THE HISTORY OF CHEMISTRY IN DOW CORNING

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Diverse Interactions – The Elements of Success
Caveat: Important work outside Dow Corning is left out!
The chemical elements and their periodic relationships
MORE CAVEATS

• I have “borrowed” shamelessly from others – especially Earl Warrick’s “Forty Years of Firsts.”

• Many thousands of people have made important contributions to the history of chemistry in Dow Corning. Unlike a good scientist, I have “selected” examples to fit my hypotheses.
MORE CAVEATS

Much of the early chemistry at Dow Corning has been documented (at most) only in proprietary, internal reports.
PHILOSOPHICAL QUESTION #1 TO PONDER DURING THIS TALK

How did diverse interactions among people, institutions, and cultures lead to today’s Dow Corning?
PHILOSOPHICAL QUESTION #2
TO PONDER DURING THIS TALK

What has driven innovation at Dow Corning in the past and what will in the future?
MY PROPOSAL FOR PAST DRIVERS OF INNOVATION AT DOW CORNING

• Military needs.
• High performance analogs.
• Environment, health, and safety.
• Cost and quality.
FORMAT FOR TODAY’S TALK

• Decade by decade perspective.
• Philosophical and psychological views.
• Outside advances in science and technology.
• Advances in Dow Corning.
• People.
• Comments about interactions.
THE 1930’s
1930’s SOUP KITCHEN
FDR SAYING THE GAME MUST GO ON
Dr. Eugene Sullivan, Director of Research at Corning, conceived that a good chemist should be able to marry brittle, inorganic, glasses with ductile, organic, resins.
Frank went into the laboratory and showed that silicon—carbon bonds were a feasible route to link organic and inorganic materials.
KIPPING’S GRIGNARD SCHEME

$\text{(C}_2\text{H}_5\text{)}\text{Br} + \text{Mg} \rightarrow \text{(C}_2\text{H}_5\text{)}\text{MgBr}$

$\text{SiCl}_4 + \text{MgBr(C}_2\text{H}_5\text{)} \rightarrow \text{MgBrCl} + \text{(C}_2\text{H}_5\text{)}\text{SiCl}_3$

$\text{(C}_2\text{H}_5\text{)}\text{SiCl}_3 + \text{MgBr(C}_2\text{H}_5\text{)} \rightarrow \text{MgBrCl} + \text{(C}_2\text{H}_5\text{)}_2\text{SiCl}_2$
HERE IS A SLIGHTLY LATER EXAMPLE FROM HYDE

\[ \text{n-C}_{18}\text{H}_{37}\text{MgCl} + \text{SiCl}_4 \rightarrow \text{n-C}_{18}\text{H}_{37}\text{SiCl}_3 \]

FRANK HYDE RECOGNIZED AS FATHER OF SILICONES

• In later years, Frank was inducted into the Inventors’ Hall of Fame in Akron both for silicones for Dow Corning and for key chemistry for opto-electronics at Corning.

• And, the American Chemical Society recognized the work with a prestigious Perkin Medal.
The concept of mixing scientific and technological disciplines started early when Ken Johannson, a physical chemist, joined Frank Hyde to look at applications for the special surface chemistry properties of silicones.
Quote from Hyman Rickover (U.S. Navy) with regard to Frank Hyde’s 990A Resin for use with fiberglass in a tape for motors and wires in submarines: “Now you’ve got something. I want it tomorrow!”
THE 1940’s AT DOW CORNING
U.S. SOCIETY IN THE 1940’S

• Minimum wage was $.43/hour.
• 55% of homes had indoor plumbing.
• The Jitterbug became a popular dance.
• Rosie the Riveter was the symbol of the working woman.
AND, MORE IMPORTANT TO DOW CORNING…

• The impossibility of isolationism for the U.S. was becoming obvious when viewing war-related activities.
• The war was also driving the need for new materials – as well as the need for substitutes for old ones. Chemistry was not in the shadows.
1945 Kurt Lewin formed the Research Center for Group Dynamics at MIT to perform experiments in group behavior.

1948 the research center moved to the University of Michigan and became a branch of the Institute for Social Research.
Bill Collings and Shailer Bass (both also prominent in later history) developed silicone research at Dow Chemical.
A joint venture was developed between Dow Chemical and Corning Glass – first with a handshake and later (1943-1944) – well after first product – official legal documents were prepared.
THE FIRST PRODUCT

Dow Corning 4 Compound, found to stop arcing on aircraft ignition wires, was developed before incorporation.

The synthesis reaction involved a cyclic siloxane pentamer catalyzed with aluminum trichloride
PROCESS CHEMISTRY TO BROADEN POSSIBILITIES AND REDUCE COSTS

The early Grignard process for formation of silicon carbon bonds was flexible but expensive.

Academic and industrial advancements elsewhere caused Mel Hunter and Art Barry at Dow Chemical to direct their research work toward application in Midland.
ANOTHER GRIGNARD EXAMPLE

$\text{HSiCl}_3 + \text{PhMgBr} \rightarrow \text{Ph}_2\text{HSiCl}$

CHARACTERIZATION OF SILOXANE BOND

Infrared spectroscopy showed a strong Si-O-Si band at 1100-1020 cm\(^{-1}\).

Dr. Mel Hunter—one of Dow Chemical's Cellosolve Researchers assigned to the silicone field. He later became Vice President and Director of Research at Dow Corning where his optimism for the future of silicones never faded.

Rick Ray McGregor was in charge of a group working on adhesives for glass brick at Malton Institute in 1937. McGregor also supervised original silicone research projects at Malton and was instrumental in bringing the silicone rubber product to Medical Research.

Dr. Eugene Sullivan was Director of Research for Corning Glass Works when he became Dow Corning’s first President. Sullivan served as President through 1964.

Working with Dr. Rick Ray McGregor at Malton Institute, Dr. Mel Hunter helped develop the intercostal sutures and became the medical device that became the foundation for Corning's original operation. With 40 patents, Dr. Warren may be best known for inventing silicone rubber.

Earl Warrick showed that polydimethylsiloxane could be reacted with organic peroxides leading to free radical crosslinking.

Just as Goodyear vulcanized polyisoprene with sulfur, Warrick’s technology allowed permanent memory of fabricated rubber.
Much later, in 1976, Warrick received the Charles Goodyear Award from the Rubber Division of the American Chemical Society.
MUCH WORK FOCUSED ON Si-C FORMATION

Art Barry played a key role in the use of a “pseudo-Friedel-Crafts reaction to attach phenyl to silicon. (U.S. Patents 2,510,853 and 2,556,462).

Later Barry and John Speier found conditions for platinum compounds catalyzing Si-H reactions with –C=C.
ALSO, ROUTES TO Si-O-C BECAME IMPORTANT

For example, Speier made discoveries relating to methods for achieving the following:

Si-Cl $\Rightarrow$ Si-O-C

Later, John Speier was recognized for this work by being named “Scientist of the Year” by “Industrial Research” magazine in 1977.
ACADEMIC PARTNERSHIPS IN THE 1940’s

A strong relationship with Penn State was initiated that resulted in many PhD scientists at Dow Corning:

- Les Tyler
- Keith Michael
- Marty Musolf
- Don Weyenberg
- Cecil Frye
- Forrest Stark
This talk is not really about engineering advancements, but it be unfair not to mention clever work by both engineers and scientists to make lab reactions into practical processes.

One famous reactor acquired the name “Big Bertha”
1940’S PROCESS TECHNOLOGY
CONCLUDING COMMENTS
FROM THE 1940’S

Much later, at the end of the twentieth century, it was broadly recognized that partnering among organization was essential.

The formation of Dow Corning in 1943 provided food for thought.
In the early 1950s, Dow Corning had a traveling exhibit that toured the U.S. Featuring the many applications of silicones, it was manned by Wayne Sanderson, George Webster and Bud Smith. (1952)
OPTIMISM ABOUT THE FUTURE

The free world must not prove itself unworthy of its own past.

Dwight D. Eisenhower
CARS OF THE 1950’S
BUSINESS PHILOSOPHY/PSYCHOLOGY

• 1954 Peter F. Drucker outlined his Management by Objectives (MBO) approach

• Late 1950's: Douglas McGregor proposed his Theory X and Theory Y assumptions of the relations between employees and organizations
IMPORTANCE OF NANOMATERIALS IN THE 1950’S

Les Tyler and Chuck Lentz kicked off an extensive effort to control the morphology of silica, synthesized from chlorosilanes and silicates, to optimize silicone elastomers.

U.S. Patent 2,676,182  (1954)
Tyler’s understanding of the importance of silanol on silica’s surface may have been tied to other interests in silanol chemistry, e.g.

\[ \text{H}_5\text{C}_6\text{-Si(OCH}_3\text{)}_3 \rightarrow \text{H}_5\text{C}_6\text{-Si(OH)}_3 \]

SILICONE ELASTOMERIC SEALANTS

Many contributed to the concept of a sealant that would be an extrudable putty and convert to a cross-linked elastomer at room temperature. A system cross-linked with ethyl silicate was patented by Frank Hyde in 1951.

U.S. Patent 2,571,039 (1951)
ORGANOFUNCTIONAL SILANES

In the 1950’s, John Speier, working with a number of other scientists, found techniques for making “organofunctional” silanes and siloxanes – with a wide variety of functional groups attached to silicon atoms directly or with carbon atoms in between.

These found use as coupling agents, adhesion promoters, drugs,....
AN EARLY EXAMPLE FROM SPEIER

PhSiH$_3$ + CH$_2$=CH(CH$_2$)$_9$NHSiMe$_3$ ➔

PhH$_2$SiC$_{11}$H$_{22}$NHSiMe$_3$

Speier, J.L., Zimmerman, R., and Webster, J., J. Amer. Chem. Soc. 78 (1957) 2278
SOLVENT RESISTANT SILICONES

In the late 1950’s, work outside Dow Corning caused people to think about solvent resistance of silicones.

- Ogden Pierce
- Eric Brown
- George Grindahl
- Yung Kim (later)
The 1960’s
ANALYTICAL TECHNIQUES

The first principle is that you must not fool yourself - and you are the easiest person to fool.

-- Richard Feynman
NEW SCIENCE DIRECTIONS IN THE 1960’S

• The 1960’s were years when questions were asked about the implications of science.

• And, at the same time, the analytical tools allowed scientists to see and measure what had to be hypothesized in the past.
SEEING AND MEASURING

We could actually measure molecular weight distributions, analyze end groups on polymers accurately, see where filler particles were in elastomers. Analytical scientists like A. Lee Smith took on new importance.
A. LEE SMITH

The Analytical Chemistry of Silicones

Edited by
A. Lee Smith
LIBRARY SCIENCE

Information scientists like Anna Colman gave Dow Corning a special competitive advantage using technology to sort and find needles in haystacks.

Anna liked to talk about her history when the soldiers returned from the war.
CAPITILIZING ON PRECISE MOLECULAR DESIGN

Keith Polmanteer and others showed how silicones could be made much stronger with precisely placed cross-links, controlled mixtures of molecular weight distributions, specialty fillers, and controlled interaction between polymer and filler.

ABILITY TO STICK ANYTHING TO ANYTHING

Ed Plueddemann developed a reputation for predicting and synthesizing the right silane for making anything stick to anything else. Ultimately, he was inducted into the Plastics Hall of Fame for this work.

ED PLUEDDEMANN
EMULSION POLYMERIZATION

Although the rubber fabrication lab joked about having a silicone rubber tree in their office area, most give credit to Don Weyenberg, Don Findlay, and later John Saam, among others, for ground breaking work on ring opening and condensation emulsion polymerization of siloxanes.
1000<sup>th</sup> PATENT APPLICATION FOR DC’S 20<sup>th</sup> ANNIVERSARY
1960’S CONCLUSIONS

This was a time when scientists and technologists more and more realized their worlds were converging – and that success depended on information flowing both ways.
The 1970’s
1970’s MORRIS MASSEY TAPES

“What You Are Is Where You Where When”

Dow Corning started early addressing values, diversity, generational conflicts, and gender.
DOW CORNING AS A GLOBAL COMPANY

Early in its history, Dow Corning appreciated the importance of using its technology to promote global sales and manufacturing.

In the 1970’s, special emphasis was given to two way flow of technology.
GLOBAL TECHNOLOGY SHARING

John Saam took block anionic copolymerization science with him to Wales in a research exchange initiative.

Tom Kendrick brought polyolefin copolymer and cross-linking science with him from Wales to Midland.
HYBRID POLYMER EMPHASIS – A PRECURSOR TO “SILICON-CONTAINING MATERIALS”
Not only were national boundaries being crossed, but much research was expended on breaking down the barriers between organic and inorganic polymers. Chi Long Lee and Gerry Gornowicz explored routes to copolymers for gas separations medical uses.
APPLICATION ORIENTED RESEARCH

The exploration of diverse science relating to applications intensified. Hal Clark, Mike Owen, Ron Baney, Keith Michael, and many others got involved in surface and optical properties of silicones for contact lenses and scratch resistant coating. And, they laid the ground work for much later work on optical materials for data transmission, optical amplification, and optical switching.
MIKE OWEN
THE 1970’S EXPANDED DOW CORNING’S SCIENCE BOUNDARIES
THE 1980’S

Environment, Health, and Safety Often the Driver of Innovation
MILESTONES IN AMERICAN CHEMICAL SOCIETY HISTORY

- **1980** The Comprehensive Environmental Response, Compensation & Liability Act (Superfund) is passed.
- **1985** Responsible Care program begins in the U.S. based on Canada's program.
DOW CORNING’S EHS HISTORY

Throughout its history, Dow Corning had realized that the inertness of its materials meant that devices made from them would last and that they should be relatively harmless to people and the environment.
A PROACTIVE DOW CORNING

Scientists like Chuck Lentz, however, started to realize that a general feeling of comfort was not enough and that we needed to start collecting scientific data. Cec Frye and Tom Lane started working on the ultimate fate of silicones in the environment.
CEC FRYE IN THE 1950’S – ORGANOSILICON BACKGROUND LED TO EHS INTERESTS IN THE 1980’S
NEW APPLICATIONS FOR CHEMISTRY

Solvent solutions were replaced with emulsions. Sealants were introduced with more benign cross-linking chemistry. Jerry Klosowski and Sam Brady became famous for marrying the chemistry of the past with the new needs.
GOVERNMENT PARTNERSHIP ON CERAMICS

Newly hired ceramics scientists and old time scientists from other fields, such as Bill Atwell and Jon Lipowitz, played key roles in manipulating synthesis, structure, and properties – as well as understanding the interrelationships.

By far the largest technical project funded externally.
CONCLUSIONS FROM THE 1980’S

Environment, health, and safety drivers catalyzed a tremendous amount of innovation.

But, there also started to develop an understanding of life cycle responsibilities as well as the need to look at risks and associated costs.
THE 1990’S
ACCELERATED CHANGE

"...in a world where outrageous is the norm, stable sensible organizations make no sense."

Tom Peters, May 1994
Partnering
CROSSING SCIENCE & TECHNOLOGY BOUNDARIES

Dow Corning’s chemists and chemical engineers found themselves often working on teams with physicists, metallurgists, electrical engineers, biologists, etc.

Udo Pernisz was showing up on publications about materials for non linear optics. Tom Lane was in the news for activities leading to a later alliance with Genencor.
1990’S A TIME FOR PURPOSEFUL CULTURE CHANGE

Dow Corning listed prominently for leader in culture change.
OVERALL CONCLUSION #1

Yes, diverse interactions among people, institutions, and cultures have led to many aspects of today’s Dow Corning.
OVERALL CONCLUSION #2

Yes, the drivers of innovation in the past will drive innovation in the future:

– Military needs
– High performance analogs
– Environment, health, and safety
– Cost and quality
Innovation will continue to become done in a more purposeful way.

– Scenario planning
– Modeling
– Interacting outside of the company
– Structured innovation
– Work flow analysis
– Designed disorder
CONTRIBUTORS

• Phil McCullough (Pictures)
• Earl Warrick’s book
• Many colleagues
• Those whose past is no longer private thanks to Google