500	130	---	79%	8.1%	No pure $SiCl_4$ separated
1131-19	Tin	600	250	---	56%	6.9%	

The major products obtained were methyltrichlorosilane and silicon tetrachloride. None of the other methylchlorosilanes were observed. No significant reaction was observed at temperatures of 500°C or below.

Copper was recognized as a catalyst, as were tin and arsenic. All of the reactions were carried out in a static bed. Quite a number of other potential metal catalysts including zinc were examined but found to be inactive. The inability to produce significant quantities of dimethyldichlorosilane or to observe the reaction of methyl chloride with silicon at temperatures below 500°C is especially puzzling. Most likely it was due to catalyst failure. Certainly the necessity of activating the silicon-copper masses was unknown at that time as was the critical cocatalyst effectiveness of zinc, tin and other components. Also absent, one might guess in retrospect, was a certain flair for organometallic synthesis.

In addition to the inability to make any of the most desirable dimethyldichlorosilane, running the Direct Process at 500°C and above greatly accelerated carbon buildup resulting in early deactivation of the silicon mass. In attempts to overcome these problems, further studies concentrated on finding new catalysts or combinations of catalysts. Only modest progress was made during the balance of 1944 and 1945. It was discovered that combinations of copper and tin catalysts would yield some dimethyldichlorosilane along with the major product, methyltrichlorosilane. However, the best results only gave a mixture of 20% dimethyldichlorosilane and 60% methyltrichlorosilane at temperatures exceeding 500°C.

Thus, after the intermittent efforts from 1942 to 1945 to develop the Direct Process for the reaction of methyl chloride with silicon metal to produce various methylchlorosilanes, the project was essentially abandoned. Adequate quantities of dimethyldichlorosilane and trimethylchlorosilane could not be produced by Strother's efforts and the process would not have been commercially feasible. Moreover, the Grignard process was not viewed as a viable alternative (Dow Corning took a more optimistic view of the Grignard process based on their raw materials position). It must have been quite distressing to realize that General Electric had already succeeded in its efforts to develop and patent this same Direct Process.

G. New Directions - Discovery of Hydrosilation

Thus, less than 3 years after the startup of the silicones program, a critical decision had to be made as to the future direction of R&D and the corresponding focus of business opportunities. Should the General Electric patents on the Direct Process for methylchlorosilanes be licensed so that products based on methylsilicones could be developed and marketed? Alternatively, should other process technologies be sought and developed which would not be dominated by the GE patents, i.,e., either a new process for methylchlorosilanes or a process leading to other alkylchlorosilanes? Or, perhaps a combination of both strategies could be pursued. These questions were not completely resolved for more than 5 years.

With the limited effort available to explore silane process chemistry at that time, pursuing both strategies was impractical. All along there had been experimental probes to develop new processes for the formation of silicon-carbon bonds. Most of this work had been unproductive. Finally, in the latter part of 1945, major success was realized with the discovery of the hydrosilation reaction. With this discovery, the production of higher alkylchlorosilanes become quite feasible. The decision was made to push ahead with this new process technology which was outside of GE's or anyone else's patents. This also had the further practical effect of focusing on new products which would not be based on dimethylsilicones. It would also lead not only to vinylsilanes, which were also accessible from the Direct Process, but also, in time, to a broad, new class of silicon compounds: the organofunctional silanes.

H. A Decision is Made - Strother Memo of 1945

The internal debate going on at this time, on hydrosilation versus the Direct Process, is disclosed in a memorandum written by Strother and coworkers at the end of 1945. In it is summarized their understanding of the then state of the silicon patent art and the known scope of the field of silicones. Because of its influence on the direction of the silicones R&D at Union Carbide in the years that followed, pertinent portions of it are reproduced here:

SILOXANES

Object:

The purpose of this memorandum is to indicate the scope of the field of organo-silicon chemistry, to evaluate the active patent art in this field, and to summarize our present research position.

Summary:

Organo-silicon chemistry appears to be potentially a field as broad as that of carbon chemistry.

The active patent art covers only a small sector of the potential field. There seems to be enough old literature to prevent any one company from monopolizing organo-silicon chemistry, even the small section on silicone resins and oils which is receiving so much publicity today.

The Laboratory has developed several interesting reactions which are believed to give us an entrée into the field.

Current Program:

   Work at this Laboratory has developed a reaction for preparing the organo-silicon halides. The method is believed to be more flexible than the General Electric reaction between hydrocarbon halides and silicon since the latter reaction requires an organic radical which is stable at high temperatures.

   Our process may be represented in the steps shown below:

1. HCl + Si $\rightarrow$ SiHCl$_3$; SiH$_2$Cl$_2$; etc. A copper catalyst is used in the reaction.

2.   (a)   SiHCl$_3$ + olefins   ----$\rightarrow$ RSiCl$_3$

     (b)   SiH$_2$Cl$_2$ + olefins   ----$\rightarrow$ R$_2$SiCl$_2$

The first step, including use of a copper catalyst, was discovered by Combes (Compt. Rend. 127, 531 (1896) and 148, 555 (1909)) and is therefore not broadly patentable. Our second step is carried out at 200-250°C and is facilitated by application of pressures of the magnitude employed in producing polyethylene. This second step is not shown in the prior art although duPont in US Patent 2,379,821 issued July 3,1945 claims the reaction between aliphatic hydrocarbons and inorganic silicon halides having at least one halogen atom of atomic weight above twenty at temperatures of at least 450°C. Aromatic hydrocarbons are disclosed in the specification of this patent. The temperature qualification is a part of all the granted claims which therefore do not read on our process. It might be pointed out that the duPont patent is concerned with the reaction of any hydrocarbon with a halogen on a silicon atom while our step 2 is concerned with the reaction of any unsaturated organic compound with a hydrogen on a silicon atom.

   It is anticipated that this reaction may be applicable to any compound containing a double bond. Should this be the case, a general method would be available for introducing various organic groups into the siloxanes. To illustrate, a siloxanyl radical on a ketone or cyanide group might produce a plasticizer with flame resistant properties.

   In addition to the siloxanes, the reactions of silicon hydrides with carbon double bonds may permit the formation of multiple silicon-carbon chains or the substitution of silicon

for carbon in any organic compounds. For example, the reaction of silicon hydrides with butadiene may give a five member ring containing silicon or, with acetylene, may give vinyl silicon hydrides capable of extensive reaction. Furthermore it is possible that the addition of a hydride to a double bond may not be confined to the silicon hydrides. In this case organic

compounds containing sodium, boron, phosphous, arsenic and the like could be prepared from their respective hydrides, NaH, B_2H_6, PH_3, or AsH_3, etc. In manfacturing these, the raw materials would be avialable within the Corporation since the hydrides for the most part are made from products of the electric furnace. It is contemplated not only that such products will necessarily find markets for themselves but also that they will serve as intermediates in chemical industry.

Conclusion:

    Only a small percentage of the possible derivatives of the siloxanes have been prepared and only a few of these are patented. While the validity of certain of these patents appears to be questionable, it should be understood that the suggestions herein on anticipation by prior art are of a tentative nature for consideration and final decision by the Patent Department. It is recommended that their opinion on this matter be sought.

    The work in this Laboratory has established a background in a field of considerable breadth. The work has already led to reactions of importance.

    The experience of several years has bred a comprehension of the extent of the industrial possibilities of organo-silicon compounds as well as other related organometallic compounds. It is felt that the business outlook will justify the utilization in additional research of the knowledge and viewpoint now acquired.

C. O. Strother

G. H. Wagner

C. W. McConnell

C. O. Strother
G. H. Wagner
C. W. McConnell:MN

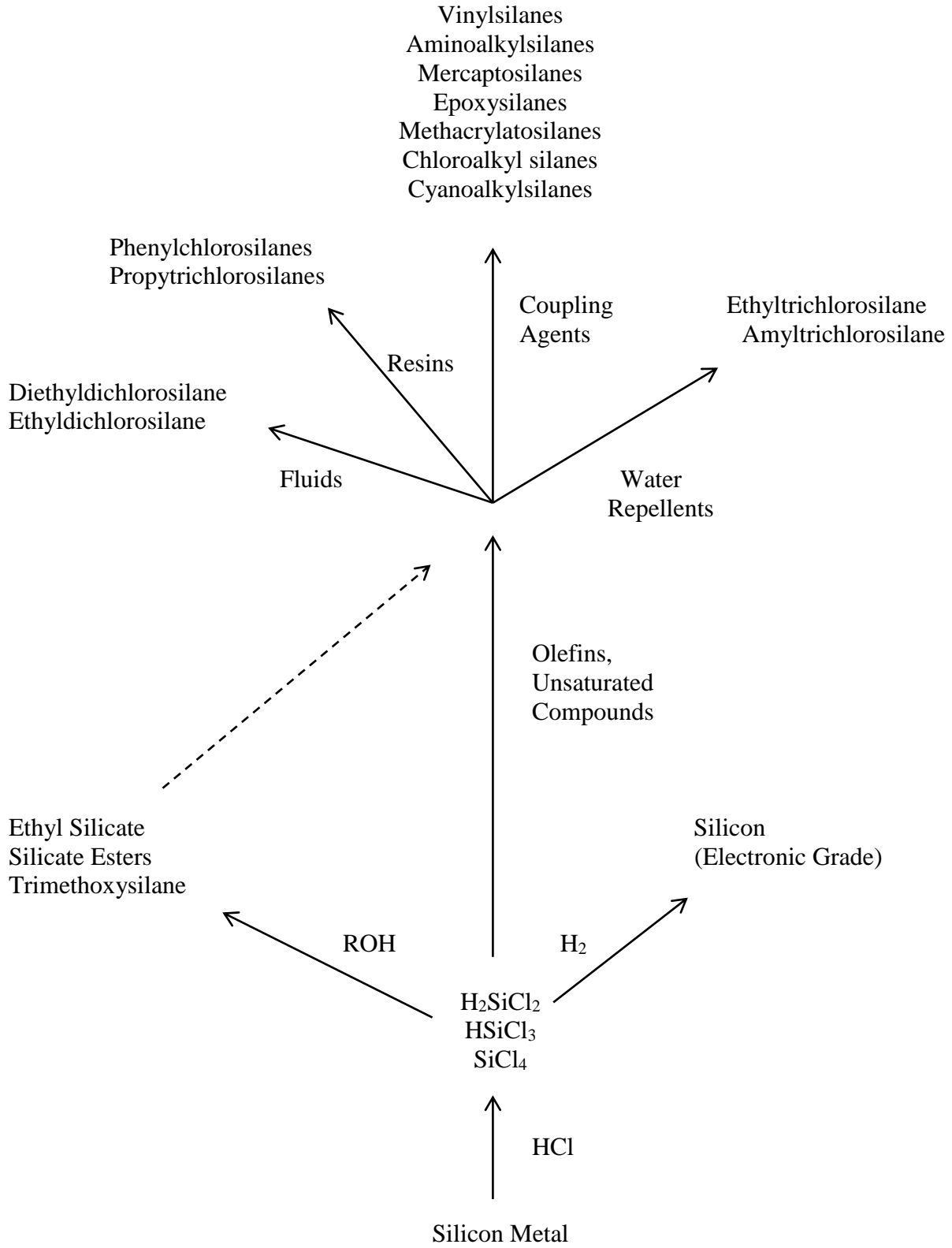Tonawanda Laboratory
December 24, 1945

The memo indicates that higher alkylsiloxanes, such as ethyl and propylsiloxanes which can be readily prepared by the hydrosilation process were not covered by any known patents. This was also apparently true for most of the higher aromatic siloxane polymers. Of more than passing interest is the prescient observation that siloxanes containing reactive functional moieties such as carboxyl, amino, thio, keto, etc., which were at that time unmentioned in the patent art, "may prove to be of great value." This early interest in the potential of organofunctional groups as modifiers for silicon compounds is further illustrated by the observation, "a siloxanyl radical on a ketone or cyanide group might produce a plasticizer with flame retardant properties". One of the more interesting speculations is on the possible analogous reactivity of other hydrides with double bonds such as NaH and B_2H_6. The latter speculation precedes the actual discovery of hydroboration by some 6 years.

This decision had two important consequences, one negative and the other positive, which are more apparent in retrospect than they were at the time. The UCC entrance into silicones, especially polydimethylsilicones, had already lagged that of Dow Corning and General Electric by at least 4 years. By concentrating almost exclusively on higher alkylsilicones for approximately an additional 5 years (1945 to 1950), the lead time of their competitors was further increased. This substantial lag time later proved to be a major hurdle to UCC's efforts to gain significant market shares in the rapidly growing silicones fluids and elastomer markets during the 1950's and the decades that followed.

The plus side of the decision turned out to be an early emphasis on hydrosilation for the formation of silicon-carbon bonds. In this area of process technology and the products that were derived therefrom, they led the way -- in contrast to the Direct Process. Some years later, Strother, who by then had left silicones for higher administrative responsibilities within the Linde organization, summarized in a flow chart how the concentration on hydrosilation by the early R&D effort in silicones influenced the new products that could be made. Most of the chart illustrates the later use of trichlorosilane as an intermediate for all sorts of silanes and for the production of transistor grade silicon. Also shown is the reaction of HCl with silicon to yield dichlorosilane which was converted to higher dialkyldichlorosilanes leading to the corresponding silicone polymers upon hydrolysis. This pioneering focus on hydrosilation chemistry led UCC to introduce organofunctional silanes and silicone-polyether copolymers (surfactants for polyurethane foam), in the 1950's. These are market areas which UCC Silicones and its successor continue to dominate world-wide some forty years after their introduction.

I.   Wagner Joins Silicones

Just prior to this same time, another important event took place -- Dr. George H. Wagner joined Neil Strother's silicones R&D group which was now beginning to expand. George Wagner had joined UCC in 1941 after graduating from the University of Iowa with a Ph.D. in physical chemistry. Shortly after joining Linde he was assigned to the automotive group

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Vinylsilanes
Aminoalkylsilanes
Mercaptosilanes
Epoxysilanes
Methacrylatosilanes
Chloroalkyl silanes
Cyanoalkylsilanes

Phenylchlorosilanes
Propytrichlorosilanes

Coupling
Agents

Ethyltrichlorosilane
Amyltrichlorosilane

Resins

Diethyldichlorosilane
Ethyldichlorosilane

Fluids

Water
Repellents

Olefins,
Unsaturated
Compounds

Ethyl Silicate
Silicate Esters
Trimethoxysilane

Silicon
(Electronic Grade)

ROH

H_2

H_2SiCl_2
$HSiCl_3$
$SiCl_4$

HCl

Silicon Metal

where he developed synthetic lubricants based on polypropylene oxide, polyethylene oxide and mixed oxide polymers.   An important early discovery by Dr. Wagner was a group of aromatic amine antioxidants allowing these fluids to be used at high temperatures. Substantial quantities of these fluids were used as synthetic lubricants in fighter planes in the Pacific campaign against the Japanese.

Although trained as a physical chemist, George had a flair and sympathy for synthetic inorganic and organic chemistry not common among physical chemists. George had minored in organic chemistry and later was president of the Organic Chemistry Club of Western New York. George was equally attracted to organic and physical chemistry. The deciding factor in his choice to major in physical chemistry was his ability in math (comment from GHW).   The gulf between physical and organic chemists is real - they might fairly be described (With a bow to Winston Churchill) as two classes of scientists separated by a common technology. The chemist who makes an easy transition between synthesis (particularly, organic) and many aspects of physical chemistry is not often found. It is fairly common for chemists to hire new chemists having similar backgrounds, i..e., organic vs. physical chemists and especially vs. chemical engineers. In keeping with its business interests, the Linde technical organization had concentrated largely in physical and inorganic chemists. Over time, as the running of the silicones R&D group gradually shifted over the next number of years from Strother to Wagner and subsequently to Don Bailey, the dominant background disciplines of the chemists joining silicones R&D changed from physical to inorganic and organic chemistry, especially with synthesis skills. These skills were to play a dominant role in UCC's leadership in coupling agents and silicone surfactants for many years.

J.   Hydrosilation Takes Off

Among the early synthetic probes for the formation of silicon-carbon bonds were the high temperature reactions of aromatics with trichlorosilane to form arylchlorosilanes and the tin catalyzed reaction of vinyl chloride with silicon forming various vinylchlorosilanes. All of this effort had become secondary with the discovery of the thermal, uncatalyzed reaction of olefins with trichlorosilane and dichlorosilane:

$$\text{(a) } HSiCl_3 + \text{Olefin} \quad \rightarrow \quad RSiCl_3$$

$$\text{(b) } H_2SiCl_2 + \text{Olefin} \quad \rightarrow \quad R_2SiCl_2$$

In the latter part of 1945 and early 1946, excellent yields were realized for these reactions when carried out at 200-250°C and moderate pressures. (Strother and Wagner, Serial No. 702,084, filed 10/09/1946). Successful reactions were carried out with ethylene, propylene, cyclohexene, butadiene, vinyltrichlorosilane, vinyl chloride, and other olefins. Reactions with acetylene and propyne-1 yielded the corresponding vinylsilanes. A general process had thus

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Picture Here

been developed for di- and trifunctional higher alkylchiorosilanes which allowed UCC to operate outside of the Direct Process patents of GE.

It was at this point (early 1946) that a major advance in the practice of hydrosilation was made with the discovery of a metal catalyst. Following a suggestion of Neil Strother, George Wagner discovered that metallic platinum was a very general and efficient catalyst for the hydrosilation of olefins and acetylenes by hydridosilicon compounds (Wagner, U.S. Patent 2,637,738, 5/05/1953):

$$HSiCl_3 + RCH=CH_2 \rightarrow RCH_2CH_2SiC1_3$$

$$H_2SiCl_2 + 2\ RCH=CH_2 \rightarrow (RCH_2CH_2)_2SiCl_2$$
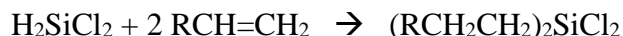
The preferred form of the catalyst was platinum supported on finely divided charcoal. The active catalyst was made from chloroplatinic acid dissolved in an aqueous slurry of charcoal which was then reduced to metallic platinum with hydrogen at atmospheric pressure. The catalyst formed in this way could be used at the level of just a few parts per million of reactants. With this highly efficient catalyst in hand, attention was directed to exploring the broad scope of the hydrosilation p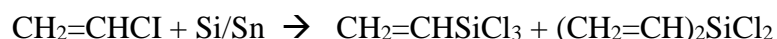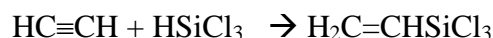rocess itself. It was almost 10 years later that Speier demonstrated that chloroplatinic acid itself was a highly efficient hydrosilation catalyst and that prior reduction to metallic platinum catalyst was unnecessary. John Speier went on to publish a series of excellent papers describing the main features of the hydrosilation process.

With an alternative process technology now in place that was commercially feasible, basic exploration of the methyl chloride silicon reaction was put on hold. UCC now could proceed to develop new families of products based on higher dialkylsiloxanes such as diethylsilicones. The technical focus was now concentrated on the reactions of HCl with silicon to produce di- and trichlorosilanes, the reactions of benzene and other aromatics to produce arylchlorosilanes and the hydrosilation of olefins to produce ethyl and higher alkylchlorosilanes.

Thus, within a year after the end of World War II, exploration was begun of the commercial potential of many new silicone products based on the newly developed hydrosilation process technology. Higher alkyltrichlorosilanes were natural intermediates for a broad class of silicone resins which now began to be examined in earnest. Diethyldichlorosilane was of particular interest for the precursor for linear silicone fluids and elastomers. Staffing was expanded accordingly with the formation of sales and development groups to complement the more fundamental R&D effort.

Along with the development of products based on alkylchlorosilanes, an interest was clearly developing in the synthesis of chlorosilanes having much more reactive organic

groups, especially olefins. Thus, particular attention was paid to the synthesis of vinylchlorosilanes. This was accomplished both via hydrosilation of acetylene and the Direct Reaction of vinyl chloride with silicon:

$$HC{\equiv}CH + HSiCl_3 \rightarrow H_2C{=}CHSiCl_3$$

$$CH_2{=}CHCI + Si/Sn \rightarrow CH_2{=}CHSiCl_3 + (CH_2{=}CH)_2SiCl_2$$

The chemical reactivity of the vinylsilanes became the focus for these new compounds. Copolymers with simple olefins such as ethylene, propylene and styrene as well as functional olefins including vinyl acetate, vinyl chloride and vinylidene chloride were all prepared. Organic reactivity of a sort that was unavailable with simple hydrocarbon modified siloxanes was a new and intriguing wrinkle. Just what directions these new reactive silanes might lead to in terms of new product opportunities was not clear in 1946 other than free radical copolymerization. A much more specific opportunity was to arise just a few years later.

The hydrosilation processes just described start with the reaction of HCI with silicon metal. The main products obtained are trichlorosilane, dichlorosilane and silicon tetrachloride:

$$HCl + Si \rightarrow HSiC1_3 + H_2SiCl_2 + SiCl_4$$
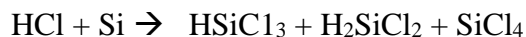
In addition to their roles as intermediates in hydrosilation processes, di- and trichlorosilanes also proved to be of considerable commercial importance for the production of high purity silicon for the electronics industry. Silicon tetrachloride led to the family of alkyl silicates and to the early production of high surface area silica. This subject will be returned to later.

A brief mention should be made at this point of an early interest in silicon metal at Linde. In 1946, Bill Eversole, working for Dr. McCandless, had explored the thermal conversion of silane to silicon metal. Among Dr. Wagner's earliest experiments was the thermal decomposition of trichlorosilane to silicon using a Vycor tube. Unfortunately, this introduced undesirable boron as an impurity. This work was to be pursued again in the 1950's and 60's with the growing interest in transistor grade silicon.

The attempted development of a family of silicone fluids based on diethylsiloxane units was the subject of considerable effort and attention for at least the next decade. This was in spite of the fact that the signing of an agreement with GE to license their Direct Process for methylchlorosilanes finally took place in 1950.

Unfortunately, in spite of intense and creative R&D efforts to solve the problems inherent in the preparation and development of commercial products based on diethylsilicones, this proved to be a dead end. This effort was not finally abandoned until the late 1950's when Dr. Leon Jehle, the then v.p. of R&D, formally ordained that the project be brought to a close. The differences in physical and chemical properties between dimethylsilicones and diethylsilicones were unexpectedly much larger than might be anticipated from the seemingly modest difference in hydrocarbon groups. Some of these differences are worth noting as they emphasize the uniqueness of the dimethylsilicone family of polymers.

During the 1940's it was known that dimethysiloxane based polymers were incompatible with organic polymers. They were also much more oxidatively stable and exhibited highly surface active properties. It was not surprising that compatibility with organic polymers increased noticeably for diethylsiloxane polymers. However, it might not be anticipated that diethylsilicones and dimethylsilicones would be mutually insoluble. It was probably expected that diethylsilicones would be less oxidatively stable. What was unexpected was that the oxidative stability of diethylsilicones was much more comparable to organic polymers rather than occupying some intermediate position. This also proved to be true for methylethylsilicones. These unanticipated properties could not be fully appreciated until processes for the polymerization of diethylsiloxanes were worked out. In this respect diethylsiloxanes also proved to be quite different from their dimethyl analogs. Dimethylsiloxane polymers are prepared by an acid or base catalyzed random scrambling of siloxane bonds known as equilibration:

$$MM + xD_4 \rightarrow MD_{4X}M$$
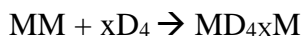
Endblocking and difunctional methylsiloxanes are randomly scrambled by strong acid or base equilibration until, at thermodynamic equilibrium, a mixture of linear and cyclic siloxanes are present. For methylsiloxanes there are about 85% linear polymers and 15% cyclics at equilibrium. For diethylsiloxanes the results are entirely different. One can not obtain linear diethylsiloxane polymers by the process of equilibration because for these polymers the thermodynamic equilibrium at atmospheric pressure favors cyclics entirely:

$$MM + XD'_4 \leftarrow MD'_{4x}M$$

Thus if a linear diethylsiloxane polymer is treated with strong acid or base under equilibrating conditions, only the diethylsiloxane cyclics would be present at equilibrium. To produce linear diethylsiloxanes it was necessary to develop other, kinetically controlled processes. This was accomplished by the base-catalyzed ring opening of diethylsiloxane cyclic trimer and by the hydrolysis and condensation of diethyldichlorosilane. Also, under high pressure and temperature, diethylsiloxane cyclic tetramer could be converted to linear polymers:

$$MM \ + \ x[(C_2H_5)_2SiO]_4 \ \rightarrow \ M[C_2H_5)_2SiO]_{4X}M$$

Oxidative stability remained a problem, however. Many antioxidant types were tried but the excellent oxidative stability of dimethylsiloxane polymers could not be matched. As oxidative stability was then believed to be the single most important property of silicone polymers, its lack in diethylsiloxanes was deemed a fatal flaw which would limit widespread utility. With the Direct Process license from GE for the production of methylchlorosilanes, diethylsilicone polymers were finally abandoned in the late 1950's.

From the perspective of the 1950's this was probably the right decision. Viewed some forty years later, it is quite possible to arrive at a different decision. While excellent oxidative stability is undoubtedly a key property of siloxane polymers, it is quite possible that diethylsiloxane polymers could have been useful for a variety of applications because of their own distinctive properties and reasonably attractive process economics. The process for ethylchlorosilanes has an important advantage over the methyls process:

$$HCl + Si \ \rightarrow \ HSiCl_3 + H_2SiCl_2 + SiCl_4$$

The main product of this reaction is trichlorosilane. However, trichlorosilane is readily converted to dichlorosilane by base catalyzed disproportionation:

$$2 \ HSiC1 \rightarrow \ H_2SiCl_2 + SiCl_4$$
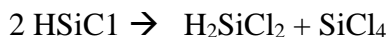
The combination of these two reactions results in the production of dichlorosilane and silicon tetrachloride. The former is then hydrosilated with ethylene to obtain diethyldichlorosilane. The silicon tetrachloride by-product can be esterified with ethanol to produce the commercially useful ethyl silicates. However, a more interesting process discovered by Wagner and coworkers is the conversion of silicon tetrachloride to trichlorosilane by reaction with silicon metal and hydrogen at elevated temperatures:

$$3 \ SiCl_4 + 2 \ H_2 + Si \ \leftrightarrow \ 4 \ HSiCl_3$$
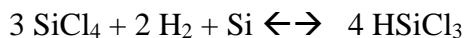
The process is reversible and essentially free of side reactions. At 500°C the product composition includes about 16% trichlorosilane. Through the combination of these reactions, the loop is closed and one should be able to obtain in excess of 90% dichlorosilane from this process which is comparable to the 90 to 95% of dimethyldichlorosilane obtained from the Direct Process. The real advantage is that diethyldichlorosilane can be purified by much simpler distillation than the expensive 100-plus plate distillation columns required for the purification of dimethyldichlorosilane.

The potential applications for ethylsiloxane polymers remain more speculative at this

point. Although lacking the oxidative stability of dimethylsiloxanes, the diethyl polymers would still be highly surface active, sharing such properties as release, antifoam, polish, water repellency, gas permeability, cosmetics. etc., etc. Possibly improved properties could include paintability, better organic compatibility and improved detergency and emulsification for surfactants based on diethylsiloxanes. With the ever increasing importance of environmental considerations, enhanced biodegradability could be another factor favoring diethylsiloxanes. These polymers would revert back to cyclics more readily under appropriate basic or acidic conditions. Oxidative breakdown to inert by-products would also occur much more readily with these polymers. At present the commercial potential for these polymers remains unexplored territory.

Along with the work on linear fluids and elastomers based on higher alkylsiloxanes, there was also carried out at the same time extensive work on resins of all types. These were based on ethyl-, amyl-, phenyl- and phenylmethylsiloxane units, none of which were derived from the Direct Process. These resins were prepared for water- proofing, electrical varnishes, high temperature paints, wire and coating enamels and other, generally high temperature, end uses. In spite of much attention over a long period of time, these all proved to have limited commercial success for UCC up until at least the 1960's.

During the late 1940's and early 1950's the R&D staff, as well as other functions, continued to expand in spite of the modest sales of commercial products. By early 1952, Silicones R&D had been underway for a decade. Sales were probably at a level of less than $200,000 annually. During the period of 1948 to 1953, Tom Welch, Sam Sterman, Tom Hart, M. H. Jellinek, R.Y. Mixer, E.O. Brimm, Tony Pater, O. K. Clarke, Dexter Huntington, R. S. Abrams, Ron Wishart, Art Pines, R. F. Kayser, Milt Dunham, Charlie Rehm, T.J. Coleman, Fran O'Connor, Vic Jex, the Pike brothers, Ron and Roscoe, Lloyd Scheafer, Dave Braun and a number of other chemists and chemical engineers joined the Silicones organization, bringing with them highly diverse training and backgrounds.

K.   Don Bailey Joins Silicones

Also entering the Linde silicones organization was Donald L. Bailey who joined Dr. Wagner's group in 1948 after receiving a Ph. D. from Penn State. There he had carried out the synthesis of vinylsilanes under the direction of Professor Frank Whitmore.

Although the commercial development work focussed on products derived from higher alkylsilanes and silicones, especially ethyl, amyl and phenylsilicon compounds (available mainly from the hydrosilation process), within Dr. Wagner's research group, emphasis continued on new chemistry. With the addition of Don Bailey, followed by Vic Jex and the Pike brothers a bit later, work began to branch out into new areas of chemistry with important long term consequences. Wagner gave his research members considerable latitude to pursue novel areas of

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Picture Here

research unrelated to their main projects as long as the latter received appropriate attention.

In the late 1940's and in the 1950's as well, there was an article of faith which guided much of the work. The mantra was "Thou Shalt Be Oxidatively Stable". New silanes were sought that would have excellent oxidative stability, especially for resins but virtually for all other purposes as well. This was illustrated by the discovery that benzene would react with trichlorosilane at high temperatures when catalyzed by boron trichloride to form a mixture of phenylchlorosilanes. It was found that phenylsilicones were even more oxidatively stable than methylsilicones. Thus the synthesis of silanes that were not oxidatively stable was not universally welcomed. Bailey's initial activities involved redistribution and disproportionation reactions of phenyl, allyl and triethoxysilanes (to produce silane). His interest in synthesis chemistry led him to the exploration of reactive organosilanes. This began with the already available vinylsilanes. Don initially examined the peroxide-catalyzed polymerization of vinyltriethoxysilane. Low molecular weight polymers were formed but did not appear to merit further interest. At this time, Bailey's interest shifted to the synthesis of other organofunctional silanes. Oxidative stability was put aside in favor of silanes and silicones capable of undergoing a number of organic reactions. Don began this work with the synthesis of amino functional silanes. These were prepared by the reaction of chloropropyl- and chlorobutylsilanes with ammonia. This subject will be resumed shortly.

L. Discovery of Vinylsilanes as Sizing Agents

Commercial developments outside of Linde 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 examined as spacers for self-sealing gasoline tanks and as non-shattering structural components. These laminates, based on unsaturated polyesters, approximated the flexural strength of equivalent weights of structural steel and were stronger and lighter than equivalent thicknesses of structural aluminum alloys.

The critical shortcoming of these laminates, which effectively prevented their commercial use, was the considerable loss in strength that they exhibited on exposure to water vapor or liquid water. The loss in strength typically amounted to about 60% whether one used either desized glass or starch-oil sized glass which was all that was available at the time. Some improvement was noted when a new sizing agent, chromium methacrylate chloride, was used. The initial flexural strength was slightly improved and the loss on humid aging was decreased to around 40%. This loss in physical strength was still unacceptably high to allow the use of these laminates in aircraft. The Air Force then (around late 1949 or early 1950) granted a contract to the Bjorksten Research Laboratories of Madison, Wisconsin to develop a superior sizing agent

if possible. Success was achieved shortly thereafter.

The breakthrough results achieved by the Bjorksten Labs were reported in a paper presented at the Spring Meeting of the Reinforced Plastics Division of the SPI at Chicago in late February and 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 reduced the loss on humid aging to 0 to 10%. The resulting laminates were now stronger after humid aging than dry chromium methylacrylate 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 for further review.

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 identical results using an undisclosed chemical via aqueous solution which was later identified as vinyltriethoxysilane. This was clearly superior to the use of vinyltrichlorosilane as it avoided HCl formation. The Owens-Corning fiberglass people present at the meeting then indicated that they also had a promising laboratory process. Plant trials were expected very shortly that 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 the 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 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 was believed that all three treatment processes were based on samples of Linde vinylchlorosilane intermediates. The decision was quickly made by Linde Silicones to enter this promising field. Based on laboratory work carried out by Murray Jellinek, aided by Dave Braun and Sarah Camiolo, new vinylsilane ester products were offered to the market place 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 silanol groups 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 polyester. 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 applicability of silane sizing agents.

To begin this work, George asked Vic Jex, a recent addition to the Research group to synthesize a silane containing an amine functionality. Perhaps fortuitously, Vic, as part of his

graduate studies, had explored the base-catalyzed cyanoethylation of sugar molecules. A base catalyzed cyanoethylation, rather than conventional platinum-catalyzed hydrosilation was the critical step in synthesizing the first amino organofunctional silane, subsequently known as A-1100:

$$HSiCl_3 + CH_2=CHCN \rightarrow Cl_3SiCH_2CH_2CN$$

$$Cl_3SiCH_2CH_2CN + 3\ EtOH \rightarrow\ (EtO)_3SiCH_2CH_2CN$$

$$(EtO)_3SiCH_2CH_2CN + 2\ H_2 \rightarrow\ (EtO)_3Si\ (CH_2)_3NH_2$$
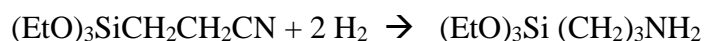
A-1100

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 gamma-aminopropyltriethoxsilane sample (A-1100) that had been prepared by Vic Jex. Subsequent tests at Owens-Coming proved the effectiveness of A-1100 as a sizing agent for epoxy resins. With the rapid industrial acceptance of Linde Silicones vinylsilane and aminoalkylsilane coupling agents in the early and middle 1950's, Linde became the leading supplier of silane coupling agents (later called organofunctional silanes), a position that UCC and its successors have maintained until the present time.

For his "----pioneering contributions to the technology of organosilicon monomers and polymers and of polyalkylene oxide lubricants" 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 was to leave silicones to assume greater responsibilities for Linde and, subsequently, for other Divisions within UCC.

At about the time of the discovery of vinylsilanes as sizing agents, Don Bailey began to explore other potential uses for these compounds. He had been aware of prior reports in the literature describing the introduction of vinyl groups into silicone elastomers where they functioned as crosslinking sites. These results were unsatisfactory as the degree of crosslinking was excessive. At about this same time, Professor Herman Mark of the Brooklyn Polytechnic Institute gave a talk in Buffalo on polymer cure and crosslinking. In it he made the observation that optimum polymer cure would result when the crosslink density approximated one per 25,000 molecular weight. Guided by this information, Bailey prepared silica filled dimethylsilicone gum stocks having the appropriate crosslinker content in the form of vinyl-

methylsilicone units. Upon crosslinking with di-tertiary butyl peroxide, he was able to obtain cured elastomers with good properties. There was sufficient interest to file a patent. However, until the problem of compression set was solved, there was no interest in developing any new products based on vinyl cured elastomers.

M. Formation of an Independent Silicones Division

By the middle of 1953, sales of resins, fluids, coupling agents, etc., continued to grow and were approaching $ 500,000, annually (Total Silicones Industry sales, mainly in the US, was perhaps in the range of $ 10,000,000). Linde management then announced the first of several steps which were to lead to an independent status for Linde Silicones. Mr. T. J. Coleman, who had been in charge of silicone engineering and small scale production, became General Manager, Silicones Department, with Mr. H.T. Ross from sales as the Assistant General Manager. The decision had previously been made to proceed with a full-scale production plant to be located at Long Reach, West Virginia. Construction of the Long Reach plant began in 1954 with the first production of chlorosilanes starting in late 1955 and the production of polymers in early 1956.

In 1956, Silicones achieved independence, becoming a separate division of Union Carbide. Silicones continued to occupy Linde laboratory facilities at Tonawanda until 1966,when a new Silicones R&D facility was completed at Tarrytown, N.Y.

The major commitments in manpower and capital investment made by UCC in a business activity that had been underway for more than 10 years and still only amounted to a few hundred thousand dollars annually, evidenced an optimism and entrepreneurial spirit that was probably not unusual for large chemical corporations in the 1950's but is no longer evident today.

N. Silicone-Polyether Copolymers - Surfactants for Polyurethane Foam

By 1953, Bailey's research interests had shifted to a project directed to preparation of silicone fibers. The initial approach was to try to introduce chain-stiffening groups into the siloxane backbone. The synthesis routes employed presented considerable difficulties and progress was discouragingly slow. Bailey then considered incorporating polyether blocks as possible chain-stiffening groups. While attempting to introduce dipropylene glycol units into the silicone chain, the observation was made that Si-O-C and Si-O-Si bonds reacted equivalently under base catalyzed equilibration conditions. This led to a convenient synthesis of alkoxy-endblocked silicones. The alkoxy-endblocked silicones were reacted with a series of hydroxyl-terminated polyethers (Ucons), which were Union Carbide products. These included polymers made from ethylene oxide and propylene oxide as well as mixtures of the two oxides.

These first known copolymers of silicones with polyethers had both linear and branched

structures:

$$EtSi(OEt)_3 + x\ (Me_2SiO)_4\ \rightarrow\ EtSi[(OSiMe_2)_y(OEt)]_3$$

$$EtSi[(OSiMe_2)_y(OEt)]_3 + 3\ R(OCH_2CH_2)_A(OC_3H_6O)_BOH$$

$$\rightarrow\ EtSi[(OSiMe_2)_yO(C_2H_4O)_A(C_3H_6O)_BR]_3 + 3\ EtOH$$
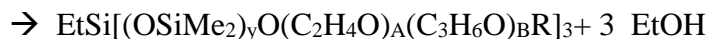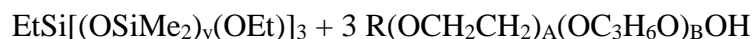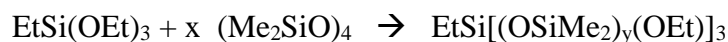
These and many other structural and compositional variations were synthesized by Bailey and F. M. O'Connor (See for example, U.S. Patent 2,834,748, issued May 13, 1958 and U. S. Patent 2,917,480, issued December 15, 1959). These new copolymers proved to be of no interest as silicone fibers, but the latter objective was quickly shelved when it appeared that these novel copolymers would have many other interesting possibilities.

Tom Welch, who came to Linde with a strong 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 and textile lubricants. The metal-on-metal lubricating properties of these copolymers were markedly improved over pure polydimethylsiloxanes.

These intriguing early results led to a period of intense examination of the potential utility of silicone-polyether block copolymers 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 the copolymers prepared via the transesterification process was their hydrolytic instability. The SiOC bonds would, when exposed to water, gradually hydrolyze, especially in the presence of acids or bases, to form separate dimethylsilicone and polyether layers.

To overcome this problem, hydrolytically stable copolymers were prepared via the platinum-catalyzed hydrosilation of polydimethylsiloxane polymers containing methylhydrogensiloxane units with allyl-endblocked 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.

O. Polyurethane Foam Undergoes a Major Technological Change

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-521 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 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 1956, 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 scaleup 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. Thus, by the latter part of the 1950's, the technical framework for the new Silicones

Division was largely completed. The use of vinyl- and aminoalkylsilane coupling agents for glass and other mineral substrates for reinforced plastics had been established, providing a major impetus for that industry. The discovery of L-520 along with the tin and amine catalysts made possible the modern form of the now enormous polyurethane foam industry. Sales of all silicone products were to reach $1,000,000 by the end of 1955. In 1956, an independent Silicones Division was formed in UCC. By the end of the 1950's, the sales of silicone surfactants for polyurethane foam and silane coupling agents were to dwarf all other UCC silicone products.

Silane coupling agents, silicone surfactants for polyurethane foam and functional fluids remained the cornerstones of the UCC Silicones Division until the business was sold in 1993. UCC Silicones had also been a major supplier of trichlorosilane to the transistor grade silicon industry during much of this same time. However, efforts by UCC Silicones to become a major factor in silicone elastomers, resin and conventional fluids were much less successful. All of these now conventional business segments were largely abandoned over time in favor of specialty products.

The question naturally arises as to why an organization which was able to develop and maintain leading positions in several specialty areas of silicones business for forty years, could not establish itself as a major player in the more fundamental segments of the industry, namely elastomer and fluids. The initial delay in entering these business segments (after Dow Corning and General Electric), further added to because of the early focus on hydrosilation, was probably the main contributing factor. Nevertheless, this same focus allowed UCC Silicones to become a very successful business while making its own unique contributions to the reinforced plastics, foamed polyurethanes, and other industries.

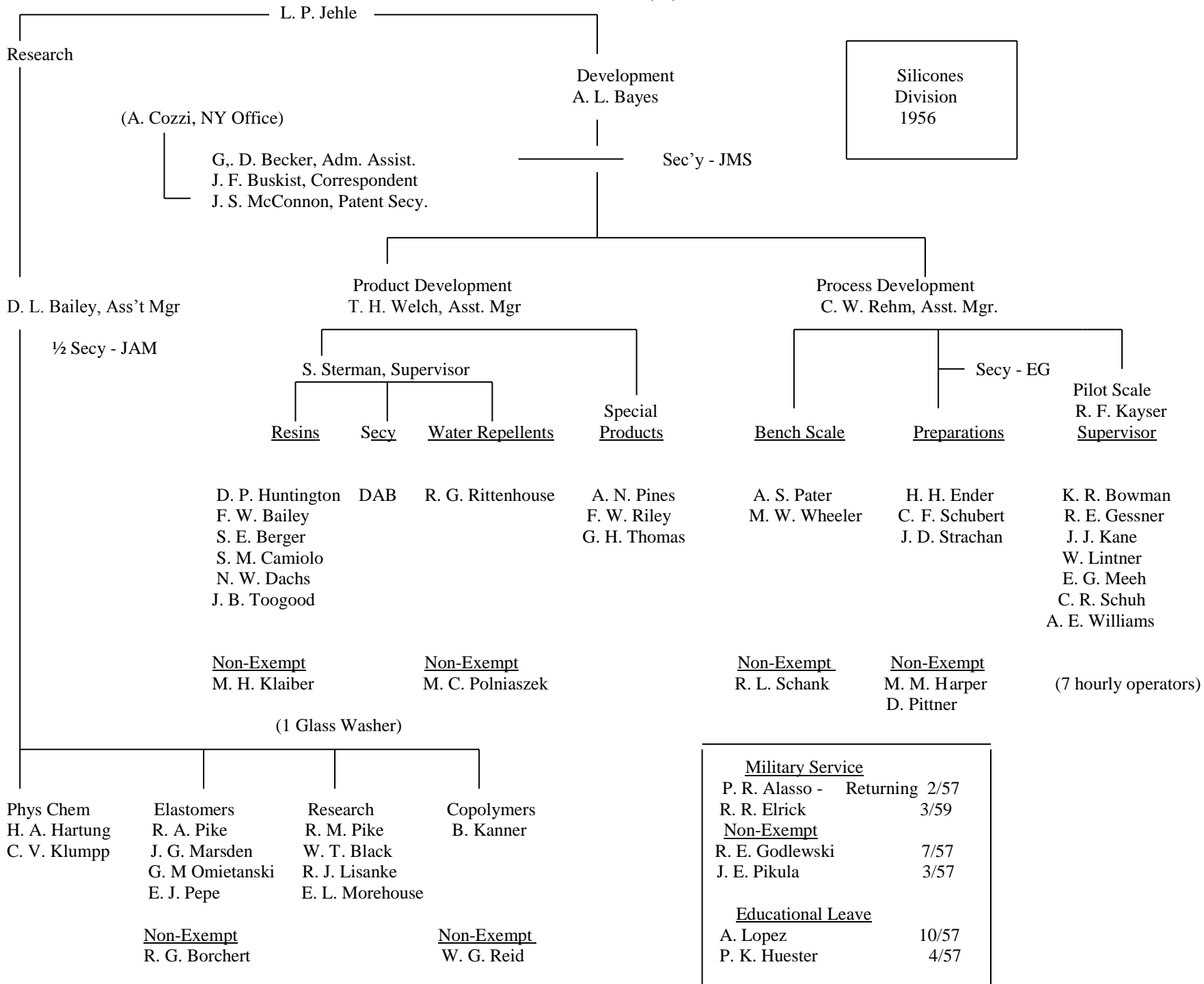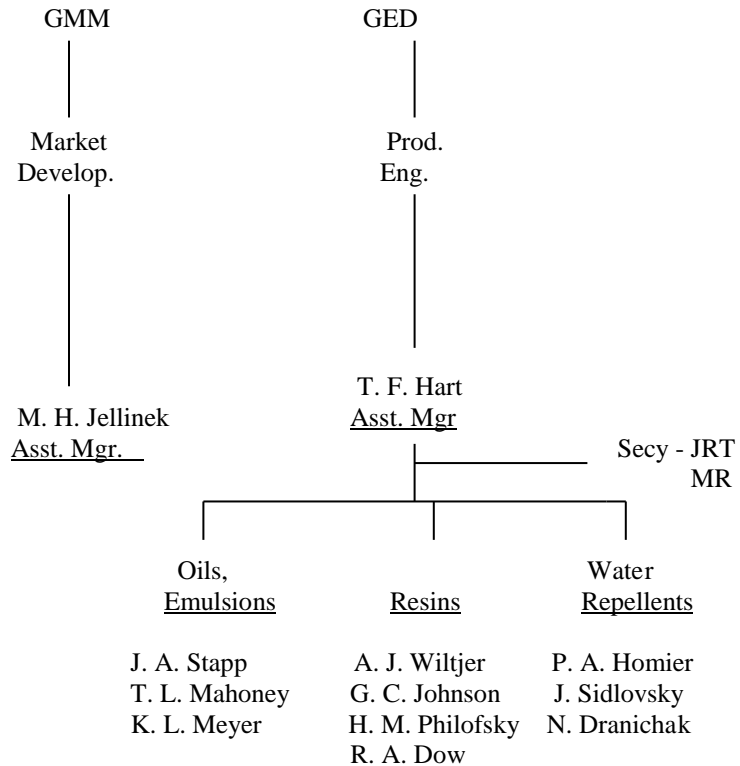A History of Silicones at Union Carbide Corporation - Part II

1957-1985

The Period of Dynamic Growth and World-Wide Expansion

The mid-1950's were a period of extraordinary change from virtually every major viewpoint for the Silicones organization at Union Carbide. It became a separate business entity, independent from Linde, with its own autonomous management structure. A major production facility was put into operation at Sistersville, West Virginia, which developed the capability of manufacturing essentially the entire known spectrum of silicon-based products. A combination of R&D pioneering discoveries and newly emerging commercial developments had placed UCC Silicones in the forefront of two novel product areas, coupling agents for reinforced plastics and surfactants for polyurethane foam. A mutually beneficial or symbiotic relationship was to develop which would fuel the rapid growth of the reinforced plastics and polyurethane foam industries while UCC Silicones was to remain their leading supplier of critical intermediates for the next several decades.

Large numbers of new personnel were added to all functions of the Silicones organization from 1955 to mid-1960's. In addition to Research and Development, such activities as Process Development, Market Development, Sales; and at the plant, Production, Production Engineering, Operations, Maintenance, Control Lab and a host of others were now formally organized and staffed. Many changes were to take place in the Silicones organization in the very dynamic period of 1956 to 1966. This was not unusual for the first decade of a newly formed Division which was feeling its way to complete independence, dealing with rapid growth and attempting to find the right slot for a number of talented personnel. A very early Organizational Chart is shown for the Silicones Division in 1956. It is quite comprehensive for an organization whose sales were extremely modest and was yet to earn its first dollar of profit! It is followed by a table of organization from the early 1960's showing the makeup, focus and relationship of Research, which, with the departure of George Wagner, was now headed by Don Bailey, and Product Development, as led by Tom Welch. It is the activities of this part of the Silicones Division which will continue to be the focal point of this history.

The growth and development of UCC Silicones from 1957 to 1985 falls more or less naturally into two distinctive periods. The first is the period of 1957 to 1965 during which the Silicones Division operated with considerable autonomy, while sharing R&D facilities with Linde. The second is the interval from 1966 to 1985 when the Silicones Division was merged with UCC Chemicals and Plastics as part of an overall plan by which UCC sought to manage its various businesses more closely. It is during this time that Silicones R&D left the Linde Tonawanda Labs and moved to Tarrytown, New York.

L. P. Jehle

Research

Development
A. L. Bayes

Silicones
Division
1956

(A. Cozzi, NY Office)

G,. D. Becker, Adm. Assist.
J. F. Buskist, Correspondent
J. S. McConnon, Patent Secy.

Sec'y - JMS

Product Development
T. H. Welch, Asst. Mgr

Process Development
C. W. Rehm, Asst. Mgr.

D. L. Bailey, Ass't Mgr

½ Secy - JAM

S. Sterman, Supervisor

Secy - EG

Pilot Scale
R. F. Kayser
Supervisor

<u>Resins</u>	<u>Secy</u>	<u>Water Repellents</u>	<u>Special Products</u>	<u>Bench Scale</u>	<u>Preparations</u>	
D. P. Huntington	DAB	R. G. Rittenhouse	A. N. Pines	A. S. Pater	H. H. Ender	K. R. Bowman
F. W. Bailey			F. W. Riley	M. W. Wheeler	C. F. Schubert	R. E. Gessner
S. E. Berger			G. H. Thomas		J. D. Strachan	J. J. Kane
S. M. Camiolo						W. Lintner
N. W. Dachs						E. G. Meeh
J. B. Toogood						C. R. Schuh
						A. E. Williams

<u>Non-Exempt</u>
M. H. Klaiber

<u>Non-Exempt</u>
M. C. Polniaszek

<u>Non-Exempt</u>
R. L. Schank

<u>Non-Exempt</u>
M. M. Harper
D. Pittner

(7 hourly operators)

(1 Glass Washer)

Phys Chem
H. A. Hartung
C. V. Klumpp

Elastomers
R. A. Pike
J. G. Marsden
G. M Omietanski
E. J. Pepe

Research
R. M. Pike
W. T. Black
R. J. Lisanke
E. L. Morehouse

Copolymers
B. Kanner

<u>Non-Exempt</u>
R. G. Borchert

<u>Non-Exempt</u>
W. G. Reid

<u>Military Service</u>	
P. R. Alasso -	Returning 2/57
R. R. Elrick	3/59
<u>Non-Exempt</u>	
R. E. Godlewski	7/57
J. E. Pikula	3/57
<u>Educational Leave</u>	
A. Lopez	10/57
P. K. Huester	4/57

GMM — Market Develop.

GED — Prod. Eng.

LJS — Elastomers

RSA — Semi-Works

M. H. Jellinek
Asst. Mgr.

T. F. Hart
Asst. Mgr

Secy - JRT
MR

Secy HA

J. P. Hamilton
Manager

Secy - JT

Oils, Emulsions
J. A. Stapp
T. L. Mahoney
K. L. Meyer

Resins
A. J. Wiltjer
G. C. Johnson
H. M. Philofsky
R. A. Dow

Water Repellents
P. A. Homier
J. Sidlovsky
N. Dranichak

Development
M. L. Dunham
C. L. Bitner
D. B. Braun
F. Fekete
W. W. Foster
J. E. Rogers
F. A. Smith
T. C. Williams

Non-Exempt
R. W. Idziur
E. E. Koslosky
H. D. Marshall

Product Engineering
J. H. Lorenz
C. F. Tripp
E. C. Schwarz

Non-Exempt
E. L. Tytka

Process Dev.& Production
R. L. Creighton
G. W. Crockwell
W. D. Eisinger
R. E. Fishlock
R. C. Maier
A. E. Schwass

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Silicones
Division
1956
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Production Engineering
O. K. Clark
K. E. Baker
D. G. Driscoll
C. E. Simpson

Non-Exempt
T. L. Gilbert

Operations
G. E. Joyce
W. J. Lee
W. A. Potocki
S. F. Michalski

(35 Hourly
Operators
2 Hourly
Yard Men)

Maintenance
S. E. Aronson
R. S. Dobein
M. H. Galliedorfer

Non-Exempt
R. O. Alonso
H. R. Fiedler
M. C. Senn
F. F. Hezen

Control Lab
R. P. Boersma

Non-Exempt
B. H.. Bazemore
J. T. Kresse
C. N. Nehrbass
J. Taranovich
S. J. Takach
N. W. Wiencek

Safety
M. J. Woodard

D. L. BAILEY

MANAGER
RESEARCH

SILICONES DIVISION

TONAWANDA LABORATORIES

FEBRUARY 15, 1964

T. C. Williams

RESEARCH SUPERVISOR
ELASTOMERS, RESINS,
SILOXANE CHEMISTRY

B. Kanner

RESEARCH SUPERVISOR
FLUIDS, MONOMERS
COPOLYMERS

G. M. Omietanski

V. G. Badding
R. L. Schank
R. L. Ostrozynski
J. D. Strachan

E. W. Bennett

J. R. Joy
E. J. Pepe
I. H. Petersen
W. G. Reid
M. L. Wheeler, Jr.

TECHNICIANS

R. C. Borchert
E. C. Lee

TECHNICIANS

E. A. Gasiecki
D. R. Kole
J. A. Lentz
R. J. Wasielewski

T. H. WELCH MANAGER PRODUCT DEVELOPMENT	SILICONES DIVISION TONAWANDA LABORATORIES FEBRUARY 15, 1964

G. J. Ciancio
ADMIN. ASST.

D. B. Braun SUPERVISOR RUBBER	D. P. Huntington SUPERVISOR FLUIDS	A. S. Pater SUPERVISOR EXPLORATORY DEVELOPMENT	S. Sterman SUPERVISOR RESINS & MONOMERS

DEVELOPMENT

O. K. Clark
C. E. Creamer
R. A. Kulakowski
W. W. Foster
W. D. Eisinger

DEVELOPMENT

E. G. Schwarz
L. Marlin
D. J. Waythomas
G. W. Douglas
E. L. Morehouse

CLASSIFED PROJECTS

F. A. Smith

M. H. Klaiber

DEVELOPMENT

G. C. Johnson
S. E. Berger
W. H. Martin
J. G. Marsden
S. L. Maher
A. N. Pines
H. H. Ender
J. E. Pikula

TECHNICAL SERVICE

G. W. Crockwell
A. G. Cavicchioli
P. R. McVicker

TECHNICAL SERVICE

R. R. Elrick
P. K. Huester
H. C. Tracy
K. E. Baker
K. L. Meyer
A. J. Sabia

TECHNICAL SERVICE

J. B. Toogood
J. C. Lang
L. P. Ziemianski

TECHNICIANS

R. E. Godlewski
G. E. Joyce
H. D. Marshall
D. Pittner
E. L. Tytka

TECHNICIANS

W. J. Fenlon
F. S. Gengo
D. L. C. Lee
W. J. McKenna
J. J. Walsh
J. Watkinson

SECRETARIES

Mrs. J. G. Besser
Miss D. J. Buchanan
Miss T. I. Bunting
Mrs. M. J. Butler
Mrs. A. E. Slerzenga
Miss J. M. Stains

TECHNICIAN

M. J. O'Hara

TECHNICIANS

R. J. Bethin
R. H. Bloom
J. P. Hawks
R. L. LaFleur
J. J. Macielag
M. C. Polniaszek
R. E. Porter

UCC Silicones was to change from a producer concentrating largely on the U.S. market to becoming a world-wide organization. In 1984, the Bhopal disaster took place in India with a great loss of life. UCC Management was under a great deal of stress and pressure to which was added the attempted takeover by GAF. This resulted in the sale of several Divisions including Agricultural Chemicals, Consumer Products and other assets. It was also at about this time that Silicones was no longer viewed as a core business for UCC. Joint ventures were sought with several other corporations the next several years and when they did not materialize, the Silicones business was eventually sold in 1993.

I. UCC Silicones During 1957 to 1965

This interval represented the beginning of very rapid sales growth both for UCC Silicones and for the entire Silicones Industry. By 1965, UCC Silicones sales had reached $ 25 million or approximately one sixth of total world production. The industry had been started in the US by General Electric and Dow Corning and was still largely an American industry. Dow Corning sales in 1965 were estimated at $ 65 million while GE sales were believed to be equal to UCC. Great Britain, Japan, France and Germany were believed to have roughly equivalent sales of about $ 10 million each.

Within UCC Silicones, the R&D organization experienced major changes both at the Tonawanda and Sistersville laboratories from 1957 to 1965. George Wagner was no longer involved with Silicones, having assumed larger responsibilities within Linde. Vic Jex had also departed to lead an R&D group in the Home and Automotive Division. The Pike brothers, Ron and Roscoe, as well as Bob Mixer and Lloyd Schaeffer were also gone. Don Bailey, who was in charge of Silicones Research at Tonawanda, transferred in 1964 to Sistersville where he was responsible for Process R&D. At Tonawanda, Tom Williams, as a Research Supervisor, was responsible for Elastomer, Fluid and Resin programs. Bernard Kanner, also as Research Supervisor, was responsible for Silicone Surfactants and Coupling Agents. Both reported initially to Don Bailey, and then in 1964, to Tom Welch, Manager of Product Development.

Also reporting to Tom Welch, were the Development Supervisors, Sam Sterman (Coupling Agents and Special Products), Dexter Huntington (Resins, Surfactants) and Milt Dunham (Elastomers). Differentiating the focus within the Research and Development groups was the emphasis on acquiring fundamental information and the exploration of new chemistry in the former and a concentration on new products and applications in the latter. The activities in both Research and Development supported the introduction of new products in the already established markets for elastomers, fluids and resins along with the newly emerging markets for coupling agents and surfactants for polyurethane foam. Each of these product arenas will be treated separately.

(A)   Polyurethane Foam Surfactants

(1)   Non-Hydrolyzable Surfactants

For several years after the initial discovery that X-520, (later, L-520), would stabilize the newly developed "one-shot" polyurethane foam formulations, it was to remain the only product for this market. Virtually all of the other major silicone manufacturers (including Dow Corning, General Electric, Shin-Etsu, ICI, Bayer, Rhone-Poulenc and Goldschmidt) scrambled to develop their own competing products. With the notable exception of Goldschmidt, all of the rest eventually dropped out of the surfactants for polyurethane foam market completely or were to remain very minor players. Goldschmidt, the smallest of all of the competitors, most closely resembled UCC Silicones, with its similar focus as a specialty silicones manufacturer.

It soon became apparent that there were considerable variations in foam stabilization performance as experienced by foam formulators, which were presumably the result of process variations in the production of L-520. Ron Wishart and Tom Hart, who were very aware of this problem through their customer contacts, were able to persuade production representatives to witness these effects and thereby understand the need for uniform and consistent product performance. The difficulties in dealing with this problem were compounded by complexities in copolymer structure and composition. The distribution of linear and branched structures in the silicone backbone were not well understood, nor was there a good understanding of the oxyethylene and oxypropylene sequencing in the pendant polyether blocks. Other gaps in understanding at the time included the mechanism of "one-shot" polyurethane foam stabilization, the complete unsuitability of organic surfactants for this purpose and why only certain silicone-polyether copolymers would stabilize such systems. Also unknown was whether the unique ability of silicone-polyether copolymers in polyurethane foam stabilization would also carry over to other surfactant properties. The continuing rapid growth of silicone surfactant sales provided the urgency to address these and other related questions. Understandably, much of the initial effort in Product Development and the Plant related to making L-520 reliably and reproducibly, which could only be determined by measuring its performance via foam tests.

A potentially troubling problem that surfaced early on was that L-520 had limited hydrolytic stability, especially under conditions that were on either the acid or base sides of neutrality. Samples of L-520 would, on standing, gradually hydrolyze and eventually separate into mutually immiscible silicone and polyether layers. This was the result of atmospheric moisture which would dissolve in L-520 over time along with the gradual development of acidic pH's because of polyether autooxidation. The obvious solution was the synthesis of silicone-polyether copolymers via hydrosilation to eliminate the hydrolytically unstable silicon-oxygen-carbon bonds. The first such copolymers were synthesized by Ingo Petersen who was in the Tom Williams group at that time.

The first commercial "non-hydrolyzable" copolymer, based on a combined R&D effort, was marketed by UCC Silicones as L-530. L-530 had been designed to be a close copy of L-520. As was the case with L-520, it made use of butanol started polyols containing equal

weights of ethylene and propylene oxides. An olefinic group was introduced by allyl capping these polyols. Because the butanol started polyols contained a small but variable amount of diol, a corresponding amount of diallyl component was introduced by allyl capping. This was undesirable and so the polyols for non-hydrolyzable copolymers had to be redesigned. These polyols were allyl alcohol started and methyl-capped based on a process that Bailey, (now at Sistersville, as Associate Director of Process R&D), introduced.

The effort in the Product Development Foam Surfactant Group was greatly strengthened at this time by the addition of Eric Schwarz, who became its Group Leader, and Ed Morehouse. Based on the synthesis efforts of Ed Morehouse, a much improved version of L-530 was developed and marketed as L-540. It was more efficient than either L-530 or L-520 although it did not have the broad processing latitude of the latter. With the improved properties realized with the introduction of L-540, further effort to improve the properties of L-520 was de-emphasized. Future efforts were to concentrate almost exclusively on non-hydrolyzable copolymers.

(2)   Rigid Polyurethane Foam Surfactants

In addition to flexible polyurethane foam, rigid polyurethane foam systems were developed for refrigeration insulation and other applications. Because of their much higher viscosity, such systems were inherently much more stable and did not require any surfactant at all for open celled slab stock. For thermal insulation, however, a fine, closed cell structure was more desirable. Of the surfactants available in the early 1960's, L-521, a copolymer having hydrolyzable silicone-polyether linkages, was clearly the best candidate. Larry Marlin, of the Product Development Group, quickly synthesized a series of non-hydrolyzable copolymers from which the improved rigid foam surfactants, L-5310 and L-5410, emerged.

(3)   Polyester Foam Surfactants

While polyether-based polyoI foam systems dominated the flexible polyurethane foam market, for some specialty applications polyester polyols proved more desirable. Due to the higher surface tension and viscosity of such systems, organic surfactants were acceptable for foam stabilization. Larry Marlin addressed the development of a silicone-polyether surfactant for such systems. The result was the introduction of L-532 for general use in polyester flexible foam formulations. L-532 quickly established itself as the industry standard for polyester foam. It combined product reliability and reproducibility, superior cell control, and eliminated the need for blending organic surfactants.

The importance of customer support and feedback was recognized quite early by Ron Wishart, Tom Hart and others, resulting in the formation of a strong Technical Service Group, led initially by Ralph Elrick, and subsequently by Charlie Rose and then Walt Rosemund. Close cooperation between Research, Product Development, Technical Service, Process Development and Production proved of critical importance allowing UCC Silicones to maintain its dominant

position in Polyurethane Foam Surfactants in spite of intense early competition. Periodic multifunctional reviews highlighted new opportunities from the field, progress in the development and introduction of new products, production scaleup experience with new and existing products, competitive activity, the development of new and better foam tests and a host of related issues. Opportunities and problems would be quickly highlighted and addressed. These meetings were not without their heated and contentious moments resulting from strongly held and opposing opinions. Fortunately, such differences were usually resolved by actions which advanced the overall business interest over any parochial interest.

(4)   Surfactant Fundamentals

Paralleling the development and introduction of new products for the polyurethane foam industry just described, Research was addressing a range of fundamental questions. These dealt with the unique position of silicone surfactants in polyurethane foam along with the behavior of silicone surfactants in general. Kanner, Petersen, (who had transferred from Williams' Group), and Reid began a broadly based program on the synthesis of silicone surfactants and the measurement of fundamental properties. In this they were aided by Professor Sidney Ross of RPI, a well known consultant in surface chemistry. In this investigation, it was decided that silicone-polyether copolymers would be synthesized in which the silicone block was a discrete moiety rather than the usual equilibrate or mixture of structures and compositions. For this purpose it was also necessary to concentrate on relatively small silicone blocks rather than the larger ones typical of polyurethane foam surfactants. As a further simplification, the polyether blocks were limited to polyoxyethylenes of low to intermediate molecular weights. The reasons for these decisions become apparent when one considers the enormous complexity and diversity of compositions present in a typical polyurethane foam surfactant. This may not appear obvious at first glance. For example, consider the silicone-polyether copolymer described by the following formulation:

$$Me_3Si(OSiMe_2)_{50}(OSiMePe)_5OSiMe_3$$
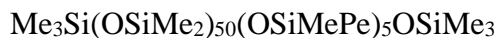
Silicone-Polyether Copolymer (A)

Where Me = methyl, and Pe = Polyether

The copolymer is derived from a silicone equilibrate and has the average composition as shown. A number of variables are inherent in such a composition. Thus the silicone backbone has a relatively broad molecular weight (Poisson) distribution. It is also expected that the diversity would increase with increasing molecular weight of copolymer (A).

The number of pendant polyether groups is an average of 5, but there are copolymers present having as few as zero pendant polyethers (relatively few, no doubt) or as many as 20 or more (also very few). Another variable is the location of the polyether groups along the silicone backbone. There are copolymers having the 5 (or more or less) polyether groups randomly distributed along the silicone backbone. The various copolymers may also have two or more vicinal polyether groups on neighboring silicon atoms in the silicone backbone.

Superimposed on the silicone block diversity of structures just described are corresponding variations in the polyether blocks. These blocks are nominally random copolymers of oxyethylene and oxypropylene units with a bridging propylene unit at one end and a methyl cap at the other. This, too, is an oversimplified depiction. As in the case of the silicone blocks, the molecular weights of the polyethers are only an average and can also be represented more or less by a Poisson distribution. Further, because ethylene oxide ring opens more rapidly than propylene oxide, under alkaline catalysis, the pendant groups are richer initially in oxyethylene units and, towards the end, are richer in oxypropylene units. Somewhere in between the copolymer is relatively random. Optical D,L-isomers should also be considered. Finally, the end groups are identified as methyl but this is also an oversimplification. Somewhere between 80 and 90% of the end groups are methyl, but the remainder are hydroxyl groups. Bill Foster of the Mathematics Support Group was asked to estimate the degree of molecular dispersity in this class of copolymers. Based on a back of the envelope calculation, it appears that no two molecules of a typical polyurethane foam silicone-polyether surfactant are identical in structure, composition and stereotacticity! It should not be surprising that analytical methods are not capable of distinguishing between "good", "bad" or "mediocre" surfactants and that foam tests are the only reliable indicators of foam performance.

Fortunately for the project, its synthesis objectives were greatly aided by some novel chemistry being developed in the Research Group. E. W. Bennett, George Omietanski and Tom Williams, who were engaged in other research projects, had discovered new processes for the controlled ring opening of dimethylsiloxane cyclic trimer.

Trimer was a coproduct of the hydrolysis of dimethyldichlorosilane which yielded a mixture of cyclic trimer, tetramer, pentamer and higher cyclics. In contrast to the other cyclics, trimer, which could readily be separated by distillation, was a highly crystalline, easily sublimable compound, which underwent certain ring opening reactions with great ease. Ev Bennett discovered that trimethylchlorosilane could be reacted with trimer to form a series of low molecular weight telomers:

$$Me_3SiCl \ + \ (Me_2SiO)_3 \ \rightarrow \ Me_3Si(OSiMe_2)_xCl$$
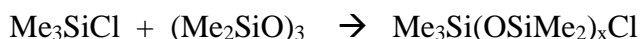
Where x = 3,6,9 etc.

Omietanski had previously discovered a related process for ring opening of the trimer to form the linear, 1,3-trimer diol in high yield and purity:

$$H_2O + (Me_2SiO)_3 \rightarrow HO(SiMe_2O)_3H$$
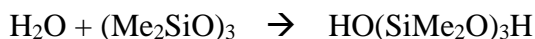
The compound, although highly reactive and prone to further condensation, could easily be distilled and stored provided that traces of acid or base were removed. It proved to be a versatile intermediate for the synthesis of mixed cyclic tetramers:

$$HO(SiMe_2O)_3H + RMeSiCl_2 \rightarrow (Me_2SiO)_3(RMeSiO)$$
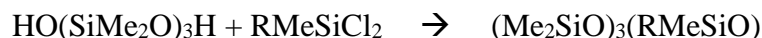
The mixed cyclic tetramer containing one methylhydrogensiloxane unit was a discrete silicone moiety useful for the synthesis of model silicone-polyether copolymers. With the aid of the intermediates available from Bennett's and Omietanski's programs, Kanner, Reid and Petersen were able to synthesize model surfactants with a considerable range of structures and compositions (Kanner, Petersen and Reid, I & E Chem., Prod. Dev. 6(2) 88-92 [1967]).

The most striking properties of these surfactants was their ability to lower aqueous surface tensions to 20-21 dynes/cm. and their outstanding wetting properties (first observed by Wally Reid). Although several copolymers exhibited excellent wetting properties, the one that was introduced commercially has the structure as shown (L-77):

$$Me_3SiOSi(Me)OSiMe_3$$
$$|$$
$$(CH_2)_3$$
$$|$$
$$(OC_2H_4)_{7\sim8}OMe$$
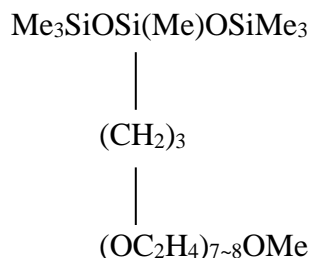
Because of its outstanding wetting properties, it became the first commercially important silicone polyether surfactant that was not used for the stabilization of polyurethane foam. Perhaps its most important use is as an adjuvant in agricultural applications.

The most striking differences between silicone and organic surfactants is evident in non-aqueous media. This is illustrated by differences in their ability to lower the surface tension of LG-56, a polyol used in the preparation of flexible polyurethane foam. It was found that typical hydrocarbon surfactants do not lower the surface tension of LG-56 while many silicone surfactants do. Surface tension lowering of polyols was a necessary but insufficient condition for the stabilization of polyurethane foam. Another important factor was surfactant structure. The best surfactants for polyurethane foam stabilization have comb structures where the silicone block has a number of pendant polyether blocks. Surfactants having an AB structure are

ineffective, while ABA surfactants are relatively inefficient (A = silicone block and B = polyether block). Most organic surfactants have an AB structure. Although some fluorocarbon surfactants lower the surface tension of polyols, they generally also have AB structures. The behavior of silicone surfactants in polyurethane foam was examined in subsequent investigations.

Although most of the study involved nonionic surfactants, some limited work was also carried out on ionic analogs.

The anionic and cationic silicones, which had analogous structures to L-77, also gave very low aqueous surface tensions and were excellent wetting agents. One rather interesting property they exhibited that was not shown by the nonionic silicone surfactants was their ability to act as aqueous thickening agents.

During 1965-66, two chemists of Hungarian background, Andy Katai and Bela Prokai, joined the Silicones Division and became members of the Kanner Group. Andy was to stay for only a short period of time, but long enough to make an important contribution to the behavior of silicone surfactants in aqueous solution.

The outstanding wetting properties of L-77 were attracting much attention and an examination of its behavior in aqueous solution was undertaken. It was observed, unexpectedly, that dilute solutions of L-77 lost their excellent wetting properties after storing for about a week. Accidental contamination by acid or base was ruled out, but it was determined that the initially neutral solution gradually became acidic on storage. Further, it was observed that the surfactant was being cleaved to form hexamethyldisiloxane and higher condensation products, accounting for the loss in wetting properties:

$$\text{L-77} \rightarrow \text{Me}_3\text{SiOSiMe}_3 + \underset{\underset{\text{Pe}}{|}}{\text{H(OSiMe}_2)_n\text{OH}}$$
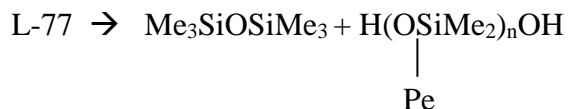
The gradual acidification of the surfactant solution was apparently the result of air oxidation of the polyether side chain generating acidic fragments. The solution was to use a neutral buffer or a hindered phenolic antioxidant, both of which worked separately or together. Unfortunately, this work was done while R&D was in transition between the Tonawanda and Tarrytown laboratories. Andy Katai also left after a rather brief stay with UCC. As a result the work was not written up nor published. These results were to be rediscovered on more than one occasion in the decades that followed.

The role of silicone surfactants in the stabilization of polyurethane foam was a subject of much speculation in the early and mid 1960's, but no definitive work had been done. It was at this time that Tom Decker, trained in surface chemistry, joined Kanner's group. His first assignment was to investigate the role of silicone surfactants in the stabilization of polyurethane foam. The conclusions drawn were quite different than would have been anticipated from earlier speculation. It led to the earliest publication involving direct observations of the role of silicone surfactants in the stabilization of one-shot polyurethane foam (B. Kanner and T. G. Decker, J. Cell. Plast. 5(1), 32-9 [1969]).

A flexible polyurethane foam system was studied and recorded using a motion picture camera. It revealed that, in the presence of a surfactant, sufficient bubbles were introduced during the initial mixing to account for all of the cells in the final foam. This was confirmed in that the nucleation of new small bubbles was not observed in the interval from initial mixing until full foam rise. In the absence of a silicone surfactant, very few bubbles, and of much larger size, were formed and quickly disappeared. The most important overall conclusions were (a) The critical initial functions of the silicone surfactant were to lower the surface tension of the system and allow the introduction and stabilization of many fine bubbles by mixing; (b) Sufficient bubbles were introduced through initial mixing in the presence of surfactant to account for all of the cells in the final foam; (c) No evidence was found for the formation of any new bubbles throughout complete foam rise, i.,e., nucleation was absent, and, (d) Based on free energy calculations, the absence of nucleation was understandable as the formation of new bubbles via nucleation was highly unfavorable thermodynamically.

(5)   MQ Resins

In addition to flexible and rigid one-shot polyurethane foam, another unrelated system, frothed polyvinyl chloride foam for carpet underlay, was beginning to attract attention in the early 1960's. It was a very fine celled, stable foam that employed as a surfactant a fairly old class of silicones known as MQ resins. MQ resins were typically made by the cohydrolysis and condensation of trimethylchlorosilane with ethyl silicate. These resins clearly had surfactant properties that were remarkably different than silicone-polyether copolymers or silicone fluids. When used in one-shot flexible polyurethane foam, they would form very closed cell foam that would shrink badly on cooling. This unusual combination of properties exhibited by MQ resins attracted the attention of Kanner, Decker and Prokai who proceeded to measure the surface properties, and, later, to determine the structure and composition of these compounds.

The unusual stability of frothed polyvinyl chloride suggested that enhanced surface viscosity might be the mechanism by which MQ resins stabilized foam. Decker proceeded to determine the surface tension and surface viscosity properties of these resins. Using standard techniques later described by Kanner and Glass (I & E Chem. 61(5), 31-41[1969]), Decker determined that MQ resins were excellent foam stabilizing surfactants because of increased surface viscosity. Increases in surface viscosity of almost a factor of ten were observed. By contrast, silicone-polyether surfactants, such as those typically used to stabilize polyurethane foam, actually decreased the surface viscosity of polyols such as LG-56.

Bela Prokai established the structure of MQ resins by synthesizing the first member of the series, M_8Q_8. M_8Q_8, unlike its higher molecular weight homologs, is a crystalline solid with a sharp melting point. Its structure was that of a cubic octamer with a silicate unit in each corner to which is bound a trimethylsilyl group. The enhanced surface viscosity is probably the result of the strong intermolecular forces present in the semicrystalline, mineral like, MQ silicate resins.

(B)　　Coupling Agents and Other Silanes

　　(1)　　Trichlorosilane

The synthesis of coupling agents, resin intermediates such as amyltrichlorosilane and even the ill-fated diethylsilicone polymers all began with trichlorosilane. In addition to its widespread use as a synthesis intermediate, trichlorosilane had its own specific commercial uses. Undoubtedly the most important was its use in the production of transistor grade silicon metal in electronics. The process was simple in concept, involving the thermolysis of trichlorosilane to silicon metal and silicon tetrachloride. The critical requirement for this purpose was to have trichlorosilane of exceptional purity, particularly with regard to certain impurities, namely boron and phosphorus. The acceptable levels of the latter impurites were so low (and were to become progressively more stringent) as to be essentially beyond the sensitivity of analytical methods available at that time.

To resolve this problem, Howard Bradley was brought in from the Analytical Department. Howard succeeded in developing ultrasensitive analytical methods for the detection of boron and phosphorus initially in the parts per million range, and, ultimately to less than a part per billion.   These methods were transferred to the Sistersville plant where they were used to monitor the purity of production batches of trichlorosilane. In time, the analytical chemists at Sistersville informed Don Bailey that they could tell when the nearby farmers were fertilizing their land by the rise in phosphorus in the trichlorosilane.

In the 1960's and 1970's, UCC Silicones became the leading supplier of trichlorosilane to the transistor silicon metal manufacturers in the U.S. Later, as these manufacturers were to back integrate by producing their own trichlorosilane, this business began to fade for UCC and eventually disappeared. A new process was developed by Don Bailey which converted trichlorosilane to silane (SiH_4) which in turn was thermolyzed to ultrapure silicon. This will be described in a later section.

　　(2)　　New Coupling Agents

The exploitation of coupling agents began with the availability of vinyltrichlorosilane, several of its esters and gamma-aminopropyltriethoxysilane (A-1100). Oxidative stability was believed to be one of the most important properties of silicon compounds in the 1950's and 60's. Therefore, among the new classes of organofunctional silanes being sought were the aromatics. The synthesis of aminophenylsilanes proved to be difficult but was solved with the use of

fluorosilane intermediates and the discovery of novel fluorosilane-chlorosilane and fluorosilane-alkoxysilane redistribution reactions. However, applications requiring aromatic organofunctional silanes failed to materialize which ended this effort.

Applications requiring a variety of aliphatic coupling agents continued to develop, spurring the synthesis of a number of new classes of these silanes. Chloroalkylsilanes were synthesized by the hydrosilation of allyl and methallyl chlorides. The corresponding esters could then be reacted with ammonia, ethylene diamine or NaSH to yield new amino and mercapto-functional silanes.

Epoxy-functional silanes were prepared by the hydrosilation of olefinic glycidyl and other aliphatic epoxides. For a long period of time, the epoxy-functional silanes were the only coupling agents whose synthesis involved trialkoxysilanes. All other coupling agents employed trichlorosilane. It turned out that the hydrosilations of many organofunctional olefins proceed in much poorer yield with trialkoxysilanes than is true for trichlorosilane, using chloroplatinic acid.

Vinylsilanes were the first silicon compounds to be used as coupling agents. They were presumed to react via free radical copolymerization with unsaturated polymers such as polyesters to form a chemical bond between the polymer and glass fiber or filler. While vinylsilanes copolymerize readily with olefins such as vinyl acetate, vinyl chloride, ethylene and the like, copolymerization with highly reactive olefins such as the acrylates, methacrylates, acrylonitrile and styrene did not proceed as well.

The need for a more reactive olefinic organofunctional silane thus became apparent. In response to a request by Sam Sterman for a more reactive olefinic silane, Kanner attempted a synthesis via metathesis of a gamma-chloropropyltrialkoxysilane. The result was unsatisfactory, with homopolymerization of the initial product a severe problem. This was resolved by running the same reaction with chloromethyltrialkoxysilane which was prepared by Ed Morehouse for another purpose. The chloromethyl compound proved to be much more reactive, allowing the metathesis to proceed under milder conditions, and avoided the homopolymerization side reaction:

$$ClCH_2Si(OR)_3 + CH_2=CHMeCOOK \rightarrow CH_2=CHMeCOOCH_2Si(OR)_3$$

A sample of the first methacryloxy-functional silane was then submitted to Sterman for evaluation by his group. Unfortunately it was evaluated in the wrong formulation so no advantage was found. The idea of a more reactive olefinic silane remained inactive until it was revived in Sam's group some time later. Sam Sterman and Art Pines approached Bailey and Kanner for their opinion of a potential new route to a methacryloxy-functional silane. It involved the hydrosilation of allyl methacrylate:

$$HSiCl_3 + CH_2=CHMeCOOCH_2CH=CH_2 \rightarrow CH_2=CHMeCOO(CH_2)_3SiCl_3$$

$$CH_2=CHMeCOO(CH_2)_3SiCl_3 + 3\ MeOH \rightarrow CH_2=CHMeCOO(CH_2)_3Si(OMe)_3$$

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After some deep thought, it was Bailey's and Kanner's collective opinion that the process would be very problematic. They reasoned that either hydrosilation would take place preferentially at the methacrylate site or both olefin sites would hydrosilate indiscriminately. Fortunately Sterman and Pines were not overly influenced by this reasoned but faulty opinion and tried the process anyway. The results were excellent. It was soon scaled up at Sistersville.

With that success, the six organofunctional silanes which were to be, until recently, the backbone of the coupling agent business, had been prepared and introduced to the market. They were the amino- and diaminosilanes, the two epoxysilanes and the vinyl- and methacryloxy-functional silicon compounds.

One experimental organofunctional silane, which did not yet gain commercial importance, is also typical of the widespread exploration of the time. Kanner and Pepe were interested in an isocyanato-functional silane because of its great reactivity with active hydrogen functions. Of the several routes they examined, the most convenient proved to be the hydrosilation of allyl isocyanate:

$$HSiCl_3 + CH_2=CHCH_2NCO \rightarrow Cl_3Si(CH_2)_3NCO$$

$$Cl_3Si(CH_2)_3NCO + 3\ ROH \rightarrow (RO)_3Si(CH_2)_3NCO$$

Unfortunately, the esterification of gamma-isocyanatopropyltrichlorosilane was not feasible at low temperatures as both the isocyanato and chlorosilyl groups reacted simultaneously with alcohols. However, a high temperature vapor phase esterification, which had been previously developed by Ev Bennett and Jeff Mui, cleanly yielded the desired isocyanato-functional silane ester.

(3)   Silanes for Antifreeze

The Consumer Products Division had marketed ethylene glycol (Prestone), as an antifreeze for automobile radiators for many years. An inhibitor was needed to control oxidative breakdown which resulted in acidic byproducts, which in turn accelerated radiator corrosion. Alkaline silicates were found to be helpful but had some problems of their own. Art Pines believed that a combination of a coupling agent with the silicate would provide a superior stabilizing additive. He then supplied the Prestone group with a series of organofunctional silanes for their evaluation. His hunch proved correct. A superior Prestone quickly resulted leading to substantial interdivisional sales from the Silicones Division to Consumer Products for many years.

(C)   Fluids

With the decision to drop diethylsilicone polymers in favor of dimethysilicones, applications of the latter finally received more attention in the late I950^{t}s. One of the most important early successes was the substantial sale of dimethysilicone oil to the Consumer Products Division of Union Carbide for use in automobile polish.

(1)   Functional Fluids

With the concurrent synthesis programs for coupling agents, it was natural to prepare new fluids having organic reactivity and to seek applications for them. Fluids were synthesized containing chloroalkyl, amino, carboxy, mercapto, vinyl, and, of course, polyether groups. Epoxy-functional fluids were found to improve the wet properties of Gypsum board and were widely used by National Gypsum and U.S. Gypsum. Fluids containing methylhydrogen siloxane units were sold to the textile industry to impart hydrophobic properties.

(2)   Gel Permeation Chromatography

On a more fundamental level, an important analytical technique was to become available as the result of an industrial-academic interaction. Professor Rodriguez, of Cornell University, spent a sabbatical at UCC Silicones, with Sam Sterman's group. One of his interests related to the use of Gel Permeation Chromatography, which was just coming into use. He proceeded to set up the first functioning GPC unit for Silicones (probably the first for all of UCC) with the help of Milt Berube. GPC was especially useful for determining molecular weight and molecular weight distributions. It was later to become an particularly effective technique in the analysis of newly synthesized or competitive silicone-polyether surfactants for polyurethane foam.

(3)   Other Specialty Fluids

With the growing success of silicone-polyether surfactants for polyurethane foam, the potential utility of these copolymers began to be explored in other applications. The development of various processes for coupling agents naturally led to the synthesis and exploitation of silicone fluids with organic reactivity as well as silicone-polyether copolymers with organic reactivity. The applications initially evaluated included antistatic agents, surfactants for emulsion polymerization, leveling agents, additives for thermoplastics, textile and paper treatment, coatings, wetting agents and antifoams. Cationic silicone surfactants were explored for their substantive properties on a variety of high energy surfaces. These included laundry softeners, automobile polishes, stain repellents and cosmetics.

Silicone antifoams were to remain relatively unsophisticated products at this time with the main emphasis on economics of use and satisfactory plant processes. Silicone oils were suitable for undemanding systems, but stable and persistent foam required silicone oil containing high surface silica which had to be heated together at high temperature. Many basic questions concerning the design of more efficient antifoams and the mechanisms by which they operated remained to be answered.

(D)   Silicone Elastomers and Resins

(1)   New Elastomers

UCC Silicones was late to enter the elastomers market with products based on di-methylsilicones in part because of the very early efforts involving diethylsilicone polymers. The effort to get the standard, methylsilicone-based products into the market place was led by Tom Williams in Research, Milt Dunham in Product Development and Ollie Clark in Process R&D. The polydimethylsilicone gumstocks which were cured with benzoyl peroxide were soon replaced by the more convenient methylvinylsilicone-modified gums cured by di-t-butyl peroxide. Elastomers having excellent low temperature properties were made by the introduction of diphenylsilicone units. Among the persistent problems was the lack of experience in making and handling gumstocks resulting in erratic reproducibility. These problems were never fully resolved over the years and were one of the contributing factors to UCC's eventual withdrawal from the silicones elastomer market.

Research efforts concentrated on the design of new elastomers having improved properties. Dimethylsilicone gumstocks are characterized by low physical properties in the absence of reinforcing fillers. This could be remedied by introduction of certain chain-stiffening units, e.g., disilylphenylene, into the silicone backbone. The synthesis of these units was carried out by George Omietanski, and involved the use of Grignard reagents. Unfortunately, a more practical synthesis could not be developed.

Fully cured dimethylsilicone elastomers are subject to a considerable loss in physical properties and excessive swell in the presence of aromatic solvents such as toluene. To overcome this problem, it was decided to try incorporating highly polar pendent groups. Omietanski and Bennett led the effort to synthesize elastomers containing methylcyanoalkyl silicone units. After considerable effort, Omietanski and Bennett were able to prepare cyanoalkylmethylsilicone-based gumstocks which could be filled and cured to give elastomers having both excellent solvent resistance and oxidative stability. However, one of the main difficulties was in the synthesis of the cyanoalkylmethyldichlorosilane intermediates.

As previously mentioned, Omietanski had developed a ring opening process for hexamethylcyclotrisiloxane to form the highly reactive trimer diol which in turn could be condensed with difunctional chlorosilanes to form various mixed cyclic tetramers. This proved to be a versatile synthetic route to incorporate many new siloxane units into silicone gumstocks. One of the more esoteric cyclics prepared by this route contained a nitroarylmethylsiloxane unit.

Although it was not of any lasting interest itself, it did have one unusual property. Typically, equilibration of such a cyclic would require base catalysis (Potassium dimethylsilanolate for several hours at 150°C). Instead equilibration was observed at about 75°C. It appeared that the polar nitro group greatly enhanced the strength of the base catalyst. Williams then observed that the same beneficial effect was obtained when small amounts of other polar solvents were added to equilibration mixtures.

Conventional gumstocks required crosslinking at elevated temperatures using free radical initiators. Systems that could be cured at much lower or even ambient temperatures appeared to offer much promise. Charlie Creamer explored such systems including one that cured through the interaction of moisture with $-SiNMe_2$ endgroups. The effort was abandoned because the potential market for such products was believed to be too small.

(2)   Resins

Silicone resins received much attention during the early years of Linde and UCC Silicones. They were prepared mainly from alkyl- and aryltrichlorosilanes or mixtures of the two. Amyl, ethyl and phenyltrichlorosilane were initially synthesized from uncatalyzed hydrosilation or other high temperature reactions. Later, the process was made more convenient by the use of platinum catalysis. The emphasis within R&D relating to resins was primarily on process development and, where possible, on thermal and oxidative stability. The applications were for electrical and electronics, paint additives, water repellents for masonry and concrete, aerospace coatings and high temperature varnishes.

Sales were reasonably attractive in the early years and it appeared that resins would remain an important business for the Silicones Division. However, as surfactants for polyurethane foam and coupling agents began to grow rapidly in the late 1950's and early 60's,

resin sales remained relatively flat. Resins were gradually deemphasized by R&D and, with the exception of a few specialty items, gradually faded out as a significant business within UCC Silicones.

II.   UCC Silicones from 1966 to 1985

During these two decades, there was more than a fifteen fold increase in sales by the Silicones Industry. The manufacture of silicones was to become truly international in scope with major participants in Germany (Wacker, Bayer, Dynamit-Nobel, Huels, Degussa and Goldschmidt), France (Rhone-Poulenc) and Japan (Shin Etsu).

The final step in the independence of UCC Silicones from Linde was the building of a separate R&D (for Product R&D only; Process R&D remained at Sistersville, W. Va.) facility at Tarrytown, New York. Construction started in 1965 with UCC Silicones R&D leaving the Linde Tonawanda labs to occupy its new facility in the Fall of 1966, with a brief sojourn at Union Carbide's nearby Sterling Forest facility.

Major organizational changes continued to take place during this period. In 1965, Ron Wishart, President of UCC Silicones, issued a five year business plan (1966-1970) coauthored with Leon Jehle, Jack Hamilton, Tom Hart and Ralph O'Connors. It was an ambitious and aggressive plan calling for major new plant investment and very substantial additions of salaried personnel. It was approved at the highest levels. Within two years the plan was obsolete.

In 1967 Union Carbide was undergoing a major reorganization. With the objective of more centralized control over the various semiautonomous operating divisions, a new Chemicals and Plastics organization was formed which absorbed these divisions. UCC Silicones was thus dissolved and became part of Chemicals and Plastics. The effects on Silicones were mixed. The nature of the Silicones business was not well understood at higher management levels. However, Silicone Surfactants for Polyurethane Foam and Coupling Agents continued to prosper as part of the Cellular and Elastomer Materials Department within C&P. Less fortunate were Silicone elastomers and resins which continued to struggle for focus and attention. After some years of inadequate growth and sales, the decision was made to essentially shut down these commodity product activities. In the case of elastomers, the business was sold to Rhone-Poulenc.

Administratively, important changes were taking place in the Tarrytown R&D management during the period of 1976 to 1981. Tom Welch retired as Director of R&D in 1976 and was replaced briefly, first by Dale Pollart from South Charleston, and then Bob Anderson from Bound Brook. Don Bailey retired in 1978 and was replaced by Jerry Barber, also from South Charleston. Sam Sterman was replaced by Phil Wolf as an Associate Director of R&D. Barber was then to replace Bob Anderson as Director of R&D. Barber continued in this role during this most important period, especially involving the major Direct Process projects.

After an indecisive decade, new capital investments were made. The long term focus, however, remained mixed and uncertain. The main sources of sales continued to be the specialty products areas of coupling agents and surfactants for polyurethane foam. Silicone fluids continued to be dominated by commodity products with a modest range of specialty products derived from the silicone surfactant and coupling agent technologies.

New facilities for the production of coupling agents were added to Sistersville at the end of the 1970's. In further support of this area and in recognition of the global nature of the Silicones business, a new plant was opened in 1982 in Termoli, Italy. Other smaller facilities were put in place in South America and in Japan as part of a joint venture. The various elements of the Silicones businesses were then recombined in the newly formed Silicone and Urethanes Intermediates Division.

To this point Silicones had grown and prospered in those businesses (particularly specialty products businesses) where it had pioneered as in coupling agents and surfactants for polyurethane foam. In spite of a great deal of effort, it remained a minor factor in those business areas where it was a latecomer. Silicone elastomers and resins had been abandoned for this reason.

Silicone fluids continued to hang on without a great deal of success. At this stage (1980), a critical decision was made affecting the entire future of UCC Silicones. It was decided to invest in a new world class (100,000,000 lb./yr. dimethyldichlorosilane) Direct Process plant. The justification for the plant was based on what was believed to be a conservative assumption, i.e., UCC Silicones could increase its market share of the commodity fluids business without upsetting the market place.

If successful, UCC Silicones would thus become a significant player in the sales of commodity fluids in addition to its established base as a manufacturer of specialty silicones products. In a sense it was a move back to an earlier phase in its history when UCC Silicones sought to be a supplier of both large scale commodity products as well as specialty products.

The proposed new plant was to be a state of the art Direct Process facility. Direct Process fundamental studies were undertaken to aid in the design of the new plant. Studies of the Direct Process had been on the back burner within the Silicones industry for a number of years. Interest in improving the process along with a better understanding of process catalysis was renewed in several of the industrial silicones R&D labs in the late 1970's and early '80's. These efforts in Silicones and Urethane Intermediates at Union Carbide were to reach a climax in 1985 and will be treated more fully in a separate section on the Direct Process.

(A)   Surfactants for Polyurethane Foam

       (1)   Frothed Polyurethane Foam

       The period of 1966 to 1985, particularly the earlier years, was especially productive for silicone surfactants for polyurethane foam. Fundamental surface studies, along with an improved understanding of how structure and composition related to surfactant properties, led to many important commercial advances.

       The fundamental work by Tom Decker on the stabilization of frothed polyvinyl chloride foam by MQ resins suggested to Eric Schwarz and Larry Marlin that the development of a frothed polyurethane foam system would lead to new commercial applications. They then proceeded over a period of months to design such a system. The difficulties were considerable, but they succeeded. The most difficult problem proved to be finding a surfactant to stabilize the frothed foam. A wide range of surfactants was evaluated without success. The only surfactant showing any promise was one based on a silicone-polyether copolymer containing terminal hydroxyl functionality:

$$Me_3SiO(Me_2SiO)_x(MeSiO)_ySiMe_3$$
$$|$$
$$(CH_2)_3$$
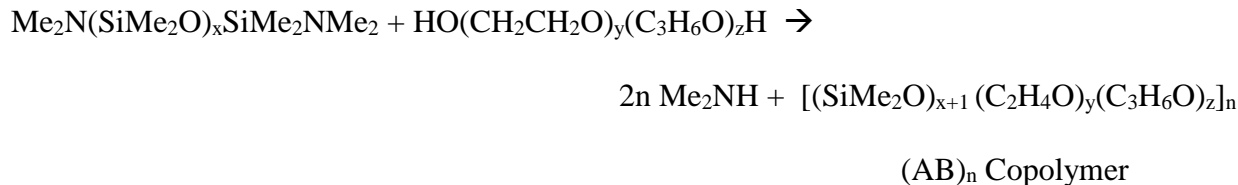$$|$$
$$(OCH_2CH_2)_zOH$$
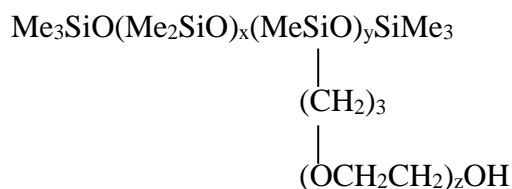
       This copolymer was a poor stabilizer for the frothed polyurethane foam system. However, when the copolymer was crosslinked by progressive additions of toluene diisocyanate, the stabilizing properties gradually improved. The best stabilizing properties were obtained just before gellation of the copolymer was reached. Commercial scale-up of such a product was, of course, impractical.

       Kanner was intrigued by this problem, wondering why it was that the performance of the copolymer improved as the degree of crosslinking increased. He asked Bela Prokai to use gel permeation chromatography to determine the molecular weight distribution of a series of surfactant copolymers having progressively increased crosslinking. The distributions proved to be quite similar for the bulk of these copolymers and differed mainly in the high molecular weight "tail" fraction, which increased modestly with increasing crosslinking.

       Speculating that this latter fraction was responsible for the improvement in stabilizing properties for the frothed polyurethane foam, Kanner concluded that a much more efficient approach would be the synthesis of a high molecular weight linear $(AB)_n$ copolymer with alternating silicone (A) and polyether (B) blocks. Copolymers of this structure had been synthesized previously by Bailey and O'Connor via a transesterification process. He then had Prokai synthesize several of these copolymers by an improved route:

(58)

$$Me_2N(SiMe_2O)_xSiMe_2NMe_2 + HO(CH_2CH_2O)_y(C_3H_6O)_zH \rightarrow$$

$$2n\ Me_2NH +\ [(SiMe_2O)_{x+1}\ (C_2H_4O)_y(C_3H_6O)_z]_n$$

$$(AB)_n\ Copolymer$$

About 6 months later, when Schwarz and Marlin had finally completed optimizing their system but could not find a satisfactory surfactant, they approached Prokai for help. Bela promptly evaluated all of the surfactants that were available in his lab and found that the only one that worked very well was the $(AB)_n$ copolymer that he had previously prepared for this purpose but lost track of in the interim. The final element, completing the frothed polyurethane foam system, was the development of a delayed action catalyst which was carried out by Dale Reedy.

Schwarz and Marlin believed that the newly developed frothed polyurethane foam system would find a widespread market for carpet underlay. Scaleup of the $(AB)_n$ copolymer was quickly transferred to Sistersville. For best surfactant performance a molecular weight in excess of 10^5 was needed. To achieve this required close control of reactant stoichiometry and reaction times of 100 hours or more. Clearly, some improvement was necessary. The question arose as to whether silyl carbamate groups (whose use Bela had noted while reading of an investigation being carried out by another Corporate Research group) might be more reactive than silylamines in this process. This was tested by Kanner's suggestion of a simple modification in Bela's synthesis route. The process was to be run under an atmosphere of carbon dioxide instead of nitrogen. By this means, the terminal dimethylaminosilyl groups would react rapidly with carbon dioxide to form the corresponding silyl carbamate groups in situ. These would then react with the hydroxyl-terminated polyethers yielding the same $(AB)_n$ copolymers as before. This would be a direct test as to whether the silyl carbamate groups would react more rapidly with the diols than the dimethylaminosilyl groups.

Within a few hours, Bela had quickly determined that under these conditions the $(AB)_n$ surfactants having the required molecular weight could be prepared in as little as 10 hours. The surfactant was successfully scaled up at Sistersville. Over the years, $(AB)_n$ copolymers have been found to be the only satisfactory candidates for frothed flexible polyurethane foam.

(2)   "Flame Retardant" Polyurethane Foam

MQ resins also proved to be the starting point for another important family of surfactants entirely unrelated to frothed polyurethane foam. MQ resins had been shown to be excellent surfactants because of their ability to raise surface viscosity. It was decided to explore the properties of MQ resins modified by the introduction of pendent polyether groups. One of these copolymers, MD'Q, (where D' contains a methyl capped pendent polyoxyethylene group), proved to be a very effective surfactant for certain 'flame retardant' flexible polyester foam systems. So-called 'flame retardant' flexible polyether foam systems were also becoming commercially important at this time.

Ordinary surfactants, which were suitable for conventional flexible polyether foam systems, proved to be unsatisfactory for 'flame retardant' foam systems. They required unduly large amounts of flame retardant additive to be used in order to pass the flame retardancy test and gave erratic results at best. With the success of the MD'Q copolymer surfactant in "flame retardant" ("FR") polyester foam, it was thought that a similar copolymer would work well in "FR" polyether foam systems. However, such copolymers proved to be completely unsatisfactory in foam systems where substantially higher molecular weight surfactants were required compared with polyester foam.

This led Kanner to speculate that the Q unit (where $Q = SiO_2$) was much more polar than dimethylsilicone units and this might be responsible for its favorable behaviour in "FR" polyester foam. This led in turn to the introduction of other polar groups into silicone-polyether copolymer surfactants. Prokai was then asked to synthesize the first of a series of polar group modified silicone-polyether surfactants:

$$Me_3SiO(Me_2SiO)_x(MeRSiO)_y(MeSiO)_zSiMe_3$$
$$|$$
$$Pe$$

R = -(CH_2)_3CN, Pe = Polyether
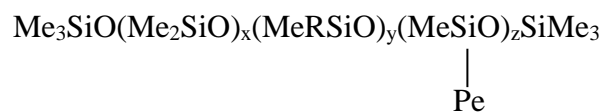
One of the first surfactants thus prepared exceeded expectations. It gave excellent performance in "FR" polyether foam. It permitted substantially lower levels of flame retardant additives to be used and it gave reliable performance. It quickly became the first commercially important surfactant for such systems. Curt Schilling was then assigned the examination of the effects of polar group substitution on "FR" response more broadly. Many other polar groups were found to give the same improvement in "FR" response. A simpler approach was later found that lowering the silicone content in the silicone-polyether copolymer gave the same response. The common factor appeared to be an inverse relationship between surfactant effectiveness in "FR" formulations and the surface tension lowering ability of the surfactant in polyol. That is, those surfactants which gave an improved response in "FR" foam did not lower surface tension as effectively as the surfactants that did not perform well in "FR" foam.

(3)   High Resilience Polyurethane Foam

During this same period the South Charleston labs were developing a much improved new flexible foam formulation having high resilience and moldability and that was also more durable. The market objective was automotive cushioning with the Inland Division of General Motors the primary target. The novel elements of the technology were the proprietary "polymer polyols" (derived from polyols to which olefins were grafted via a free radical process) and

which had higher primary hydroxyl endgroups. The combination of higher viscosity and higher reactivity gave inherently self-stabilizing foam with a high closed cell content. In this respect the new foam formulation behaved similarly to the much earlier prepolymer polyurethane foam systems. Essentially the same type of surfactant was required to give an open celled foam. Eric Schwarz and Ed Morehouse developed the first surfactant products that gave open celled high resiliency foam for the automotive market. Many subsequent surfactants were then developed by Schwarz, Morehouse and Prokai to maintain UCC's leading position in the HR foam market.

(4)   New Surfactant Processes

The processes for the synthesis of both hydrolyzable and non-hydrolyzable silicone-polyether surfactants involved silicone and polyether reactants, catalysts and a substantial amount of aromatic hydrocarbon solvent. The latter was present to partially compatibilize the otherwise immiscible reactants. The solvent subsequently had to be removed by distillation and cleaned up so that it could be recycled. A project had started in the Sistersville Process R&D group to synthesize silicone surfactants in the absence of solvent. The initial objectives were to reduce process costs, eliminate the cleanup and recycling of solvent and increase kettle capacity (that is, to produce more copolymer per kettle run). In addition to these features, it also became evident that the copolymers produced by this process had different, and, in some ways, superior properties to conventionally prepared surfactants. The project was then transferred to Tarrytown to further explore this last aspect.

Gerry Murphy, who had recently joined Kanner's group after graduating from M.I.T., assumed responsibility for this project. Murphy was the latest in a series of highly motivated and talented graduates trained in Dietmar Seyferth's group at M.I.T. to join the Kanner group. Over more than a decade, Jeff Mui, Bela Prokai, Gerry Murphy, Scott Eschbach and Steve Vick were to make many important contributions during their stay in Kanner's group. They also were to go onto highly successful careers within UCC and elsewhere. For this UCC is greatly indebted to Professor Seyferth for the excellent training they received under his guidance at M.I.T

Murphy proceeded to explore the synthesis of non-hydrolyzable copolymers prepared in the absence of solvent. He confirmed the main features of the process as carried out at Sistersville. The improved process costs which resulted from the absence of solvent, were overshadowed by the changed nature of the copolymer being synthesized. The distribution of copolymer structures which resulted from this process were clearly different than the copolymers prepared by the process involving solvents. As a result, the surfactants synthesized by this process had significantly broader processing latitude, a property of considerable commercial importance. However, the process gave erratic results making it unsuitable for scaleup at that time. This problem was finally solved later by Dale Reedy and others at Sistersville.

(B)   Direct Processes

        (1)   Methylchlorosilanes

        For the first 20 years of its operation at Sistersville, the characteristics of the Direct
Process for methylchlorosilanes improved modestly, but remained relatively unchanged. The
selectivity of the process (ratio of D/T; where D and T represent di- and trifunctional
chlorosilanes) was in the range of 8 to 12, the induction period on startup was erratic and
uncontrollable, the effectiveness of the copper catalyst was highly variable and unpredictable and
the state of chloride and silicon efficiencies and waste disposal handling left much to be desired.
It was against this background that Don Bailey began a program in the middle 1970's to examine
some of the fundamentals of the Direct Process. Jeff Mui, who had transferred from Tarrytown,
and others in Bailey's group at Sistersville carried out the experimental work.

        Because of the erratic and unpredictable activity of the copper catalyst, it was necessary
to screen individual batches of copper at the bench before they could be approved for use in
production. Various improved methods of activating the silicon/copper mass were also sought.
Hydrogen chloride etching of the silicon/copper mass proved to be very effective in minimizing
the induction period although it had no effect on the catalytic activity of individual batches of
copper itself. That problem would be resolved subsequently in cooperation with Tarrytown. In
addition to reducing the induction period of startup, hydrogen chloride etching also improved the
selectivity factor from about 12 to 20 or more. The amount of methyltrichlorosilane, the least
desirable of the major methylchlorosilanes, was thereby substantially reduced.

        Bailey had also been interested in the Direct Reaction of ethanol with silicon. Mui
examined the process in a bench scale fluidized bed reactor. The reaction would start
promisingly but would quickly stop with deactivation of the silicon/copper mass. Dehydration of
ethanol apparently resulted in passivation of the silicon particles. Further studies of this short
term project were then discontinued.

        It was at this point in the late 1970's that the decision was made to replace the Sistersville
Direct Process reactor with a state of the art unit capable of producing 100,000,000 lbs./yr. of
dimethyldichlorosilane. The objective was to have a Direct Process unit as efficient as any in the
world. A program to achieve this objective consisted of two separate but simultaneous
approaches. The first was through internal R&D and the second was to examine and possibly
license competitive technology. Ultimately, internal R&D proved to be at least equal to, if not
superior to, any competitive technology.

        The output of the proposed new plant would be used to supply product needs arising from
a modestly increased world share of the silicones fluids market. The main need for the increased
production capacity would thus be filled by increased sales of commodity silicone fluids

products. This was in sharp contrast to the specialty products nature of UCC Silicones main businesses arising from silicone surfactants and silane coupling agents. If successful, this would lead to UCC silicones becoming a significant supplier of commodity as well as specialty products. Its implementation would require the largest investment by far ever made in silicones.

This decision to proceed with this project proved to be the most important decision ever made effecting the entire future of silicones at UCC (other than perhaps the original decision to begin work on silicon chemistry made by Neil Strother in 1942).

Although the work in support of a new Direct Process unit was to receive much attention for the next several years throughout much of the silicones organization, the focus here will be on what went on in the research group.

The first significant advance was the hydrogen chloride etching of the silicon-copper masses, developed at Sistersville under Don Bailey's direction. It had minimized the induction period observed during startup and had considerably improved selectivity (D/T) of the methylchlorosilanes produced.

One of the main remaining problems was the unpredictable and highly variable catalytic activity of different batches of the copper catalyst. Ken Lewis, who was in Kanner's Group at Tarrytown and Tom Childress of Sistersville jointly attacked this problem. Suspecting that the variable concentration of some trace metal might be responsible for the variations in observed catalytic activity, Ken had a series of copper samples, as supplied by Tom, analyzed for a broad range of trace metal content. There was no correlation between the concentration of various trace metals and catalytic activity with the dramatic exception of tin.

The reaction rates of silicon/copper masses varied directly with the logarithm of tin concentration. With the proper tin content and the appropriate Sn/Zn ratio, every batch of copper catalyst could be made to be essentially equally effective with excellent reaction rates and selectivities. Further, the amount of copper needed could be dramatically reduced from high levels which were typical at that time, to as little as 0.5% or less. With the now known importance of tin and the ratio of tin and zinc, the selectivity ratio of D/T could be further increased to 30 or more. The details of this work are fully described in U.S. patent 4,864,044 (1989) by K.M. Lewis and T.E. Childress and in "Catalyzed Direct Reactions of Silicon", Ed. by K.M. Lewis and D.G. Rethwisch, chapter 1, pp 13-16 (1993), Elsevier.

In addition to the production of methylchlorosilanes, the new plant (which was to be located at South Charleston) also contained facilities for the hydrolysis of dimethyldichlorosilane to cyclics and OH fluids along with the efficient recycling of HCl by reaction with methanol to form methyl chloride.

The startup and operation of the new plant was beset with many difficulties including erratic behaviour and failure to meet many design specifications. Unfortunately, in the last phase of plant design, a number of changes were instituted to reduce costs. The effects of these changes

had not been properly evaluated before their implementation. The design flaws were gradually corrected over a period of many months. By 1985 the plant was at last meeting its design criteria. This story will be temporarily suspended at this point as it has moved chronologically ahead of other important research on the Direct Process on which we will now focus our attention.

(2)   Reactions of Secondary Amines with Silicon ("Tris" Project)

A great deal of other research was being carried out on other novel aspects of the Direct Process both preceding and simultaneously with the massive effort on methylchlorosilanes. The work by Bailey and coworkers at Sistersville in about 1976 has already been described. With the newly available and highly reactive Si/Cu masses developed at Sistersville, Kanner proposed a broad project to explore new Direct Reactions of silicon at Tarrytown. With one or two minor exceptions, this was the first such project since the days of Strother and Wagner some 30 years earlier. Just as their work was supported by corporate rather than divisional funding, the new project was also supported by Corporate Exploratory and Basic Research funds.

William B. Herdle joined Kanner's group in Fall of 1977 with the assignment of carrying out this new project. The initial phase of this work was to examine the reactions of secondary aliphatic and aromatic amines with silicon. Dimethylamine was to be the first candidate. The first experiments by Bill Herdle with dimethylamine were discouraging. The only products isolated resulted from the catalyzed cracking of dimethylamine to form small amounts of bis(dimethylamino)methane. However, after reactivation with HCl of the silicon/copper mass, the first traces of a silicon-containing product were isolated. It soon became clear that the process was being run at an excessively high temperature. When run at 275 - 300° C, an excellent reaction was observed:

$$Me_2NH + Si/Cu \rightarrow (Me_2N)_3SiH + (Me_2N)_4Si + H_2$$

The principal product was tris(dimethylamino)silane or "tris". The reaction proved to be extraordinarily sensitive to traces of moisture and oxygen which had to be rigorously excluded. Just as the process economics of the Direct Process for methylchlorosilanes was far superior to other processes, the Direct Process for "tris" was equally superior to any other known process for the preparation of silylamines.

Remembering his work on the ethanol-silicon reaction at Sistersville, Bailey suggested that the combined reaction of dimethylamine and ethanol with silicon should be tried. Unlike the fluidized bed reaction of ethanol with silicon which died out rapidly, the mixed reaction proceeded very well yielding a series of mixed functional silanes:

$$Me_2NH + EtOH + Si/Cu \rightarrow (Me_2N)_{3-x}(EtO)_xSiH$$
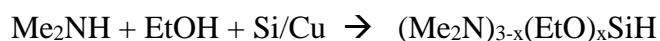
Because of the broad commercial potential of this new Direct Process of silicon, the details of this new process along with the chemistry of "tris" were intensively examined at the Tarrytown, Sistersville and South Charleston laboratories over the period from 1980 to 1985. This resulted in more than 150 patents issued in the U.S. and abroad. The details of the "tris" Direct Process are fully described in "Catalyzed Direct Reactions of Silicon", Ed. by K.M. Lewis and D.G. Rethwisch, ch. 20, Elsevier (1993). A preliminary report on the reaction chemistry of "tris" was presented at the Eighth International Symposium on Organosilicon Chemistry held the week of June 7, 1987 at Washington University, St. Louis, Mo. and published in Silicon Chemistry, Ed. by J. Y. Corey, E. R. Corey and P .P. Gaspar, Ch. 12, Ellis Horwood (1988). Much of the chemistry of "tris" related to new coupling agents or improved processes for coupling agents and is covered in that section.

(3)   Methylhydrogenchorosilanes

With the greatly increased selectivities now made possible in the Direct Process, the concentrations of methyldichlorosilane and especially dimethylchlorosilane might well be substantially reduced and could be expected to be in future short supply. Ken Lewis addressed this problem. He successfully modified the Direct Process for methylchlorosilanes to produce much larger quantities of methylchlorohydridosilanes by introducing hydrogen as a coreactant along with certain cocatalysts:

$$MeCl + H_2 + Si/Cu\ (Ni,Cr)\ \rightarrow\ MeSiHCl_2 + Me_2SiHCl + Me_2SiCl_2 + MeSiCl_3$$

Instead of being produced in quantities of 5% or less, as is normally experienced in the Direct Process for methylchlorosilanes, the addition of controlled amounts of certain metals, especially nickel and chromium causes the methylchlorohydridosilanes to be produced at levels of 70% or more. Typically, methyldichlorosilane can be made at levels of 50% or more while dimethylmonochlorosilane is obtained in quantities of 20% or more. Both methyldichlorosilane and dimethylmonochlorosilane are needed as intermediates in the synthesis of organofunctional fluids, surfactants and other copolymers The process is fully described in U.S. patent 4,973,725, (1990) by Lewis, Cameron, Larnerd and Kanner.

(C)   Coupling Agents and Other Monomers

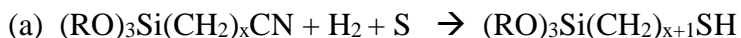(1)   New Processes for Sulfur and Amino Functional Coupling Agents

In the 1960's, the tire industry was beginning to experiment with other fillers besides carbon black for their products. Silicas were an obvious choice. For silica filled systems, a sulfur functional silane would be an appropriate choice as a coupling agent. Automobile tires then, as now, were either all black or had white sidewalls. With silica as the filler, it would be possible to
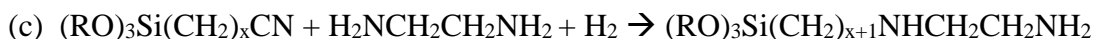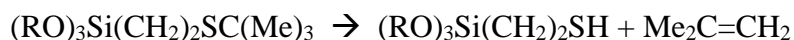
use a wide variety of sidewall colors to match the color of the car itself. None of this materialized then, but in the late 1960's the potential of such a large market justified the synthesis of a number of sulfur functional silanes. One of the first was a disilyl polysulfide which was already known in Europe:

$$2 \ (EtO)_3Si(CH_2)_3Cl + Na_2S_x \rightarrow [(EtO)_3Si(CH_2)_3]_2S_x$$

Several other good processes were also developed in Kanner's group, especially by Jeff Mui for both sulfur and amino-functional silanes:

(a) $(RO)_3Si(CH_2)_xCN + H_2 + S \rightarrow (RO)_3Si(CH_2)_{x+1}SH$

Reductive Thiolation

(b) $(RO)_3SiCH=CH_2 + (Me)_3CSH \rightarrow (RO)_3 Si(CH_2)_2SC(Me)_3$

$(RO)_3Si(CH_2)_2SC(Me)_3 \rightarrow (RO)_3Si(CH_2)_2SH + Me_2C=CH_2$

(c) $(RO)_3Si(CH_2)_xCN + H_2NCH_2CH_2NH_2 + H_2 \rightarrow (RO)_3Si(CH_2)_{x+1}NHCH_2CH_2NH_2$

Reductive Amination

Mui had found that the reduction of cyano groups with hydrogen and sulfur would yield mercapto-functional silanes in excellent yield (a). He also developed a second process for mercaptosilanes. It involved the free radical catalyzed addition of t-butyl mercaptan to olefinic silanes followed by cracking to yield the corresponding mercaptosilane and isobutylene (b). During this same period of new silane syntheses, John Kilgour, also in Kanner's group, developed an efficient process for diamino-functional silanes involving the reductive amination of cyanoalkylsilanes (c).

(2) Coupling Agent Processes Derived from "Tris"

(a) Synthesis of Trialkoxysilanes from "Tris"

With the discovery of a proprietary and economical Direct Process for the production of "tris", a major effort was launched to exploit its potential as an intermediate for a broad range of organosilicon compounds, especially coupling agents. This project began in 1979 and continued until the end of 1985. Within Dr. Kanner's group, Bill Herdle, Steve Vick, Dennis Sepelak, Steve Hopper, Curt Schilling, Rick King, Jeff Mui, Nan Chu, Ken Lewis and Jennifer Quirk all contributed to various phases of this project. Also engaged at Sistersville were Don Bailey, George Omietanski, Frank Mendicino, Barry Tan and others. Design of process equipment and economic analyses were provided by members of the South Charleston Engineering function. This massive effort led to the issuance of more than 175 patents in the U.S. and worldwide. Those aspects relating to coupling agents are reported here.

The exploration of 'tris" as an intermediate involved both reactions of the SiH and the SiN groups with the latter receiving attention first. The uncatalyzed reactions of "tris" with primary, secondary and tertiary alcohols were examined initially by Steve Vick and then Dennis Sepelak. The stoichiometric reactions with methanol and ethanol gave a broad mixture of silanes including methyl and ethyl silicate along with unreacted "tris":

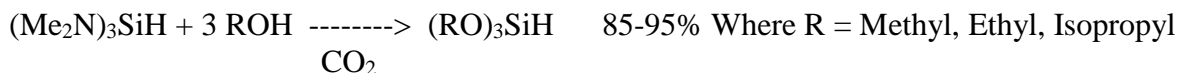$$(Me_2N)_3SiH + 3\,MeOH \quad \rightarrow \quad (MeO)_{3-x}(Me_2N)_xSiH + (MeO)_4Si$$
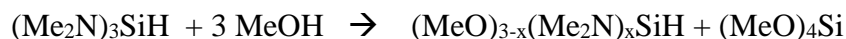
Apparently, once the first dimethylamino group was displaced, the succeeding reactions were more rapid. Reactions with isopropanol gave similar results.

Tertiary butanol, however, showed no signs of reaction even at reflux. Remembering the excellent results that Prokai had obtained using carbon dioxide as a catalyst for (AB)n copolymers, Kanner suggested its use to Dennis Sepelak. The results were particularly gratifying:

$$(Me_2N)_3SiH + 3\,t\text{-BuOH} \quad \xrightarrow{\quad CO_2 \quad} \quad (t\text{-BuO})_3SiH$$
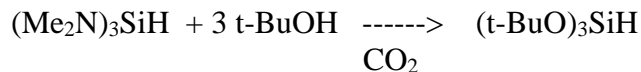
The reaction of tertiary butanol with "tris", catalyzed by a trace of carbon dioxide, was exothermic and nearly quantitative, yielding only tris(t-butoxy)silane with no silicate byproduct. Similar catalysis of primary and secondary alcohols, carried out by Sepelak and then Hopper, gave similar results:

$$(Me_2N)_3SiH + 3\,ROH \xrightarrow{\quad CO_2 \quad} (RO)_3SiH \quad 85\text{-}95\% \text{ Where R = Methyl, Ethyl, Isopropyl}$$
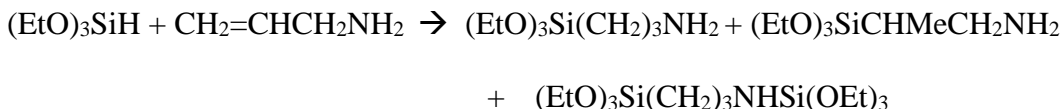
Thus a versatile process was available for the preparation of primary, secondary and tertiary trialkoxysilanes. Economically, it appeared more attractive than esterifying trichlorosilane, which was the process of choice at that time.

It had become apparent at about the same time that trimethoxysilane could also be made from the reaction of methanol with silicon although important problems over the next decade remained to be solved. The synthesis of triethoxysilane via the reaction of ethanol with silicon had also appeared in Japanese patents but was not tackled for a number of years. As for the synthesis of triisopropoxysilane and tri-t-butoxysilane, this process, involving the reaction of the corresponding alcohols with silicon, is as yet, unknown.

Other displacement reactions were also examined, establishing the generality of the alcoholysis process. Oximes and hydroxylamines reacted smoothly, showing a similar pattern of carbon dioxide catalyzed displacement reactions with "tris".

(b)   Synthesis of A-1100 from Triethoxysilane

With an effective and general process for the economic synthesis of alkoxysilanes, a broad program was then initiated to examine the general synthesis of the most important coupling agents starting from trialkoxysilanes. Nan Chu began this approach with the platinum catalyzed reaction of triethoxysilane with allylamine to give A-1100:

$$(EtO)_3SiH + CH_2=CHCH_2NH_2 \rightarrow (EtO)_3Si(CH_2)_3NH_2 + (EtO)_3SiCHMeCH_2NH_2$$

$$+ \quad (EtO)_3Si(CH_2)_3NHSi(OEt)_3$$

The reaction gave only fair yields of gamma-aminopropyltriethoxysilane (A-1100), but, more importantly, also yielded significant amounts of the undesirable beta-isomer along with some side reactions. Various other forms of platinum catalysis were examined by Nan, but to little avail. Jennifer Quirk subsequently examined the process using rhodium and other catalysts and was able to obtain much cleaner results, obtaining A-1100 that was virtually free of the beta-isomer and other side reactions.

(c)   Synthesis of A-174

gamma-Methacryloxypropyltrimethoxysilane (A-174) is another of the more commercially important coupling agents which is made starting from trichlorosilane. Nan Chu examined the synthesis of A-174 from trimethoxysilane. The laboratory and commercial production of A-174 is particularly sensitive to polymer formation. This problem is more serious when trimethoxysilane is the intermediate. Nan was able to define reaction conditions for a reliable and reproducible process. She also established most of the conditions for making A-174
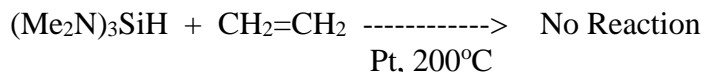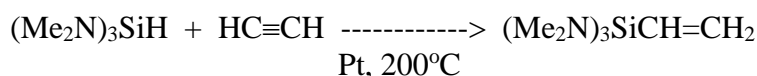
via a continuous process. The process was picked up by George Omietanski at Sistersville, where he contributed several important modifications in optimizing the final process.

There were still some important problems to be solved as in the hydrosilation of acrylonitrile or allyl chloride by trialkoxysilanes. However, it had become clear that in time virtually all of the commercially important coupling agents could be or would be made from trialkoxysilane interniediates with process economics that were superior to the trichlorosilane processes. The need for trichlorosilane as an intermediate for these silanes would thus disappear over time.

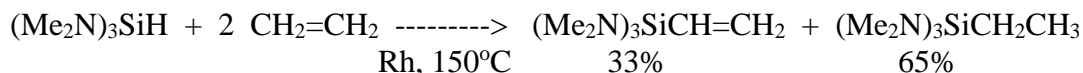(d)   "Tris" as an Intermediate for New Coupling Agents

While the preparation of coupling agents starting with trialkoxysilanes derived from "tris" was of more immediate commercial importance, the hydrosilation chemistry of "tris" itself was to prove more interesting. Jennifer Quirk, showing her usual flair for exploratory synthetic chemistry, assumed responsibility for this program. Her efforts would result in a number of novel coupling agents and other silanes as well as new insights into hydrosilation and related chemistry.

Jennifer quickly discovered that "tris" did not undergo hydrosilation with simple olefins using platinum catalysis under typical hydrosilation conditions. Even at elevated temperatures "tris" did not react with ethylene, using platinum. Under similar conditions, "tris" did react with acetylene to yield vinyltris(dimethylamino)silane:

$$(Me_2N)_3SiH \ + \ HC{\equiv}CH \ \text{------------>} \ (Me_2N)_3SiCH{=}CH_2$$
$$\text{Pt, 200}^o\text{C}$$

$$(Me_2N)_3SiH \ + \ CH_2{=}CH_2 \ \text{------------>} \ \text{No Reaction}$$
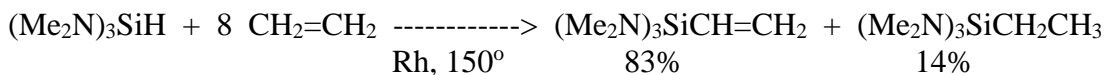$$\text{Pt, 200}^o\text{C}$$

Hydrosilation of Tris(dimethylamino)silane

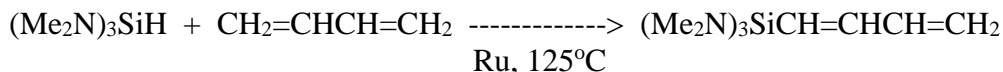In order to successfully react "tris" with ethylene, it was necessary to use rhodium catalysts:

$$(Me_2N)_3SiH \ + \ 2 \ CH_2{=}CH_2 \ \text{--------->} \ (Me_2N)_3SiCH{=}CH_2 \ + \ (Me_2N)_3SiCH_2CH_3$$
$$\text{Rh, 150}^o\text{C} \qquad 33\% \qquad\qquad 65\%$$

$$(Me_2N)_3SiH + 8\ CH_2=CH_2 \xrightarrow{\quad Rh,\ 150^o \quad} (Me_2N)_3SiCH=CH_2 + (Me_2N)_3SiCH_2CH_3$$
$$83\% \qquad\qquad\qquad 14\%$$
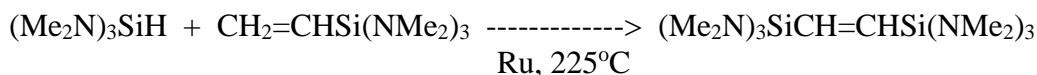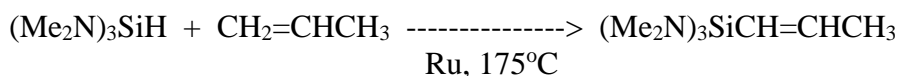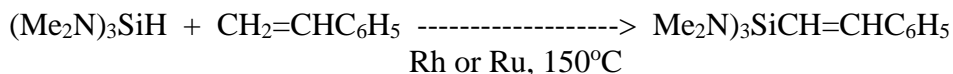
With stoichiometric amounts of ethylene, ethyltris(dimethylamino)silane was the dominant product. Large excesses of ethylene favored the formation of vinyltris(dimethyl-amino)silane. Rhodium and ruthenium were clearly catalyzing a condensation reaction rather than hydrosilation. The reaction proved to be general for olefins.

CONDENSATION REACTIONS WITH SUBSTITUTED OLEFINS

$$(Me_2N)_3SiH + CH_2=CHC_6H_5 \xrightarrow{\quad Rh\ or\ Ru,\ 150^oC \quad} Me_2N)_3SiCH=CHC_6H_5$$

$$(Me_2N)_3SiH + CH_2=CHCH_3 \xrightarrow{\quad Ru,\ 175^oC \quad} (Me_2N)_3SiCH=CHCH_3$$

$$(Me_2N)_3SiH + CH_2=CHSi(NMe_2)_3 \xrightarrow{\quad Ru,\ 225^oC \quad} (Me_2N)_3SiCH=CHSi(NMe_2)_3$$

$$(Me_2N)_3SiH + CH_2=CHCH=CH_2 \xrightarrow{\quad Ru,\ 125^oC \quad} (Me_2N)_3SiCH=CHCH=CH_2$$

The reaction path followed by rhodium and ruthenium catalyzed reactions of olefins with hydrosilanes was greatly influenced by the steric crowding around silicon.
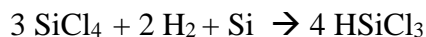
$$R_3SiH + 10\ CH_2=CH_2 \xrightarrow{\quad Rh,\ 120\text{-}200^oC \quad} R_3SiCH=CH_2 + R_3SiCH_2CH_3$$
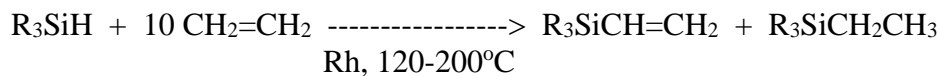
R_3SiH	Products	
Cl_3SiH	0%	96%
$(MeO)_3SiH$	26%	65%
$(EtO)_3SiH$	28%	59%
$(Et)_3SiH$	76%	18%
$(i\text{-}PrO)_3SiH$	77%	15%
$(Me_3SiO)_2MeSiH$	81%	13%
$(t\text{-}BuO)_3SiH$	92%	5%
$(Me_3N)_3SiH$	96%	3%

(3)   Trichlorosilane; Silane for Silicon Transistors

In the 1960's and 70's, UCC Silicones had been a major supplier of trichlorosilane to the manufacturers of transistor grade silicon. This market gradually disappeared as the various manufacturers began to make their own trichlorosilane.

In the 1970's solar energy received a lot of attention as a potential long term alternative to oil and natural gas. Governmental agencies sponsored research programs in support of new processes for solar grade silicon. In response to this, Don Bailey and Bill Breneman initiated such a program. They quickly developed a three step process starting with the base-catalyzed disproportionation of trichlorosilane to generate silane, followed by the recycling of the byproduct silicon tetrachloride by means of high temperature hydrogenation to regenerate trichlorosilane:

$$4 \ HSiCl_3 \ \rightarrow \ SiH_4 \ + \ 3 \ SiCl_4$$

$$3 \ SiCl_4 \ + \ 2 \ H_2 + \ Si \ \rightarrow 4 \ HSiCl_3$$

$$SiH_4 \ \rightarrow \ Si \ + \ 2H_2$$

The second step of the process was based on earlier work of George Wagner. The final step involved the thermolysis of silane yielding high purity silicon metal. The "closed loop" process proved to be very efficient and produced silicon metal that was significantly higher in purity than the Siemens process. The program ultimately graduated, largely through the efforts of Jim Lorenz, from Silicones, where it lacked support, to Linde. From there it was put into production, with the considerable aid of Bill Breneman, who left Silicones to pursue this project, becoming Chief Design Engineer for the new plant, which is in operation at Moses Lake, Washington. The successful operation of this process/plant led to the first Kirkpatrick Award for the organization and its variously named successors.

(D)   Fluids

Silicone fluids continued to be dominated by the sale of commodity products. Receiving increasing attention were the organofunctional fluids, silicone-polyether copolymers for non-polyurethane foam applications and silicone fluids containing both organofunctionality and polyether groups. These specialty fluids, although the focus of much R&D, made only minor contributions to the overall sales of silicone fluids during this period.

(1)   Antifoams

The most important antifoam products continued to be silicone fluids containing small amounts of high surface area silica. Understanding of defoaming mechanisms and the role of high surface area silica were at a primitive level and remained so until Ravi Kulkarni joined Kanner's group after receiving a Ph.D. in surface chemistry from Columbia University. Ravi began fundamental studies on antifoam behaviour. The excellent progress being made was continued when he and Mike Rosen transferred to Des Goddard, who had joined UCC Silicones to form a Surface Chemistry Skill Center.

Although silicone oil/silica combinations were and remain the most effective antifoams for most purposes, there are foaming systems that can be effectively treated with certain silicone-polyether copolymers. Fermentation systems are an excellent example. Fermentation processes to produce certain drugs and other products are frequently accompanied by excessive foaming. Conventional antifoams can be used but they are inferior to certain copolymers. Silicone-polyethers, which have cloud points below room temperature, are especially desirable to control foaming in fermentation reactors. They are foam control agents rather than antifoams in that they limit rather than eliminate foam. Their most important property, however, is that they enhance oxygen transmission thereby increasing the productivity of the fermentation process.

(2)   Silicone-Polyether Copolymers for Non-Polyurethane Applications

The use of silicone-polyethers for foam control agents in fermentation processes was one of the first to be explored in an effort to broaden the usefulness of these copolymers. Over time, these surfactants, along with other copolymers were modified with amino, epoxy and other organofunctional groups, and were developed for applications such as coating additives, cosmetics and personal care, pulp and paper, textiles, polishes and agriculture. The technology supporting these efforts grew out of R&D activities in Coupling Agents and Polyurethane foam.

(3)   PCB Transformer Retrofill

Polychlorinated biphenyls were widely used in the 1960's and 70's as heat transfer fluids. They were used in many electrical transformers for this purpose. When the carcinogenic properties of PCB's became recognized, ways were sought to eliminate this use. Dick Atwood and others at Tarrytown sought to develop a procedure to flush PCB filled transformers and to fill them with silicone fluids. An efficient process was developed which filled transformers with silicone fluid leaving only trace levels of PCBs. This activity was eventually spun off as a separate business to service these electrical transformers under the Unison name.

(4)   Iron Oxide Stabilized Oils

Polydimethylsiloxane silicone oils have excellent oxidative and thermal stability compared to most hydrocarbon based polymers. However, these silicone fluids will oxidize rapidly and gel at service temperatures of 200ºC or higher. Silicone oils derived from phenylmethylsiloxane units have superior oxidative stability and can withstand temperatures up to 250ºC. These more stable fluids are substantially more expensive to manufacture, however.

Attempts to improve the oxidative stability of methylsilicone based fluids have centered around the introduction of various antioxidants. The most effective of these was a mixture of iron oxides. The iron oxides were introduced through a cumbersome method involving the addition of iron salts of fatty acids followed by the removal of the organic residues through air oxidation. The process, though effective, was tedious and left the iron oxides in the form of an unsightly sludge. To solve this problem, Bob Neale, a fine organic chemist who had transferred from the UC Research Institute to join Kanner's group, explored several alternative techniques to introduce iron oxides into silicone oils. The first approach proved to be quite successful. Iron pentacarbonyl, added to silicone oils at very low concentrations, was thermally decomposed and oxidized at relatively low temperatures. The result was a stable dispersion of colloidal iron oxides. The stability of polydimethylsilicone fluids was increased to many hundreds of hours at 250ºC using iron oxides at levels of 100 parts per million. The colloidal dispersions of iron were stable indefinitely and gave silicone fluids an attractive burgundy color.

(E)   Elastomers

UCC Silicones attempts to develop a viable silicones elastomers business lasted until about the early 1970's. Prominent in this activity were Milt Dunham, Dave Braun and Warren Crockwell in Product Development, Tom Williams and Charlie Creamer in Research, Jim Lorenz in Tech Service and Dick Kayser as Product Manager.

An opportunity to establish a position in RTV cured elastomers was missed early on because of the mistaken belief that the market would be too small to be of interest. A number of other innovative elastomer products were developed both in Research and Development which resulted in some limited successes. As a relative latecomer, the UCC silicone elastomer effort had to scramble to catch up. This was considerably complicated by the need for close coordination between Research, Product Development, Process R&D, Technical Service and Customer requirements, while maintaining control of economics. A particularly daunting problem were the difficulties in scale-up from the laboratory to plant production of specification grade products. In retrospect, this effort might have been successful with a combination of some additional patience, and, more importantly, a more tightly focussed effort limited to specialty, higher margin products.

Final Events - A Summing Up

UCC Silicones had evolved by 1980 into a largely specialty products manufacturer, more through happenstance than design. During this time, there had been no formal strategy other than the 5 year plan drawn up in 1965 (and which was quickly abandoned). The decision to build a world class methylchlorosilane plant was not the logical outgrowth of any existing strategy. It was justified by a projected expansion of UCC's commodity fluids business rather than any significant growth of its specialty fluids position. Thus, the decision to make the largest investment in its history was not to support its strengths but rather to support a business where it was a minor player.

The new methylchlorosilane plant had gone through a two year shakedown period. In spite of many earlier problems, the plant was finally producing methylchlorosilanes with rates and selectivities that exceeded plant specifications and laboratory results. The hydrolysis unit was equally proficient, producing hydrolyzate containing 80% or more cyclics. The decision to shut the plant down was therefore not based on any performance deficiency.

The period was a very difficult one for Union Carbide. There was the Bhopal disaster in 1984, which placed further plant incidents and safety problems under intense scrutiny by the press. There was the understandable desire to avoid, at almost any cost, any further potential releases of hazardous materials. The new methylchlorosilane plant, because of the nature of its products and its location near a high population center, was closely scrutinized. The decision was then made to shut the plant down. The raw material intermediates needed for UCC Silicones products could be purchased from other major silicones manufacturers. The plant shutdown and its associated investment loss, however, created serious doubts as to the desirability of retaining silicones as part of UCC Chemicals business. In 1985, it was once again merged with a much larger unit, the Specialty Chemicals Division.

Synopsis – 1985-2000

After the closing of the Direct Process plant, changes took place in the UCC Silicones top management and it received a new name, OSi. OSi was eventually sold to the investment bankers, Donaldson, Lufkin, and Jenrette (DLJ) in 1993, and prospered as an independent business, allowing DLJ to do the same by selling OSi to Witco in 1995. Witco joined Crompton & Knowles in a 1998 merger, with the combined CK Witco being renamed Crompton Corporation in 2000.

During the 1985-2000 period, numerous changes also occurred in the R&D organization. Research efforts acquired more customer focus and R&D objectives became more aligned with those of the various business segments. Larry Jarrett became the Research Director, with facilities at Tarrytown, Sistersville, South Charleston, and Geneva. The basic/exploratory group of B. Kanner at Tarrytown ceased to exist, as did the surface science group of D. Goddard, aided and abetted by an attractive early retirement program. The Applications portion of the urethane foam surfactants R&D effort shifted from Tarrytown to South Charleston, concurrent with the Union Carbide divestiture of its polyols business in the late 1980's.

The more focussed R&D effort contributed to continuation of the company's historical dominance of the organofunctional silanes and urethane foam surfactants businesses, with silicone fluids maintaining strength in specialty areas. Other pretenders to becoming viable businesses received attention for substantial time periods, but faded under the harsh lights of economic reality. These included the preceramic polymer effort, federally funded for eight years, and ultimately licensed. Also, Plastics Additives Systems (PAS), which was formally a Union Carbide business with a broad silicone/silane product portfolio, was formed and then reabsorbed by the organofunctional silanes area.

The specifics of technical successes in 1985-2000 can not be presented in the same detail as earlier work since such discussion leads to proprietary sensitivities and involves unexpired patents. The greatest effort and the greatest success both relate to the production of trimethoxysilane from silicon metal and methanol , and downstream products from trimethoxysilane, for which this organization received its second Kirkpatrick Award. Other general areas of fundamental or commercial significance include:

-       Silicon-containing Automotive Topcoats

-       New/Known Sulfur Silanes for Silica-filled Tires

-       Continuous Hydrosilation Processes

-       New Aminosilanes

-       Difunctional Silanes

-       Waterborne Silanes

-       Trisiloxane Agricultural Adjuvants

-       Fundamentals of Silane Hydrolysis and Condensation

-       CASelects/Organosilicon Chemistry

-       High Yield Hydrosilation of Allyl Chloride

The future likely holds as much change as the past few years, and as much unpredictability.