NASA TECHNICAL MEMORANDUM

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CHEMICAL RESEARCH PROJECTS OFFICE: FUNCTIONS, ACCOMPLISHMENTS, PROGRAMS

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Moffett Field, Calif. 94035

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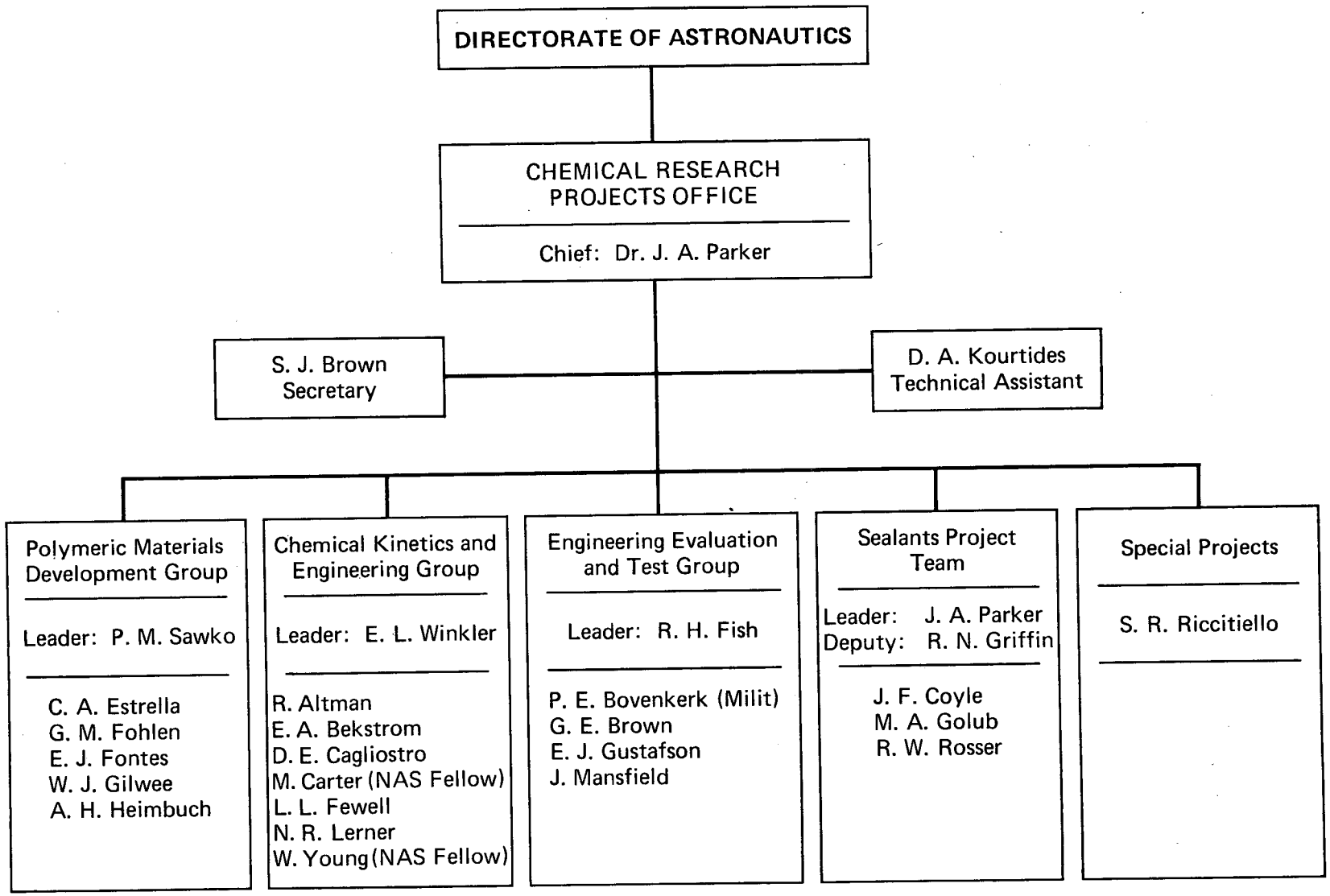
FUNCTIONAL (LINE) ORGANIZATION



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 liason 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 and application for civil applications:
   a. Development of morphine drug detector.
   b. Development of fire-protective coatings for LPG railroad tank cars.
   c. Development of improved brake linings for heavy duty use automotive vehicles and trucks.
   d. Development of refurbishment techniques for railroad ties.
   e. Development of high rise building fire safety concepts.
   f. Pollution control studies for internal combustion engines and other power plants.

ACCOMPLISHMENTS

1. Research Achievements:
   a. Discovery of new energy transfer process in macromolecules.
   b. Identification of nitro-aromatic amine derivatives as intumescent agents.
   c. Establishment of new techniques and materials for analytically modeling of polymer pyrolysis processes.
   d. Spectroscopic characterization for indole charge transfer process.
   e. Microstructural changes in diene polymers during pyrolysis.
   f. Identification of new thermochemical mechanisms of flame inhibition resulting from spectroscopic studies of hydrogen halides in diffusion flames.
   g. Identification and characterization of silicon carbide as the major char component of the Apollo spacecraft heat shield after entry.

h. Development of thermally stable polymers from the reaction of N,N' Bis(p-nitrophenyl) sulfamide and p-Benzoquinone dioxime acid mixtures.
i. 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.
j. 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. Development of fire-retardant foams:
      (1) Semi-rigid urethane(5I).
      (2) Reinforced urethane(5I-10AQ-B, 5A-43).
      (3) Semi-rigid isocyanurate.
      (4) Flexible neoprene modified urethane.
      (5) Low and high density polybenzimidazole.
      (6) Low density polyimide.
   b. Development of intumescent fire-retardant formulations:
      (1) Coatings for structural protection and for thermal-protection of weapons.
   c. Basic parameters for new dangerous drug detector.
   d. Ablative and thermal structures for LEM.
   e. Development of isocyanurate foam-intumescent coating system and comcept to increase survivability in aircraft ground crash fires.
   f. Development of low density 5A43 reinforced urethane-composite system to protect Navy aircraft from fires initiated from incendiary projectiles.
   g. Development of new brake lining materials based on high temperature polymeric composites with improved performance characteristics.
   h. Development of non-smoking fire-resistant foams (polyimide and polybenzimidazole).
   i. Development of fire-resistant, char-forming clear polymers, i.e., phenolphthaline polycarbonate, and cured tetrafunctional epoxy resin for application as windows and canopies for aircraft.
   j. Catalytic conversion of water-hydrocarbon fuel mixture to methane gas using commercially available catalysts.
   k. Development of bismaleimide resin composite structures; development of room temperature cure bismaleimide coatings.
   l. Development of low cost polybenzimidazole prepolymer.
   m. Development of low density polybenzimidazole foam for cryogenic and high temperature insulation applications.

3. Applications:
   a. Application of intumescent coatings adjacent to center jet engine of Lockheed L-1011 aircraft to protect aircraft structure from jet engine fires.
   b. Application of urethane foam in the intergral fuel tank assembly of Navy A-4 aircraft to achieve fuel systems cook-off protection against carrier deck fires and to reduce ballistic threat levels and in the wing fuel tank of Marine A-4 aircraft to reduce ballistic

threat levels.

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, Sidewinder 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 MSC 737 test program.

ENGINEERING EVALUATION TEST GROUP

Activities:

1. Analysis of materials applications problems:
   a. Identification of application requirements and constraints for advanced aerospace materials.
   b. Selection of combinations of key properties required for specific applications.

2. Design testing programs to evaluate materials for specific applications such as fire protection of commercial and military aircraft:
   a. Establish materials use specifications and design criteria for utilization of fire-retardant materials in aircraft.
   b. Develop screening programs for specific materials.

3. Conduct thermal, mechanical and other tests needed to screen materials developed by Chemical Research Projects Office:
   a. Measurement of thermal properties of high-temperature materials, and fire-resistant materials.
   b. Measurement of the mechanical properties of advanced aerospace materials.

4. Provide metallic and non-metallic materials physical testing as a service function for other research activities at the Center.

5. Conduct environmental and physical testing of state-of-the-art commercial materials and present results for comparison with NASA-produced materials for in-house evaluation.

6. Engineering evaluation of improved polymeric aircraft brake materials.

POLYMERIC MATERIALS DEVELOPMENT GROUP

Activities: Development of polymeric composites.

1. Material and process development and pilot level production of non-metallic materials for evaluation and other test programs.
2. New pilot processing methods for heterocyclic polymers and curable polyphenylene composites.
3. Preparation of nitroaniline derivatives for intumescent coatings.
4. Preparation of polyisocyanurate, polyurethane and polyimide foams.
5. Preparation of bismaleimide composites and room temperature cured fire-resistant coatings based on copolymers of bismaleimide and acrylonitrile.
6. Development of char-forming fire-resistant clear polymers for aircraft windows and canopies.
7. Preparation of preliminary materials and process specifications for materials developed.

CHEMICAL KINETICS AND ENGINEERING GROUP

Activities: Chemical kinetics, thermal-oxidative degradation of polymers and catalytic studies.

1. Chemical Kinetics:
   a. Chemical kinetics of complex gas-phase reactions and evaluation of fuel-fire kinetics and quenching mechanics.
   b. Kinetics studies of reactions in organic systems such as energy transfer and quenching reactions of halogenated hydrocarbons and scission and cross-linking reactions of polymeric materials.
   c. Development of solid fire extinguishing compounds i.e., definition of mechanism of fire extinguishing action of solid fire extinguishers for jet engine fire and definition of efficiency of fire extinguishment of existing and new solid fire-extinguishing compounds.

2. Thermal degradation studies of polyphenylene and other high temperature polymers by electron spin reconance; studies of the pyrolysis and offgassing products of high temperature polymers.

3. Methanation studies of hydrocarbon fuels for reducing polution of emissions produced from internal combustion engines and other power plant systems; studies of catalytic surfaces.

SEALANT PROJECT TEAM

Activities: Development of high temperature elastomers for aircraft fuel tank sealants.

1. Synthesis and vulcanization of sealant compositions.
2. Study of thermal degradation and stress relaxation of candidate sealants.
3. Microstructural characterization of candidate sealants.
4. Development of analytical models for prediction of sealant service life.
5. Compounding and evaluation of dynamic and thermophysical properties of filled sealants.
6. Study of interaction of titanium structures with sealants.
7. Evaluation of sealants using simulated flight tank assembly.
8. Pilot production, processing, and compounding of candidate sealants.

9. Flight testing of selected sealants.

CONTRACTS AND GRANTS

Current:

1. Study for synthesis of optically clear polymeric materials for high-temperature windows; Dow Chemical Co., NAS2-6388.
2. Design, development and delivery of a prototype protable detector of morphine in urine; Whittaker Corp.
3. Development and Evaluation of room temperature curing, fire-resistant coatings based on selected bismaleimides; Battelle Memorial Institute, NASW-1948.
4. Study of aircraft fire safety: Flame spreading across materials, Princeton University, NA2-6705.
5. Study of refractory modified high temperature structural composites, synthesis and properties; Lockheed Aircraft Corp., Lockheed Missile and Space Co., NAS2-7060.
6. Characterization of polybenzimidazole composite foams; Whittaker Corp. R and D Division, NAS2-7112.
7. Study of oxygen atom recombination on quartz surfaces; Stanford Research Institute, NAS2-6776.

Completed:

1. A study involving the characterization, synthesis and production of polybenzimidazole prepolymer; ESSO Research and Engineering Co., NAS2-6159.
2. Theoretical and experimental investigation of ignition and combustion mechanisms in polymer materials in both air and enriched atmospheres; Marshall Industries, NASW-1921.
3. Research on toxicity of pyropysis products of foams, intumescent coatings and Fluorel; University of Utah, NAS2-6063.
4. Study to formulate intumescent coating compositions; Hughes Aircraft Co., NAS2-6349.
5. Synthesis, physiochemical and biological measurements of a series of indole compounds; University of San Francisco, Grant NGR-05-029-066.
6. Kinetics of reaction of the by-products of ablative materials; Stanford Research Institute, NAS7-472.
7. Fire protective materials application program; AVCO Corporation, NAS2-5428.
8. Synthesis of organic compounds containing nitrogen; Dow Chemical Co., NAS2-4893.
9. Study and production of polybenzimidazole laminates and billets; Lockheed Missiles and Space Company, NAS2-5521.
10. Study to fabricate encapsulated halogen-containing compounds; National Cash Register Company, NAS2-4886.
11. Ablation testing of PBI; Aerotherm Corporation, NAS2-5794.
12. Synthesis of nitro-aromatic amine compounds as intermediates for intumescent coatings and polymers; Dow Chemical Company, NAS2-4893.
13. Fire-retardant foam materials testing program; Lockheed Aircraft Corporation, NAS2-4815.
14. Study for development of improved char forming heat shields; Narmco, NAS7-340.
15. Thermal control coatings systems; Dyna-Therm Corporation, NAS2-3237.

CONTRACTS AND GRANTS

16. Para-polyphenylene and composites; Rocketdyne Corporation, NAS2-3710.
17. Polydimethylphosphonitrile polymers as thermal control coatings; W. R. Grace Company, NAS2-4028.
18. Study of vapor release and fire suppression of encapsulated fire-retardant compounds; Atlantic Research Corporation, NAS2-4988.
19. Study of low density fire-retardant materials; University of Utah, NAS2-5553.
20. Synthesis and characterization of model polymers for use in the investigation of char forming hear shields; Dow Chemical Company, NAS7-344.
21. Thermophysical and chemical characterization of charring ablative materials; Battelle Memorial Institute, NAS7-342.
22. Experimental and analytical studies of radiation-only pyrolysis of model char forming polymers; Stanford Research Institute, NAS7-341.
23. Thermochemical characterization of modern polymers to be used in the investigation of fundamental ablation mechanisms of char-forming heat thields; IITRI, NAS7-343.
24. Ablation materials study; Hughes Aircraft Company, NAS2-2739.
25. The Kinetics of reactions of the by-products of ablative materials at high temperatures and the rate of heat transfer between hot surfaces and reactive gases; Stanford Research Institute, NAS7-2739.
26. A review of oxidative degradations of certain heterocyclic polymers; Stanford Research Institute, NAS2-6464.
27. Development and installation of fire-retardant foam; AVCO Corporation NAS2-6489.
28. Study to optimize gellant polymer-water systems for control of hypergolic fires; Dow Chemical Company, NAS2-6532.
29. The synthesis of monomers for high-temperature resistant polymers; Wartburg College, Grant NGR16-005-001.
30. Synthesis of polymers with high residues at high temperatures; University of Notre Dame, Grant NGL-15-004-028, NGL-15-004-001.
31. Formulation and production of intumescent coating compositions; Hughes Aircraft Company, NAS2-6387.
32. Material Screening test program, Aerotherm Corp., NAS2-5794.

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4. Parker, J. A., Fohlen, G. M., Sawko, P. M. and Griffin, R. N., Jr.: The Use of Acid Salts,of p-Nitroaniline as a Component of Intumescent Coatings, SAMPE Journal, August/September 1968.
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8. Pope, R. B., Riccitiello, S. R., and Parker, J. A.: Development and Evaluation of a Polyurethane Foam System for Ablative Protection at Low Heating Rates. Journal of Spacecraft and Rockets, 6, 506 (1969).
9. Parker, J. A., Riccitiello, S. R., Gilwee, W. J., and Fish, R.H.: Development of Polyurethane for Controlling Fuel Fires in Aircraft Structures, SAMPE Journal, p.41, Vol. 5, No. 3, April/May 1969.
10. Dickey, R. R., Lundell, J. H., and Parker, J. A.: The Development of Polybenzimidazole Composites as Ablative Heat Shields. Journal of Macromolecular Science Chemistry, A3, 753 (1969).
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14. Golub, M. A.: Photocylization of 1,2-Polybutadiene and 3,4-Polyisoprene. Macromolecules, 2, 550 (1960).
15. Neel, C. B., Griffin, R. N., Jr., and Millard, J. P.: Studies Related to Satellite Thermal Control: Measurements of Earth-Reflected Sunlight and Stability of Thermal-Control Coatings. Solar Physics, 6, 235 (1969).
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17. Cagliostro, D. E., Riccitiello, S. R., and Parker, J. A.: A Kinetic Model for the Acid-Catalyzed Decomposition of Delrin. Journal of Macromolecular Science, Chem., A 3 (8),1601, (1969).
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23. Riccitiello, S. R., Fohlen, G. M., and Parker, J. A.: The Thermal Reactions of Bis-(4-nitroanilino)-Sulfone and p-Benzoquinone Dioxime Acid Mixtures. Journal of Polymer Science, A-1,9 317 (1971).
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26. Riccitiello, S. R., Fish, R. H., Parker, J. A., and Gustafson, E. J.: Development and Evaluation of Modified Polyisocyanurate foams for Low-Heating-Rate Thermal Protection. Journal of Cellular Plastics,7, 91 (1971).
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30. Sung, M. and Parker, J. A.: Amphetamines: Correlation of Activity with Stability of Molecular Complexes. Proceedings of the National Academy of Sciences, 69, 1346 (1972).
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32. Golub, M. A.: Photochemistry of Unsaturated Polymers, NASA Technical Memorandum, X-62, 201, May 1971; Pure and Applied Chemistry, 30, 105 (1972).
33. Golub, M. A. and Gargiulo, R. J.: Thermal Degradation of 1,4-Polyisoprene and 1,4-Polybutadine. Polymer Letters, 10, 41 (1972).
34. Cagliostro, D. E., Goldstein, H. and Parker, J. A.: Silica Reinforcement and Char Reactions in the Apollo Heat Shield. Journal of Spacecraft and Rockets (AIAA) No. A4323 (1972).
35. Sung, M. and Parker, J. A.: Molecular Complexes of Methoxyindoles with 1,3,5-Trinitrobenzine and Tetracyanoethylene. Proceedings of the National Academy of Sciences, 69, 1196 (1972).
36. Collins, G. R. and Riccitiello, S. R.: An Anomalous Reaction of Aceto-4-(or 6-) Nitro-2, 5-Xylidies with Hydrochloric Acid. Journal of Organic Chemistry, in press.
37. Golub, M. A. and Sung, M.: Thermal Cyclization of 1,2-Polybutadiene and 3,4-Polyisoprene. Polymer Letters, to be submitted.
38. Sawko, P. M.: "Intumescent Paint Containing Nitrile Rubber", U.S. Patent applied for.
39. Riccitiello, S. R.: Reactions of Quinone Dioxime and 4-Nitroso Diphenyl Amine with H_2SO_4. U.S. Patent applied for.
40. Parker, J.A. and Fohlen, G. M.: Intumescent Paints. U.S. Pat. No. 3535130 (October 20, 1970).
41. Parker, J. A. and Riccitiello, S. R.: Modified Polyurethane Foams for Fuel Fire, U.S. Pat. 3549564 (Dec. 22, 1970).

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43. Sawko, P. M., Parker, J. A. and Fohlen, G.M.: Fire Supression System for Fuel Tank Applications. U.S. Patent applied for.
44. Sawko, P. M.: Polymeric Vehicles as Carriers for Sulfonic Acid Salt of Nitrosubstituted Aromatic Amines. U.S. Patent 3663436. (May 10, 1972).
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46. Parker, J. A.: High Temperature Resistant Polymer. U.S. Patent applied for.
47. Sung, M. and Parker, J. A.: Molecular Complexes Between Methoxyamphetamines and Riboflavin Derivatives. To be submitted for publication in the proceedings of the National Academy of Sciences.

PRESENTATIONS AND SPECIFICATIONS

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2. Parker, J A.: Need for Characterization and Process Control of Low Density Composites for Aerospace Application. Presented at 11th National Plastics Exposition and Conference of the Society of Plastics, New York, June 8, 1966.
3. Winkler, E. L. and Parker, J. A.: Thermal Analysis of Low-Density Char Forming Composites Useful as Ablative Heat Shields. Presented at San Francisco Science Symposium-Thermal Analysis of Polymers, October 16-17, 1966.
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12. Parker, J. A.: "Weapons Safety". Presented at the Second Symposium on Increased Survivability of Aircraft. February 17, 1970.
13. Parker, J. A.: NASA Developments in Fire Prevention and Protection. Presented at Coco Beach, Florida. February 24-25.
14. Parker, J. A.: Impact in the 70's. Presented at the Washington Industrial Arts Association in Pullman, Washington, March 21, 1970.
15. Parker, J. A.: Thermodynamics of the Ignition and Combustion Process. Apollo 13 Review Board, May 1970.
16. Neel, C. B.,and Fish, R. H.: Protection of Aircraft in Ground Crash Fuel Fires. Presented at the Polymer Conference Series, University of Utah, June 25, 1971.
17. Golub, M. A.: Photochemistry of Unsaturated Polymers. Presented at the IUPAC Conference on Chemical Transformations of Polymers, Bratislava, Czechoslovekia, June 1971.
18. Parker, J. A.: New Fire-retardant Foams and Intumescents. Presented at the Wesrec Fireproofing and Safety Symposium, Los Angeles, May 27, 1972.
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20. Fohlen, G. H.: Intumescence: The Use of Some Aromatic Nitrogen Compounds to Provide in Situ Fire Protection. Presented at the American Chemical Society, New Orleans, Dec. 4, 1970.
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24. NASA-ARC Specifications for Fire-Retardant Foams.
25. Fire Retardant Foams Developed to Support Fuel Fires, NASA-Ames Tech. Support Package 68-10358.
26. Parker, J. A. and Kourtides, D. A.: Aerospace Polymers for Public Use. To be submitted to the AIAA, 14th Structures, Structural Dynamics and Materials Conference, Williamsburg, Va., March 20-22, 1973.

RTOP NO.	PROGRAM OFFICE	J.O. NUMBER T-8	DIRECT PROF. MAN YEARS	DIRECT SUPPORT MAN YEARS	TOTAL DIRECT MAN YEARS	TOTAL R and D$	NET R and D$
501-31-71 AST FUEL TANK SEALANTS	RA-Jones RW-Deutsch	J.O. T-5456 T-501-31-71-01 Synthesis J.O. T-5455 T-501-31-71-02 Characteriza-tion J.O. T-5454 T-501-31-71-03 Testing	Parker: Supervisor Kourtides 0.1 Griffin 0.8 Coyle 0.7 Golub 0.3 Rosser 1.0 Fish 0.1 NAS FELLOW (1.0) 3.0		3.0	$398,686	$370,000
501-38-19 FIRE RETARDATION	RO- Ransone	J.O. T-501-38-19-01	Fish 0.5 Kourtides 0.7 Gilwee 0.5 Coyle 0.3 2.0	Gustafson 1.0 Brown 1.0 2.0	4.0	$119, 248	$ 81,000
501-21-22 POLYMERS	RW-Deutsch	J.O. T-2750 Polymers 501-21-22-02 J.O. T-4514 Flammability 501-21-22-03 J.O. T-5467 MATERIALS DEGRADA-TION 501-21-22-04	Sawko 0.6 Fohlen 1.0 Heimbuch 1.0 Kourtides 0.2 Cagliostro 0.2 Lerner 0.3 Altman 1.0 Young NAS(1.0) FELLOW Lerner 0.7 Fewell 1.0 Carter (1.0) (NAS 8.0 Fellow)	Fontes 1.0 Estrella 1.0 Code R Support 4.0	12.0	$160,744	$ 46,000
501-38-12 TIRE TRACTION AND BRAKING	RO- Ransone	J.O. T-4706 Tires; 501-38-12-02 J.O. T-4511 Brakes; 501-31-12-01	Golub 0.7 Mansfield 1.0 Mansfield 1.0 Gilwee 0.3 2.0	2.0	4;0	$ 49,248	$ 11,000

RTOP NO.	PROGRAM OFFICE	J.O. NUMBER T-8	DIRECT PROF. MAN YEARS	DIRECT SUPPORT MAN YEARS	TOTAL DIRECT MAN YEARS	TOTAL R and D$	NET R and D$
501-31-90 FIRE RETARDANT MATERIALS FOR MILITARY PROGRAMS	RW- Deutsch USN/NWC	J.O. T-5463 T-501-31-90-01	Fish 0.4 Gilwee 0.2 Sawko 0.4 Military (1.0) (Bovenkerk) 1.0	2.0	3.0	$ 41,686	$ 13,000 $ 25,000
770-18-02 FIRE SAFETY, AIR POLLUTION REDUCTION, HEALTH CARE	RD- Ginter	J.O. T-4316 Fire Safety 770-18-02-01 J.O. T-770-18-02-(81) J.O. T-5288 Air Pollution Reduction 770-18-02-03	Riccitiello 0.6 Griffin 0.2 Cagliostro 0.8 Winkler 1.0 2.6	1.0 Bekstrom 1.0 2.0	4.6	$118,985	$ 75,000
502-37-02-01 SSV HEAT SHIELD AND INSULATION MATERIALS	RS- Tischler	J.O. T-4535 TP Materials 502-37-02-01	Riccitiello 0.4		0.4		
141-93-02 TECHNOLOGY UTILIZATION	KT- Hamilton	J.O. T-5265 Drug Detector 141-93-02-01 J.O. T-5264 Railroad Applications, Auto Brakes 141-93-02-01					
797-92-02-15		J.O. K-5015 797-92-02-15 Maint. Bldgs. and Equipm.					
TOTALS			17.0	14.0	31.0	$913,597	$571,075