Applications of Aerospace Technology in Industry

A TECHNOLOGY TRANSFER PROFILE

PLASTICS

ACKNOWLEDGEMENTS

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Much of the information was gathered with the assistance of NASA in-house and contractor personnel who participated in the development and application of the technology discussed.

APPLICATIONS OF AEROSPACE TECHNOLOGY IN INDUSTRY

A TECHNOLOGY TRANSFER PROFILE

PLASTICS

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Industrial Economics Division
Denver Research Institute
University of Denver

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PROFILE HIGHLIGHTS

With an average growth rate of 11 to 15 percent per year since the early 1940's, plastics has become one of the nation's fastest growing industries. A significant part of the progress made during the last decade in high temperature polymer development must be credited to technology developed under NASA sponsorship. The formulation of pyrrones by chemists at Langley Research Center in 1964, for example, defined the state-of-the-art in thermal stability and radiation resistance. They have long-term stability at 500° F and can withstand up to ten times the amount of radiation that degrades other polymers.

While trying to develop ablator binders and adhesives for NASA, a California aerospace firm discovered a new method of processing a class of plastic materials known as polyimides. The new process eliminates the generation of water and volatile byproducts, permits rapid curing and simplifies storage. The resulting polymer, named P13N, has high temperature strength and is impervious to a variety of chemicals.

During 1964, while attempting to develop new materials for rocket thrust chamber ablators, a NASA contractor discovered a new class of thermosetting plastics. While unsatisfactory for ablator applications, its potential for use in other situations was immediately obvious. The material, called HYSTL, is noted for its processing simplicity, long shelf life at ambient temperatures, workability and rapid curing. HYSTL has high thermal strength, good chemical stability and good radiation stability. The original contractor has recently invested $1, 500, 000 to form a company to market this material.

These developments and others like them are excellent examples of contributions to the space program which are producing, as an additional dividend, a wide range of benefits for the private sector of the national economy.

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INTRODUCTION

In the recent past, there has been increasing interest in determining the actual influence of NASA-sponsored research on new polymer formulations and refinements, as well as plastics product design and processing. The value of cataloging and measuring such space program transfers to the plastics field is twofold: it provides a storehouse of information for economic growth and it also makes the technology transfer process more understandable and manageable. When government funding stimulates technology to extend its limits -- as during World War II when great strides were made in reinforced plastics manufacture and design -- the entire economy ultimately benefits through technology transfer. The space program, a program of massive technological advance, has undertaken to expand and speed the transfer process.

New plastics technology bred out of the space program has moved steadily into the U. S. economy in a variety of organized and deliberate ways. It is the transfer of new plastics know-how into the plants and eventually the products of American business that is the chief concern of this report. How does plastics technology developed by NASA laboratories and NASA contractors transfer to the rest of the scientific and industrial community? How does time affect this transfer process? What hinders or speeds the process?

These and many other questions present themselves when technology transfer is studied in any field, but because plastics have become such an important element of our economy and because they have played such a vital role in the space program, close study of the transfer process in this field is valuable.

SECTION I. AN OVERVIEW OF THE PLASTICS INDUSTRY

In a relatively short time plastics, as a family of materials, has evolved into one of the nation's (indeed commercial history's) fastest growing industries. Developing from a scant 6 million pounds per year consumption rate in 1922 to an estimated 19 billion pounds in 1970, plastics now ranks as one of the few billion dollar industries in the United States. Since the early 1940's, plastics' growth has been spectacular, averaging 11 to 15 percent per year during that period. (See Figure 1-1.)

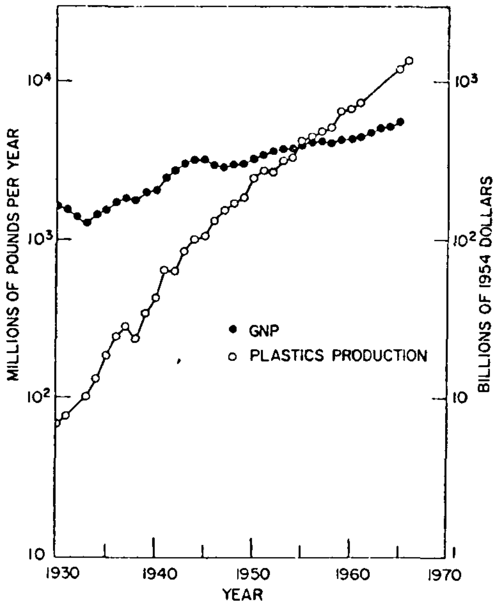

Figure 1-1. United States Plastics Production and Gross National Product Plotted as Logarithms vs Time. Source: Rosato, et al. (1969, p. 2).

The plastics industry is expected to continue this growth in the next two decades.

According to McGraw-Hill's economics department, for example, plastics materials will be the number one industrial growth area in the period from 1967 to 1982, registering a 568 percent gain over that time; interestingly enough, the number two growth area is plastics products with an estimated 378 percent gain, 88 percent ahead of the nearest gainer.

By 1975, per capita consumption of plastics in the United States and Canada will reach 128 pounds, up from 2 pounds in 1940. It has also been forecast that by 1983 plastics production will exceed that of steel on a cubic volume basis; it will exceed all paper products by 1990; and in the year 2000 will surpass the largest volume material-- lumber. According to the formula used by various economists, it is calculated that by the year 2000 plastics will comprise three-quarters of all engineering materials in terms of volume.

Characteristic of an industry that is growing at a very rapid rate, much change has occurred in the structure of the plastics field (see Attachment I). For many years, new products and applications for plastics were largely initiated by such resin producers as DuPont, Union Carbide, Dow, and Goodrich, but during the past 15 years the end-product innovation emphasis has shifted to industrial plastics users like Ford, North American Rockwell, and Grumman Aircraft Engineering Corporation. The properties and formulations of certain plastics have become familiar enough and manageable enough for innovation to proceed successfully at the user level.

A B. F. Goodrich official commented recently that "15 years ago we were the initiators of 75 percent of all the products that came on the market using our vinyl. That percentage today has dropped to about 25 percent. This doesn't mean that we have slacked off on our research necessarily, but that vinyl has become a commodity material with common properties." It is also true that the same drop in resin-producer innovation has occurred within the other workhorse resin areas, such as polystyrene, polyethylene, phenolic, and polypropylene, all resins that exceed a yearly consumption rate of one billion pounds. Of course, resin producers, most of whom are linked to major chemical companies, necessarily remain the big powers in influencing pricing, materials formulation, and much basic polymer and processing research.

As might be expected in a dynamic and fast-growing industry, there has been considerable consolidation. Many resin producers have moved into the processing of film and sheet products for packaging, as well as the actual packages. Similarly, some large industrial users-- Ford with its Mount Clemens, Michigan vinyl plant is a good example-- have integrated backwards into resin compounding. Many custom-molding operations have been absorbed by resin producers and industrial users, but custom molders still account for the lion's share of resin consumption.

In some markets for plastics, growth has been especially rapid and strong. Within the past two years, for example, the furniture industry has embraced plastics with keen interest. As a result, many major furniture producers are now building their own plastics processing plants. A few are processing on a custom basis for the entire furniture industry. According to Plastics World Magazine, it is expected that resin consumption in this market will reach one billion pounds in 1970, up from 400 million pounds in 1966.

The automotive segment of the transportation market also represents a prime growth area for plastics as Detroit auto makers seek ways to cut costs, hold down weight, and gain more design freedom. Approximately 1.2 billion pounds of plastics will go into U.S. auto production in 1970, with average per-car use at approximately 120 pounds. This is up from 660 million pounds in 1967 or 75 pounds per car at that time. Construction and packaging markets continue to dominate plastics consumption, with construction alone accounting for 4.8 billion pounds in 1970 and packaging consuming 4.5 billion pounds.

With resin consumption expected to top off at the 60-billion-pound mark by 1980, many of the smaller markets for plastics will doubtless expand considerably, thus strong growth should occur in appliances, medical applications, agricultural uses and recreational products. Paralleling this growth is a similar expansion trend in plastics processing machinery and chemical additives necessary to manufacture plastics products.

Not many industries today possess the growing power of plastics. When this industry is viewed in the light of technology transfer, it can readily be seen that it must be receptive to new formulations and processing techniques if growth predictions are to be attained. Before plastics can reach the 60-billion-pound mark, higher processing speeds must be developed; this, in turn, will require new resin formulations as well as machinery development. Higher temperature limits for polymers must be achieved, and even greater strengths must be built into materials.

Resin producers and other major contributors of basic polymer formulations and processing innovations continue to pour funds into polymer research. Indications are that new polymer formulations will continue to emerge as chemists seek to tailor molecules to market needs.

As will be shown in Section II, NASA work in formulating new polymer modifications is quite relevant to certain needs of the plastics industry. An important point to remember is that the technical contributions also clearly served the primary purposes of the space program.

SECTION II. REPRESENTATIVE NASA CONTRIBUTIONS TO THE PLASTICS FIELD

NASA contributions to the plastics field can be viewed as important additional dividends of space program research and development. The chief aim of the space agency's work has been to satisfy program objectives, but the technology developed has multiple uses. Three specific advances out of the total body of NASA contributions to the plastics field are examined in this section. All three are formulation improvements in high temperature materials and they serve to illustrate the nature and extent of the NASA research effort. Other NASA advances, however, such as development of fire retardant and fire resistant materials, or of adhesives, or of composite materials, could just as well have served this illustrative function.* Selection of the high temperature advances was purely a matter of convenience and should be viewed as only representative of the many NASA advances in the plastics field.

The first high temperature contribution, the independent discovery and subsequent development of pyrrones, is important to high temperature applications up to 1,000°F. The second, P13N, represents a breakthrough in the processing of polyimides. The third, HYSTL, is a new thermoset formulation that exhibits exceptional resistance to corrosive chemicals at moderately elevated temperatures. After examining these key contributions to the plastics field, the section concludes with an analysis of their potential significance to the industry.

NASA Contributions to High Temperature Polymer Chemistry

A significant part of the progress made during the last decade in high temperature polymer development must be credited to technology developed under NASA sponsorship. The formulation of pyrrones by chemists at Langley Research Center in 1964, for example, defined the state-of-the-art in thermal stability and radiation resistance. High-density moldings configured with these materials possess useful tensile properties at 1,000°F for short periods of time. The ability of pyrrones to sustain massive radiation doses is exceptional, about 10 times greater than the next best polymer.

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* More detailed information on the full range of NASA contributions to the plastics field is presented in Attachment II and in Exhibits I and II of Attachment III.

Formed by condensing a tetraamine with a dianhydride, the pyrrone structure incorporates both the bensimidazole and the polyimide groups as fused rings. In addition, much of the polymer is double-stranded. This means that two adjacent bonds must be broken to rupture the polymer chain. Synthesized by NASA five years ago, pyrrones still represent the best combination of thermal and radiation resistant properties of any organic polymers that have been tested.

NASA-sponsored research is also responsible for the development of a polyimide prepolymer which represents a significant step forward in the processability of polyimides. Known as P13N, this material is commercially available from the Geigy Chemical Corporation, which purchased world-wide license rights from TRW which actually carried out the developmental work. P13N, unlike other polyimide prepolymers, does not give off water during the cure cycle. It has good shelf life and gives a fully imidized structure when cured.

P13N employs a thermal rearrangement rather than a dehydration step to achieve a final state of cure. This type of reaction, while novel, is not limited to the synthesis of polyimides, but can be used to prepare thermally stable polymers containing other functional groups as well, such as silicones, esters, amides, or even fused, ladder-type ring systems. The technology embodied in P13N may well represent as significant a contribution to the field of high temperature plastics as did the development of epoxy or phenolic resins.

The third NASA contribution under discussion here is HYSTL, also developed by TRW under NASA sponsorship. This material, prepared from a commercially available viscous liquid prepolymer, can be readily chain extended to give an elastomeric composition. In this latter form, it can be mixed, molded, or extruded, and gives prepregs with excellent drape characteristics. The prepolymers possess a large number of vinyl side chains and can be cured with peroxides to give the thermally stable, chemically resistant, thermosetting resin called HYSTL. Because the properties of the intermediate elastomer can be varied over a wide range, HYSTL provides manufacturers with more processing flexibility than is available with other thermosetting compositions.

Significance of These Contributions

While the three key NASA contributions to high temperature polymer chemistry cited above have not yet produced large-scale, immediate commercial effects in the plastics industry, nonetheless these advances have advanced the state-of-the-art in temperature capability, in improved polyimide processability, and in a wider range of processing choices for thermosetting resins. The technical significance of these contributions can be seen in "trend-line" presentations shown in Figures 2-1 and 2-2. These "trend-line" presentations demonstrate that certain plastic material limitations have indeed been extended, introducing a new area for plastic applications.

The HYSTL development perhaps comes closest to bringing immediate benefit to the commercial world of plastics because much work already has been devoted to making thermosets more readily processable. Machinery manufacturers have been developing and offering thermoset injection molding machines, and a number of thermoset resin producers now provide injection moldable grades of phenolic and other thermosetting materials. Injection molding was, until recently, the exclusive domain of thermoplastics. General Electric's "Genal" is perhaps the best known example of this. In addition to resin producer and machinery maker efforts, at least three companies at the processor level are building up thermoset extrusion businesses. Prominent among them is Thermoplastics Processes, Inc., a well-known New Jersey custom extrusion firm, which has designed and built its own equipment. York, Inc., a division of the Budd Company, also figures strongly in this development. There is little question that HYSTL with its extended temperature capability will come to the attention of those resin producers, machinery manufacturers, and processors who are pursuing the mass-production thermoset manufacturing business.

A combination of polyimide and pyrrones as a high temperature insulation for wire has been developed by Hughes Aircraft. That work, sponsored by the Air Force, has been cited by Industrial Research Magazine as one of the most important research developments of 1969. The Microdot Corporation demonstrated production feasibility for both P13N and the pyrrone as wire coating materials, an important secondary result.

Conclusion

In Section IV of this report, actual transfers of technology centering around the three key NASA polymer contributions are identified. Section III reviews the transfer mechanisms employed by NASA to publicize the existence and availability of the new plastics technology.

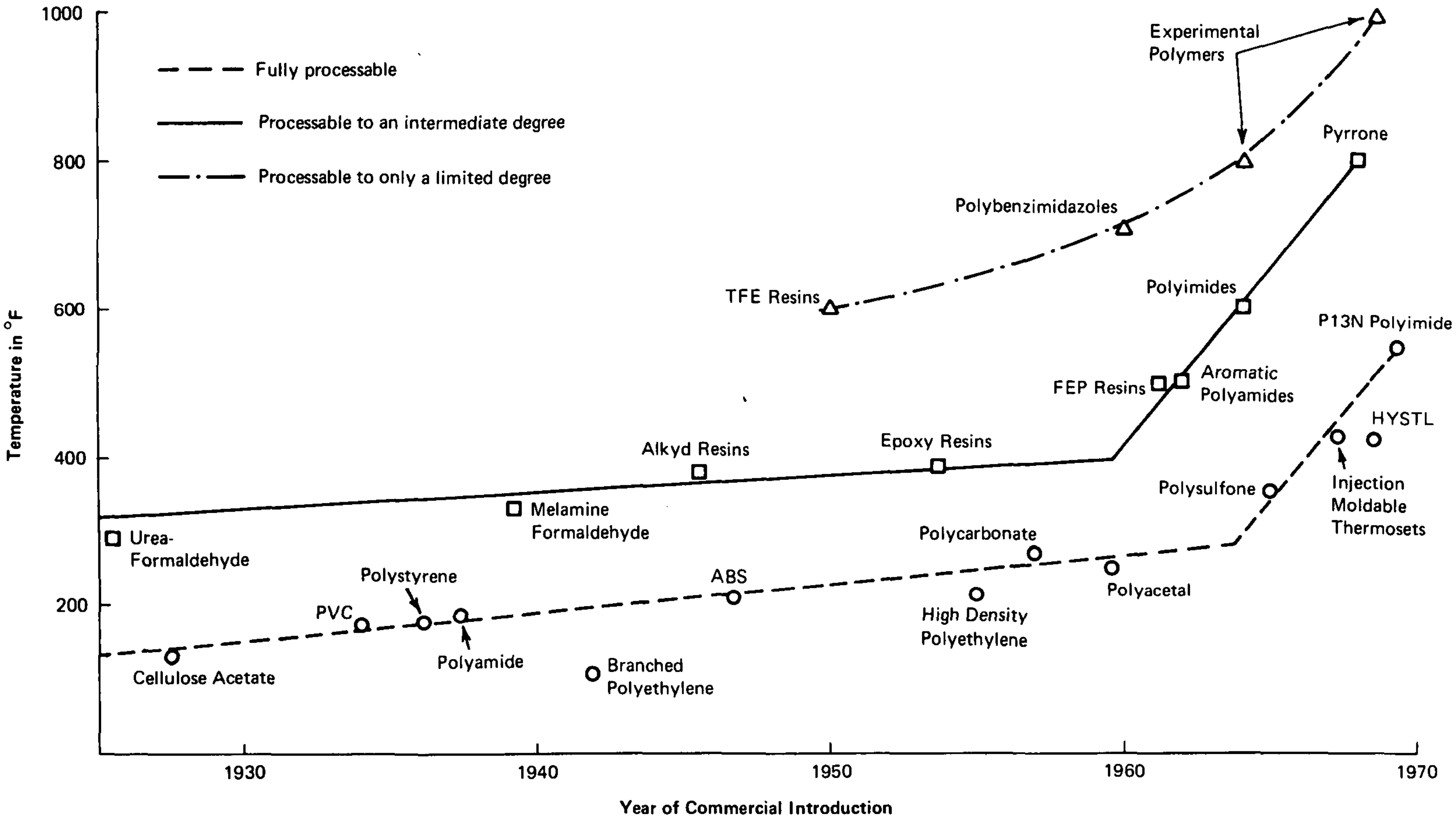

Figure 2-1. Improvement of Long Term Thermal Stability of Polymers With Respect to Their Processability

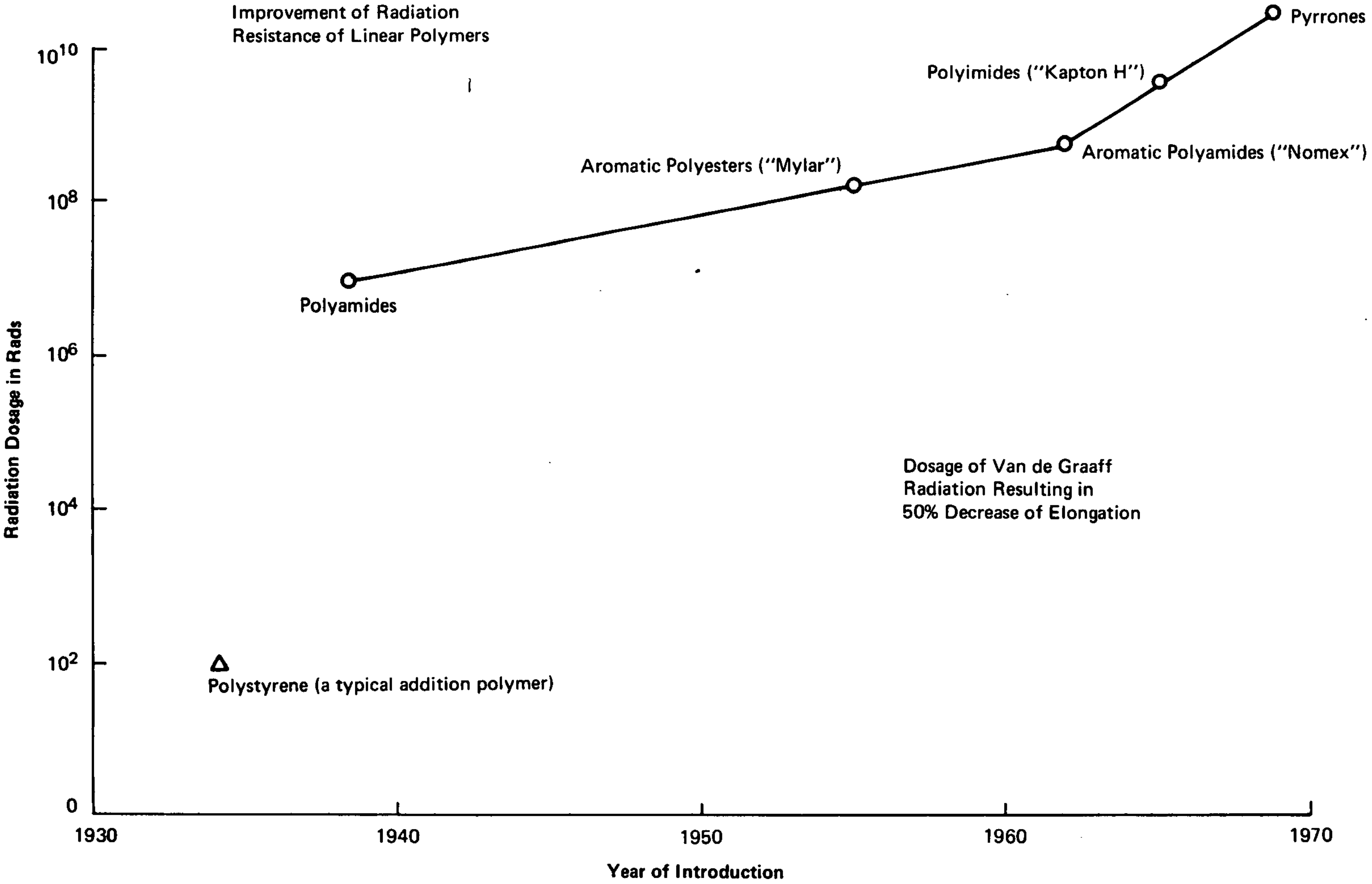

Figure 2-2. Improvement of Radiation Resistance of Linear Polymers

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SECTION III. NASA CHANNELS USED TO DISSEMINATE CONTRIBUTIONS

NASA's total effort at technology transfer is substantial. It embraces publications, services and other special techniques. In relating NASA technology transfer to the plastics industry, this section focuses on NASA-funded publications: Contractor Reports, Technical Translations, and other Special Publications (Figure 3-1).

PUBLICATION	SCOPE	PREPARED BY
CONTRACTOR REPORTS (CR)	Generated under NASA contract or grant that resulted in a significant contribution to a field of knowledge	Contractor or grantee author
TECHNICAL REPORTS (TR)	Contains important, complete, & lasting additions to available knowledge	NASA authors primarily in Centers, also Headquarters
TECHNICAL TRANSLATIONS (TT-F)	Information first published in another language deemed worthy of distribution in English by NASA	Commercial translation contractors
TECH BRIEFS AND TECHNICAL SUPPORT PACKAGES (TSP'S)	Most commonly used channel for announcing an innovation and explaining its basic concepts and principles	NASA and contractor authors
TECHNICAL MEMORANDUMS (TM-X)	Given limited distribution because data are preliminary, or not widely available by decision of Center or Headquarters	NASA authors primarily in Centers, also Headquarters
TECHNICAL NOTES (TN)	Less broad in scope than TR but nevertheless valuable	NASA authors primarily in Centers, also Headquarters
SPECIAL PUBLICATIONS (SP)	Publications of widespread interest & importance; Histories & Chronologies; Management, Evaluation, & Analysis Standards; Compilations, Charts & Tables; Bibliographies, & Other Reference Works	NASA and contractor authors
NASA personnel obtain from: Center Technical Library or Headquarters Technical Library	NASA, DOD & other Government contractors obtain from: NASA's Scientific & Technical Information Facility, P.O. Box 33, College Park, Md. 20740	Publicly available items are purchased from: The National Technical Information Service, 5285 Port Royal Road, Springfield, Va. 22151, and/or Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

Figure 3-1. NASA Scientific and Technical Information Publications

To gain some idea of the amount of plastics technology reported in these various NASA documents, Table 3-1 shows the number of titles relating to plastics research which appeared in each publication category from 1963 through 1969.

TABLE 3-1. NASA PUBLICATIONS PUBLICIZING SPACE PROGRAM CONTRIBUTIONS TO THE PLASTICS FIELD: 1963-1969

	TYPE OF NASA PUBLICATION							
YEAR OF PUBLICATION	Contractor Reports	Technical Reports	Technical Translations	Tech Briefs*	Technical Memorandums	Technical Notes	Other Special Publications	TOTALS
1963	0	0	0	3	0	3	1	7
1964	27	0	4	4	5	3	3	46
1965	44	47	35	16	11	8	6	167
1966	86	50	64	24	15	12	0	251
1967	94	93	21	24	24	24	1	281
1968	77	64	4	8	35	16	1	205
1969	52	16	11	23	7	16	0	125
TOTALS	380	270	139	102	97	82	12	1,082

*The subject of close study in this section.

A representative view of the scope of plastics technology appearing in NASA's transfer program can be obtained by examining the content of Tech Briefs for the past seven years. Tech Briefs are representative because they publicize many of the commercially valuable innovations resulting from NASA research efforts. Since 1963, 102 Tech Briefs have been prepared and disseminated which deal with NASA plastics work. To better examine their relevance to the plastics field, the titles in Attachment III have been arranged under two headings: new formulations (Exhibit I) and new applications (Exhibit II). Tech Briefs reporting new plastics formulations are of primary concern to resin producers and those conducting basic polymer research; those announcing new processing or design applications are likely to have broader immediate transfer potential because plastics processors and machinery manufacturers constitute a larger group. New formulations, however, may prove to have the greater long-term significance.

In addition to its various publication programs, NASA has transferred its new plastics technologies through other special techniques. Of particular interest are the activities of NASA's six Regional Dissemination Centers (RDC's). RDC's, established at universities or not-for-profit research institutes (See Figure 3-2), use computer search-and-retrieval services to facilitate transfer to client organizations. The North Carolina Science and Technology Research Center (STRC), for example, has provided literature search and problem-solving assistance to a number of companies in the plastics industry. Attachment III, Exhibit III, presents an example of STRC's literature search activities in this field.

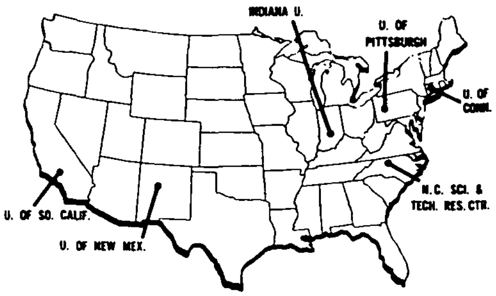

Figure 3-2. NASA's Six Regional Dissemination Centers

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SECTION IV. A TRANSFER PROFILE

After reviewing the variety of NASA plastics-related publications issued from 1963 through 1969 in Section III, the next step is to see how certain documents have been used by persons outside the space program. This will illustrate the role such documents play in the technology transfer process, as well as indicating the different ways NASA plastics contributions have been applied by commercial firms.

To identify and validate specific transfer activity, a total of 589 questionnaire contacts were completed with individuals who had ordered Technical Support Packages (TSP's) associated with plastics-related Tech Briefs. Those individuals were contacted six months after they had requested the TSP's. TSP requestors were asked to describe how they had used the information received.

The varying responses were classified as being in one or another of three transfer stages. Stage one transfers involved recognition of opportunity and a search for additional information to determine relevance to professional activities. Stage two transfers included cases involving laboratory verifications of theory or design ideas. Stage three transfers included those situations in which organizations were either market testing prototypes or using new products or processes in their in-house operational activities.

While almost all (93 percent) of the persons contacted indicated their transfer activities were in stage one (see Figure 4-1), approximately five percent had advanced to stage two, and another two percent of the cases involved stage three transfer activities.

In addition to classifying the cases by transfer stage, they also were categorized as continuing or having been terminated. In a case involving P13N technology, for example, Westinghouse Electric Corporation's Research and Development Center in Pittsburgh had progressed into stage two and was continuing. A group manager said he is directing the company's search for a wire coating that could withstand excessive external heating. (See "P13N" Transfer Example File Summary, Attachment IV.)

Another case, involving the Clairex Corporation of New York City, had progressed to the third transfer stage and was continuing. Clairex engineers had been able to develop an improved thermosetting material used in a photocell housing by employing information on

HYSTL received from NASA. (See "HYSTL" Transfer Example File Summary, Attachment IV.)

A transfer of pyrrone technology involved the Aerospace Group of of the Hughes Aircraft Company, which has developed two products based on the material and is working on a third. This transfer had advanced into stage three and was continuing. (See "Pyrrones" Transfer Example File Summary, Attachment IV.)

Although only three transfer cases involving NASA-developed polymer formulations have been discussed here, other contributions are summarized in Attachment IV. Attachment IV also contains cases that illustrate transfers of new processing or design applications.

The profile presented in Figure 4-1 is obviously time-related. It is a single synoptic view, after only six months, of what is actually a continuing transfer process.

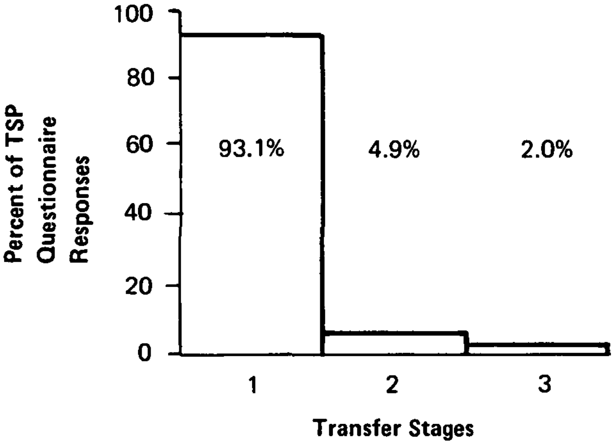

Figure 4-1. Transfer Profile of 589 Persons Using TSP's Related to the Plastics Field

Some feel can be gained for the time scale and effort involved in the transfer of technology to full commercial use by considering the development of DuPont's "Delrin" acetal resin which, for example, required $50 million in research during the 1950's. The development of "Delrin" involved no complex transfer of technology from a government agency to the private sector; rather, it was a company-directed, deliberate R&D and marketing effort. "Delrin" required 300 man-years of laboratory research and three years of field testing involving 250 companies before the material proved commercially successful. In formulating new plastics materials like "Delrin," such time requirements from innovation to adoption are not unusual.

Product development centering around the processing and design of plastics end-products also takes time. Anderson Window Company invested $4 million and 10 years of research and development effort in its successful attempt to develop and market a vinyl-clad window. After many design and processing failures, the company finally developed a new process for the extrusion-coating of wood that resulted in a marketable product in 1966.

This section, then, reflects the status of Tech Brief-related transfers of NASA plastics technology at a specific point in time. It also provides a necessary insight into the time required for industrial development of materials formulation and processing or design applications involving plastics end-products.

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SECTION V. A FOCUS ON ISSUES

This description of NASA contributions to the plastics field and the identification of specific communication channels leading to transfer examples has been an experiment in its own right. The experiment dealt with the following four issues centering around the nature of technology transfer in the context of the plastics field.

First, an attempt was made to demonstrate that while commercial and technical activities in the plastics industry are enormous, technical contributions flowing from NASA research are bonuses not anticipated by the plastics industry. Those contributions have had, and may continue to have, a marked effect on the expansion of plastics application possibilities.

Second, only three NASA contributions advancing the state-of-the-art in high temperature polymers were developed in this presentation. This small sampling represents only a fragment of the total contributions NASA has made, as evidenced by the statistical summary of the research reported in Section III. Space agency contributions extend completely across the spectrum of the plastics field and include dozens of materials formulations and hundreds of new processing and design applications.

Third, an effort was made to develop a more useful definition of the transfer process by identifying different transfer stages and then drawing a profile of those stages. The significance of the profile, appearing in Section IV, is not just that it identifies examples of technology in transit; it also demonstrates that some NASA contributions already are making significant impact despite the brief amount of time that has elapsed since their initial development.

Finally, this presentation notes the fact that widespread commercial exploitation of new technology is not entirely determined by the nature of the contributions or by the operation of the communication channels themselves. Instead, widespread commercialization is finally determined by economic and market factors. It should be recognized, however, that effective communication of valuable new technology to those responsible for achieving commercial success is an essential step in the technology transfer process.

What should be clear from the preceeding sections is that in the pursuit of its primary space goals, NASA has developed certain necessary plastics technology which will have a substantial long-term impact on the plastics industry and which, at this point in time, is already well along on the transfer road.

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ATTACHMENT I

A Brief History of the Plastics Field*

1831 Earliest description of styrene reported.

1834 Liebig first isolated melamine.

1835 Pelouze nitrated cellulose.

1835 Regnault prepared vinyl chloride.

1839 Goodyear discovered vulcanization of rubber.

1844 Cellulose acetate studied in Europe.

1845 Schonbein nitrated cellulose in the presence of sulfuric acid.

1847 Berzelius made first polyester.

1859 Butlerov described formaldehyde polymers.

1859 Chlorination of rubber produced hard plastics.

1862 Baldwin's compression mold patented.

1865 Schutzenberger acetylated cellulose.

1870 Hyatt's basic celluloid patent issued.

1872 Baumann reported polymerization of vinyl chloride.

1872 Bayer reported reaction between phenols and aldehydes.

1872 Hyatt brothers patented first plastics injection molding machine.

1879 Gray granted patent for first screw extruder.

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* Based on D. V. Rosato, W.K. Fallon, and D. V. Rosato. Markets for Plastics. New York: Van Nostrand Reinhold Co., 1969, Appendix B.

1879 Polymerization of isoprene into rubber occurred.

1892 Cross and Bevan developed viscose silk.

1894 Cross and Bevan produced industrial process for manufacture of cellulose acetate.

1899 Smith published patent on phenolformaldehyde composition.

1901 Smith discovered alkyd resins by reaction of glycerol and phthalic anhydride.

1909 Leo H. Baekeland granted his "heat and pressure" patent for making phenolic resins usable (patent applied in 1907).

1912 First emulsion polymerization patent applied to isoprene.

1918 John patented urea-formaldehyde condensation resins.

1921 Rayon introduced commercially.

1927 Cellulose acetate introduced commercially in U.S.

1927 Polyacrylate introduced commercially.

1928 Urea-formaldehyde introduced commercially.

1931 Patents issued to Formica (urea-formaldehyde surface on phenolic-paper core, etc.) which provided the major start for the Formica decorative laminate business.

1931 Carothers discovered neoprene.

1931 DuPont injection molding started.

1934 Polyvinyl chloride introduced commercially.

1936 Rohm & Haas Co. introduced "Plexiglas" acrylic sheet molding powders.

1936 Polystyrene introduced commercially.

1937	Polyamide introduced commercially.
1939	Melamine-formaldehyde introduced.
1940	Dow Chemical Co. introduced its vinylidene chloride "Saran" and Oscar Meyer & Co. used it to revolutionize packaging of meat.
1940	RP industry basically started with the use of glass fiber to reinforce plastics.
1941	Whinfield and Dickson invented polyethylene glycol terephthalate (Terylene).
1942	Polyester introduced commercially.
1942	Polyethylene introduced in U.S.
1943	Fluorocarbon introduced.
1944	ABS (acrylonitrile-butadiene-styrene) plastic developed by UNIRoyal, Inc.
1947	Epoxy introduced commercially.
1950	First large scale production started of Teflon (PTEFE).
1954	Ziegler produced polyethylene without pressure.
1955	Phillips Petroleum Co. disclosed its new process of polymerizing ethylene under low pressure.
1955	Polypropylene introduced commercially.
1959	Polycarbonates introduced commercially.
1959	Polyformaldehyde introduced commercially.
1961	Vinylidene fluoride introduced commercially.
1963	Polyimides introduced commercially.
1964	Polyimide introduced as a fabricated product.

1964 Polyphenylene oxide introduced commercially.

1964 Pyrrones first prepared.

1965 Parylene introduced commercially.

1965 Polysulfone introduced commercially.

1968 Pyrrones introduced commercially.

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ATTACHMENT II

NASA CONTRIBUTIONS TO THE FIELD OF PLASTICS

This review of NASA contributions to the plastics field began with an analysis of in-house research, contractor research and university programs. The principle challenge of the review was to identify concentrated and continuing areas of research. In general, the review showed a strong materials emphasis because of mission requirements for high strength, high temperature and low weight structures.

The broad range of NASA in-house research projects conducted within the plastics field is illustrated by the list of selected project titles in Table II-1. While the citations are in no way exhaustive of center programs, they confirm the breadth of the contributions.

TABLE II-1. SELECTED TITLES ILLUSTRATING BREADTH OF NASA IN-HOUSE POLYMER RESEARCH

NASA Center	Title
Marshall	Development of Polymeric Fuel Tank Sealants for Advanced Aerospace Vehicles Fractography of Polytetrafluoroethylene (PTFE) A Preliminary Evaluation of Silane Coupling Agents as Primers and Additives in Polyurethane Bonding Procedures Development of Siloxane Containing Epoxy Polymers for Electrical Circuit Embedment Applications
Lewis	Synthesis of Ultrahigh Molecular-Weight Poly(ethylene Terephthalate) Glass-, Boron-, and Graphite-Filament-Wound Resin Composites and Liners for Cryogenic Pressure Vessels Effect of Film Processing on Cryogenic Properties of Poly(ethylene Terephthalate) Compatibility of Several Plastics and Elastomers with Sodium Potassium and Rubidium
Langley	A Study to Determine the Presence of Voltage Breakdown Due to Proton Irradiation in Polymeric Materials Imidazopyrrolone/Imide Copolymers Synthesis and Thermal Stability of Benzimidazole Aromatic Imide Copolymers An Exploratory Study of a New Class of Stepladder and Ladder Polymers -- Polyimidazopyrrolones Cross-Linking of Polyvinylidene Fluoride by Gamma Radiation
Ames	The Effects of Molecular Structure on the Thermochemical Properties of Phenolics and Related Polymers Description and Applications of Fluorel L-3203-6 Synthesis of Ferrocene-Nitrogen-Containing Polymers with Conjugated Bonds High Temperature Polyimides for Electrical Equipment

All in-house NASA documents were separated into one or another of three groups according to the type of contribution:

1. Formulation (basic material research)
2. Evaluation (processing developments)
3. Application (development of functional designs)

The formulation category of contributions was chosen for further study because it appeared new formulations would be more easily related to transfer examples and to the plastics industry as well. Certain areas of formulation research were obvious candidates for in-depth development for purposes of this document. Candidate areas included fire retardant and resistant materials, semi-permeable membranes, radiation resistant materials, high temperature polymers, adhesives and composite materials.

The area of high temperature polymers was finally chosen to illustrate the extent and nature of NASA research in the field of plastics. A discussion below of the state-of-the-art in high temperature polymers precedes a specific discussion of NASA contributions.

High Temperature Polymers -- The State-of-the-Art

Ten years ago the upper temperature limit for useful polymeric materials was about 400°F. This limit was characteristic of a number of thermosetting resins, such as phenolics and certain epoxies. Teflon, a 20-year-old white elephant, held the tantalizing possibility of reaching much higher temperatures, since it showed great stability up to 600°F. Unfortunately, it showed little else; it could not be dissolved or extruded, there was no way to crosslink it, and it could not be made to stick to anything else. The best thermoplastics were polyamides and polycarbonates. They possessed excellent processing characteristics, but as resins they began to soften below 300°F. Because of the demand, primarily by NASA and the Air Force, for lightweight structural materials that would still be useful at 500-1,000°F, there was already considerable activity in the laboratory to develop new polymers that might function in this temperature range.

A significant advance was made in 1962 when the DuPont company announced they had prepared a high molecular weight, wholly aromatic polyamide. Fibers formed from the polymer showed superior long-term stability up to 500°F. Trademarked "Nomex," these fibers are self-extinguishing, and when heated in a flame form a char rather than melt. Nomex has been in full commercial production since 1966.

The idea of going to aromatic structures in order to obtain improved temperature resistance was a logical one, since it is known that the introduction of benzene rings increases chain stiffness and raises the melting point, both of which enhance thermal stability. A price had to be paid for these improvements, however, and the price was in the processability of the resulting polymer. It was found that most of these aromatic polyamides decomposed at about their melting point, so could not be extruded or easily molded. They are difficult to dissolve, a typical solvent being boiled dimethylacelamide containing 3 percent calcium chloride. Hence, there has been considerable effort to synthesize polymers that not only have good thermal stability but can be easily processed as well. To date, a completely satisfactory solution to this problem has not been achieved.

By way of illustration, the aromatic polysulfones, introduced commercially by Union Carbide in 1965, are some of the most temperature resistant polymers that are still true thermoplastics. Yet their maximum service temperature is only about 350°F, above which they begin to soften. Their glass transition temperature is about 375°F. On the other hand, new types of polymers, such as the polyimides and the polybenzimidazoles, which show excellent thermal stability above 500°F, also exhibit processing limitations that are in many cases as severe as those of the aromatic polyamides.

Nevertheless, polyimides are one of the most promising classes of high temperature polymers that have been developed. First introduced commercially in 1964 by DuPont, they are prepared by the condensation of a diamine with a dianhydride. The resulting polyamide, because it possesses additional carboxylic acid groups, is fairly soluble in highly polar solvents such as dimethylformamide. Thermal or catalytic dehydration yields the polyimide. A typical reaction sequence is given in Figure II-1.

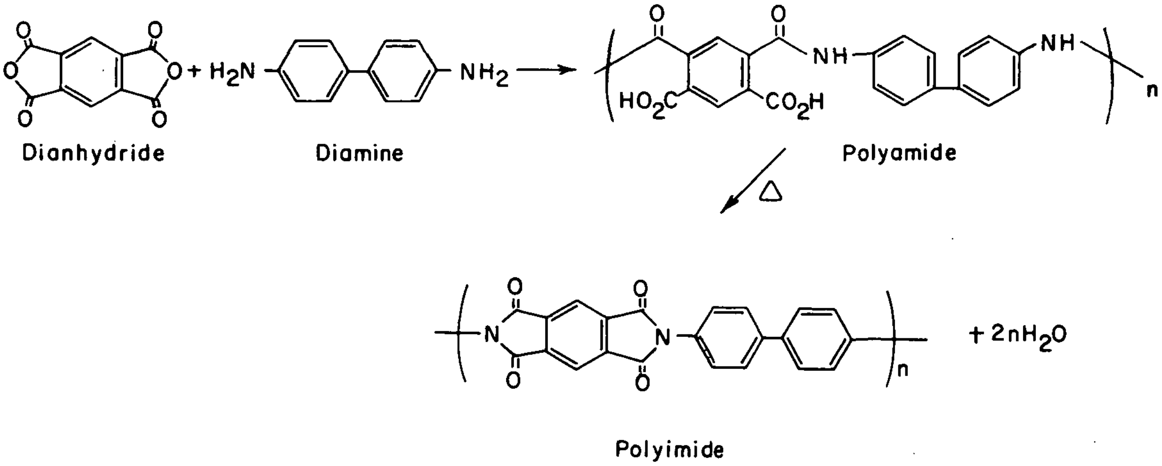

Figure II-1. Polyimide Synthesis.

Once formed, polyimides are no longer soluble; but, because they are prepared by way of a soluble precursor, they can be fabricated into films and fibers, and are commercially available as films, varnishes and molding powders. It has been estimated that the service time of Kapton H, DuPont's polyimide film, can be measured in years at 500°F, in months at 575°F, and in days at 700°F.

Polybenzimidazoles are one of a considerable number of heteroaromatic polymers that were prepared during the past decade. Most of these materials showed considerable thermal stability but at the present time are of theoretical interest only. Polybenzimidazoles, however, have undergone sufficient development to be available on a semicommercial basis. They are formed by the condensation of aromatic tetraamines with dicarboxylic esters (Figure II-2).

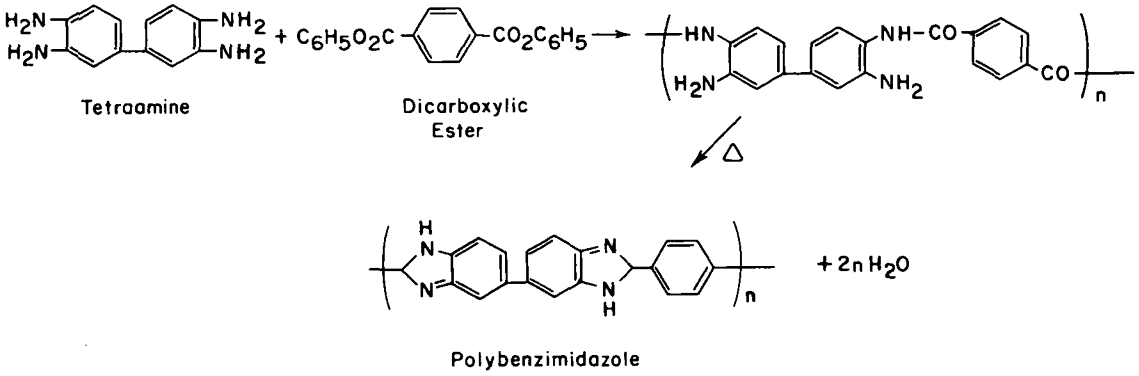

Figure II-2. Polybenzimidazole Synthesis.

An amino polyamide is apparently an intermediate which, on further heating, dehydrates to give the polybenzimidazole. Although some of these polymers have shown remarkable thermal stability, their full utilization has been hampered by processing difficulties. For example, an inert atmosphere during curing is required for the development of ultimate properties. Although fibers have been prepared, polybenzimidazoles have been used primarily in laminate compositions and as adhesives.

A new class of polymers independently discovered and subsequently developed by NASA personnel appears to be even more thermally stable and shows remarkable resistance to ionizing radiation as well. Known as pyrrones, these polymers are formed by condensing a tetraamine with a dianhydride (Figure II-3).

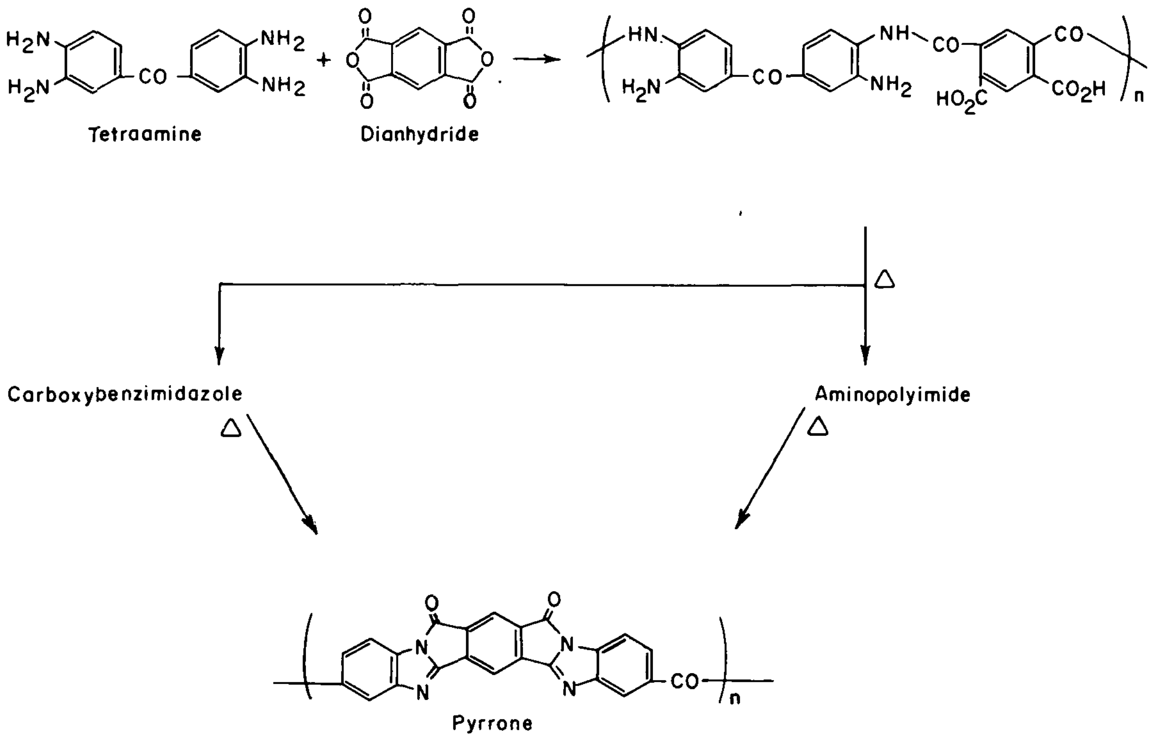

Figure II-3. Pyrrone Synthesis.

The pyrrone structure incorporates both the benzimidazole and the polyimide groups as fused rings. Moreover, much of the polymer is double stranded; this means that two adjacent bonds must be broken to rupture the polymer chain. Certain of these polymers show no significant weight loss when heated in air at 1, 000°F. Although first synthesized by NASA scientists five years ago, they still exhibit the best combination of thermal and radiation resistant properties of any organic polymers that have been tested.

The foregoing has outlined one of the most fruitful areas of investigation in the field of high temperature polymers. The development of these materials represents only a fraction of the research conducted in the whole field. Fluorinated resins with improved processing characteristics have been developed. Fully fluorinated elastomers also have been prepared and ways have been found to improve the mechanical properties of silicones. A number of new types of linear aromatic polymers have reached the marketplace. These include polyphenylene oxides, polysulfones, and coatings of polymerized para-xylylene (Parylene). A number of experimental organoinorganic polymers have been discovered, some of which hold promise for future development. Among them are phosphonitrilic polymers, ferrocene containing polymers and silazanes. All of these developments were made, at least in part, because of a desire for different properties in heat and radiation resistant materials.

Figure 2-1 in Section II relates thermal stability with processability for most of the polymers that have been developed during the past 40 years. It should be noted that the degree of temperature performance for many of these polymers can vary over a considerable range depending upon the way they are formulated. Their upper thermal limit also depends upon their actual application. Polyimides, for example, can be used for extended periods at 550°F and for shorter lengths of time at 700°F to 800°F. Finally, it must be realized that cost and processability are two crucial variables that also must be taken into account if meaningful comparisons are to be made. Concerning processability, for example, polymers may be separated into three categories. Soluble, melt-processable thermoplastics, such as polystyrene, make up the first category. Thermosetting resins, along with many of the newer types of linear aromatic polymers, may be placed inan intermediate processability category. Polymers which, because of their solubility characteristics or the way they are formed, may be placed in the third category. In some cases further development of a polymer has moved it from the third to the second, or from the second to the first category of processability. Such movement occurred in the case of perfluorinated resins.

NASA Contributions

The preceding brief state-of-the-art summary in high temperature polymer technology has not attempted to delineate systematically the role NASA has played in the overall development of the plastics field. In a very real sense, such a task is impossible. In any field in which there is a great amount of research activity, one organization's contributions might be overshadowed by those from another organization that occur at a later date, while still being a critical stepping-stone in the overall development process. In retrospect, it can only be said that both organizations have been contributors to the state-of-the-art.

Pyrrones. It is impossible to point to certain important areas of technological development that have occured under NASA sponsorship, and to attempt by way of example to fit them to the overall picture. One important contribution has been the independent discovery and subsequent development of pyrrones.* These materials were first prepared by NASA chemists at Langley Research Center. Subsequent formulation studies resulted in the prepolymer now being available as a varnish and a molding powder. A chemically blown pyrrone foam has been formulated. All have been commercially available on a limited basis, although they are expensive. On a purely utilitarian basis, the pyrrones represent the state-of-the-art with respect to thermal stability and radiation resistance. High-density moldings formulated from these materials still possess useful tensile properties at 1,000°F, more than 100 degrees higher than formulations using currently available polyimides. Their ability to withstand massive doses of radiation is also exceptional, being about 10 times better than that of the next best polymeric material (see Figure 2-2 of text).

These materials may represent a breakthrough in that they are "stepladder" polymers; that is, a significant portion of their chain is double stranded. Indeed, one can write paper reactions which give pyrrones that are completely double stranded. Since in actual practice such compounds (i.e., full ladder structure) are too intractible to be useful, a number of compromises have been made in commercially available materials -- compromises that permit flexibility and solubility at the expense of ultimate thermal stability. Nevertheless, the concept of useful ladder-type polymers is now firmly established, and the possibility for further improvements by molecular manipulation is now practical.

P13N. A new polyimide formulation that represents a significant advance in terms of the processability of this type of polymer is also a direct result of NASA-sponsored research. Codenamed P13N,

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* Work at the Langley Research Center resulted in a patent being granted in the name of the inventor, Vernon L. Bell, Jr. (Patent No. 3,518,232 issued June 30, 1970). Independently, work performed by DuPont resulted in a patent to the inventor -- Baufler (Patent No. 3,414,543 issued December 1968) for a similar formulation. Subsequent copolymer patents and development of methods to mold pyrrones were the result of NASA-sponsored work (See, e.g., Patent No. 3,532,673, in the name of inventors Vernon L. Bell, Jr. and George F. Pezdirtz, both of the NASA Langley Research Center).

it is commercially available from the Geigy Chemical Corporation, a licensee of TRW, the contractor who actually carried out the development work for NASA. A serious drawback to using any of the polymers that are ultimately formed by a cyclizing dehydration step (this includes polyimides, polybenzimidazoles and pyrrones) has always been that thermal stability is directly dependent upon the degree to which this cyclization reaction occurs. Completion of the reaction might take hours in a carefully programmed post-cure cycle if a thick specimen is being fabricated, since diffusion of volatiles formed in this final step must be slow enough to prevent void formation in the curing matrix. In addition, solutions of these polyimide-acid prepolymers may be sensitive to moisture and oxygen, necessitating storage in carefully sealed containers and immediate use once they are exposed to the atmosphere. All of these disadvantages have been overcome in a very elegant way by the development of P13N, which is a polyimide prepolymer. The material is essentially a difunctional vinyl monomer which already possesses preformed imide groups.

When P13N is heated, it undergoes thermal rearrangement to yield a highly crosslinked, thermally stable polyimide. A typical structure for the prepolymer is given in Figure II-4.

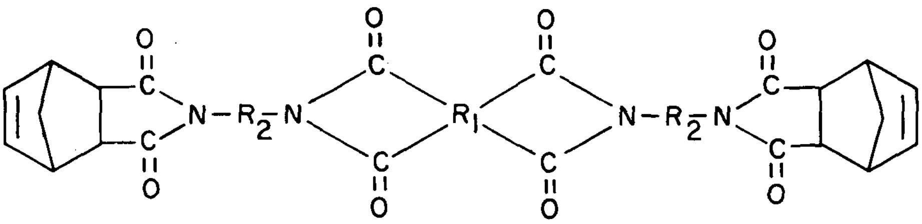

Figure II-4. A Typical P13N.

During the curing process no volatiles are evolved; a completely imidized polymer is formed. The cure time, which depends on the rate of heat transfer into, rather than the rate of water diffusion out of, the polymer interior, is much faster. This technology is significant for a number of reasons. Most obvious, of course, is the fact that there is now an easy way to fabricate a material that formerly required a considerable amount of special handling. This development alone should permit polyimides to be used in a great many more applications. Equally important is the method that has been employed to provide crosslinking functionality. Cyclopentadiene has been condensed with an olefin to give a Diels-Alder adduct (P13N) which, when heated, rearranges to give a thermally stable crosslinked resin. This type of curing reaction, while novel, need not be limited to the synthesis of polyimides, but can be used to prepare thermally stable polymers containing other functional groups as well, such as silicones, esters, amides, or even fused, ladder-type ring systems. The technology embodied in P13N may well represent as significant a contribution to the field of high temperature plastics as the development of epoxy or phenolic resins.

HYSTL. HYSTL is another material that was developed, again by TRW, as a direct result of NASA sponsorship. It is commercially available from the HYSTL Development Company, a joint venture of TRW, Inc., and Commonwealth Oil Refining Company. HYSTL is made from a viscous liquid prepolymer which can be readily chain extended to give an elastomeric composition. In this latter form it can be mixed, molded, or extruded, and gives prepregs with excellent drape characteristics. The prepolymer possesses a large number of olefinic side chains and can be cured with peroxides to give a highly crosslinked, thermosetting resin. This final product shows excellent chemical resistance, thermal stability, and electrical resistivity when compared with other polymers in its class. Because the elastomer can be modified to provide a wide range of properties, HYSTL provides a manufacturer with a great deal more processing flexibility than is available with other thermosetting compositions.

It is difficult even to estimate the total significance of the technological developments that have been discussed in these three examples with respect to the entire plastics industry. Neither the concepts involved, nor the materials themselves, have been in existence long enough to have had more than the very earliest concrete indications of their eventual major impact.

The three examples of NASA-sponsored technology that have been discussed represent three different types of technological contributions to the whole field. Pyrrones are a new class of polymers which incorporate a number of structural features that lead to thermal stability and radiation resistance. They are expensive and not readily fabricated, and their use is generally limited to situations where extreme conditions prevail. When the situation warrants, pyrrones are being employed. A recent study of high temperature electrical wire coatings reported that a polyimide film coated with pyrrones gave the most satisfactory results. These polymers represent the case in which a certain degree of processability has been sacrificed for exceptional properties in two specific performance areas.

With HYSTL, processability, rather than extreme thermal stability, is the significant contribution. (See again, text Figure 2-1 in which an attempt was made to view the plastics field both in terms of thermal stability and processability.) The thermal properties of HYSTL resins should not be underestimated, however. The material can be used for applications in the 350°F to 450°F temperature range. Because of its superior electrical properties, it is in an excellent position to compete with lower temperature polyimides. Its primary market, however, will undoubtedly be that served by today's thermosets, such as phenolics and epoxies. Although technology is currently being developed which permits certain thermosetting resins to be handled in some ways like thermoplastics (injection molding is now possible, for example), HYSTL, because of its very versatile processing characteristics, may well capture a significant share of this market.

The development of P13N also represents an improvement in processing characteristics. It is considerably more than this however. It represents an entirely new way of forming thermally stable polyimides that eliminates most of the shortcomings of earlier methods.

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ATTACHMENT III

EXHIBIT I. NEW PLASTICS FORMULATIONS ANNOUNCED IN NASA TECH BRIEFS

Tech Brief Number	Tech Brief Title
63-10612	Metals Plated on Flourocarbon Polymers
65-10016	Adhesive for Vacuum Environments Resists Shock and Vibration
65-10164	Irradiation Improves Properties of an Aromatic Polyester
65-10288	Organic Reactants Rapidly Produce Plastic Foam
65-10374	Plastic Plus Stainless-Steel Fibers Make Resilient, Impermeable Material
66-10043	Polymer Film Exhibits Thermal and Radiation Stability
66-10111	Storage-Stable Foamable Polyurethane is Activated by Heat
66-10121	Compound Improves Thermal Interface Between Thermocouple and Sensed Surface
66-10185	Improved Adhesive for Cryogenic Applications Cures at Room Temperature
66-10194	Silazane Polymers ShowPromisefor High-Temperature Application
66-10259	Substituted Silane-Diol Polymers Have Improved Thermal Stability
66-10395	Composite Gaskets are Compatible with Liquid Oxygen, Resist Compression Set
66-10487	Adhesive for Polyester Films Cures at Room Temperature, Has High Initial Tack
66-10646	Process Produces Chlorinated Aromatic Isocyanate in High Yield
67-10016	Dispersion of Borax in Plastic is Excellent Fire-Retardant Heat Insulator
67-10100	Synthesis of Various Highly Halogenated Monomers and Polymers
67-10132	Static Electricity of Polymers Reduced by Treatment with Iodine
67-10168	*Isostatic Compression Process Converts Polyaromatics into Structural* Material
67-10197	New Class of Thermosetting Plastics Has Improved Strength, Thermal and Chemical Stability
67-10429	Adhesives for Laminating Polyimide Insulated Flat Conductor Cable
67-10593	Solvent Permits Solid Curing Agents to be Used at Room Temperatures
67-10634	Photovoltaic Effect in Organic Polymer-Iodine Complex
67-10647	Synthesis of Pure Aromatic Glycidyl Esters for Use as Adhesives
68-10358	Fire Retardant Foams Developed to Suppress Fuel Fires
68-10360	Fiberglass-Reinforced Structural Materials for Aerospace Application
69-10072	Refractory-Metal Compound Impregnation of Polytetrafluoroethylene
69-10074	Adhesive for Cryogenic Temperature Applications
69-10118	New Rapid-Curing, Stable Polyimide Polymers With High-Temperature Strength and Thermal Stability
69-10299	Heparin Insolubilized with Crosslinking Agent
69-10511	Thermally Conducting Electron Transfer Polymers
69-10559	Development of Improved Potting and Conformal Coating Compounds
69-10580	Silphenylene Elastomers Have High Thermal Stability and Tensile Strength
69-10636	Synthesis of Polyethers of Hexafluorobenzene and Hexafluoropentanediol
69-10744	Production of Crystalline Polymers via Liquid Crystal Monomers

ATTACHMENT III

EXHIBIT II. NEW PLASTICS APPLICATIONS ANNOUNCED IN NASA TECH BRIEFS

Tech Brief Number	Tech Brief Title
63-10387	Portable Flooring Protects Finished Surfaces, Is Easily Moved
63-10564	A Technique for Making Animal Restraints
63-10568	Plastic Molds Reduce Cost of Encapsulating Electric Cable Connectors
63-10579	Small Foamed Polystyrene Shield Protects Low-Frequency Microphones from Wind Noise
63-10613	Cryogenic Waveguide Window is Sealed with Plastic Foam
64-10068	Mechanical Properties of Plastics Predetermined by Empirical Method
64-10151	Plastic Films for Reflective Surfaces Reproduced from Masters
64-10178	Machine Tests Crease Durability of Sheet Materials
64-10280	Servo System Facilitates Photoelastic Strain Measurements on Resins
65-10004	Screening Technique Makes Reliable Bond at Room Temperature
65-10046	Wide-Aperture Solar Energy Collector is Light in Weight
65-10088	Fiberglass Parts Cured During Filament Winding Eliminates Oven, Saves Time
65-10065	Spherical Model Provides Visual Aid for Cubic Crystal Study
65-10090	Compact Assembly Generates Plastic Foam, Inflates Flotation Bag
65-10136	Vapor Pressure Measured With Inflatable Plastic Bag
65-10172	Aluminum Alloys Protected Against Stress-Corrosion Cracking
65-10177	Epoxy-Resin Patterns Speed Shell-Molding of Aluminum Parts
65-10256	Hollow Plastic Hoops Protect Thermocouple in Storage and Handling
65-10367	Flexible Plastic Ring Assembly Makes Durable Shaft Seal
65-10386	Drill Bit Design Assures Clean Holes in Laminated Materials
65-10396	Adhesive-Backed Terminal Board Eliminates Mounting Screws
66-10017	PTFE-Aluminum Films Serve As Neutral Density Filters
66-10080	Nylon Shock Absorber Prevents Injury to Parachute Jumpers
66-10081	Polytetrafluoroethylene Lubricates Ball Bearings in Vacuum Environment
66-10137	Rotating Mandrel Speeds Assembly of Plastic Inflatables
66-10147	Polymer Deformation Gauge Measures Thickness Change in Tensile Tests
66-10152	Nylon Bit Removes Cork Insulation without Damage to Substrate
66-10153	Argon Purge Gas Cooled by Chill Box
66-10334	Strippable Grid Facilitates Removal of Grid-Surfaced Conical Workpiece from Die
66-10387	Self-Supported Aluminum Thin Films Produced by Vacuum Deposition Process
66-10390	One-Piece Transparent Shell Improves Design of Helmet Assembly
66-10451	Reusable Chelating Resins Concentrate Metal Ions from Highly Dilute Solutions
66-10455	Mylar Film Eliminates Silk Screening of Equipment Panels
66-10588	Plastic Tubing Protects Flexible Copper Hose
66-10609	Film Coating Permits Low-Force Scribing
66-10681	Thin Plastic Sheet Eliminates Need for Expensive Plating
67-10045	Resistance Heating Releases Structural Adhesive
67-10054	Method Accurately Measures Mean Particle Diameters of Monodisperse Polystyrene Latexes
67-10113	Nonwoven Glass Fiber Mat Reinforces Polyurethane Adhesive

EXHIBIT II. NEW PLASTICS APPLICATIONS ANNOUNCED IN NASA TECH BRIEFS (Continued)

Tech Brief Number	Tech Brief Title
67-10227	Photosensitive Filler Minimizes Internal Stresses in Epoxy Resins
67-10264	Inexpensive Cryogenic Insulation Replaces Vacuum Jacketed Line
67-10302	Improved Compression Molding Process
67-10381	Machining Heavy Plastic Sections
67-10383	Polarized Light Reveals Stress in Machined Laminated Plastics
67-10409	Scribable Coating for Plastic Films
67-10432	Vibration Damping Composition has Flush-Away Feature
67-10526	Dynamic Valve Seal is Reliable at Cryogenic Temperatures
67-10542	Plastic Shoe Facilitates Ultrasonic Inspection of Thin Wall Metal Tubing
67-10596	Epoxy Resins Produce Improved Plastic Scintillators
67-10600	Dynamic Captive Plastic Seal
67-10613	Polystyrene Cryostat Facilitates Testing Tensile Specimens under Liquid Nitrogen
68-10040	Heat-Shrink Plastic Tubing Seals Joints in Glass Tubing
68-10063	Plastic Preforms Facilitate Fabrication of Welded Cordwood Electronic Modules
68-10132	Improved Molding Process Ensures Plastic Parts of Higher Tensile Strength
68-10318	Compressible Sleeve Provides Automatic Centering for Grinding or Turning of Cylinders
68-10406	Fiberglass Prevents Cracking of Polyurethane Foam Insulation on Cryogenic Vessels
68-10523	Evaluation of a Fluorocarbon Plastic Used in Cryogenic Valve Seals
69-10012	Microwave Interferometer Controls Cutting Depth of Plastics
69-10049	Teflon-Packed Flexible Joint
69-10066	Fractography Can Be Used to Analyze Failure Modes in Polytetrafluoroethylene
69-10310	Precision Mounting for Instrument Optical Elements Provided by Polyimide Bonding
69-10330	Simple Test Indicates Degree of Cure of Polyimide Coatings
69-10366	Instrumentation for Nondestructive Testing of Composite Honeycomb Materials
69-10406	Quick-Set Temporary Bonding Clamps
69-10408	Self-Lubricating Gear
69-10450	Improved Fire Resistant Radio Frequency Anechoic Materials
69-10519	Flared-Tube Fittings with Replaceable Seat Inserts
69-10530	A Method for Observing Gas Evolution During Plastic Laminate Cure
69-10540	Improved Primer for Bonding Polyurethane Adhesives to Metals
69-10615	Design of Multilayer Insulation Systems
69-10649	High-Pressure Seals for Rotary Shafts

ATTACHMENT III

EXHIBIT III. A LIST OF TYPICAL LITERATURE SEARCHES PERFORMED FOR THE PLASTICS INDUSTRY BY THE NORTH CAROLINA SCIENCE AND TECHNOLOGY RESEARCH CENTER

New Developments in Polymer Chemistry and Physics
Polyethylene Terephthalate
Exposure of Plastics and Polymers to Light Sources
Design Criterion for Reinforced Plastics
Use of Polyethylene in Reinforced Plastics
High Temperature Resistant Polymers and Plastics
High Temperature Polymers and Plastics Containing Boron
Polyethylene Foaming and Molding
Vacuum Forming of Plastics
Treatment of Polyethylene with Gamma Radiation
Chemically Resistant Polymers
Plating of Polymers
Fibers and Reinforced Plastics
Polymerization of Polymer for Fibers
Bonding of Polyethylene
Semiconductor Organic and/or Polymeric Materials
Mechanical Properties of Plastics
Plastic Pressure Vessels
Fluorine Polymer Adhesives and Elastomers
Plastics Forming
Metallic Coating on Plastics
Extrusion of Ceramics, Plastics and Plastics Composites
Flame Retardant Additives for Plastics
Adhesive Bonding of Polyester Fibers to Rubber
Photocell Indicator of Polymer Density
Polymerization of Fiber-producing Materials
Hysteresis in Polymer and Fibers
Effect of Aging on Fibers and Polymers
Polyvinyl Chloride and Polypropylene
Plastics Bearing

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ATTACHMENT IV

SUMMARY OF TECHNOLOGY TRANSFER REPORTS INVOLVING NASA-GENERATED PLASTICS TECHNOLOGY

NASA CONTRIBUTIONS	TRANSFER STAGES†					
	1		2		3	
	Cont.*	Term.	Cont.	Term.	Cont.	Term.
FORMULATIONS						
• HYSTL		2782** 2882 9267 11259		1550	11194 12760 42552	
• LOX-Compatible Adhesive					42937	
• LOX-Compatible Plastic				42936		
• Nylon-Filled Epoxy-Polyamine						27958
• P13N			42934		31988 42550	
• Polyurethane Foam		21798	42935	20138		
• Pyrrones	42930 42931 42932		9267 44079		42928 42929	
• Thermally Conducting Electron Transfer Polymers	43005	43004				
APPLICATIONS						
• Captive Plastic Seal					4574	
• Fluorel Flameproofing					43001 43002	
• Nonflammable Polyimide Plastic Laminates					43003	
• Plastic Gasket					5737	

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* The action status, continuing or terminated, of transfer cases at the time DRI-PATT contacted users. Cases are classed as terminated when (a) no further adaptation or adoption is contemplated, (b) a better technical alternative has been found, or (c) continued transfer activity is not economically feasible.

** Numbers in columns refer to PATT case numbers.

† At the time the plastics presentation was developed, the transfer process was defined to include three "stages": awareness, evaluation, and in-house use or prototype testing. With the development of subsequent presentations, a fourth transfer stage--"marketing"--was added.

HYSTL

TECHNOLOGY TRANSFER EXAMPLE SUMMARY

During 1964 a major aerospace contractor began work on a Lewis Research Center contract to develop new materials for rocket thrust chamber ablators. A new class of thermosetting plastics resulted from the research; and while it was unsatisfactory for ablator applications, its many unique properties were immediately obvious for other purposes. The material is noted for its processing simplicity. It has a long shelf life at ambient temperatures in an intermediate rubber stage, is workable in the precured state and cures rapidly. The end product has high thermal stability and strength at high temperatures, good chemical stability and stiffness, and unusual electrical properties and radiation stability. Title to the invention was waived to the aerospace firm, and a Tech Brief was published in 1967. Since then NASA has received more than 400 inquiries concerning the material.

In 1968 the aerospace firm helped establish a new company that would form and market plastic products incorporating the new material. Agreement was also reached with a major Japanese chemical firm to supply basic ingredients, in return for marketing rights in Japan. More than $1, 500, 000 has been invested in the commercial development of the new plastic. When it became commercially available, the price of the new material was approximately $1 per pound; potential reductions by as much as 50 percent are expected, as economies are achieved. The aerospace subsidiary firm is now perfecting a processing method that will allow forming the material into auto body parts. A maker of microwave ovens intends to utilize the plastic for trays for microwave ovens, where the material's radiation stability will be valuable. Experiments conducted for a clay pipe manufacturer indicate that a composite material with as little as 15 percent or less of the new plastic has considerable strength when molded into pipe fittings. They have excellent potential for transporting corrosive materials, including sewage (42552).

The NASA Tech Brief has been used by many other firms with varying success. One company (12760) developed a plastic housing for a photocell used for sun attitude control for unmanned rockets. The plastic was able to withstand the great thrust and vibration that had caused earlier models of the photocell to disintegrate. Another firm (11194) formulated a modification of the plastic and used it to coat an oil temperature sensor, and anticipated that the increased value of the device would amount to $100, 000 in annual sales.

A casket manufacturer (11259) evaluated the Tech Brief for possible innovations in casket material. This firm wanted an inexpensive plastic that could be easily cast rather than injection-molded, and the evaluation of the Tech Brief produced a negative judgment concerning the likely cost of the innovation. A maker of grinding wheels (9267) also decided against using this plastic as a binder for diamond grinding wheels. Evaluation of alternative plastics continues with the firm, and one of the new candidates is another NASA-originated plastic, called pyrrones.

Control Numbers

Tech Brief Number: 67-10197
NASA Center: Lewis Research Center
PATT Case Numbers: 9267, 11194, 11259, 12760, 42552
TEF Number: 6
Date of Latest Information Used: August 3, 1970

LOX-COMPATIBLE ADHESIVE

TECHNOLOGY TRANSFER EXAMPLE SUMMARY

A California firm (42937), working under NASA contract, developed a structural adhesive system suitable for use with liquid oxygen. The work centered around the preparation of fluorinated polyurethanes and the synthesis and testing of various monomers and prepolymers.

As a result of its work, the firm has made several patent applications. One such patent application deals with the preparation of tetrafluor-m-phenylenediamine, a precursor of a liquid oxygen compatible, fluorinated polyurethane adhesive. Although there are no plans to use the diamine in meeting specific commercial needs, it may be useful with other specialized resins produced by the firm.

While expenditures to prepare the chemical for possible commercial applications have been modest, the firm has sold two pounds at $145 per pound to other research and development organizations.

Control Numbers

Tech Brief Number:	None
NASA Center:	Marshall Space Flight Center
PATT Case Number:	42937
TEF Number:	314

Date of Latest Information Used: August 12, 1970

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LOX-COMPATIBLE PLASTIC

TECHNOLOGY TRANSFER EXAMPLE SUMMARY

A Southern chemical company (42936) performed basic research on polymers with the objective of developing new types of elastomers that would retain basic properties under temperature conditions created by contact with liquid oxygen. A chemist employed by the firm said that he thought that a process for synthesizing 1-2 difluorethylene would yield the desirable properties; however, the polymer did not have the required flexibility or resistance to attack in the presence of liquid oxygen. Management personnel said that the polymer might have properties of value in commercial applications and received a patent waiver from NASA in 1965.

After spending more than $5, 000 in analyzing the commercial potential of the manufacturing process, the company officials decided the market was not favorable and abandoned the waiver and development project. Manufacturing costs were quite high, especially in relation to the attainable new properties. Because little information concerning the cryogenic plastic research was available, the company recently published its research findings.

Control Numbers

Tech Brief Number:	None
NASA Center:	Marshall Space Flight Center
PATT Case Number:	42936
TEF Number:	A - Plastics

Date of Latest Information Used: August 12, 1970

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NYLON-FILLED EPOXYPOLYAMINE

TECHNOLOGY TRANSFER EXAMPLE SUMMARY

Employees of Telecomputing Corporation, under contract to NASA's Western Operations Office, devised a method of formulating an adhesive that cures at room temperature and maintains effective bonding at cryogenic temperatures. The method entails adding one part of powdered nylon filler to two parts of an epoxypolyamine resin. As described in a 1966 Tech Brief, the nylon filler also markedly improves the adhesive strength and toughness of the epoxypolyamine resin.

A small California firm (27958), engaged in custom compounding of epoxy resins, silicones, and polyurethanes for high and low temperature uses, employed the Tech Brief to guide preparation of a proposal and sample material for a potential client. When the client abandoned his project the proposal was rejected. Although he foresees no additional applicability of the Tech Brief in his work, the general manager of the firm estimated that the document saved him 40 to 50 hours of research time while preparing the sample and proposal.

Control Numbers

Tech Brief Number:	66-10185
NASA Center:	Western Operations Office
PATT Case Number:	27958
TEF Number:	295

Date of Latest Information Used: August 13, 1970

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P13N

TECHNOLOGY TRANSFER EXAMPLE SUMMARY

Polyimides, well-known as high temperature polymers, were first introduced in 1961 by DuPont. They are among the most thermally stable organic polymers in existence, retaining their properties under long-term use at 500 °F and short-term use at even higher temperatures. In addition, polyimides are insoluble and infusible, have excellent radiation resistance and machining qualities, are inflammable,and are resistant to organic solvents and acids. They may be degraded by alkalies and tend to absorb water, which affects their electrical properties.

The common method for formulating polyimides is by a condensation reaction, which releases unwanted volatiles and water. While trying to develop ablator binders and adhesives under contract to NASA's Lewis Research Center, a theoretical chemist employed by a major California aerospace firm discovered a way to process a polyimide by an additive reaction. The method eliminates the evolution of water and volatiles; in addition, it permits rapid curing and simplifies storage and handling of the precured material. The resulting polymer, codenamed P13N, has high temperature thermal strength and stability and is impervious to a variety of chemicals. It should be widely applicable for uses in ablators, supersonic aircraft structures, jet engine components, circuit boards, flexible electrical cable insulation, and as a high temperature adhesive. P13N can be molded easily for applications in seals, self-lubricating bearings, valve seats and bushings. A Tech Brief describing the polymer was published in 1969.

NASA waived title to the invention to the contractor (42550). The firm developed commercial manufacturing processes, procedures for industrial processing, and introduced in limited quantities one product form, P13N. Subsequently, an exclusive license was taken by a large international chemical corporation. It is expected that this new arrangement will lead to a more expanded market and further development of the polymer.

A major electrical motor manufacturer (31988) is attempting to use P13N to develop a wire insulation for DC motors subject to abnormal external heat conditions. In another application effort, an aerospace firm is evaluating the polymer for use in the SST (42934).

Control Numbers

Tech Brief Number: 69-10118
NASA Center: Lewis Research Center
PATT Case Numbers: 31988, 42550, 42934
TEF Number: 217
Date of Latest Information Used: August 3, 1970

POLYURETHANE FOAM

TECHNOLOGY TRANSFER EXAMPLE SUMMARY

While performing research on heat shieldmaterials, scientists at Ames Research Center invented a lightweight, fire-retardent plastic foam. As described in a 1968 Tech Brief, the material is a semirigid or rigid polyurethane foam having uniformly dispersed in it a halogenated polymer. When heated, the material chars and hydrogen halide is evolved. The char layer and released gases help quench the flame. The density of the foam can be varied from 2 to 50 pounds per cubic foot, enhancing the versatility of the material for fire protection in aircraft, spacecraft, homes, autos, boats, trains, and in industries such as petrochemicals, paint and chemical processing, and laboratories. NASA has received almost 100 inquiries since issuing a Tech Brief describing the foam.

An Eastern manufacturer (20138) used the TSP to develop material for controlling an induced explosion in a production process. The foam performed adequately in controlling the explosion, but it also had undesirable side effects and was therefore rejected as a possible solution to the problem. The Department of Labor of an Eastern state (21798) has the TSP on file for reference concerning fire safety. A large aerospace contractor (42935) is evaluating the foam for aircraft fireproofing potential. If the studies funded by NASA are fruitful, the firm will extend its explorations into potential commercial applications.

Control Numbers

Tech Brief Number:	68-10358
NASA Center:	Ames Research Center
PATT Case Numbers:	20138, 21798, 42935
TEF Number:	17

Date of Latest Information Used: August 13, 1970

PYRRONES

TECHNOLOGY TRANSFER EXAMPLE SUMMARY

Aerospace requirements for materials with exceptional resistance to heat, light, and radiation pose a never-ending research problem. In 1965 a Langley Research Center scientist, Vernon Bell, independently discovered a new class of aromatic/heterocyclic step-ladder and ladder organic polymers, designated "pyrrones." These thermosetting resins result from the reaction of an aromatic tetra-amine with an aromatic dianhydride. At an intermediary stage the polymer has a structure like nylon, and through a thermal-curing process it forms a polybenzimidazole (PBI) or polyimide (PI) before evolving to the pyrrone structure. The resulting combination of PBI and PI structures yields a polymer with greater rigidity than either PBI or PI, with exceptional thermal and radiolytic stability. The polymer is nonflammable and can be heated to incandescence without burning. Long-term stability to 500°F and short-term stability to 1,000°F suggest the heat resistance qualities of the new polymer. Up to ten times the amount of radiation that degrades other polymers can be withstood by pyrrones. The material has great potential for use in high temperature films, coatings, adhesives, resins for laminates and filament windings. Pyrrone moldings are easily filled with reinforcing materials and produce very hard machinable surfaces.

A NASA Technical Note (TN D-3148) was issued in 1965, followed by Tech Brief 66-10043. Interest was immediate and widespread, but few inquirers were decisively motivated to pursue their own development activities. A Southern company (42930) wanted to evaluate the material for use in production processes for a defluorinated phosphate feed supplement. Acid by-products and high temperatures (to 1,700°F) commended the use of a heat-stable plastic. The firm still wishes to purchase such material, and low price is a major criterion in evaluation of various alternatives. An Indiana electrical cable manufacturer (42931) also would like to purchase a material with pyrrone's characteristics, but has similarly been unable to locate a source. A major chemical company (42932) has been interested in pyrrones for over three years, but has been unable to obtain adequate information.

The unavilability of pyrrones, which slowed early attempts to transfer the technology, may end soon. Two major aerospace contractors (42928, 42929) have recently produced evaluation batches of the material. Both of these contractors acquired their pyrrone formulating capabilities through contract work under a Langley program of collaboration with industry and universities to explore the application potential of pyrrones. Both firms are also continuing in-house programs to find commercial uses for pyrrones, with emphasis on laminates, bearing applications (42929) and electrical cable coatings (42928). Another aerospace company is comparing pyrrones with polyimides for SST applications (44079). In addition, an abrasive grinding wheel manufacturer is evaluating pyrrones for use as a binder for diamond grinding wheels (9267).

Control Numbers

Tech Brief Number: 66-10043
NASA Center: Langley Research Center
PATT Case Numbers: 9267, 42928, 42929, 42930, 42931, 42932, 44079
TEF Number: 5
Date of Latest Information Used: September 3, 1970

THERMALLY CONDUCTING ELECTRON TRANSFER POLYMERS

TECHNOLOGY TRANSFER EXAMPLE SUMMARY

Advances in electronic circuitry, such as subminiaturization of components and modular circuit construction have been accompanied by serious problems in environmental protection, mechanical shock, radiation and temperature. Some potting compounds provide good mechanical shock and radiation protection; but because they are poor heat conductors, and therefore act as thermal insulators, they often cause poor electronic performance.

In 1969, scientists employed by McDonnell-Douglas Corporation published a Tech Brief summarizing the results of their work under NASA contract, which resulted in new polymeric materials that exhibit outstanding thermal conductivity in addition to excellent shock protection and electrical resistance. The thermal conductivity of the polymers is larger by a factor of 10 than that of most organic polymers; and their electrical resistivity is about double that of other charge-transfer polymers.

The president of a small Eastern plastics firm (43004) inquired about commercial use of the invention, but upon evaluating the market potential of the material, decided that he could not afford the substantial investment necessary to market it. In another application effort, a major aerospace contractor (43005) with greater financial resources is evaluating the technical information for potential commercial use.

Control Numbers

Tech Brief Number: 69-10511
NASA Center: Goddard Space Flight Center
PATT Case Numbers: 43004, 43005
TEF Number: 325
Date of Latest Information Used: August 20, 1970

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CAPTIVE PLASTIC SEAL

TECHNOLOGY TRANSFER EXAMPLE SUMMARY

Cryogenic temperatures impose especially difficult conditions for the functional integrity of most plastics and elastomers used in seals. In order to obtain zero leakage of cryogenic materials, a seal must have total surface conformity; but the very low temperatures cause plastics to become brittle, shrink, and lose resiliance with the result that a seal using these materials does not perform well.

An engineer employed by a NASA contractor invented a "captive plastic seal" that achieves total surface conformity. For cryogenic applications, teflon provides ideal sealing characteristics when its extrusion under pressure is contained by abrasion-resistant metal rings. The surfaces to be sealed are tightly compressed; the resulting pressure on the teflon exceeds its compressive yield point and causes it to act as a fluid flowing into adjacent surface irregularities to provide sealing. The reusable seal thus minimizes requirements for "super-finishing" sealing surfaces and it can accommodate misalignment and surface separations. It operates under fluid pressures to 12, 500 psi and temperature ranges from -450°F to +550°F.

The basic invention was described in a 1967 Tech Brief. In August 1967, a waiver was granted to the contractor. He, in turn, licensed a California plastics manufacturer (4574) to produce and market the device. Initially, only one size was produced; but the firm now offers a full range of standard sizes. Captive plastic seals may be used for all flange-type plumbing, and as components in hydraulic systems, hazardous fluid systems and cryogenic systems.

Control Numbers

Tech Brief Number:	67-10600
NASA Center:	Marshall Space Flight Center
PATT Case Number:	4574
TEF Number:	207

Date of Latest Information Used: July 27, 1970

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FLUOREL FLAMEPROOFING

TECHNOLOGY TRANSFER EXAMPLE SUMMARY

Fluorel, a copolymer of hexafluoropropene and vinylidene fluoride, is a nonflammable elastomer available under various names from several major chemical companies. NASA's search for flameproof materials for the interior of Apollo command modules culminated with fluorel, which was also used for walls and furnishings in the mobile quarantine facility used after the moon flights.

Two rubber manufacturers were involved in projects that yielded modifications of basic fluorel for the Apollo applications. Both are pursuing nonspace applications, largely in aircraft interiors but also in oceanographic and other oxygen-rich environments. One of these firms (43002) anticipates a large market in such applications where price is not a decisive factor and safety is a primary consideration. Some aircraft are already equipped with structural and decorative fluorel materials supplied by this firm. The other company (43001) has achieved promising initial test results with aircraft wire bundle coatings and carpeting and tile for aircraft galleys. A serendipitous by-product of the company's ongoing development work with fluorel is a new potting compound consisting of several polymers, some of them proprietary with the firm. The compound will not burn and cures at room temperature. If it passes tests being conducted by several aircraft manufacturers, it will constitute a major advance in the state-of-the-art, since no existing potting compounds are nonflammable.

<u>Control Numbers</u>

Tech Brief Number:	None
NASA Center:	Manned Spacecraft Center
PATT Case Numbers:	43001, 43002
TEF Number:	324

Date of Latest Information Used: August 20, 1970

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NONFLAMMABLE POLYIMIDE PLASTIC LAMINATES

TECHNOLOGY TRANSFER EXAMPLE SUMMARY

A California aerospace firm (43003) became involved in developing a new fireproof polymer in 1968, following the Apollo 7 fire. Under NASA contract, the firm discovered a new process for formulating a preimpregnated B-stage polyimide by dissolving a commercially available material, N-methyl pyrrolidone (NMP) solvent, to form a 12-15 percent solution. The resulting PI structural laminate is self-extinquishing in 16.5 psia pure oxygen. The patented process requires rigorous controls, since NMP boils at 395°F and water condensation occurs. Reinforced with glass laminate material, the PI can be cast in an RTV silicone rubber coated mold, and it is readily tooled at temperatures to 600°F. It is dimensionally stable, so shrinkage is easily predictable. Low outgassing properties assured its safety for use in an Apollo food storage container. Flame tests have demonstrated the nonflammability of the PI in 16.5 psia pure oxygen. Compared with aluminum, the material has superior strength-to-weight ratios and is far less costly for making complex parts.

The firm has made more than 3,000 Apollo parts in more than 50 design configurations, ranging from battery terminal covers to large protective panels. Commercial possibilities are being investigated for fireproofing applications in aircraft, autos, marine vehicles, furnaces, fuel systems, engines, electrical components and railroad tank cars.

Control Numbers

Tech Brief Number:	None
NASA Center:	Manned Spacecraft Center
PATT Case Number:	43003
TEF Number:	326

Date of Latest Information Used: August 20, 1970

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PLASTIC GASKET

TECHNOLOGY TRANSFER EXAMPLE SUMMARY

Axial joints incorporating metals of differing hardness, or metal alloys with an affinity for each other, in close stressful contact often deteriorate because of fretting. Expensive plating of the mating surfaces has been a common remedy. In 1966, R. L. Stremel of North American Aviation, under contract to NASA, discovered that an ordinary thin plastic sheet could be interposed between the mating surfaces and completely eliminate the fretting.

A Tech Brief describing the plastic gasket technique was used by a materials engineer, employed by an Ohio power equipment manufacturer (5737), to help solve a fretting problem. In the process, he tested a variety of plastic materials. He discovered that teflon was too soft; he rejected polyphenylsulfide because it squeezed out of the joint. Nylon, which passed all laboratory tests, is now being field tested by an airline. Early research with the airline has been aimed at increasing the maintenance-free time of gasket units from 1,000 hours to 5,000 hours.

Control Numbers

Tech Brief Number:	66-10681
NASA Center:	Marshall Space Flight Center
PATT Case Number:	5737
TEF Number:	236

Date of Latest Information Used: August 3, 1970

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