CHEMICAL RESEARCH PROJECTS OFFICE FUNCTIONS
ACCOMPLISHMENTS PROGRAMS

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CHEMICAL RESEARCH PROJECTS OFFICE
FUNCTIONS ACCOMPLISHMENTS PROGRAMS

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MISSION

The Chemical Research Projects Office conducts basic and applied research in the fields of polymer chemistry, polymeric composites, chemical engineering and biophysical chemistry. Primary objectives are to achieve fire safety and human survivability as they relate to commercial and military aircraft, high-rise buildings, mines and rapid transit transportation. The Office responds to national problems, when possible, by identifying the nonmetallic materials and chemistry needed for the solution of the problem and by participating in the development and application of these materials.

Research and development are therefore performed to develop a strong technological base which supports both the aerospace and domestic needs of the nation. Skills are maintained and developed in the areas of polymer synthesis and characterization, the development and processing of polymeric materials composites, and the basic analytical chemistry and instrumentation needed to support the above activities. A scientific interdisciplinary approach is commonly used in the solution of problems. New and improved materials systems and other fire control systems (e.g., high temperature polymeric foams, composites and fire extinguishing systems) are developed primarily for aerospace applications and can also often be applied to national domestic needs. The Office acts as a liaison between Center scientists and the Engineering community and assures that relevant technology is made available to other NASA Centers, agencies and industry. Before this technology can be transferred, in many cases, bench scale to full-scale tests are conducted of the aircraft systems and sub-systems which have been modified or retrofitted with the Ames' developed materials in order to demonstrate the improvements in performance obtained through the utilization of these materials and fire control measures.

PURPOSE

1. To identify the chemical research and technology required for solutions to problems of national urgency, synchronous with the aeronautics and space effort.
2. To conduct both basic and applied interdisciplinary research on chemical problems, mainly in areas of macromolecular science and fire research.

3. To provide productive liaison with the engineering community and effective transfer of technology to other agencies and industry.

SCOPE

1. **Transportation safety in human environments:**
   a. Fire control in vehicles and structures.
   b. Development of high performance aircraft tire and brake materials.
   c. Development of high temperature elastomers for fuel tank sealants for advanced supersonic and conventional aircraft.
   d. Fire extinguishing methods.
   e. Toxicity studies of fire-retardant materials.

2. **Space exploration and advanced aircraft progress:**
   a. Development of advanced aerospace materials.
   b. Materials for environmental extremes—Entry Thermal Protection.
   c. Fire-resistant, functional, nonmetallic materials for aircraft applications.

3. **Technology utilization for civil applications:**
   a. Utilization of skills in combustion, heat transfer and fluid mechanics to simulate the heating environment associated with accidental liquid propane gas (LPG) fires and application of this characterization to LPG railroad tank cars via a fire test facility.
   b. Utilization of the technology of high temperature materials development for reentry for application to high temperature friction materials, e.g., automobile brakes.
   c. The application of high temperature fire resistant materials technology for mine safety; structures and coatings applications in work coordinated with the Bureau of Mines.
d. Utilization of the technology base developed for aircraft crash-fire survivability for application to fire refuges for high rise dwellings.

e. Development of microanalytical chemical systems and the application of chemical modeling to biomedical problems, e.g. morphine detector.

f. Application of the technology base developed for aircraft interior materials to rapid transit systems.

g. Utilization of computer technology for mapping liquid natural gas spills in inland harbor areas.

ACCOMPLISHMENTS

1. Research Achievements:

a. Demonstrated that the stable free radicals which are formed during high temperature curing of poly-p-phenylene contribute largely to the long term thermal oxidation of this polymer, and the establishment of the limits of service of organic polymers for high temperature uses.

b. Characterized the molecular weight distribution of a new class of polyaromatic ethers and found a relation with their heats of reaction.

c. Demonstration of a structure-properties relationship to increase the Tg by 125° without limiting the mechanical properties when indane is substituted for bisphenol-A in the polycarbonate polymer. The char yield increases, high impact strength and good transparency are maintained and a reduction in flammability is obtained.

d. It has been found that phenolphthalein can be copolymerized with bisphenol-A to yield a polymer which is processable and with increased char yield and Tg and a much reduced flammability.

e. The heat penetration of a laser impulse was found to be inversely proportional to the degree of aromaticity in a polymer.

f. Discovery of new energy transfer process in macromolecules.

g. Identification of nitro-aromatic amine derivatives as intumescent agents.

h. Establishment of new techniques and materials for analytical modeling of polymer pyrolysis processes.
i. Spectroscopic characterization for indole charge transfer process.

j. Microstructural changes in diene polymers during pyrolysis.

k. Identification of new thermochemical mechanisms of flame inhibition resulting from spectroscopic studies of hydrogen halides in diffusion flames.

l. Identification and characterization of silicon carbide as the major char component of the Apollo spacecraft heat shield after entry.

m. Development of thermally stable polymers from the reaction of \( N,N' \) bis(p-nitrophenyl) sulfamide and p-benzoquinone dioxime acid mixtures.

n. Discovery of the linear correlation of the association constants of 1:1 complexes of methoxy amphetamines and 1,4 dinitrobenzene to the threshold hallucinogenic dose in humans.

o. Discovery of the effectiveness of gellant polymer-water system (polyacrylamide formulated with suitable scavengers for fuel components) to control hypergolic fires of \( N_2O_4 \) and hydrazine.

2. Developments:

a. Developed a new aircraft tire retread formulation with improved heat build-up and heat blow-out properties.

b. Developed a new method for screening solid fire extinguishants.

c. Chemical fire extinguishing systems have been developed for jet engine nacelles while engine is running under high air velocity.

d. Development of a new class of intumescent coatings, 45B3 and 313, and flexible versions of the same.

e. Development of high molecular weight perfluoroalkylene ether-heterocyclic polymers as promising high-temperature fuel tank sealants.

f. Development of a low-density PBI foam for aircraft interiors and fuselage and for general application.

g. Development of a polyimide foam for thermal insulation and fire resistance.

h. An instrumental system for comprehensive evaluation of evolved gases, smoke and toxicity of pyrolyzed nonmetallic materials has been developed. (T-4 Facility).
i. Environmental stabilization of polyurethane baffle foam by the use of coatings.

j. Development of fire-retardant foams:
   (1) Semi-rigid urethane (51).
   (2) Reinforced urethane (51-10AQ-B, 5A-43).
   (3) Semi-rigid isocyanurate.
   (4) Flexible neoprene modified urethane.
   (5) Low and high density polybenzimidazole.
   (6) Low density polyimide.

k. Development of intumescent fire-retardant formulations: Coatings for structural protection and for thermal-protection of weapons.

l. Basic parameters for new dangerous drug detector.

m. Ablative and thermal structures for LEM.

n. Development of isocyanurate foam-intumescent coating system and concept to increase survivability in aircraft ground crash fires.

o. Development of low density 5A43 reinforced urethane-composite system to protect Navy aircraft from fires initiated from incendiary projectiles.

p. Development of new brake lining materials based on high temperature polymeric composites with improved performance characteristics.

q. Development of non-smoking, fire-resistant foams (polyimide and polybenzimidazole).

r. Development of fire-resistant, char-forming clear polymers, i.e., phenolphthalein polycarbonate, and cured tetrafunctional epoxy resin for application as windows and canopies for aircraft.

s. Catalytic conversion of water-hydrocarbon fuel mixture to methane gas using commercially available catalysts.

t. Development of bismaleimide resin composite structures; development of room temperature cure bismaleimide coatings.

u. Development of low cost polybenzimidazole prepolymer.

v. Development of low density polybenzimidazole foam for cryogenic and high temperature insulation applications.
w. Development of methodology for assessing the toxic threat level of pyrolysis gases produced from aircraft interior materials.

3. **Applications:**

a. Development of replica windows for Boeing 737 aircraft with improved impact and fire resistance through the use of a new kind of transparent, laminate, polyaromatic type polymer.

b. Urethane, void space, ballistic foam (5A-43) developed for use on Navy A-4 aircraft qualified and being used on the Fairchild A-10 fighter aircraft. The same material is also used on the McDonnell Douglas F-15 aircraft for ballistic protection against high velocity fragments.

c. Application of intumescent coatings and urethane foam to the F-15 Gun System to prevent catastrophic explosions resulting from fire and fire propagation of ignited rounds.

d. Application of intumescent formulations to explosive devices and missiles to achieve cook-off protection against fires (U.S.N. 500 lb. bombs, Harpoon missile and 20 mm gun pod).

e. Application of intumescent formulations and urethane foam for thermal protection of the Space Shuttle Vehicle during ascent phase.

f. Application of bismaleimide laminate-polyimide foam composite structures as fire-resistant bulkheads for crash-fire protection of aircraft.

g. Application of fire-retardant foams as accoustical insulation for aircraft.

h. Utilization of Ames fire-resistant materials in the JSC 737 test program.

i. Development of fire-resistant panels for aircraft interiors consisting of bismaleimide laminate and polybenzimidazole foam (or polyquinoxaline foam).

**POLYMER RESEARCH AND DEVELOPMENT GROUP**

The activities of this group support the aerospace and non-aerospace programs, and its objectives are specifically established for the purpose of providing a sound technology base.
1. The synthesis and characterization of new and improved polymers include:
   a. Fire-resistant polymers of the polyphosphazene series (inorganic) for flexible foams, moldings and coatings.
   b. Transparent and fire-resistant polycarbonates of the bisphenol series (aromatic groups substituted on the pivotal carbon atom) which can be used for aircraft windows, canopies and coatings. The phenolphthalein polycarbonate has also been synthesized and studied.
   c. Sealants for aircraft fuel tanks include new elastomers such as s-triazine and other heterocyclic linked perfluoroalkylene ethers.
   d. Elastomers (synthetic rubber) for aircraft tires having higher temperature and stress service involve the study of vinyl polybutadiene and trans polypentenamer.

2. The thermal degradation of polymers and polymeric composite systems is being investigated as related to fires aboard commercial and military aircraft.
   a. The mechanisms of degradation of fire-resistant polymers are being studied to determine the underlying thermochemistry responsible for flammability, toxicity and smoke formation. The fire-resistant polymers of interest are the polybenzimidazoles, polyquinoxalines, polyphenylenes and polybismaleimides.
   b. The toxic effects from the gases and smoke which arise from the pyrolysis of polymeric materials are determined for both neat polymers and the total polymeric composite system as used in aircraft structures. Animal assays are used to assess the toxicological effects of the pyrolysis products.
   c. Chemical fire quenching mechanisms are being studied to develop an understanding of the processes which will lead to the development of dry chemical systems specifically engineered to aircraft engine and interior fires.

3. Fire modeling studies on polymers are performed to determine ignition and quenching processes.

4. The synthesis of polymers via heterogeneous catalysis with very high stereoregularity is being studied with a view toward possible space processing and/or manufacturing applications.

5. The physical chemistry of certain classes of compounds having biological activity and forming charge-transfer complexes has been studied, e.g., indoles and phenylisopropylamines.
ADVANCED MATERIALS DEVELOPMENT GROUP

Formulation, processing and development of polymeric materials and composite systems are provided by this group as model and prototype specimens for chemical and engineering tests. Polymers derived from both NASA aerospace technology and industry are used to develop films, coatings, foams, composites and laminates for a variety of purposes, as listed below. Primarily, material systems are being developed which have greater fire-resistance and thermal insulative properties and a significant decrease in the toxicity of the pyrolysis products.

1. Interior aircraft fuselage panels are being developed which possess improved fire-resistance and insulative properties and decreased toxicity levels of pyrolytic products. These panels will also be used for the lavatories as secondary structures in the aircraft. Low density composites consisting of a honeycomb structure filled with polybenzimidazole foam and laminated on both sides with bismaleimide-glass material is one of the candidates for this purpose.

2. Transparent laminates of epoxy-boroxine and polycarbonates are being developed for use as aircraft windows and canopies. These laminates have greater impact strength and fire-resistance and also much greater laser resistance than materials currently being used.

3. Development work is being performed to make films and coatings from fire-resistant polycarbonates such as the phenolphthalein and fluorene polycarbonates.

4. Internal ballistic foams are being developed from polyphosphazene polymers and external ballistic foams developed from polybenzimidazole.

5. Advanced coatings for cook-off protection of ordnance and missiles in a fire environment are being developed through the use of intumescent materials.

6. New tire treads for aircraft are being developed using vinyl polybutadiene and trans polypentenamer as new elastomers.

7. Work is being performed to develop a carbodiimide foam for fire-resistance as part of a materials system for mine safety application.

8. Drum type brake linings are being developed, with a view toward disc brake pad application, utilizing NASA developed materials. New binder materials being studied are polybismaleimide, branched polyphenylene and polyquinoxaline. Potassium titanate fibers offer advantages over asbestos fibers which are being investigated.

9. New sealant material systems are being developed for aircraft fuel tanks. Formulation and processing parameters are being established for the use of perfluoroalkylene ethers cross-linked with heterocyclic agents such as s-triazines and oxadiazole.
10. Fire-resistant, flexible polyphosphazene-foam is being developed as candidate material for use in aircraft interior furnishings.

ENGINEERING MATERIALS AND FIRE TEST GROUP

The function of this group is to design and perform the appropriate tests on prototype material systems (models) with respect to fire dynamics and retardation, fire safety, thermal protection and toxicology as applied to sub-system models of aircraft. The development of methods and criteria for fire testing is also a function of this group. Also, the physical and mechanical properties of material systems are determined.

1. Work is being conducted to define the operating and testing parameters of a fire test facility to be constructed at Ames. Included will be the definition of the safety requirements, type of heat and fire source for testing, scrubbing of smoke exhaust and other parameters. Design of the facility will permit the testing of various aircraft configurations and components under varying conditions which simulate an aircraft interior or exterior fire.

2. Criteria for large scale fire tests for aircraft secondary structures are being developed. Fire tests will be conducted on lavatories, cargo bays and interior panels and furnishings.

3. Toxicological tests are conducted on new and improved fire-resistant polymers, composites and aircraft sub-systems and the results compared with those obtained from state-of-the-art materials currently used in aircraft interiors which are subjected to the same tests. Smoke and gas samples tested are derived from (a) full-scale fire tests (flaming and smoldering) of complete materials systems, and (b) controlled pyrolytic degradation (aerobic and anaerobic) of neat polymeric materials.

4. Design studies are performed to develop interior fuselage panels which have better fire-resistant properties and produce less smoke and toxic gases than currently used materials. A composite laminate consisting of polyquinoxaline foam in a polybismaleimide honeycomb laminated between two sheets of polybismaleimide-fiberglass has been developed as a candidate panel material.

5. Analytical models to predict fire environments and mechanism of fire inhibition and propagation are being developed.

6. New and improved dry chemical systems for fire quenching are being developed and tested for engine nacelle and cargo bay fires.

7. The analysis of materials applications problems is performed by (a) identification of application requirements and constraints for advanced
aerospace materials, and (b) selection of combinations of key properties required for specific applications.

8. Thermal, mechanical and physical tests are conducted to screen materials (neat polymers, polymeric composites and material systems) developed by the Chemical Research Projects Office. The state-of-the-art commercial materials are tested in a similar manner and the results are compared with those of the NASA-produced materials.
PUBLICATIONS


5. M. A. Golub: "Type II Thermal Cyclization in 1,2-Polybutadiene and 3,4-Polyisoprene." Polymer Letters, 12, 615 (1974).


25. M. A. Golub and R. J. Gargiulo: "Thermal Degradation of 1,4-Polysisoprene and 1,4-Polybutadiene." Polymer Letters, 10, 41 (1972).


49. M. A. Golub: "Photolysis of 1,4-Dichlorobutane Sensitized by the \( n,\pi^* \) Singlet State of Acetone." Journal of the American Chemical Society, 91, 4925 (1969).


PATENTS


CONTRACTS AND GRANTS

Current:


5. "Development of Design Criteria for a Fire Test Facility," University of California, Berkeley, NSG-2026-B.


Completed:


6. "Determination of Possible Relationships Between Spin Concentration and Rate of Oxidation," Stanford Research Institute, NAS2-8027.


PRESENTATIONS AND SPECIFICATIONS


4. M. A. Golub: "Thermal Cycloaddition of 1,2-Polybutadiene and 3,4-Polyisoprene." Presented at Western Regional Meeting of the American Chemical Society, San Francisco, Calif., October 16-18, 1974.


