Flame Retardant Fibers for Human Space Exploration – Past, Present, and Future

Introduction

The National Aeronautics and Space Administration (NASA) has led in the development of unique flame retardant fibers for human spaceflight since the beginning of the Apollo program.

After the Apollo 1 fire which killed Command Pilot Virgil I "Gus" Grissom, Senior Pilot Edward H. White II, and Pilot Roger B. Chaffee from cardiac arrest on January 27, 1967, the accident investigators found severe third degree burns and melted spacesuits on the astronauts bodies. NASA immediately initiated an extensive research program aimed at developing flame retardant and flame resistant fibers for the enriched oxygen atmosphere of the Apollo crew cabin. Fibers are flame retardant when they have been modified by chemical and thermal treatments. Fibers are flame resistant when they are made of inherently flame resistant materials (i.e. glass, ceramic, highly aromatic polymers).

Immediately after this tragic accident, NASA funded extensive research in specifically developing flame retardant fibers and fabrics. The early developmental efforts for human spaceflight were for the outer layer of the Apollo spacesuit. It was imperative that non-flammable fabrics be used in a 100% oxygen environment. Owens-Corning thus developed the Beta fiber that was immediately used in the Apollo program and later in the Space Shuttle program.

Aside from the urgent need for protective fabrics for the spacesuit, NASA also needed flame retardant fabrics for both clothing and equipment inside the spacecraft. From the mid-1960s to the early 1980's, NASA contracted with many companies to develop inherently flame retardant fibers and flame retardant finishes for existing fibers. Fluorocarbons and aromatic polyamides were the polymers of great interest for the development of new inherently flame retardant fibers for enriched oxygen environments. These enriched environments varied for different space programs. For example, the Apollo program requirements were for materials that would not support combustion in a 70%/30% oxygen/nitrogen environment at 6.3 pounds per square inch (psi). The Skylab program flammability requirements were set at 80%/20% oxygen/nitrogen ratios at 5 psi.

While many fibers produced under several NASA contracts were never used, a few have become commercial products. The intent of this paper is to present the developmental history of some of these new or modified textile fibers. These developmental efforts are presented at various levels of details depending on the source of the historical records.

Development of Beta Fiber

"With the Apollo Program which started in 1961 and ended in 1972, unique requirements for strength, flame resistance, and drape (a characteristic of flexibility and suppleness) were imposed on textiles used in spacecraft and in the lunar environment. In order to accommodate these extreme conditions, Owens-Corning, under NASA contract, developed the extra fine filament fiber, Beta Fiberglass®. "This inorganic fiber is nonflammable in a 100% oxygen environment. It has a service temperature between -300ºF and 900ºF (-184ºC and 482ºC) and is degraded at 1550ºF (843ºC). The unique characteristic of Beta fiber was an extremely fine diameter of 3.5 to 3.8 microns resulting in low bending stiffness, a necessary condition for making fabrics with high drape. In today's textile terminology the "Beta fiber", as it has become to be known in the aerospace industry, would be called a microfiber.

With further enhancement through the addition of Teflon coating, Beta multifilament yarns became easier to weave, and the overall abrasion resistance of the glass fabrics was also improved. The enhanced Beta Fiberglass® fabric, more than any other fabric, has been used throughout the Apollo and Space Shuttle programs. The woven Beta fabrics were selected for the outer layer of Apollo space suits and flight suits, for the interior liner of the Apollo command module, and for several crew equipment items and fire protective covers. The largest use of Beta fabric in the Space Shuttle Program's Orbiter was the contamination control cover of the cargo bay. Between 1967 and 1990 approximately 10,450 lb. of Beta fabrics were used in the Apollo, Skylab, Apollo-Soyuz, Space Shuttle, and Spacelab programs combined.

Today, with the International Space Station, the need for glass fibers is even greater than before, due to the long exposure of materials to space radiation and space particles. Glass and ceramic structures have excellent resistance to the atomic oxygen present in Low Earth orbit, whereas atomic oxygen will provoke the inevitable degradation of organic materials over time. On the other hand, the need for the original Beta fiber is gone because glass fabrics are no longer used in the space suit. By the mid 1990's, Owens Corning or Dodge Fibers in Hoosick Falls, NY (Oak Fluorglas Division) could no longer sustain the production of a material that had one customer. The need to tailor a garment out of glass fabric ended after the Apollo program. A new spacesuit had been developed for the Space Shuttle program. This space suits would be used for several missions as opposed to Apollo suits made for each mission." (Orndoff, 2016)

<u>Development of Aromatic Polyamide Fiber for Enriched Oxygen Environment from the 1960s to the 1990s</u>

In 1969, The NASA Manned Spacecraft Center in Houston contracted with the Monsanto Research Corporation, a Subsidiary of Monsanto Co. Dayton Laboratory to develop, test, and modify flame resistant fibrous materials (John Mann Butler, Albert Y. Garner, Archie E. Follett, Monsanto Research Corporation). The Monsanto Research Corporation chemists were tasked with developing polymers which were inherently nonflammable in pure oxygen atmosphere at 6.2 and 16.5 psia.

The goal of this project was to develop a non -flammable fiber with mechanical properties similar to those of nylon. The initial effort consisted in preparing highly halogenated aromatic polyesters, determine their solubility, cast films, and test their flammability in an oxygen atmosphere at 6.2 psia. Several polymers were produced by interfacial polymerization. The first film successfully that was cast from poly-tetrabromobisphenol-A-chloromethylphosphonate was tested for flammability. However, this film manufacturing success did not translate into a fiber spinning success. The films were either nonflammable and insoluble or soluble and flammable. In addition to solubility which is needed for fiber spinning, infusibility was also needed to avoid dripping of the polymer when it was heated. Hence, different co-polymers were developed.

The researchers found that co-polymers containing 20% to 50% tetrabromodihydroxybenzophenone, in contrast to the polytetrabromobisphenol carbonates, were soluble, and could be extruded into thin films and fibers. While this result was promising, solubility, flammability, and strength of some of the new materials were still major issues.

After this period of research, because of the problems of solubility associated with the first polymer, the research shifted towards the synthesis of nitrogen-containing polymers because of the solubility problems associated with the first polymers. A series of aromatic polyamides and polyimides were synthetized and tested for flammability. The researchers found that while the monomers should be highly halogenated, it was not necessary that they be completely halogenated. The halogenated polyimides had low molecular weight and formed friable films. Among the halogenated polyamides, the brominated analog of Nomex, poly(4,6-dibromo-m-phenylene-4,6-dibromoios-phtalamide), had the good linear symmetry and chain packing needed for fiber formation.

By the end of the contract 59 different polymers had been produced and tested. Poly(4,6-dibromo-m-phenylene-4,6-dibromoiso-phtalamide) or tetrabromo-Nomex and poly(4,6-dibromoisophtalic anhydride.) were found to be the most promising for producing strong films and fibers.

Work on the halogenated aromatic polyamides continued with another contract with NASA (Robert Cass, Monsanto Research Corporation, 1972). The general goal of this contract was to further develop flame resistant organic fabrics. The specific objective was to develop a treatment for various textile structures made of aromatic polyamides and polybenzimidazole (PBI).

During this research effort, different compounds were evaluated and two new polymers were introduced as binders, Fluorel and Kel-F. Three additives were also evaluated: Dechlorane Plus 25[1], Firemaster 45 BT[2], and Hexabromobenzene[3]. Kel-F appeared to be a better binder because it is hydrogen-free. However, its viscosity made it more difficult to formulate into a coating. A higher concentration of Dechlorane was required with Fluorel than with Kel-F in order for the film to be self-extinguishing.

Research continued using various combinations of phosphorus oxyhalide and thermal treatments on commercially available aromatic polyamide fabrics. The flammability and mechanical properties of these fabrics were satisfactory.

Following these efforts, a series of other contracts with Monsanto and Albany International Research Company led to more improvements in the treatments of aromatic polyamide such that a variety of new fabrics were produced first for evaluation at NASA, and later use in Skylab.

Development of Polybenzimidazole Fibers

The development of polybenzimidazole fibers was performed by Hoechst Celanese under US government contracts from the Department of Defense and NASA. This work led to the production of PBI multifilament and staple fibers used in several space programs. Yarns made of multifilament fibers were used in tethers, belts, and restraints in the Apollo program. Staple fibers were used in many applications ranging from apparel fabrics for use in Skylab to stowage partitions in the Space Shuttle program.

Development of Chlorofluoroethylene (CTFE/TFE) Fibers

During the early 1970's NASA contracted several companies to develop flame resistant fibrous materials. Under contract number NAS 9-12257, the Plastics Division of Allied Chemical Corp. developed experimental copolymers of Chlorofluoroethylene (CTFE) and tetrafluoroethylene (TFE) that could

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[1] Hooker Industrial Chemicals
[2] Michigan Chemical Company
[3] Michigan chemical Company

potentially be spun into fibers and monofilaments. The objective of the contract was to produce yarns that could meet the NASA/Apollo program flammability requirements at 70/30% O2/N2 ratios at 6.2 psi.

The first spinning trials made by Allied Chemical Corp. were successful. This allowed Fabric Research Laboratories in Dedham, MA, under NASA contract No. NAS9-13673, to produce an experimental quantity of CTFE/TFE copolymer.

NASA Thus led the development of flame resistant fibrous materials under Contract NAS 9-12418. The focus of this effort was to produce the optimum multifilament and monofilament yarns made of the new CTFE copolymer developed by Allied Chemical Corp.

Development of Polyimide Fiber

With the advent of Upjohn 2080 polyimide resin in mid-1974 {US patent No. 3,708,458} by the Upjohn Company, D.S. Gilmore Laboratories, Industrial Division, North Haven, Connecticut, NASA initiated the research for the development of polyimide fibers. NASA contracted Southern Research Institute (contract No. NAS9-14475, Contract period: February 10, 1975 to October 19, 1976) to develop the technology for processing fine denier continuous filament fiber from the 2080 polyimide resin.

Under this contract, Southern Research Institute was required to produce continuous fibers that could be bundled into multifilament yarns, and had the following properties:

1. Physical and Mechanical Properties
    a. 2.2, 4.4. and 6.6 dtex (2, 4, and 6 Denier)
    b. 4.4-5.5 grams per dtex (4-5 grams per denier) breaking tenacity
    c. 15% to 35% elongation
2. Flammability
    a. Non-burning or self-extinguishing when tested in accordance with a 10.0 psia and 31% O2-69% N2 environment per category A, NHB 8060.1A
    b. Off-gassing, toxicity, and odor acceptable per NHB 8060.1A
    c. Stability in vacuum acceptable per SP-R-0022

The development was done is three phases: fiber development, resin pigmenting and fiber dyeing, and fibrous structures development.

The fiber development effort consisted in experimenting with both dry and wet spinning methods. In addition, post-drawing treatments were investigated to estimate a range of applications of the new fiber. Resin pigmenting and fiber dyeing were evaluated for the same reason. Finally, yarns and fabrics were produced for testing.

Since the Upjohn polyimide resin had good retention of its tensile strength at high temperature, a Limiting Oxygen Index of 40, and a specific gravity less than of CTFE copolymer, it was expected that the fiber would had many NASA applications.

Under contract with Albany International Research Co. (Contract No. NAS9-13673)[4], pilot plant quantities of continuous filament yarns in various deniers were produced as well as cut staple fibers. The staple fibers could be spun into yarns on commercial equipment. Consequently, tapes, braids,

[4] Albany International Research Co. (formerly Fabric Research Laboratories, Inc.) operates as a subsidiary of Albany International Corp.

knitted and woven fabrics were produced in sufficient quantity for evaluation at the Johnson Space Center. Last, dyes and finishes were applied to the fabrics in an effort to provide a range of colors for astronaut's clothing.

The last of fiber research effort in the 1990s was driven by the need to have films and fabrics that could resist the atomic oxygen present in Low Earth Orbit. One fiber, TOR™, a co-polymer of polyimide, was developed by Triton Systems Inc. (TSI) for that purpose. The small and newly founded company received funding from NASA in 1992 in response to the findings from the Long Duration Exposure Facility (LDEF). After the LDEF was retrieved from its six years in space, NASA scientists found that virtually all polymeric materials exposed to ultraviolet radiation and atomic oxygen were severely degraded. The LDEF findings raised concerns about using new polymer composite materials in the future space station. TOR™ is a space durable polymer that can withstand the damaging effects of ultraviolet radiation and atomic oxygen as well as extreme thermal cycles. In 1996, TOR™ thin films were flown on the MIR station as part of the Passive Optical Sample Assembly (POSA-I) experiment. After this experiment, 2 grams per denier (18 grams per tex) fibers were developed for making sewing threads, braided and woven fabrics.

These polyimide fabrics are not used in the International Space Station program. On the other hand, expanded polytetrafluoroethylene (E-PTFE) and polybenzimidazole (PBI) fibers have been used since they were developed, fabrics made with these fibers have been used in all NASA space programs until the International Space Station program.

<u>The International Space Station Period</u>

Many other fabrics were developed over the 56 years of human spaceflight. For the most part, these fabrics were made of blended yarns in an attempt to combine properties from their different components. For example, polybenzoxazole (PBO) was blended with Nomex or polyimide (P84) for improving its abrasion resistance. Similarly, Beta Fiberglass® yarns were blended with various polymeric fiber yarns to obtain core/sheath type fabrics which have a good combination of flame resistance, UV and atomic oxygen resistance, as well as other desired mechanical properties. These blended fabrics are examples of the continuous research effort at NASA for developing fabrics for use in extreme environments.

<u>Human Exploration of Deep Space in the 2030s?</u>

Unfortunately, the resources available to NASA for a trip to Mars cannot compare to those used to enable the landing on the Moon. Fifty years ago the textile industry produced, exclusively for NASA, fibers and fabrics specifically needed to go to the moon. The US government, in the geopolitical context of the 1960s, created a favorable environment to encourage the industry to produce new textile fibers for protective applications.

The textile fiber manufacturers, in addition to conducting research for the US government, invested some of their resources to build plants to produce the most promising new fibers. Owens-Corning built a two-story plant to draw, with the assistance of gravity, the Beta fiber to micrometer scale. Likewise, Hoechst-Celanese dedicated an entire facility to produce PBI filaments.

Fibers like the Beta glass have disappeared because they were no longer needed for industrial or apparel applications. The Beta fiber developed for a one-time-use protective outer layer of the Apollo spacesuit was too expensive for use in the market of protective fabrics. Other glass fibers, not quite as fine as

Beta, satisfy our current commercial applications. Likewise, PBI staple fiber yarns blended with other flame retardant yarns satisfy the demand of today's protective clothing markets.

NASA will need new fibers and fabrics for living in the Orion capsule and for residing in a habitat on the Martian surface. The fibers that are needed will have to meet additional requirements for missions of long duration over three years. The astronauts apparel will have to meet not only flammability requirement but also comfort, aesthetic, and other functional requirements. There will be new logistical requirements that did not exist in previous space programs. Today, all astronauts' apparel is disposed of after a short usage period without laundering capability. The same practice represents an unaffordable logistical burden for long human space missions.

With the commercialization of space and the beginning of space tourism, a new industry is growing and needs the same materials NASA is using. There may be new incentives for the textile industry to invest in supporting the aerospace industry, and lead new fiber developments to open the door of a new market sector of space explorers.

References

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