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An Accidental Discovery: Teflon (Polytetrafluoroethylene)

A Brief History

Polytetrafluoroethylene (PTFE), more commonly known by its DuPont trademark Teflon, is a polymer in extensive use all over the world. The discovery of Teflon was an example of divine providence.[7] Dr. Roy Plunkett had been hired by Kinetic Chemicals to find a fluid suitable as a refrigerant. Plunkett had chosen a synthesis pathway that required a reaction of tetrafluoroethylene (C_2F_4) with HCl to produce a desired refrigerant, $CClF_2CHF_2$.[7] On April 6th, 1938, when Plunkett's assistant tried to empty a cylinder filled with gaseous tetrafluoroethylene (TFE), the flow-meter was not registering any outflow. The weight of the container, however, indicated that TFE remained in the cylinder. Plunkett used a hacksaw to slice the container open. On the interior of the container was a white waxy powder.[7]

Immediately after the discovery Plunkett and other DuPont chemists went about identifying the waxy powder. They discovered that the white waxy substance was a polymer, a repeating chain of chemical units, with a wide variety of unusual properties. PTFE was chemically inert, not reacting with any acids, bases, or solvents.[7] PTFE did not degrade upon heating; it was stable to 300ºC for extended periods of time. PTFE was a good insulator with a low coefficient of friction.[3]

Its chemical structure explains why PTFE is inert; the Carbon-Fluorine bonds present through polymer are very strong, protecting the polymer from any chemical interaction.[8] PTFE showed promise in heavy industry, chemical handling, and electronics acting as a lubricant, non-reactive coating, and insulator respectively.[1-4, 8] PTFE'S discovery coincided with the outbreak of World War II; the US government classified PTFE's patent records, ensuring that Axis powers would not have access to the useful compound.[8]

First Applications

In the race to build an atomic weapon, it was necessary to separate fissionable Uranium from its less fissionable isotope through a process using UF_6, an extremely corrosive gas.[4] PTFE's high resistance to corrosive materials made it the perfect reactor liner for this separation process. Large quantities of PTFE were manufactured to serve as a lining for the separation process.[4, 8] PTFE played a major role in the race for the atomic bomb; without it, the US would have been severely handicapped in its attempts to create a nuclear weapon.

Plunkett was granted a patent for PTFE in 1941.[7] After World War II, PTFE was quickly incorporated into everyday life: PTFE served as everything from an insulator, a lubricant, and non-stick cookware.[8] PTFE and the techniques to produce it were further developed to serve heavy industry; suspensions of PTFE, for example, were employed as lubricants for large pieces of machinery. PTFE served as a cost-effective lubricant or joining piece in machinery. PTFE was relatively expensive to produce in the 1950s; this cost was, however, countered by PTFE's low rate of degradation.[8]

Due to its novel chemical characteristics of inertness and low coefficient of friction, PTFE found widespread use as a coating on cookware.[4] Non-stick cookware was met with widespread approval and quickly sold out.[7]

The First and Only Choice

Outer space is a harsh and unforgiving environment; low temperatures render most substances useless as their chemical properties are only stable within terrestrial temperatures and pressures. However, in outer space, PTFE has come to the rescue. Materials were needed to create impermeable seals so that astronauts would not be exposed to the vacuum of space; rubber, which was unsuitable as it becomes brittle at cryogenic temperature, was replaced by Teflon seals and joints on space suits.[2] Due to its low thermal conductivity, PTFE is also used as an insulator on the space shuttle.[2]

Many structures are subject to environmental degradation. For example, bridges are subject to rusting, especially when near an ocean or building materials can disintegrate from the high heat and UV radiation present in the desert. One novel solution for preventing corrosion is illustrated by the use of PTFE in the Statue of Liberty.[2] The Statue of Liberty is made of copper covering steel; it is subject to extensive corrosion because it is situated close to the sea. To prevent the inner stainless-steel structure from corroding, a layer of PTFE is inserted to serve as a barrier to corrosion.

PTFE can strengthen materials that alone, cannot act as building materials, heightening their heat resistance and lowering their electrical conductivity. Fiberglass is a versatile building material that can be made into a cloth-like fabric. When coated with PTFE, this fabric meets building codes because it is stable and flame-retardant; as a result, structures such as the United Kingdom’s Millennium

Dome have been constructed from this PTFE-dipped fiberglass, providing stunning architecture not possible with other materials.[6]

Because it has high heat resistance and low electrical conductivity, Teflon is a good insulator for electrical wiring. Because PTFE does not burn easily, it does not pose a risk in starting electrical fires. PTFE-insulated wires meet building codes.[1] PTFE is also used to insulate fiber-optic cables, as used, for example in the transatlantic optical telephone cable. Teflon's resistance to corrosion creates a barrier between the fragile optical cables and salty seawater laden with biological and chemical particulates. Telecommunications are in the process of phasing out copper wiring in deference to PTFE-coated fiber-optic cables.[1]

PTFE's chemical inertness has made it a candidate for medical applications because following numerous medical trials, Teflon is biologically inactive.[5] A PTFE-paste, a suspension of Teflon in a gel, was used in surgical procedures for the vocal cords and as well as hip replacements. The paste provides a non-reactive space filler in the vocal cavity, allowing the vocal cords to have enough tension for speech. In the hip joint, PTFE fulfills its familiar role as a lubricant, slowing the wear of artificial hip joints.[5] PTFE has also been used to patch perforated human aortas, thereby saving a lives.[5]

As it has with other industries PTFE has made its way into textiles, where it has revolutionized the industry. Gore-Tex, a patented layering of PTFE and nylons, provides superior breathability and weather resistance. US Special Forces, exposed to extreme weather, use Gore-Tex and other PTFE-based fabrics.[8] Because it does not bond with other materials, Teflon is used to stain-proof fabrics in a patented process called “Scotch Guarding.” Teflon-coated fabrics are marketed by many companies that produce garments, rugs, and furniture. DuPont markets a Teflon-coated carpet that is advertised to 40% easier to clean than standard carpeting. PTFE protects from stains and deterioration.[8]

Scaling Up

The synthesis of PTFE has changed over the years. The original preparation was an accidental free radical polymerization of TFE

$$XCF_2 = CF_2 \rightarrow -(CF_2 - CF_2)_n - .$$

This reaction is dangerously exothermic, so the DuPont chemists developed safer synthesis routes. Due to its non-reactive nature, PTFE cannot be manufactured using condensation polymerization. Instead PTFE is synthesized using suspension polymerization. In suspension polymerization liquid TFE is combined with an initiator chemical and put into a solution of purified water and then agitated, forming beads of PTFE and heating the solution. While PTFE can be synthesized in this way the molding is quite different from that of other plastics, PTFE is very viscous when heated and as such does not flow well and is not well suited for traditional molding. PTFE moldings are cast using ram-extrusion, pushing solid masses of Teflon through a metal die, creating rope-like fibers of PTFE that can be further processed into films, textiles or powders.[8] The length of the polymer chain (the number of repealing groups) can be tailored for individual industrial needs. The temperature and concentration of the reactants during synthesis can be manipulated, producing longer or shorter chains of PTFE. Longer polymer chains are more effective as a fabric while short chains are more useful for lubricants.[3]

Applications of PTFE as an engineering material have not been exhausted. Its favorable properties make it the first or only choice in many applications. PTFE has opened the door to a future where former mechanical restraints no longer prevent successful production.

On an April day in 1938 the world changed. The serendipitous discovery by a young chemist would soon significantly affect production in most industries. Teflon created a world where spacewalks are possible and where brownies don't stick to pans. Teflon created a world where, thanks to non-corroding pacemakers, hearts keep on beating. The most slippery material known to man has deeply affected many aspects of technology toward improving our standard of living.

1. Avakian, P., and Ferro, R. Dielectric Properties of Fluoropolymers. In *Modern Fluoropolymers: High Performance Polymers for Diverse Applications;* Scheirs, J., Ed.; Wiley: New York, 1998; p 91-101

2. Banks, B. A. The Use of Fluoropolymers in Space Applications. In *Modern Fluoropolymers: High Performance Polymers for Diverse Applications;* Scheirs, J., Ed.; Wiley: New York, 1998; p 103-113

3. Brewis, D. M. and Mathieson, I. Adhesion Properties of Fluoropolymers. In *Modern Fluoropolymers: High Performance Polymers for Diverse Applications;* Scheirs, J., Ed.; Wiley: New York, 1998; p 166-190

4. Khaladkar, P. R. Fluoropolymers for Chemical Handling Applications. In *Modern Fluoropolymers: High Performance Polymers for Diverse Applications;* Scheirs, J., Ed.; Wiley: New York, 1998; p 311- 326

5. Laustriat, S.; Geiss, S.; Becmeur, F.; Bientz, J.; Marcellin, L.; Sauvage, P. Medical History of Teflon Eur. Urol. **1990**, 17, 301-303

6. Mossman, S. *Fantastic Plastics: Product Design and Consumer Culture*; Black Dog Publishing: London, 2008.

7. Plunkett, R. The History of Polytetraflouroethylene: Discovery and Development. In H*igh Performance Polymers: Their origin and Development*; Seymour and Kirshenbaum, Ed.; Elsevier, New York 1986; p 261-266

8. Sperati, C. Polytetrafluoroethylene: History of its Development and Some Recent Advances. In H*igh Performance Polymers: Their origin and Development*; Seymour and Kirshenbaum, Ed.; Elsevier, New York 1986; p267-278