FluoroConsultants Group, LLC

Roy Plunkett's World

Every story about fluoropolymers begins with the serendipitous discovery of Roy Plunkett in 1938 when he inspected a small cylinder of tetrafluoroethylene and found no pressure. He was trying to develop fluorinated refrigerants for automobiles and other uses. He had the cylinder cut open and found a white powder which was characterized and found to be polytetrafluoroethylene. The rest is history.

The first time I heard the story I was not sure whether it is true or not because a lot of tales transform over time with the real story getting lost. I went looking for the story and found out there was a lot more to the story and the world in which the discovery was made. I am going to tell you about personalities and events in Roy Plunkett's world.

Roy came from a poor farm family in New Carlisle, Ohio. He went to Manchester College in North Manchester, Indiana just when the Great Depression was starting. Roy shared a room with an older student named Paul. Roy graduated with a bachelor of art in chemistry in 1932 and followed Paul to graduate school at the Ohio State University. Roy and Paul both earned masters and PhD degrees from the Ohio State University within two years of each other. Roy joined the DuPont Central Research in 1936 where Paul had been working since 1934. Paul was working for Wallace Carothers, the inventor of nylon and neoprene, in the nascent field of synthetic macromolecules.

Roy Plunkett went to Kinetic Chemical Co., a joint venture that DuPont and General Motors had set up to produce safe refrigerants to replace ammonia and sulfur dioxide. Roy was given a laboratory in DuPont's Jackson Laboratory on the shore of Delaware River in Deep Water New Jersey. Roy's laboratory was across the hall from Charlie who was a young chemist and had a strong interest in synthesizing new organic compounds. Roy was trying to expand the line of fluorocarbons known as Freon® for the explosive growth of automobile production at GM.

It must have been exciting to be involved with polymers during late 1930's. The field of polymer science was taking shape at the academic and industrial centers. There were heated arguments at technical meetings where opponents and proponents of various theories on polymer argued over the finer points of their beliefs. They could have sold tickets to these meeting so that people could hear Herman Mark, Karl Meyer and Herman Staudinger passionately debate the principles of polymer science. Everyone finally agreed with Staudinger and Carothers hypothesis: Polymers are not aggregated collections of small molecules but long chains of small molecules linked by covalent bonding.

Mark, Meyer and Staudinger ended doing quite well. Meyer stated the rubber-like elasticity theory in 1932. Staudinger published his influential book *Die Hochmolekularen Organischen Verbindungen, Kautschuk und Cellulose* in 1932. (High Molecular Organic Compounds, Natural Rubber and Cellulose). He received the Nobel Prize for chemistry in 1953. Herman Mark and Meyer published Hochpolymere Chemie in 1940 (Natural and Synthetic High Polymers, 1942). You may have heard of Mark-Houwink equation and the brilliant tenure of Professor Mark at the Polytechnic University in Brooklyn, New York.

On April 6, 1938 on the day that Roy Plunkett found the TFE cylinder without pressure, there was a small commotion in his lab. What was this slippery white powder? He had time and presence of the mind to pause and ask the question. There was no relentless pressure to meet next month's deadline because people understood success in research needed a low stress work environment. At any rate, Charlie came to Roy's lab when he heard the racket that the occupants were making. He later said, "On another occasion, at Jackson Laboratory, across the Delaware River in New Jersey where I worked, I noticed commotion in the laboratory of Roy Plunkett, which was across the hall from my own. I investigated and witnessed the sawing open of a cylinder from which was obtained the first sample of Teflon® fluoropolymer." These are words that I have taken from Charlie Pederson's 1987 Nobel Lecture. You see Charlie invented new crown ether compounds and was awarded the Nobel Prize for it in 1987.

Roy Plunkett sure lived in heady times. Before long after his 1938 discovery the world would be engulfed in the bloodiest battles ever fought in the human life. World War II was looming in the picture. Of course, the polymer that Roy had found was not useful for much of anything because it melted at over 340˚C and when it did melt it just sat there in a ball of clear gel and would not flow. The polymer did not dissolve in anything and did not seem to react with any acid, base or solvent that people tried. It was not at all clear whether any one would ever find use for this intractable slippery powder. Nonetheless Paul was rewarded for his curiosity and moved out of refrigerant business into a management role for manufacturing of a very successful chemical, *tetra ethyl lead*. That is right, the old poisonous octane booster which has been phased out for some time now.

The circle of Roy's contemporaries began falling apart just like the peace in Europe. In 1937 Wallace Carothers, the gifted Harvard Chemist who has been wooed to DuPont for frontier breaking research, died prematurely. He did not share the 1953 chemistry Nobel Prize with Staudinger only because this prize is not awarded posthumously. He not only invented nylon and neoprene but advanced the field of polymer science. Roy's roommate at Manchester College and Ohio State, Paul, left DuPont in 1938 for the University of Cincinnati, later Exxon Corporation, Goodyear Tire and Rubber Company, Cornell University, Mellon Institute and Stanford University. Paul Flory, an Illinois boy and the son of a clergyman, was awarded the Nobel Prize for chemistry in 1974.

War time needs rescued Roy Plunkett's discovery from oblivion. At the time the Manhattan Project was a secret program aimed at beating the Nazi Germany in the development of atom bomb. The project was headed by General Groves who was an extremely competent and dedicated man. He was always looking for new materials to meet the novel need of the Manhattan Project. General Groves heard about PTFE properties and its resistance to different chemicals. The Project badly needed corrosion resistant materials for the uranium enrichment process. U-235 (0.7% atomic) had to be separated from U-238 using differential diffusion of UF_6. Now a-days thousands of centrifuges are used for separation of the two isotopes. UF_6 is highly corrosive, even to most metals while PTFE stands up to it. Upon verification PTFE was placed under a national "Secrecy Order" by the US Patent Office. Only one patent with little content was issued to DuPont to recognize its rights to the invention in 1941.

The next time that PTFE was heard about was after the war in 1946 under the now famous trademark of Teflon®. Du Pont had learned a great deal from the intense effort to produce PTFE for the Manhattan Project. It was now ready to move from the pilot plant to a commercial manufacturing operation. The end of World War II had freed resources devoted to the effort and the focus was shifted to meeting the unending needs of the US and the world.

Roy Plunkett began to receive the recognition that his discovery deserved after applications were developed for PTFE and copolymers of TFE in the 1950's and 1960's. DuPont had a major celebration at the 25th anniversary of the discovery of Teflon® in 1963. Roy Plunkett received innumerous honors and was toasted by the world in 1988 at the 50th anniversary of his discovery. Dr Plunkett's own words describing the impact of his discovery are the most fitting tribute that we could pay to him.

"*The discovery of polytetrafluoroethylene (PTFE) has been variously described as (1) an example of serendipity, (2) a lucky accident and (3) a flash of genius. Perhaps all three were involved. There is complete agreement, however, on the results of that discovery. It revolutionized the plastics industry and led to vigorous applications not otherwise possible.*" (From speech at American Chemical Society Meeting, New York, April 15-18, 1986)

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