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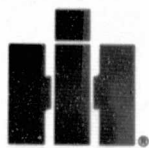
# Development of Fire-Resistant, Low Smoke Generating, Thermally Stable End Items for Commercial Aircraft and Spacecraft Using a Basic Polyimide Resin

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FIRE-RESISTANT, LOW SMOKE GENERATING,  
THERMALLY STABLE END ITEMS FOR COMMERCIAL  
AIRCRAFT AND SPACECRAFT USING A BASIC  
POLYIMIDE RESIN Final (Solar Turbines

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# **Development of Fire-Resistant, Low Smoke Generating, Thermally Stable End Items for Commercial Aircraft and Spacecraft Using a Basic Polyimide Resin**

**Final Report**

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# TABLE OF CONTENTS

| <u>Section</u> |  | <u>Page</u> |
|----------------|--|-------------|
|                | SUMMARY  | 1           |
| 1              | PROGRAM SCOPE AND OBJECTIVES   | 3           |
| 2              | BACKGROUND AND PROGRAM APPROACH  | 7           |
| 3              | EXPERIMENTAL PROCEDURES  | 9           |
|                | 3.1 Selection of Raw Materials   | 9           |
|                | 3.2 Purification of Raw Materials  | 9           |
|                | 3.3 Synthesis of the Liquid and Powder Precursors  | 11          |
|                | 3.3.1 Monomeric Liquid Precursors  | 11          |
|                | 3.3.2 Polyimide Foam Precursors  | 12          |
|                | 3.3.3 Reactions  | 12          |
|                | 3.4 Flexible Resilient Foams   | 17          |
|                | 3.5 Low Density Wall and Panel High Strength Floor Panels  | 22          |
|                | 3.6 Thermal Acoustical Insulation  | 25          |
| 4              | EXPERIMENTAL RESULTS   | 27          |
|                | 4.1 Flexible Resilient Foams   | 27          |
|                | 4.1.1 Task I - Advanced Polyimide Synthesis  | 27          |
|                | 4.1.2 Task II - Foaming Studies  | 47          |
|                | 4.1.3 Task III - Scale-Up Processes  | 68          |
|                | 4.1.4 Task IV - Characterization and Selection of Polyimide Foam Compositions                                  | 89          |
|                | 4.1.5 Task V - Sample Preparation  | 95          |
|                | 4.2 Product II - Low Density Wall Panels   | 97          |
|                | 4.2.1 Task I - Optimization of Rigid Polyimide Foam Panels   | 97          |
|                | 4.2.2 Task II - Development of Techniques for Producing Rigid Panels With Low Core and High High Density Skins | 101         |
|                | 4.2.3 Task III - Optimization of Low Core, High Density Skin Technology  | 106         |

# TABLE OF CONTENTS (Contd)

| <u>Section</u> |  | <u>Page</u> |
|----------------|--|-------------|
| 4.2.4          | Task IV - New Configurations and Reinforcements  | 119         |
| 4.2.5          | Task V - Process Parameters and Screening of Candidates  | 119         |
| 4.2.6          | Task VI - Advanced Testing   | 124         |
| 4.2.7          | Task VII - Sample Preparation  | 124         |
| 4.3            | Product III - High Strength Floor Panels   | 126         |
| 4.3.1          | Task I - Optimization of the Rigid Polyimide Foam Panel  | 126         |
| 4.3.2          | Task II - New Rigid Panel Configuration  | 128         |
| 4.3.3          | Task III - Process Parameters and Screening of Candidates  | 132         |
| 4.3.4          | Task IV - Advanced Testing   | 134         |
| 4.3.5          | Task V - Sample Preparation  | 136         |
| 4.4            | Product IV - Thermal Acoustical Insulation   | 137         |
| 4.4.1          | Task I - Advanced Polyimide Synthesis  | 137         |
| 4.4.2          | Task II - Foaming Studies  | 138         |
| 4.4.3          | Task III - Development of Thermal Acoustical Insulation by Coating and Foaming a Polyimide Resin on Fiberglass or Mats | 139         |
| 4.4.4          | Task IV - Preparation of Thermal-Acoustical Insulation Materials and Selection of Candidates                           | 149         |
| 4.4.5          | Task V - Final Characterization of Thermal Acoustical Materials  | 157         |
| 4.4.6          | Task VI - Fabrication of Samples for Submittal to NASA-JSC   | 158         |
| 5              | RECOMMENDATIONS FOR FUTURE WORK  | 161         |
|                | REFERENCES   | 163         |

## LIST OF FIGURES

| <u>Figure</u> |   | <u>Page</u> |
|---------------|---|-------------|
| 1             | Program Schedule  | 5           |
| 2             | Program Flow Diagram  | 6           |
| 3             | 55 Liter Reactor for the Preparation of Polyimide Liquid Resin        | 11          |
| 4             | Bench-Scale Arrangement for the Preparation of Liquid Resin           | 12          |
| 5             | Blue M Industrial Oven  | 13          |
| 6             | Blue M Vacuum Oven  | 14          |
| 7             | Spray Dryer   | 15          |
| 8             | IR Spectrum of 1702-1 Foam Resin (Powder Precursor)                   | 15          |
| 9             | IR Spectrum of 1702-1 Foam (Uncured)                                  | 16          |
| 10            | IR Spectrum of 1702-1 Foam (20 Minute Cure)                           | 16          |
| 11            | IR Spectrum of 1702-1 Foam (90 Minute Cure)                           | 16          |
| 12            | Gerline Moore 5 kW Microwave Oven, Model 4115                         | 18          |
| 13            | Fatigue Tester  | 19          |
| 14            | Vapor-Temperature Controlled Relative Humidity Chamber                | 19          |
| 15            | NBS Smoke Density Chamber   | 20          |
| 16            | 15 kW Microwave Oven (GFE)  | 20          |
| 17            | Research Pilot Plant Facility at Solar                                | 21          |
| 18            | Electrically Heated Circulating Oven (Despatch)                       | 21          |
| 19            | Preparation of Rigid Panel From Continuous Carbon Mat                 | 23          |
| 20            | Fabrication of Rigid Panels From Glass Fibers Filled Polyimide Resins | 23          |

## LIST OF FIGURES (Contd)

| <u>Figure</u> |   | <u>Page</u> |
|---------------|---|-------------|
| 21            | ABBE Double Shaft Mixer   | 24          |
| 22            | Direct Screw Withdrawal Apparatus   | 24          |
| 23            | Fatigue Test; DADPE Modified Terpolyimide Foam at the End of 15,000 Cycles. Foam 1710-1-9                               | 31          |
| 24            | Fatigue Test; Terpolyimide Foam at the End of 20,000 Cycles Foam 1720-1-24  | 35          |
| 25            | Recticulated Foam Derived From 1701-1 Precursor   | 37          |
| 26            | Polyimide Foam (1720-1) at the End of Humidity Test (30 Days)   | 40          |
| 27            | Fatigue Resistance of Foams Derived From 1702-1 Precursors Modified With Various Surfactants                            | 42          |
| 28            | AS-2 Surfactant Concentration; Effect on Fatigue Resistance   | 43          |
| 29            | X-3-6 Surfactant Concentration; Effect on Fatigue Resistance  | 43          |
| 30            | X-3 Surfactant Concentration; Effect on Fatigue Resistance  | 43          |
| 31            | Flexible, Resilient Polyimide Foams; Effect of Surfactant Concentration (AS-2) on Compression Set Loss                  | 45          |
| 32            | Effect of AS-2 Surfactant on Cellular Structure of Flexible, Resilient Polyimide Foams (1703-1)                         | 46          |
| 33            | Effect of Surfactant Concentration on Compression Set Loss of Aliphatic Diamines Modified Polyimide Precursors (1720-1) | 46          |
| 34            | 1720-1 Foam - Rough Cut   | 50          |
| 35            | Polyimide Foam (1720-1) Produced at Spray Dryer Outlet Temperature of 63-70°C   | 52          |
| 36            | Foam Produced From Spray Dried 1720-1 Precursors After 20,000 Cycles Fatigue  | 52          |
| 37            | Spray Dried Powder Resin Collection System  | 53          |
| 38            | Timed-Impact Vibrator for the Spray Dryer   | 53          |
| 39            | Polyimide Foam Produced by Microwave in a One-Step Process  | 57          |
| 40            | Effects of Powder Loading on Properties of Polyimide Foams  | 61          |

## LIST OF FIGURES (Contd)

| <u>Figure</u> |   | <u>Page</u> |
|---------------|---|-------------|
| 41            | Effect of Powder Loading on Aliphatic Terpolyimide Foams (1720-1)   | 62          |
| 42            | Effect of Preheat Temperature (2 Min.) on Compression Set Loss of 1701-1 Polyimide Foams Modified With 0.015 Percent AS-2                           | 63          |
| 43            | Effect of Preheat Temperature on Rise of Polyimide Foams Derived from 1701-1 Precursors   | 64          |
| 44            | Effect of Preheating Powder Precursor on the Cellular Structure of Polyimide Foams  | 64          |
| 45            | Effect of Preheat Time on Compression Set Loss (250°F) of 1701-1 Polyimide Foams  | 65          |
| 46            | Effect of Foaming Time on Compression Set Loss of Aliphatic Terpolyimide System (1720-1)  | 67          |
| 47            | Seat Cushion and Foam Derived From 1720-1 Precursor   | 69          |
| 48            | Effect of Curing Temperature on 90% Compression Set Values of Foams Derived From 1701-1 Precursors Modified with 0.015% and 0.02% AS-2 Respectively | 70          |
| 49            | Effect of Curing Temperature on 90% Compression Set Values of Foams Derived From 1701-1 Precursors Modified with 0.35% and 0.05% AS-2 Respectively  | 71          |
| 50            | Polypropylene Mold for Use in Foaming Polyimide Precursors to a Shape   | 75          |
| 51            | Microwave Foaming Methods   | 76          |
| 52            | Comparison of Finished Foams From 2.2, 4.4 and 8.8 kg Powder Charge (1702-1)  | 78          |
| 53            | Foam Samples by Microwave Curing at 8.8 kg of Powder Charge (1702-1)  | 79          |
| 54            | 1701-1 Foam Produced From 10 kg of Powder Precursor in 15 kW Microwave Oven   | 80          |
| 55            | Particle Size Distribution of 1720-1 Precursors   | 83          |
| 56            | Final Prototype Production Samples, 1720-1  | 85          |

## LIST OF FIGURES (Contd)

| <u>Figure</u> |  | <u>Page</u> |
|---------------|--|-------------|
| 57            | Final Prototype Production Samples, 1720-1   | 86          |
| 58            | Effect of Microwave Power, kW/kg, on Cellular Structure of 1720-1 Foams  | 88          |
| 59            | Fatigue Damage of Polyimide Foams After 10,000 Cycles - 1701-1, 1702-1 and 1720-1                                | 93          |
| 60            | Fatigue Damage of 1701-1 Foam at High Surfactant Concentration   | 93          |
| 61            | Foam Cores Made With Carbon Mats and Glass Strands   | 98          |
| 62            | Wall Panels Produced From VMA Carbon Mat   | 100         |
| 63            | Fabrication of Rigid Low Density Panels From Powder Polyimide Precursors in a One-Step Microwave Process         | 102         |
| 64            | Effect of L-170 on Compressive Strength of Low Density Rigid Panels  | 103         |
| 65            | Fabrication of Rigid Low Density Panels From Liquid Polyimide Precursors in a One-Step Microwave Process         | 104         |
| 66            | Wall Panels by Powder Microwave Process; Effect of Glass Strands Loading on Foam Contraction During Fire         | 108         |
| 67            | Wall Panels by Liquid Microwave Process; Effect of Fiber Length on Foam Contraction                              | 110         |
| 68            | Wall Panels by Liquid Microwave Process; Effect of Fiber Concentration on Foam Contraction                       | 111         |
| 69            | Comparison of Cellular Structure of Panels Made With Unsized Glass Strands and Type 405 Sizing Glass Strands     | 113         |
| 70            | Burnthrough Resistance of Wall Panels With Integral Woven Glass Skin. Five Minutes Exposure to a Mapp Gas Burner | 114         |
| 71            | Wall Panel Core by Microwave Process Having Density Less than 80 kg/m <sup>3</sup>                               | 115         |
| 72            | Example of Blocking Material (30% C-15X Microballoons) and Direct Screw Withdrawal Test Specimens                | 117         |
| 73            | Blocking Material Machined to a Feather Edge   | 117         |

## LIST OF FIGURES (Contd)

| <u>Figure</u> |  | <u>Page</u> |
|---------------|--|-------------|
| 74            | Wall Panel With Integral Blocking Material Edge  | 118         |
| 75            | Scale-Up of Low Density Wall Panel Core  | 121         |
| 76            | Pyrex Foaming Rig Installed in the 15 kW Microwave Oven  | 121         |
| 77            | Full Size Wall Panel Cores   | 123         |
| 78            | Finished Wall Panel  | 123         |
| 79            | Curved Wall Panel With High Density Edge   | 124         |
| 80            | 1702-0 Glass Reinforced Rigid Foam; Effect of Sizing on Foam Properties  | 127         |
| 81            | 1702-0 Glass Reinforced Rigid Foam Owens Corning 832 Sizing; Effect of Glass Concentration on Foam Properties  | 128         |
| 82            | 1702-0 Glass Reinforced Rigid Foam Owens Corning 405 Sizing; Effect of Glass Concentration on Foam Properties  | 128         |
| 83            | Polyimide Foam Filled Nude Nomex Honeycomb   | 130         |
| 84            | Floor Panel Core - One-Step Microwave Process  | 132         |
| 85            | Floor Panel Core - One Step Microwave Process  | 135         |
| 86            | Floor Panel Cores With Unidirectional Glass Skins  | 135         |
| 87            | 1702-1 Polyimide Resin Spray Coated and Foamed on Owens Corning PF 105-700 Fiberglass 20 x 20 cm. Effect of Loading on Burn Test   | 140         |
| 88            | 1702-1 Polyimide Resin Spray Coated and Foamed on Owens Corning PF 105-500W Fiberglass. Effect of Foaming Time on Flame Resistance   | 141         |
| 89            | 1702-1 Polyimide Resin Spray Coated and Foamed on Owens Corning PF 105-500W Fiberglass. Difference Between Flame Impingement on Coated Side and Flame Impingement on Uncoated Side | 141         |
| 90            | 1702-1 Polyimide Foam. Effect of Foaming Time on Contraction During Burn Test  | 144         |
| 91            | 1702-1 Polyimide Foam. Effect of Glass Microballoons on Contraction During Burn Test   | 144         |



## LIST OF FIGURES (Contd)

| <u>Figure</u> |   | <u>Page</u> |
|---------------|---|-------------|
| 92            | 1702-1 Polyimide Foams. Effect of Fillers on Contraction During Burn Test                                 | 145         |
| 93            | Effect of Fillers on Burnthrough Characteristics of Polyimide Foam  | 146         |
| 94            | Thermal Acoustical Foam Derived From 1702-1 Precursors Modified With Glass Fibers and Microballoons       | 147         |
| 95            | Mapp Gas Burner Test Set-Up   | 149         |
| 96            | Polyimide Coating Configurations on Foams (1710-1)  | 152         |
| 97            | Thermal-Acoustical Insulating Foam - Before and After Burnthrough Test at NASA-JSC                        | 154         |
| 98            | Effect of Grinding and Blending the Fiberfrax on Cellular Structure of Thermal-Acoustical Polyimide Foams | 155         |

## LIST OF TABLES

| <u>Table</u> |  | <u>Page</u> |
|--------------|--|-------------|
| 1            | Aromatic Diamines Used in Advanced Terpolyimide Systems  | 29          |
| 2            | Properties of Advanced Aromatic Terpolyimide Systems   | 30          |
| 3            | Aliphatic Diamines Used in Advanced Terpolyimide Systems   | 32          |
| 4            | Aliphatic Terpolyimide Foam Precursors and Foam Characteristics  | 33          |
| 5            | Properties of Advanced Copolyimide Systems   | 37          |
| 6            | Flexible, Resilient, Polyimide Foams; Effect of Molar Concentration of 2,6DAP on Compression Set Loss Values                 | 38          |
| 7            | Hydrolytic Stability of Flexible, Resilient Polyimide Foams at 74°C and 90% Relative Humidity                                | 39          |
| 8            | Hydrolytic Stability of Flexible, Resilient Polyimide Foams at 60°C and 100 Percent Relative Humidity                        | 40          |
| 9            | 1702-1 Resin Systems - Foam Properties   | 42          |
| 10           | Flexible, Resilient Polyimide Foams; Effect of Surfactant Concentration on Compression Set Loss of 1701-1 and 1702-1 Systems | 45          |
| 11           | Summary of Spray Dryer Study   | 49          |
| 12           | Effect of Outlet Temperature   | 50          |
| 13           | Effect of Conductive Fillers on Foaming Temperature of 1702-1 Precursors   | 54          |
| 14           | Effect of Carbon Concentration on Foaming Behavior of 1702-1 Precursors  | 55          |
| 15           | Effect of Microwave Power on Foaming and Curing Behavior of 1702-1 Precursors  | 56          |
| 16           | Effect of Powder Loading on Foaming and Curing Behavior of 1702-1 Precursor  | 56          |

## LIST OF TABLES (Contd)

| <u>Table</u> |  | <u>Page</u> |
|--------------|--|-------------|
| 17           | Substrates, Effect on Foam Properties  | 58          |
| 18           | Foaming Behavior of 1702-1 Precursors at Various Power Outputs   | 60          |
| 19           | Effect of Powder Loading on Properties of Polyimide Foams Derived From 1702-1 Precursors               | 61          |
| 20           | Effect of Preheat Temperature on Properties of Polyimide Foams Derived From 1701-1 Precursors          | 63          |
| 21           | Selection of Optimum Process Parameters for Flexible, Resilient Polyimide Foams                        | 72          |
| 22           | Properties of Polyimide Foams Produced in an Open Mold   | 74          |
| 23           | Summary of Scale-Up Study in NASA 15 kW Microwave Oven (1702-1 Resin)                                  | 78          |
| 24           | Scale-Up of 1720-1. Effect of Particle Size on Foam Properties   | 82          |
| 25           | Effect of Thickness on Foaming Behavior of 1720-1 Precursors   | 84          |
| 26           | Selection of Optimum Process Parameters for Flexible, Resilient Polyimide Foams (15 kW Microwave Oven) | 90          |
| 27           | Mechanical Properties of 1701-1 Polyimide Foams  | 92          |
| 28           | Mechanical Properties of 1702-1 Polyimide Foams  | 92          |
| 29           | Mechanical Properties of 1720-1 Polyimide Foams  | 92          |
| 30           | Scale-Up Proccses: Flexible Resilient Foams 1720-1 Resin Test Data                                     | 95          |
| 31           | Scale-Up Process: Flexible Resilient foams 1720-1 Resin  | 96          |
| 32           | Summary of Rigid Panel Reinforcement Study   | 98          |
| 33           | Results of Surfactant Addition to Carbon Reinforced Rigid Foam   | 100         |
| 34           | Screw Withdrawal Testing of Low Density Rigid Panels   | 101         |
| 35           | Evaluation of Process Parameters for Fabrication of Low Density Wall Panels by the Liquid Proccss      | 105         |

## LIST OF TABLES (Contd)

| <u>Table</u> |  | <u>Page</u> |
|--------------|--|-------------|
| 36           | Effect of Crosslinking Additives on Strength of Low Density Panels Made by the Liquid Process                        | 105         |
| 37           | Effect of Glass Strand Length on Properties of Low Density Rigid Foams   | 107         |
| 38           | Wall Panels by Liquid Microwave Process; Effect of Glass Strand Length on Foam Contraction and Compressive Strength  | 109         |
| 39           | Wall Panels by Liquid Microwave Process; Effect of Glass Concentration on Foam Contraction and Compressive Strength  | 110         |
| 40           | Wall Panels by Liquid Microwave Process; Effect of Glass Fiber Sizing on Foam Concentration and Compressive Strength | 112         |
| 41           | Effect of Sizing on Properties of Wall Panels  | 112         |
| 42           | Wall Panels by Liquid Microwave Process; Effect of Woven Glass Skins on Foam Properties                              | 113         |
| 43           | Screw Withdrawal Test of Blocking Material   | 116         |
| 44           | Water Absorption Testing of Blocking Material  | 118         |
| 45           | B-Staging Parameters for One Step Wall Panels  | 119         |
| 46           | Process Parameters for the Fabrication of Large and Small Wall Panel Cores by the Liquid Process                     | 120         |
| 47           | Process Parameters for the Fabrication of Wall Panel Cores by the Powder Process                                     | 122         |
| 48           | Summary of Results - Low Density Wall Panels   | 125         |
| 49           | Mechanical Properties of Rigid Panels Made With Various Reinforcements   | 127         |
| 50           | Advanced Testing Results - Floor Panel   | 136         |
| 51           | Acoustical Attenuation of Standard and Polyimide Foams Insulation  | 138         |
| 52           | Acoustical Attenuation of Standard and Polyimide Resin Coated Fiberglass Insulation                                  | 142         |
| 53           | Effect of Glass Strands and Microballoons on Foam Contraction During Burn Test                                       | 145         |

## LIST OF TABLES (Contd)

| <u>Table</u> |   | <u>Page</u> |
|--------------|---|-------------|
| 54           | Effect of Milled Fibers on Foam Contraction During Burn Test  | 148         |
| 55           | Effect of Glass Strands and Milled Fibers on Foam Contraction During Burn Test                        | 148         |
| 56           | Burnthrough Resistance of Crosslinked Polyimide Foams (1710-1)  | 151         |
| 57           | Burnthrough Resistance of Polyimide Foams (1702-1) at Different Concentrations of Fiberfrax           | 156         |
| 58           | Burnthrough Resistance of Polyimide Foams (1702-1) at Different Concentrations of Glass Milled Fibers | 156         |
| 59           | Summary of Results - Thermal Acoustical Insulation 1701 Resin 3% AS-2                                 | 158         |

## SUMMARY

The following paragraphs contain a summary of the significant accomplishments generated during the course of the contract effort.

- The task dealing with Advanced Polyimide Synthesis has produced a new terpolyimide precursor which can be foamed by microwave methods and yields foams possessing the best seating properties. This new precursor has been selected as the final candidate for use in seating applications.
- The molecular ratio of the heterocyclic diamine in the basic copolyimide resin has been varied over specific ranges, each producing foams of different flexibility. Foams produced at high molecular ratio show significantly improved mechanical properties and best compression set.
- A continuous process has been developed which permits production of polyimide powder precursors in large quantities. This process is based on spray drying techniques.
- The most critical parameter of the spray drying process is the temperature of the air bed through which the atomized liquid polyimide is injected to effect rapid vaporization of the solvents. The powder precursors obtained at various temperature ranges produce foams having different indentation load deflection properties for use in a variety of seating applications.
- Polyimide powder precursors modified with conductive fillers interact with the microwave field. This interaction produces sufficient thermal energy to cause foaming and curing of the polyimide precursors in a one-step process using a 5 kW microwave oven.
- A microwave oven (GFE) having dimensions of 1.83 x 1.83 x 3.66 m (6 x 6 x 12 ft) and a power output of 15 kW has been selected for fabrication of large size foam samples. The unit has been used for large scale development work and for production of prototype foam samples.
- Microwave foaming and curing in a one-step process has been accomplished with unmodified polyimide precursors using high microwave outputs in the range of 12-15 kW.
- Microwave foaming processes using free rise and constrained rise techniques have been successfully carried out in the 15 kW microwave oven to produce both flexible and rigid foams.

- The constrained rise foaming process permits fabrication of rigid foam panels with improved mechanical properties and almost unlimited density characteristics. Polyimide foam core rigid panels have been produced by this technique with woven fiberglass fabric bonded to each side of the panel in a one-step microwave process.
- The fire resistance of polyimide foams has been significantly improved by the addition of ceramic fibers to the powder precursors. Foams produced from these compositions are flexible, possess good acoustical attenuation and meet the minimum burnthrough requirements when impinged by high flux flame sources.
- Foaming processes obtained by pulsing the microwave power ON and OFF for predetermined periods of time yield foams with homogeneous cellular structure practically free of reticulation and flaws. This process has been adapted to foam the candidate materials selected in the execution of this program.
- Optimum foam compositions and processes have been selected and candidates fully characterized for each of the products under study. These candidates meet the program goal with the exception of few specific instances.

# 1

## PROGRAM SCOPE AND OBJECTIVES

This program has been devised to investigate and optimize the properties of polyimide foam compositions evaluated in two previous programs funded by NASA-JSC and to provide cost effective large scale processes for fabrication of fire-resistant, low-smoke emitting open cell polyimide foams for use in the following types of aircraft cabin structures.

- . Flexible, resilient foams
- . Low density wall panels
- . High strength floor panels
- . Thermal acoustical insulation

This program has been organized to proceed with investigations of all these products concurrently or as closely as possible and has resulted in significant benefit from the transfer of technology between the various tasks.

The major objective of this program is the fabrication of these products in shapes and sizes for replacement of conventional more flammable structures presently used in aircraft interiors. Major considerations in the execution of this program have been given to fire-containing and low-smoke emitting properties, however, durability, specific strength, weight and ease of manufacturing have been important technical objectives.

Another major objective is to obtain improvement of the properties of these products where deficiencies have been recognized and reported (Ref. 1 and 2). This has been attempted by modification of the polymer structure to obtain improved mechanical properties and by innovations designed to overcome specific deficiencies.

Unlike conventional cellular materials, the materials under study in this program must combine three important attributes:

1. Inherent non-burning characteristics
2. No discernible smoke formation
3. No incapacitating cabin environments

Solar Turbines International, during the past twelve years, has developed polyimide compositions that have been adapted to a variety of engineering applications. These compositions have been processed by thermal or microwave



techniques into flexible and rigid open cell polyimide foams possessing a wide range of mechanical and physical characteristics. This technology has been applied to the fabrication of the products recommended in this study and offers a solution to the problem of flammability of materials used for interior aircraft applications.

This program consists of five major work phases which describe the general objectives of the work plan for optimizing and scale-up each of the different products and for fabricating final prototypes for submittal to NASA-JSC. The work plan constituting the various objectives of the program and their milestones is shown in Figure 1 and a flow diagram describing the interactions of the various tasks is presented in Figure 2. The work phases are outlined below:

- The work dealing with Product I, Flexible Resilient Foams, starts with studies of modification of the polymer structure with aliphatic and aromatic diamines to produce polyimide precursors yielding foams with improved fatigue and compression set characteristics. This task will be followed by evaluation of most effective methods to manufacture these precursors in large volume and of foaming techniques easily adaptable to continuous processes.
- The work dealing with Product II and Product III, Low Density Wall and High Strength Floor Panels, entails optimization of the rigid foam core and foam filled honeycomb panels developed under NAS9-15050 followed by studies of new techniques to fabricate rigid panels possessing various shapes and multiple density characteristics. The specific requirements for low density wall panels and high strength floor panels will be given separate consideration. However, the study of both will be pursued concurrently to benefit from technology transfer between the two tasks.
- The work dealing with Product IV, Thermal Acoustical Insulation, involves optimization of the acoustical properties and dimensional stability of polyimide foams developed under NAS9-15050 by alteration of the resin system by chemical and physical methods and entails considerable transfer of technology from the task dealing with flexible resilient foams. Alternate systems will be developed by coating conventional glass batting or glass fibers with a polyimide resin to impart fire hardening properties to the glass.
- The final task dealing with Reporting and Coordination, covers the effort necessary to report the program status and includes two mid term and one final presentation to acquaint NASA-JSC technical personnel with the progress of the program.

The overall technical content of the program was scheduled to cover a period of 24 months starting from December 15, 1977 and included an additional two months for final draft and submittal.

A two months extension of the period of performance was requested and the extension approved by NASA-JSC. This request was the result of a six months



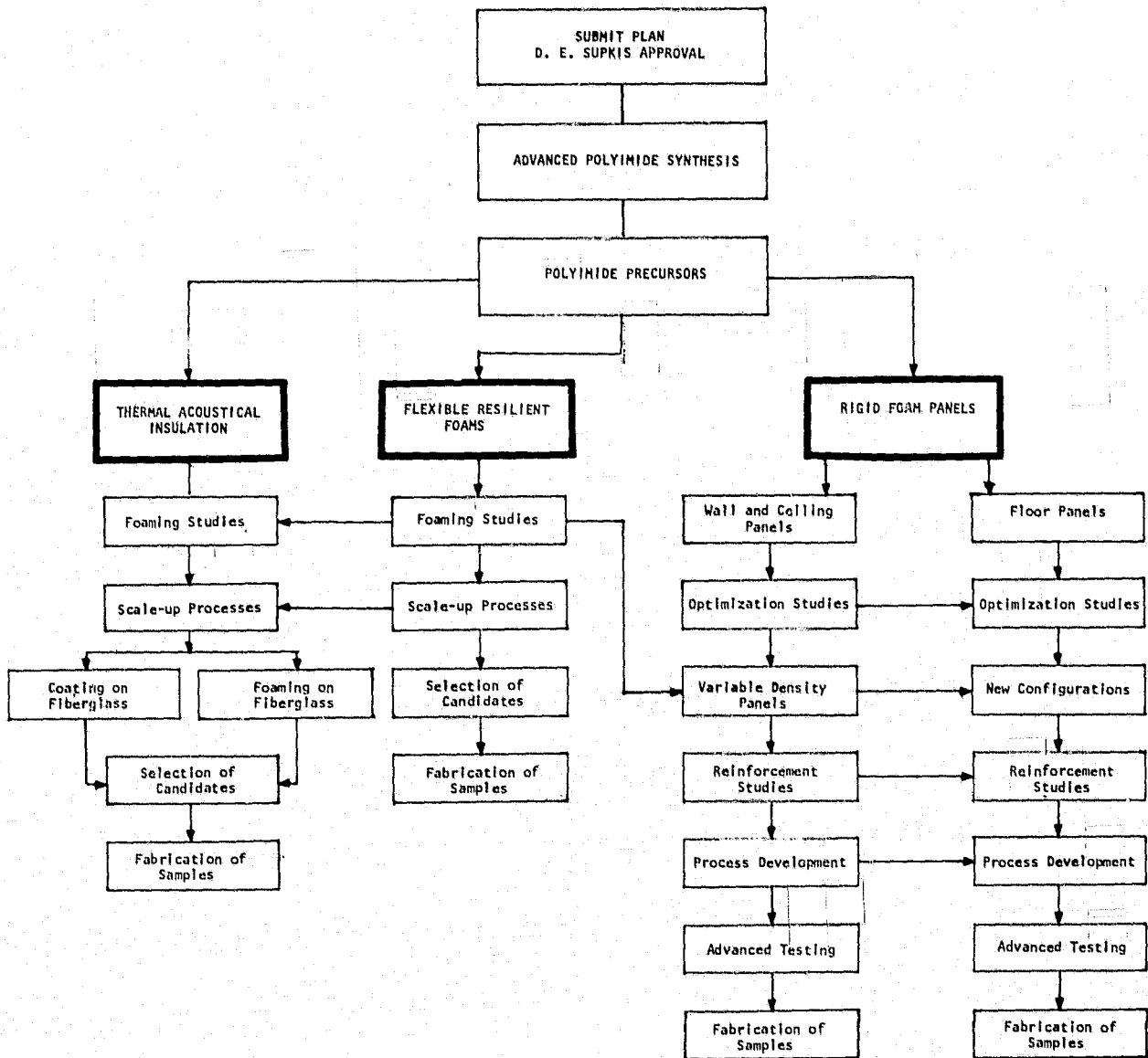


Figure 2. Program Flow Diagram

## 2

### BACKGROUND AND PROGRAM APPROACH

Solar Turbines International, an Operating Group of International Harvester, has developed the basic technology for formulation of light weight, heat- and fire-resistant low smoke-generating polymers for containment of fuel fires. This technology is based on polyimide chemistry. A significant effort has already been devoted to this technology in two previous programs funded by NASA-JSC. In the first program (Ref. 1), the major deficiencies of the polyimide flexible resilient foam were identified, namely fatigue strength, resistance to high humidity, and production cost. The major emphasis of a second program (Ref. 2), resulted in significant improvement of foam properties as they relate to hydrolytic stability, fatigue resistance, and cost. Various other concepts of polyimide materials were also investigated (Ref. 2) and significantly advanced hardware was produced. The products included, in addition to the flexible resilient foams, thermal acoustical insulation, floor paneling, wall paneling, molded shapes and coated fabrics. These products met many of the requirements but were deficient in certain areas which were clearly identified. Some of these deficiencies are reported below for each of the products studied (Ref. 2).

The flexible resilient foams were deficient in fatigue properties and their cellular structure was found to be affected by scaling up the foam slab to large sizes. The size effect was clearly a result of the lower output of the microwave oven which, for a large mass of foaming material, was not sufficient to heat the rising foam homogeneously and efficiently.

The acoustical absorption characteristics of the thermal acoustical insulation foam were found to vary over a wide range of values with minimum correlation to chemical, mechanical or physical properties of the foams.

Various concepts of floor and wall paneling have been investigated, namely, the compressed foam configuration and the foam filled honeycombs. The compressed foam products were shown to be deficient in weight characteristics.

Despite some limitations of these polyimide materials, the properties demonstrated in previous studies represented a technological advancement in the art of polyimide development, processing and fabrication and warranted additional effort. This effort dealing with upgrading the polyimide materials already characterized and developed under the two programs funded by NASA-JSC was directed toward improved foaming compositions, definition of property relationships, refinement of selected foaming processes, new configurations and new methods of fabrication more adaptable to large scale production. Since all these products were expected to be produced from essentially the same polyimide resin precursor or obtained from it with minor modification,

the proposed program was organized to proceed with investigations of all items concurrently or as closely as possible. Significant benefits have accrued from the transfer of technology between these products and significant saving in time and material has derived from preparation of the resins in larger lots. This approach was possible due to the adaptability of the polyimide resins to processing in a wide variety of forms, densities and configurations.

# 3

## EXPERIMENTAL PROCEDURES

This section outlines the experimental procedures and includes selection of raw materials (Sec. 3.1), purification of raw materials (Sec. 3.2), synthesis of the liquid and powder polyimide precursor (Sec. 3.3), and description of fabrication and test procedures for the products outlined in the sequence: flexible resilient foams (Sec. 3.4), low density wall and high density floor panels (Sec. 3.5), and thermal acoustical insulation materials (Sec. 3.6).

### 3.1 SELECTION OF RAW MATERIALS

The availability of a wide range of aromatic and aliphatic diamines and tetracarboxylic acid dianhydrides enables the mechanical and thermal properties of most polyimide resins to be varied within wide limits. The selection of the raw materials for the type of polyimide materials under development in this program was limited to those reactants possessing low dissociation constants as covered under one or more of Solar's existing patents. However, the present program has been carried out to include the use of more reactive diamines to benefit from the use of long chain reactants which are known to lead to increased flexibility and elasticity of the final polymer. The most promising diamines, dianhydrides and chemicals used in this phase of the program and their relevant physical properties are listed below.

### 3.2 PURIFICATION OF RAW MATERIALS

- 2,6 Diaminopyridine - This highly purified diamine (MP 120-122°C, 248-252°F) was obtained from Reilly Tar and Chemicals and used without purification.
- 4,4'Diaminodiphenyl sulfone - This highly purified diamine (MP 175-176°C, 347-349°F) was obtained from Roussel Corp. and used without purification. The same material obtained from RSA Corp. (MP 171-173°C, 340-343°F) required recrystallization from isopropyl alcohol solutions before use.
- Methylene dianiline - This commercial grade diamine (MP 90-92°C, 194-197.6°F) was obtained from Allied Chemicals Co. and used without purification.

- 3-3' Diaminodiphenyl sulfone. This diamine (MP 167-170°C, 332-338°F) was obtained from Aldrich Chemicals and used without purification.
- Thiodianiline. This purified diamine (MP 221-229°C) was obtained from Research Organic/Inorganic and used without purification.
- 4,4'Diaminodiphenyl ether - This polymer grade diamine (MP 188°C, 370.4°F) was obtained from Research Organic/Inorganic and used without purification.
- 2,6 Diaminotoluene - This highly purified diamine (MP 105°C, 221°F) was obtained from Aldrich Chemicals and used without purification.
- 2,4 Diaminotoluene - This material (MP 90°C, 208.4°F) was obtained from Aldrich Chemicals and used without purification.
- The aliphatic diamines, which included 1,3 diaminopropane, 1,4 diaminobutane, 1,8 diaminoctane and 1,12 diaminododecane were obtained from Aldrich Chemicals and were used without purification.
- 1,6 Diaminohexane - This 98 percent pure diamine (MP 39-40°C, 102-104°F) was obtained from Celanese Chemical Company and used without purification.
- The diamines which included Jeffamine D-230, D-400, D-2000 and AP-22 were obtained from Jefferson Chemicals. All these diamines were used without purification.
- All alcohols were obtained from the Mallinkrodt and used as received.
- The surfactants FSB, X-3, X-3-6, and AS-2 were obtained from E. I. Dupont de Nemours; FC-430 and FC-431 from 3M Company; DC-190, DC-193, and DC-196 from Dow Corning; L-5410 and L-5340 from Union Carbide. All surfactants were used as received. Other specialty chemicals used in the report were obtained from Aldrich Chemicals.
- Pyromellitic Dianhydride - This product (MP 283-286°C, 539-546°F) was obtained from Aldrich Chemicals and used without purification.
- Benzophenone 3,3',4,4'Tetracarboxylic acid dianhydride - This product was obtained from the Gulf Oil Co. Chemical Division. The off white material was slurried in warm acetone and dried at 120°C (248°F) to yield a material (MP 225-226°C, 437-439.5°F) suitable for synthesis of polyimide precursors.
- The glass fibers, glass mats and glass strands were obtained from Owens Corning Fiberglas.

### 3.3 SYNTHESIS OF THE LIQUID AND POWDER PRECURSORS

The following procedures are typical of those used to prepare the polyimide precursors.

#### 3.3.1 Monomeric Liquid Precursors

The dianhydride (1.0 mole) was added to 240 ml of alcohol in a one-liter, three neck flask, equipped with thermometer, mechanical stirrer and reflux condenser. The mixture was then refluxed for 60 minutes to ensure complete esterification. The diamines were added to the ester solution and the mixture heated to 60-65°C (140-149°F). Alcohol, based on the dilution ratio required, was added at this stage along with additives, if any. The 55 liter reactor for the preparation of liquid precursors in large lots is shown in Figure 3. The bench scale arrangement located in a newly equipped laboratory is shown in Figure 4.

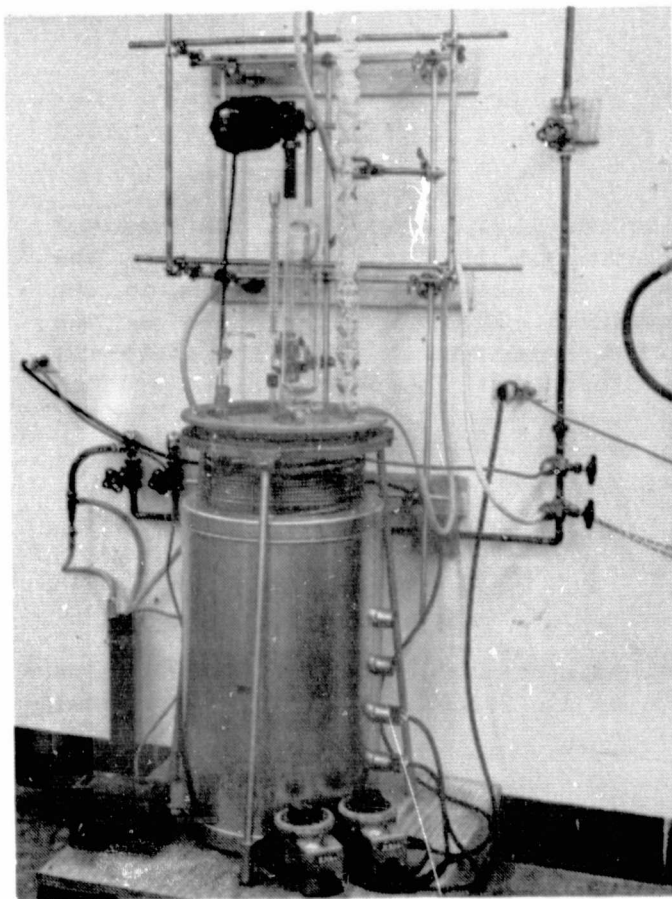


Figure 3.

55 Liter Reactor for the  
Preparation of Polyimide Liquid  
Resin

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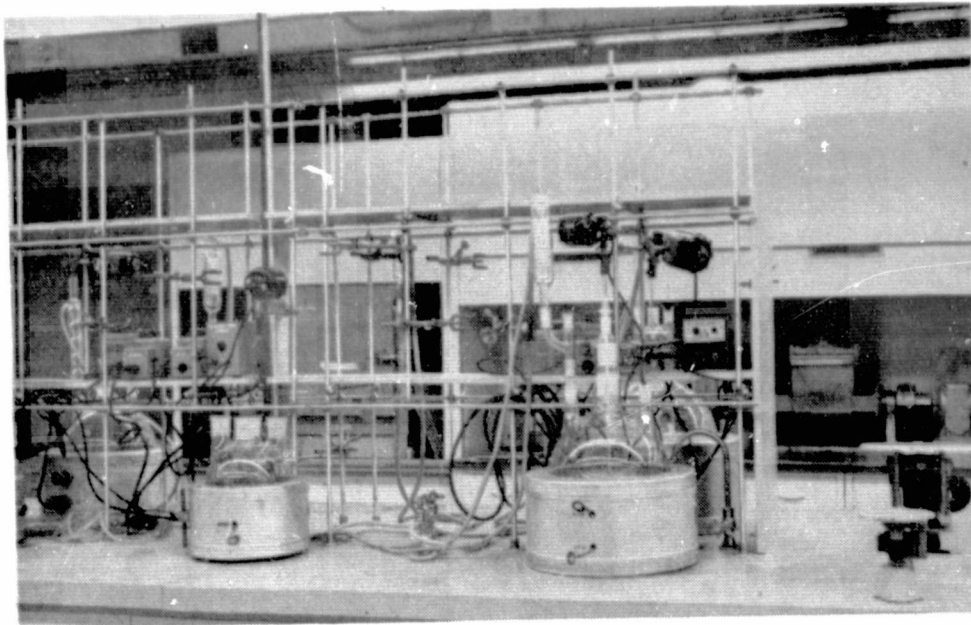


Figure 4. Bench-Scale Arrangement for the Preparation of Liquid Resins

### 3.3.2 Polyimide Foam Precursors

The procedure used to prepare foam precursors from liquid resins was carried out by a spray drying process.

The spray dryer was operated by feeding the liquid resin into the atomizer and the feed was manually adjusted throughout the operation to keep the outlet temperature below 100°C (212°F). The powder was collected in the glass jar mounted under the cyclone separator. When full, the glass jar was emptied in separate plastic bottles. The experimental work leading to the selection of the parameters for spray drying will be described in Section 4.1.2 dealing with Foaming Studies of flexible resilient polyimide foams. The circulating air oven, the vacuum oven used in processing of the powders, and the spray-dryer are shown in Figures 5, 6 and 7 respectively.

### 3.3.3 Reactions

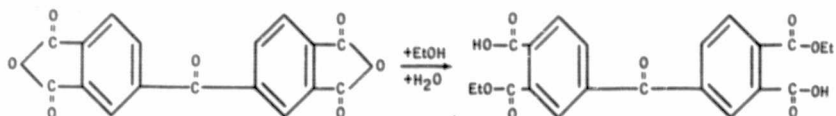
The reactions that occur during the synthesis of the liquid and powder resins and subsequent foaming are too complex to be described here. The general model is presented below:



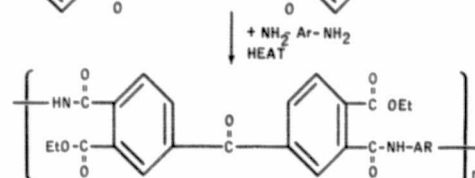
Figure 5.

Blue M Industrial Oven

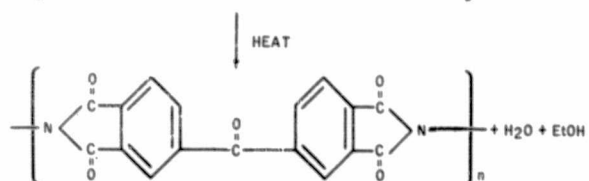
(i) Esterification:



(ii) Amidization:



(iii) Imidization:



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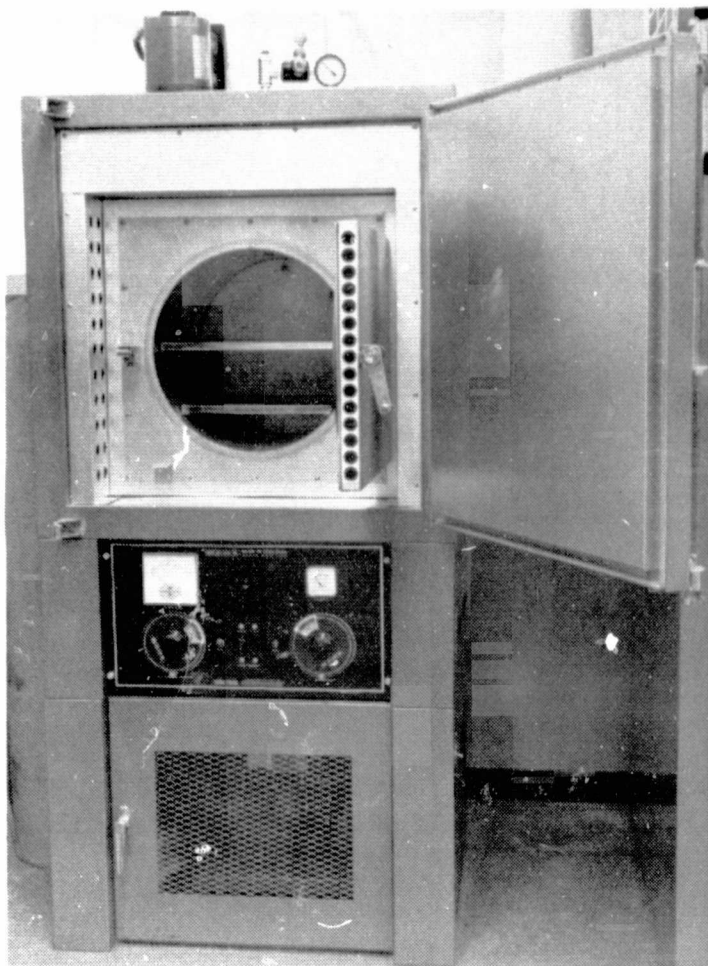


Figure 6.

Blue M Vacuum Oven

Infrared Spectroscopy was used to follow the progress of the reactions of imidization. Precursors and foams were made into powders which were then used to make KBr wafers. These were then analyzed on a Beckman Model IR 8 grating spectrophotometer. The disappearance of the primary amino group bands from  $3300\text{ cm}^{-1}$  to  $3500\text{ cm}^{-1}$  as the polymerization proceeds from precursor (Fig. 8) to uncured foam (Fig. 9) to cured foam (Fig. 10), indicates that the nitrogens are reacting to form imide bonds. In addition, the amide peak at  $1675\text{ cm}^{-1}$  which is very strong in the precursor (Fig. 8), weaker in the uncured foam (Fig. 9) and weakest in the cured foam (Fig. 10) also indicates that the imide bond is being formed. The amide peak does not totally disappear due to the presence of a ketone peak in the same region. Finally, the presence of bands at  $1785\text{ cm}^{-1}$ ,  $1725\text{ cm}^{-1}$ , and  $720\text{ cm}^{-1}$  in the foams (Figs. 9, 10, and 11) definitely indicates the formation of the imide bonds. A 20 minute cure time was shown to be sufficient by comparing Figure 10 and 11 and noticing the lack of visible change despite the additional 70 minutes of curing time.

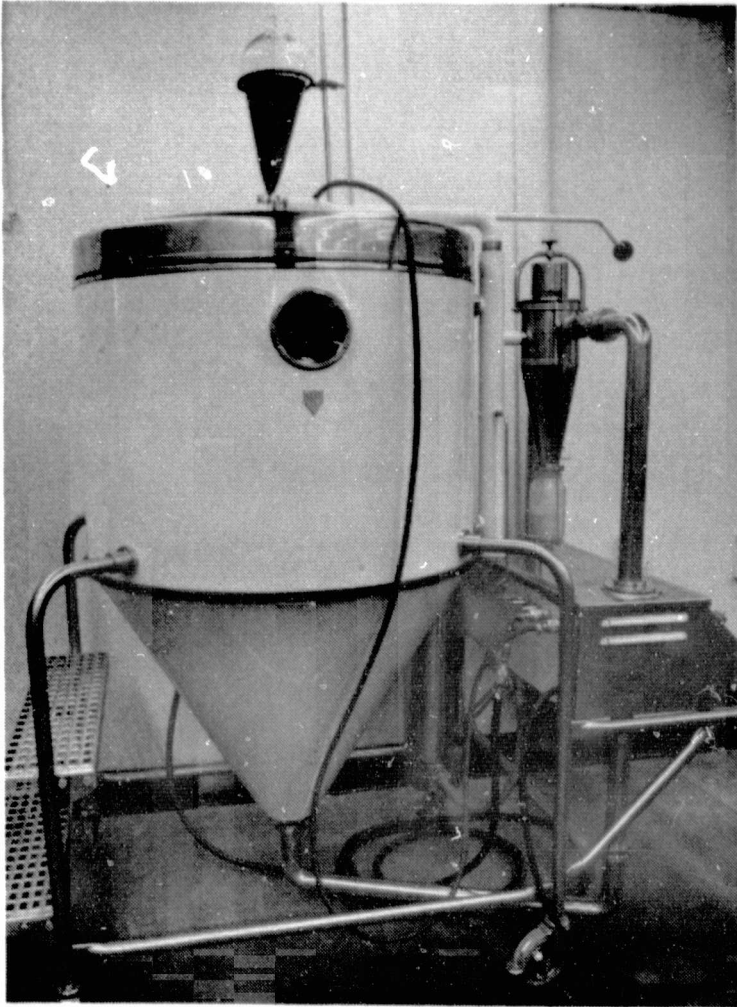


Figure 7.  
Spray Dryer

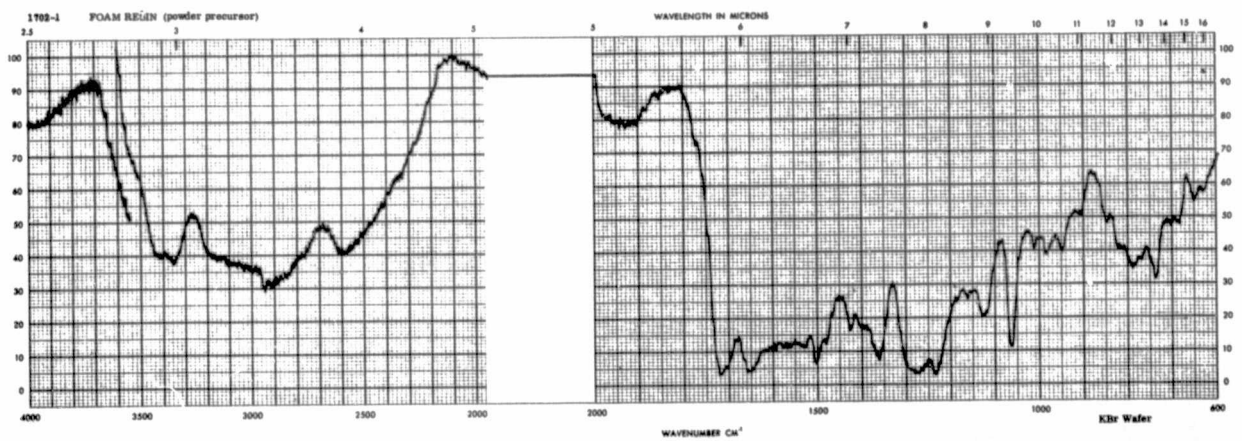


Figure 8. IR Spectrum of 1702-1 Foam Resin (Powder Precursor)

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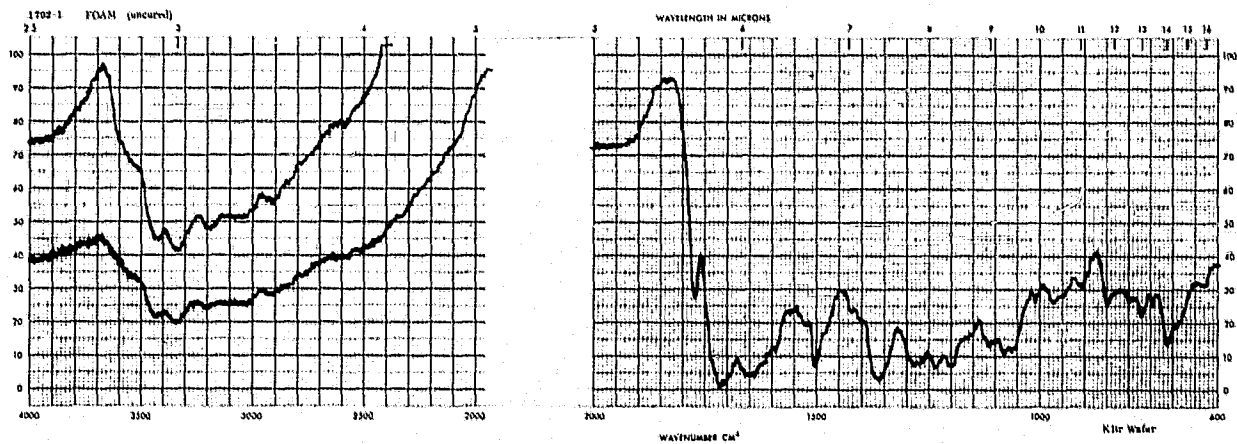


Figure 9. IR Spectrum of 1702-1 Foam (Uncured)

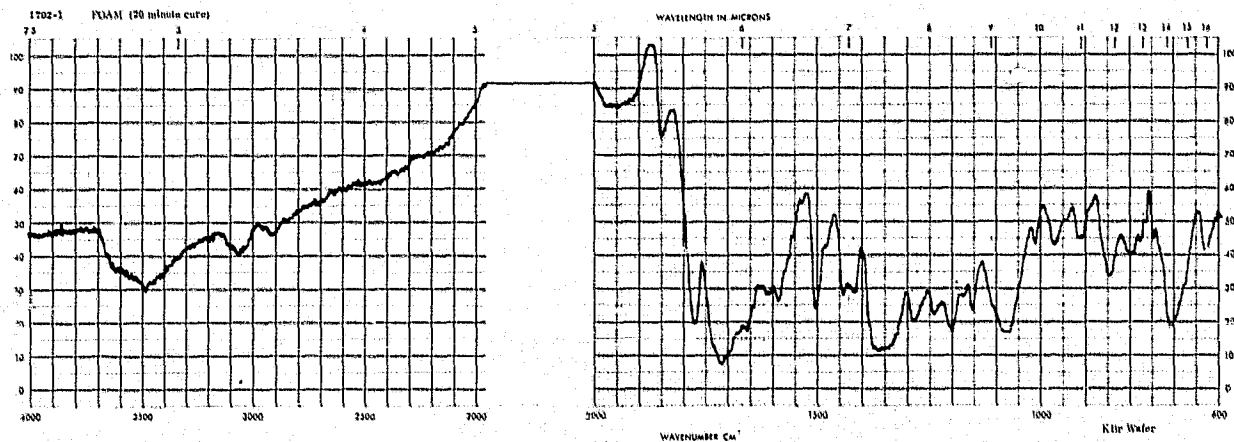


Figure 10. IR Spectrum of 1702-1 Foam (20 Minute Cure)

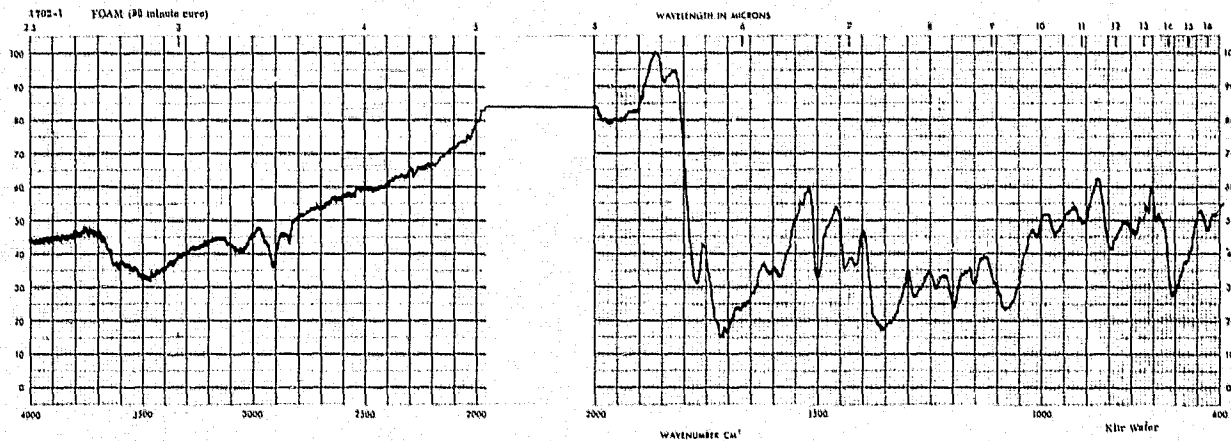


Figure 11. IR Spectrum of 1702-1 Foam (90 Minute Cure)

Some preliminary work to determine the molecular weight equivalent of the powder precursor was done using a diazo type titration with external indicator. Early results indicate a chain length for these precursors of about 20-30 molecules.

### 3.4 FLEXIBLE RESILIENT FOAMS

These foams were produced from the powder polyimide foam precursors using a Gerling Moore Batch Cavity Model 4115 microwave oven operating at a frequency of 2450 MHz and a power of 5 kW.

The precursor was laid on a suitable substrate and placed in the microwave cavity at room temperature. After a period of exposure to the high frequency radiation the powder expanded to a homogeneous cellular material which was further processed by heating it at 287.7°C (550°F). The 5 kW Gerling Moore Batch Cavity Model 4115 is shown in Figure 12. After this curing step the foam achieved maximum resiliency and flexibility.

For each of the foam processed, the foam rise, cellular structure, resiliency, striations, density, fatigue, compression set and flammability characteristics were determined to screen the most promising foam precursors and foaming processes.

Resiliency was determined by the ball rebound method according to the procedure described in ASTM Designation D-1564, Suffix B, using a tester fabricated and calibrated with the same procedure.

The compression set of the foams at 90 percent compression was determined according to the same ASTM Designation D-1564, Method B, using two steel plates held parallel to each other by clamps and the space between the plates adjusted to the required thickness by means of spacers.

The resistance of the foam to cyclic shear-loadings (fatigue test) was determined in accordance with ASTM Designation D-1564, Procedure B, with the exception that examination and measurement of the foam for loss of thickness was made at 10,000 and 20,000 cycles. The fatigue tester was constructed in accordance with the same ASTM Designation and is shown in Figure 13.

Mechanical tests, which included tension and elongation, dry heat, tear resistance and indentation load deflection were carried out using an Instron Universal Test Machine in accordance with ASTM Designation D-1564 which covers standard methods of testing of slab flexible urethane foams.

Humidity tests were carried out in a vapor-temperature Controlled Relative Humidity Chamber. This is a mechanical convection controlled humidity tester manufactured by Blue M Company. Using this chamber, foam samples were subjected to 100 percent relative humidity at a dry bulb temperature of 74°C (165°F) for a period of seven days. Performance of the test samples was detected qualitatively by embrittlement or degradation of the cellular structure and quantitatively by ball rebound resiliency method and weight change. Figure 14 shows the humidity chamber.



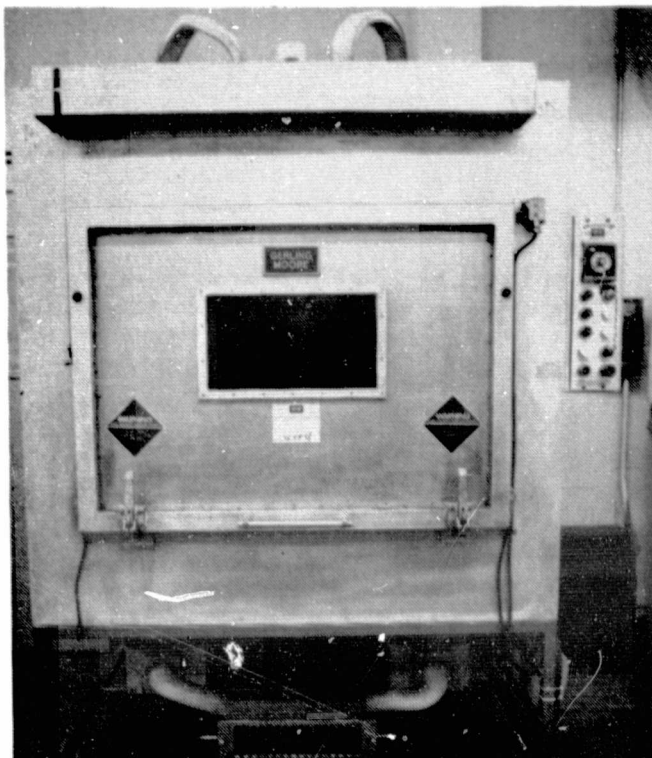


Figure 12.

Gerling Moore 5 kW Micro-  
wave Oven, Model 4115

The flammability characteristics of the foams were obtained by determination of the smoke density in accordance with the NBS procedure utilizing the NBS Smoke Density Chamber (Ref. American Instrument Co., Aminco Catalog No. 4-5800, Instruction No. 941). The NBS Smoke Density Chamber is shown in Figure 15. The relative flammability of the foams were determined by measuring the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that will just support combustion of the material (LOI). The test apparatus for this determination was prepared in accordance with ASTM Designation D-2863. Thermogravimetric analysis of the foams, determined in air, was conducted by the West Coast Technical Service, Cerritos, California.

Density tests were made in accordance with ASTM Designation D-1564, Suffix W. Other tests involved visual observation of the products for cellular structure, foaming behavior and imperfections.

Large scale fabrication of prototype production samples of polyimide foams was carried out in the 15 kW microwave oven (GFE) having dimensions of 1.83 x 1.83 x 3.66 meters (6 x 6 x 12 feet). The oven is shown in Figure 16. This oven was installed in a Research pilot plant facility shown in Figure 17. Figure 18 shows an electrically heated circulating oven for curing the foams by thermal methods. This oven is equipped with a moveable cart to carry out large foam slabs from the microwave oven into the thermal oven for the curing process. The two ovens are installed in series for ease of operation.

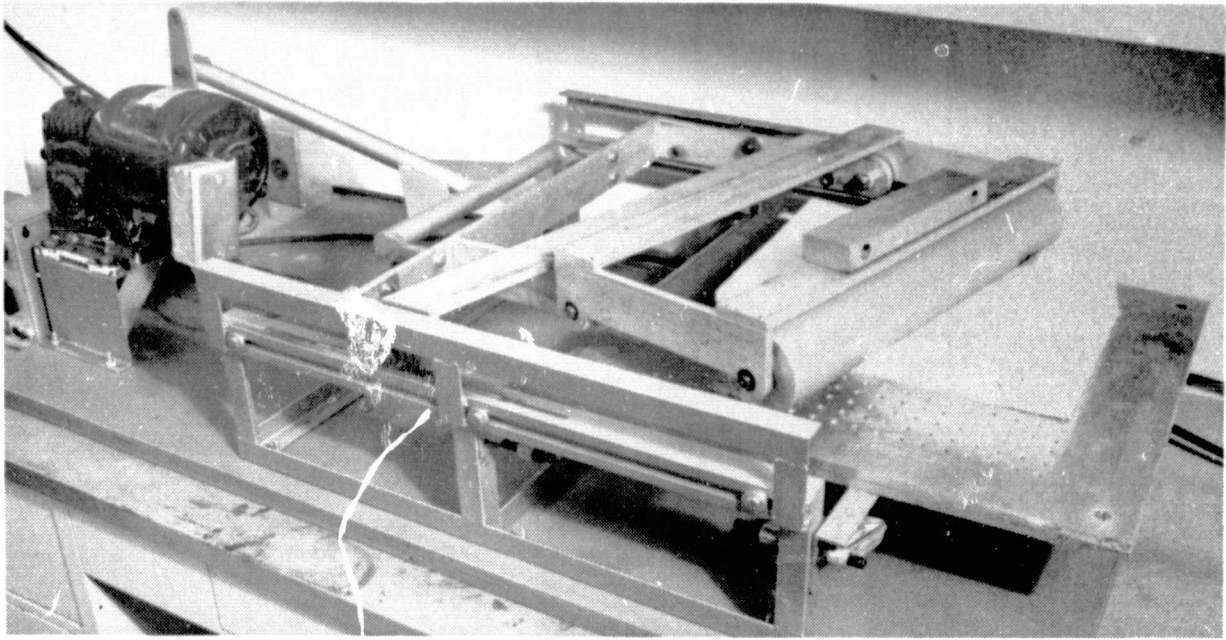


Figure 13. Fatigue Tester



Figure 14.

Vapor-Temperature Controlled  
Relative Humidity Chamber

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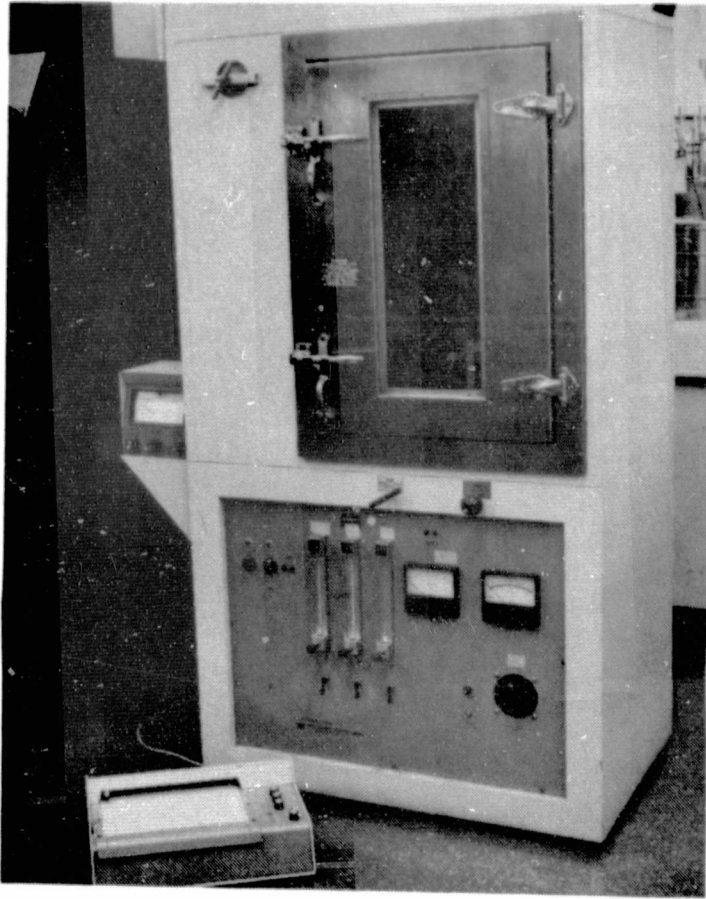


Figure 15.

NBS Smoke Density Chamber

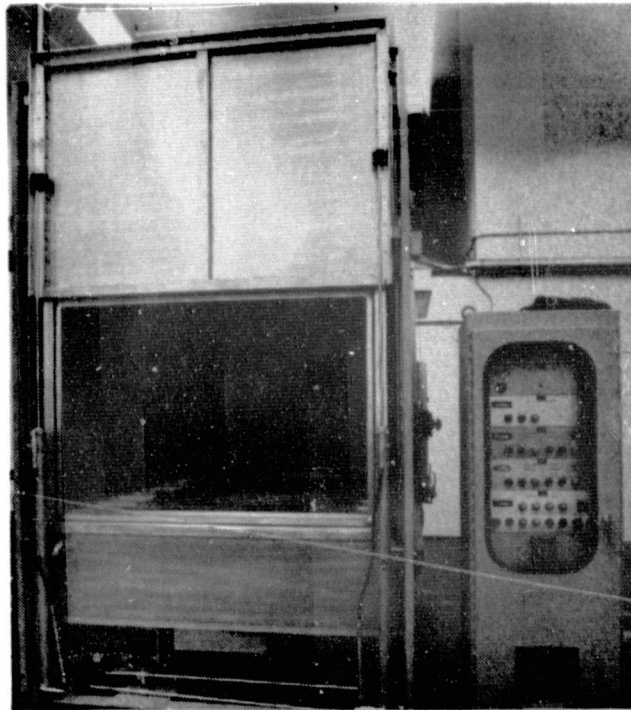


Figure 16. 15 kW Microwave Oven (GFE)



Figure 17. Research Pilot Plant Facility at Solar



Figure 18. Electrically Heated Circulating Oven (Dispatch)

### 3.5 LOW DENSITY WALL AND HIGH STRENGTH FLOOR PANELS

The procedure for preparation of the liquid polyimide resin precursors for fabrication of wall and floor panels is essentially that described in Section 3.3. The major effort of this task involved improvement of the mechanical properties of the foams and reduction of the weight characteristics through the use of a variety of methods, which included:

- a) reinforcing fillers
- b) addition of surface active agents or additives
- c) modification of process parameters

Two processes were used to fabricate rigid panels; the free-rise thermal process and the microwave process.

The free-rise thermal process consisted of compounding the liquid resin with selected fillers in a variable speed mixer until the fibers or fillers were thoroughly wetted. This mixture was then spread out on aluminum foil over a specified area, depending upon the final density and thickness desired, and the solvent removed by drying in a circulating air oven at 70-93°C (160-200°F). The compositions were then foamed at a temperature of 287.7-315°C (550-600°F) and cut to the desired thickness or compressed in a platen press. The rigid panels were produced from short fibers or continuous low density materials such as carbon mat. Figure 19 shows the sequence of steps for preparation of rigid panels from mats (left) followed by foaming (center) and compression (right). Figure 20 shows the steps for fabrication of rigid panels reinforced with glass fibers. The wet composition spread over aluminum foil (right) and the foam panel (left) are shown.

The microwave process consisted of compounding the liquid resins with selected fillers in a variable speed mixer (Fig. 21) until the fibers and/or fillers were thoroughly wetted. Glass cloth (120 style) wetted with resin, was placed on a sheet of aluminum foil. The resin mixture was then spread out over a specified area depending upon the final density and thickness desired. The top surface of the panel was then covered with another piece of wetted glass cloth. Solvent was removed by drying the wet panel in a circulating air oven at 82°C (180°F) for 120 minutes. The aluminum foil was removed from the dried panel and the sample placed between two sheets of Teflon coated glass cloth. A more advanced drying technique was developed later in the program. This involved drying the wet panel in a microwave cavity. The dried panel obtained by either method was further processed by foaming and curing. Foaming of the panel was carried out in the microwave oven at a power output of 5.0-10 kW between two sheets of microwave compatible material. The samples were cured in a circulating air oven at a temperature of 287.7°C (550°F) for 30 minutes and cut to the desired dimensions. Fabrication of low density core, high density skin wall panels by the new microwave process is illustrated in Figure 63 shown in Section 4.2.2. Further improvements of the process were attained by foaming the core and bonding glass fabric on both sides of the core simultaneously by microwave processing.

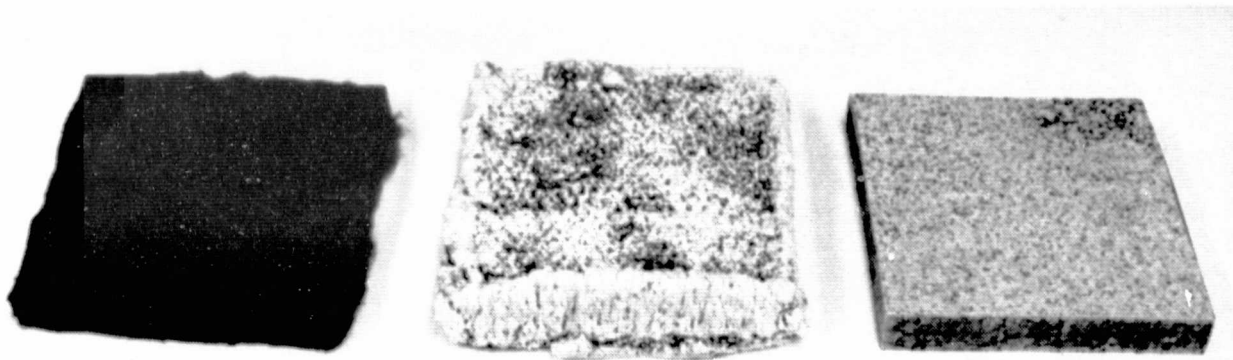


Figure 19. Preparation of Rigid Panels From Continuous Carbon Mat

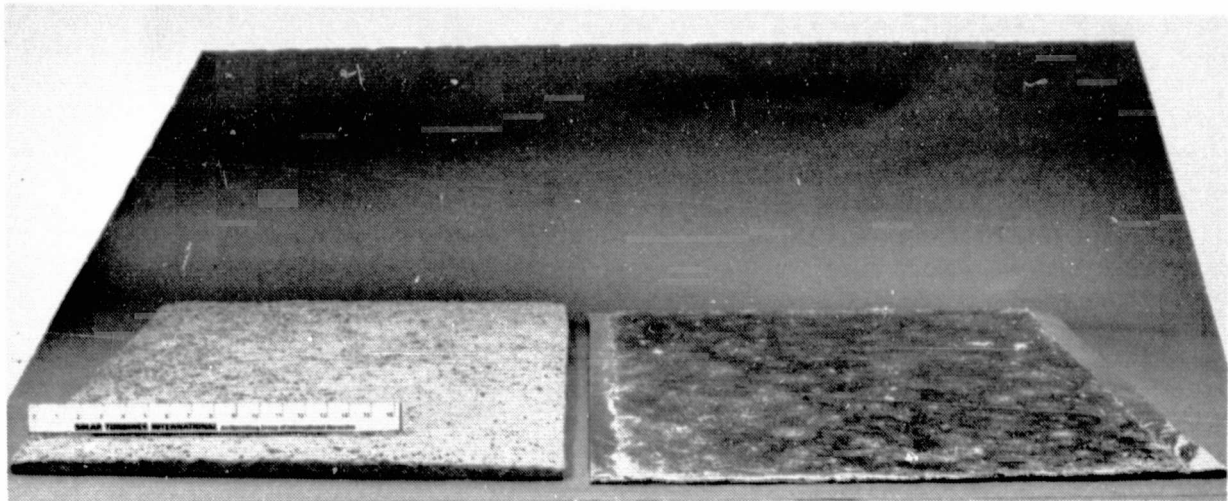


Figure 20. Fabrication of Rigid Panels From Glass Fibers Filled Polyimide Resins

Each significantly important rigid foam candidate was evaluated to determine the effectiveness of various fillers, resins and processes for screening and further optimization. Initial tests included visual observation followed by density, compressive strength and screw withdrawal. Compression tests were carried out using the procedure described in ASTM-C365. The apparatus used was an Instron model TM-SM with a full scale load range of 500 kg and crosshead speed range of 0.05 to 10.0 cm/min. Direct screw withdrawal tests were made using the procedure and apparatus described in ASTM D-1761 (Fig. 22). Determination of the flexural strength was carried out by a modified form of MIL-STD-401 using a test specimen size of approximately 7.5 x 17.5 cm (29 x 6.9 in.).

The burning characteristics of the rigid panels were obtained by horizontal burn test observing flame penetration at various time intervals for a duration of up to 10 minutes when the specimens were subjected to a Meker

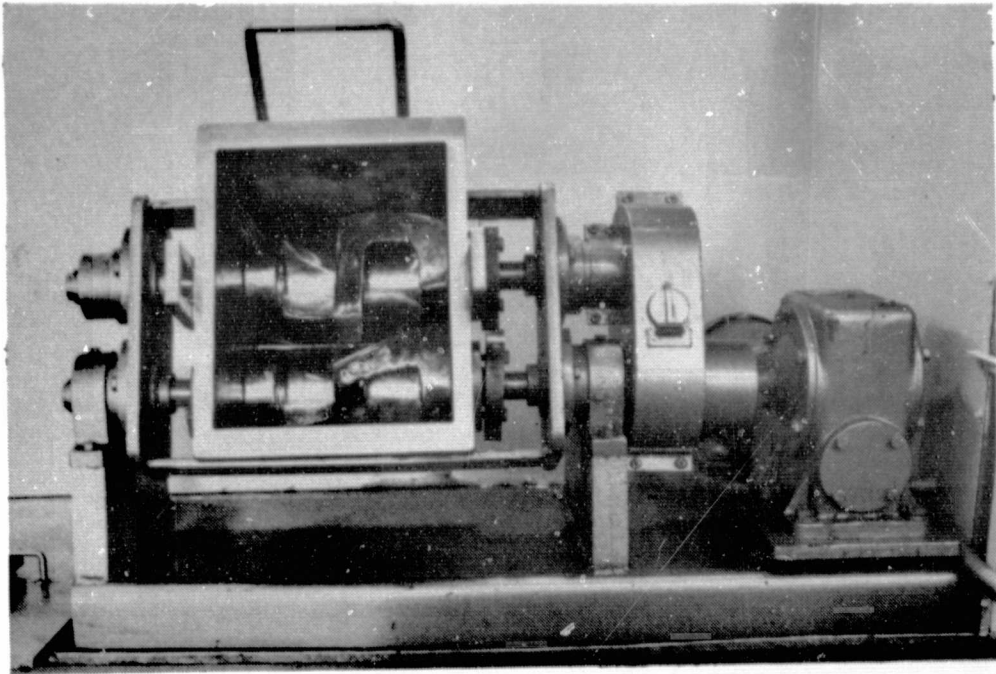


Figure 21. ABBE Double Shaft Mixer

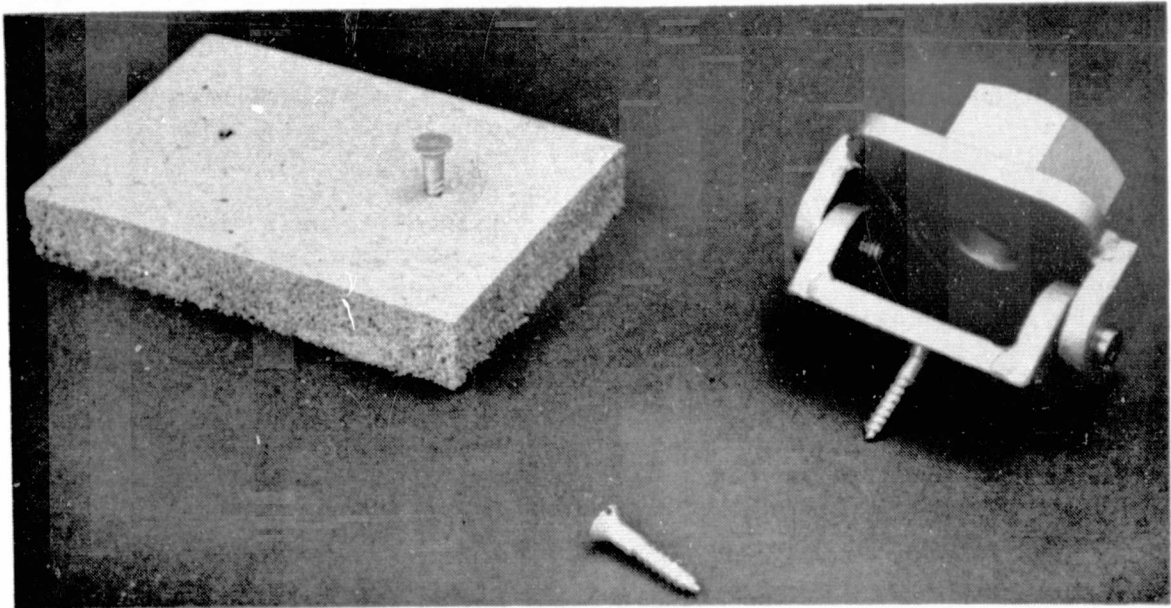


Figure 22. Direct Screw Withdrawal Apparatus



burner, by determination of the smoke density in accordance with the NBS procedure and by measuring the relative flammability of the panels by determination of the oxygen index (LOI).

### 3.6 THERMAL ACOUSTICAL INSULATION

These foams were produced from essentially the same polyimide foam precursors and same process used for the flexible resilient foams. Glass fibers, glass microballoons and other additives were compounded into the powder by milling on a ball mill or by blending in a high speed blender. These compositions were foamed by microwave techniques.

Thermal-acoustical insulation materials were also produced by coating and foaming a polyimide resin on one surface of Owens Corning PF-105 fiberglass insulation presently used in commercial aircraft. The liquid resin precursors were applied by spray techniques using a deVilbiss spray gun with a fluid tip D and foaming carried out by thermal processes at 287.7°C (550°F).

After foaming, the materials obtained from each of the processes described above were characterized by determination of foam rise, cellular structure, density, fire resistance and foam contraction during burn tests. Foam contraction was determined by measuring the loss of width of 15.25 x 5.0 cm samples (6 x 2 in.) after exposure to a Meker burner for one to five minutes and the burnthrough resistance was measured by evaluation of the burnthrough time on 22.8 x 22.8 cm samples (9 x 9 in.) exposed to the same conditions. A more effective Mapp Burner was used in the last phase of the program after it was found that the laboratory results did not correlate with those obtained in the NASA-JSC Fire Test Rig which uses a higher velocity flame. A discussion of these results is presented in Section 4.4.3.

Wicking characteristics were obtained by the procedure described in document QR6-4501, "Development of Fire-Resistant, Low Smoke Generating, Thermally Stable End Items for Aircraft and Spacecraft", Section 5-13, under the caption "Wicking of the Material as Received". Samples were cut from the foam material with the six inch length in the direction of roll and parallel to the width of the roll. Tests were carried out at room temperature and at 49°C (120 ± 5°F) for a period of seven days. Progress of the test was recorded qualitatively by visual inspection every 24 hours with respect to penetration of water above water line and formation of precipitate. At the end of the test period, samples were inspected under microscope for any physical distortion of cellular structure submerged in water.

The acoustical absorption coefficient of the polyimide foams was measured using a Type 4002, Bruel and Kjaer Standing Wave apparatus in conjunction with a signal generator and a sound level recorder.

Breaking strength was determined in accordance with Federal Specification CCC-T-191b, Method 5100 modified as described in document QR6-4674-7, Section 5-10.

The corrosive properties of the materials on aluminum, and the flammability, chemical and vibrational properties were carried out in accordance with the

procedures described in document QR6-4674-7, Sections 5-10, 5-11 and 5-12 respectively.

The resistance of the final candidates to burnthrough was determined in the NASA-JSC Fire Test Rig. The flame source was a modified oil burner, Lennox Model OB-32. The flame impinged one side of the foam at a temperature of 1093°C (2000°F) while the cold face temperature was measured (262°C, 500°F maximum) for five minutes or until burnthrough occurred.

# 4

## EXPERIMENTAL RESULTS

This section is divided into four parts to improve clarity. The first part (Sec. 4.1) covers experimental data pertinent to flexible, resilient foams followed, in order, by low density wall panels (Sec. 4.2), high strength floor panels (Sec. 4.3), and thermal acoustical insulation (Sec. 4.4).

### 4.1 FLEXIBLE RESILIENT FOAMS

The effort of this task starts with advanced polyimide synthesis. The task involves the modification of copolyimide precursors with aromatic and aliphatic diamines to produce terpolyimide systems characterized by greater chain flexibility and improved fatigue and compression set characteristics. This task is followed by a study of process parameters for the preparation of foam precursors by spray drying techniques and respective foams by microwave foaming. This study continues with scale-up of selected polyimide foam compositions to define the optimum parameters for an economically viable process to produce production size foam samples which are characterized in a subsequent task to select the optimum seating foam candidate or candidates.

#### 4.1.1 Task I - Advanced Polyimide Synthesis

The study of compositional characteristics of polyimide foams has shown (Ref. 2) that the presence of a heterocyclic diamine is necessary to produce flexible and resilient foams. The minimum concentration of the heterocyclic diamine was also found (Ref. 2) to change from system to system depending upon the type of aromatic diamine used. With this in mind, new polyimide compositions have been evaluated in this program by alteration of the basic formulations with new aromatic and aliphatic diamines to form terpolyimide resins. In the study dealing with alteration of the resins with aromatic diamines, the concentration of the heterocyclic diamine was kept constant hoping to achieve improved contribution to flexibility and elasticity of the foams. In the study dealing with alteration of the resins with aliphatic diamines, the concentration of the heterocyclic diamine was varied over a wide range to gain more knowledge from this new family of polyimide resins.

During the course of these studies, it has been also shown that surface active agents improve bubble stability and produce more homogeneous cellular structure. Study of these additives and their effect on the physical and



mechanical characteristics of the foams has continued to be a task of major importance.

A discussion of the experimental study carried out is presented succinctly in the sequence:

1. Aromatic terpolyimide systems
2. Aliphatic terpolyimide systems
3. Effect of molar ratio of 2,6DAP
4. Hydrolytic stability
5. Additive studies
6. Modification with fatty acids

### Aromatic Terpolyimide Systems

The principal objective of this task is to modify the copolyimide resins with aromatic diamines to produce terpolyimide resins and to study the contribution of such modifications on cellular structure, foaming behavior and mechanical properties of the foams with special consideration to fatigue resistance and compression set.

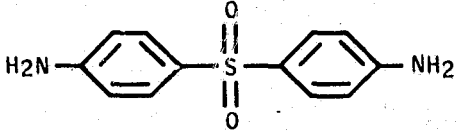
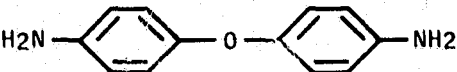
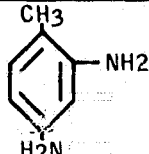
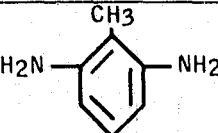
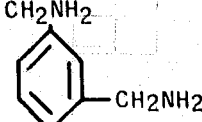
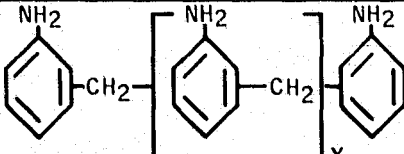
A terpolymer is the product of simultaneous polymerization of three different monomers, or of the grafting of one monomer to the copolymer of two different monomers. Three diamines are required to make a terpolyimide system and their presence was expected to give foams with more flexibility due to the highly disordered structure of the molecular chain.

The aromatic terpolyimide resins developed in the extension of this program are identified by the code 1710-1. The modification with aromatic diamines was effected by varying the molar concentration of the aromatic diamine already present in the system to accommodate the inclusion of a second aromatic diamine while keeping the molar concentration of the heterocyclic diamine constant. Three different concentrations of the third diamine were used to study each terpolyimide system.

A total of six different aromatic diamines were used to synthesize the new terpolyimide systems, followed by their complete evaluation for physical and mechanical characteristics with particular emphasis on compression set loss values. These aromatic diamines were selected on the basis of their availability, chemical structure and ability to produce foams possessing a wide range of physical and mechanical properties. These diamines and their chemical structures are listed in Table 1.

Table 1

## Aromatic Diamines Used in Advanced Terpolyimide Systems

| AROMATIC DIAMINE              | ABBREVIATION    | STRUCTURE   |
|-------------------------------|-----------------|---|
| 4, 4' DIAMINODIPHENYL SULFONE | DADPS           |     |
| 4, 4' DIAMINODIPHENYL ETHER   | DADPE           |     |
| 2, 4 TOLUENE DIAMINE          | TDA             |    |
| 2, 6 DIAMINO TOLUENE          | DAT             |     |
| M - XYLYLENE DIAMINE          | XDA             |  |
| POLYMETHYLENE POLYPHENYLEMINE | JEFFAMINE AP-22 |   |

X = 0, 1, 2

Table 2 presents the properties of foams including compression set data derived from each terpolyimide system. All terpolyimide systems were made with 0.1 percent surface active agent of the X-3 type. Terpolyimides made with diaminodiphenyl sulfone were eliminated from further study because of incompatibility.

Terpolyimides made with diaminodiphenyl ether gave foams which were flexible, resilient, and possessed homogeneous cellular structure, but an increase in the concentration of DADPE caused striations during foaming. The compression set properties of these foams improved with an increase of the molar concentration of DADPE although the values do not meet the requirements for the

Table 2

## Properties of Advanced Aromatic Terpolyimide Systems

| Foam Resin Number | Mole Ratio      | Density           |                     | Resiliency Ball Rebound | % Loss After 30 Minutes Recovery | Type of Foam  |
|-------------------|-----------------|-------------------|---------------------|-------------------------|----------------------------------|---|
|                   |                 | kg/m <sup>3</sup> | lbs/ft <sup>3</sup> |                         |                                  |   |
| 1710-1-4          | 1:0.3:0.65:0.05 | --                | --                  | --                      | --                               | Flexible, resilient, DADPS not compatible                                 |
| 1710-1-5          | 1:0.3:0.55:0.15 | --                | --                  | --                      | --                               | DADPS not compatible  |
| 1710-1-6          | 1:0.3:0.40:0.30 | --                | --                  | --                      | --                               | DADPS not compatible  |
| 1710-1-7          | 1:0.3:0.65:0.05 | 10.9              | 0.68                | 50-60                   | 58.0                             | Flexible, resilient, good homogeneous cellular structure                  |
| 1710-1-8          | 1:0.3:0.55:0.15 | 19.9              | 1.24                | 60-70                   | 50.0                             | Flexible, resilient, good homogeneous cellular structure, some striations |
| 1710-1-9          | 1:0.3:0.4:0.30  | 16.8              | 1.05                | 70                      | 48.4                             | Flexible, resilient, good structure; some striations                      |
| 1710-1-10         | 1:0.3:0.65:0.05 | 8.2               | 0.51                | 60-70                   | 52.5                             | Flexible, resilient; homogeneous cell structure                           |
| 1710-1-11         | 1:0.3:0.55:0.15 | 8.7               | 0.54                | 90                      | 49.1                             | Flexible, resilient; homogeneous cell structure; some striation present   |
| 1710-1-12         | 1:0.3:0.4:0.30  | 12.2              | 0.76                | 60                      | 51.7                             | Flexible, resilient; flaws and striations                                 |
| 1710-1-13         | 1:0.3:0.65:0.05 | 8.17              | 0.51                | 80-85                   | 44.4                             | Flexible, resilient, homogeneous cellular structure                       |
| 1710-1-14         | 1:0.3:0.55:0.15 | 9.77              | 0.61                | >90                     | 39.4                             | Flexible, resilient, homogeneous cellular structure                       |
| 1710-1-15         | 1:0.3:0.4:0.3   | 9.93              | 0.62                | 80                      | 40.8                             | Flexible, resilient, medium size cellular structure with some flaws       |
| 1710-1-16         | 1:0.3:0.65:0.05 | 9.93              | 0.62                | 75-80                   | 59.0                             | Flexible, resilient, fine cellular structure                              |
| 1710-1-17         | 1:0.3:0.55:0.15 | 18.42             | 1.15                | 60                      | 52.4                             | Flexible, resilient, fine cellular structure, flaws and striations        |
| 1710-1-18         | 1:0.3:0.4:0.3   | 18.74             | 1.17                | 55-60                   | 44.3                             | Semi-rigid and hard foam with flaws                                       |
| 1710-1-19         | 1:0.3:0.7       | 6.41              | 0.4                 | 60                      | 45.3                             | Flexible, resilient, homogeneous cellular structure                       |

program (the goal is 15 percent loss maximum). Foams prepared from these terpolyimides were tested for fatigue resistance. These foams retained the minimum limit of resiliency at the end of 15,000 cycles without loss of foam integrity or excessive tear, but the loss of thickness was 30 percent. A foam fatigued for 15,000 cycles is shown in Figure 23.

Foams produced from terpolyimides made with 2,4 toluene diamine show signs of incompatibility at higher concentrations of 2,4 toluene diamine and the compression set values were poor. Similarly, terpolyimide systems made with 2,6 diaminotoluene, m-xylene diamine and polymethylene polyphenylamine did not show any significant contribution to better compression set properties.

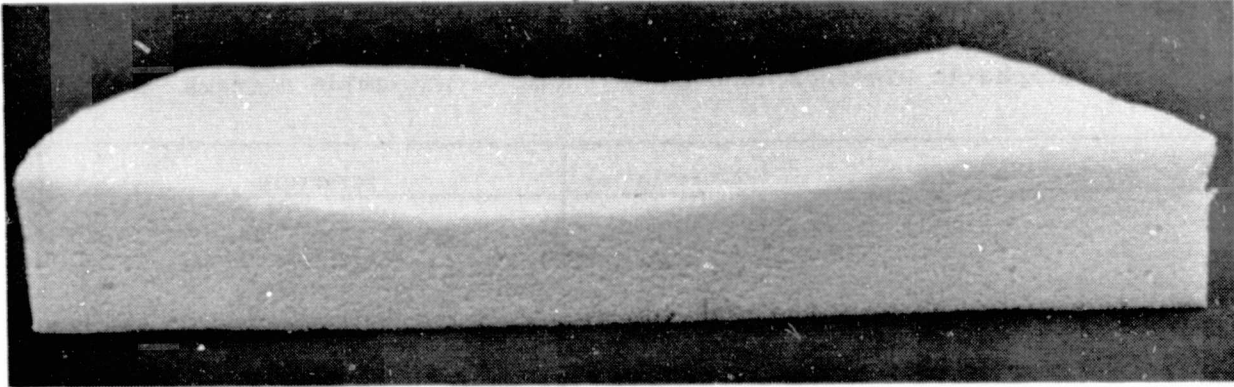


Figure 23. Fatigue Test; DADPE Modified Terpolyimide Foam at the End of 15,000 Cycles. Foam 1710-1-9

The data clearly showed that the work carried out in this task did not produce suitable foam candidates for use in seating applications. Therefore, the work on the synthesis and subsequent scale-up of aromatic terpolyimides was discontinued in the seventh month from the beginning of this program to concentrate on other important tasks. The study of the terpolyimide systems made with polymethylene polyphenylamine (Jeffamine AP-22) was carried along further as new applications were developed from this system in thermal acoustical insulating foams due to its low cost, availability and ability to produce foams with superior thermal resistance. However, even this candidate was abandoned as will be discussed in Section 4.4.

#### Aliphatic Terpolyimide Systems

The objective of this task involved the modification of the copolyimide resins with aliphatic diamines to produce terpolyimide resins and to study the contribution of these modifications on cellular structure, foaming behavior, and mechanical properties of the foams with particular reference to fatigue resistance and compression set properties. This type of terpolyimide resin is identified in this program with the code 1720-1.

To allow for the addition of the aliphatic diamines in the molecular structure, the amount of aromatic diamine was first reduced in proportion to the amount of aliphatic diamine added. All aliphatic terpolyimide systems were made with 0.1 percent surface active agent of X-3 type. The aliphatic diamines used in this study are listed in Table 3 along with their chemical structure. Table 4 presents the properties of foams obtained from these diamines. This table is separated into seven major groups based on the ratios of aromatic to aliphatic diamines.

Experiment Group 1 covers the work involving all eight of the aliphatic diamines under study. The precursors were prepared at an aliphatic diamine ratio of 0.1. In general this group exhibited better compression set values and higher density than foams produced from the unmodified resin.

Table 3

Aliphatic Diamines Used in Advanced Terpolyimide Systems

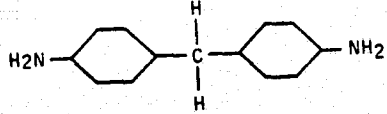
| Aliphatic Diamine                                | Abbreviation | Structure   |
|--|--------------|---|
| 1,3Diaminopropane (Propyl)                       | PDA          | $\begin{array}{c} \text{H} & \text{H} & \text{H} \\   &   &   \\ \text{H}_2\text{N} - \text{C} - & \text{C} - & \text{C} - \text{NH}_2 \\   &   &   \\ \text{H} & \text{H} & \text{H} \end{array}$  |
| 1,4Diaminobutane (Butyl)                         | DAB          | $\begin{array}{c} \text{H} & & & \text{H} \\   & & &   \\ \text{H}_2\text{N} - \text{C} - & (\text{CH}_2)_2 - & \text{C} - \text{NH}_2 \\   & & &   \\ \text{H} & & & \text{H} \end{array}$   |
| 1,6Diaminohexane (Hexa)                          | DAH          | $\begin{array}{c} \text{H} & & & \text{H} \\   & & &   \\ \text{H}_2\text{N} - \text{C} - & (\text{CH}_2)_4 - & \text{C} - \text{NH}_2 \\   & & &   \\ \text{H} & & & \text{H} \end{array}$   |
| 1,8Diaminooctane (Octa)                          | DAO          | $\begin{array}{c} \text{H} & & & \text{H} \\   & & &   \\ \text{H}_2\text{N} - \text{C} - & (\text{CH}_2)_6 - & \text{C} - \text{NH}_2 \\   & & &   \\ \text{H} & & & \text{H} \end{array}$   |
| 1,12Diaminododecane (Dodeca)                     | DAD          | $\begin{array}{c} \text{H} & & & \text{H} \\   & & &   \\ \text{H}_2\text{N} - \text{C} - & (\text{CH}_2)_{10} - & \text{C} - \text{NH}_2 \\   & & &   \\ \text{H} & & & \text{H} \end{array}$  |
| Jeffamine Series<br><br>D-230<br>D-400<br>D-2000 |              | $\begin{array}{c} \text{H} & \text{H} & & \text{H} & \text{CH}_3 \\   &   & &   &   \\ \text{H}_2\text{N} - \text{C} - & \text{C} - & \left[ \text{O} - \text{C} - \text{C} \right] & \text{NH}_2 \\   &   &   &   \\ \text{CH}_3 & \text{H} & \text{H} & \text{H} \end{array}$ <p>X = (approx)</p> <p>2.6<br/>5.6<br/>33.1</p> |
| PACM-20  |              |   |

Table 4

## Aliphatic Terpolyimide Foam Precursors and Foam Characteristics

| Foam Resin Number | Density             |                   | 90% Compression Set<br>% Loss After<br>30 Minutes Recovery | Resiliency<br>Ball Rebound | Foam Characteristics                                |
|-------------------|---------------------|-------------------|--|----------------------------|---|
|                   | lbs/Ft <sup>3</sup> | kg/m <sup>3</sup> |  |                            |   |
| 1702-1            | 0.538               | 8.6               | 52   | 55                         | Flexible, resilient, good structure                 |
| <u>Group 1</u>    |                     |                   |  |                            |   |
| 1720-1-1          | 1.44                | 23.0              | 46   | 50                         | Flexible, resilient, good structure                 |
| 1720-1-8          | 1.31                | 21.1              | 63   | 45                         | Flexible, resilient, good structure                 |
| 1720-1-2          | 1.36                | 21.8              | 48   | 55                         | Flexible, resilient, good structure                 |
| 1720-1-3          | 0.943               | 15.1              | 39   | 50                         | Flexible, resilient, good structure                 |
| 1720-1-4          | 1.62                | 25.9              | 42   | 50                         | Flexible, resilient, striated                       |
| 1720-1-5          | 1.11                | 17.8              | 21   | 70                         | Flexible, resilient, large cell size, brittle       |
| 1720-1-6          | --                  | --                | --   | --                         | Poor foam, collapsed on heating                     |
| 1720-1-7          | --                  | --                | --   | --                         | Poor foam, collapsed and degraded on heating        |
| <u>Group 2</u>    |                     |                   |  |                            |   |
| 1720-1-12         | 0.840               | 13.4              | 40   | 40                         | Flexible, resilient, good structure                 |
| 1720-1-9          | 1.25                | 20.0              | 53   | 53                         | Flexible, resilient, good structure                 |
| 1720-1-13         | 0.817               | 13.1              | 47   | 55                         | Flexible, resilient, good structure                 |
| 1720-1-10         | 1.40                | 22.4              | 43   | 35                         | Flexible, resilient, good structure                 |
| 1720-1-14         | 3.32                | 53.0              | 46   | 70                         | Flexible, resilient, poor structure                 |
| 1720-1-11         | --                  | --                | --   | --                         | Brittle, very large cell size, poor foam            |
| <u>Group 3</u>    |                     |                   |  |                            |   |
| 1720-1-15         | --                  | --                | --   | --                         | Rigid foam, collapsed and degraded on heating       |
| 1720-1-16         | 1.48                | 23.7              | 63   | 50                         | Flexible, resilient, fair structure                 |
| 1720-1-17         | 1.37                | 21.9              | 71   | 50                         | Flexible, resilient, fair structure                 |
| 1720-1-18         | 1.33                | 21.2              | 58   | 45                         | Flexible, resilient, good structure                 |
| 1720-1-19         | 0.778               | 13.5              | 45   | 70                         | Flexible, resilient, good structure                 |
| <u>Group 4</u>    |                     |                   |  |                            |   |
| 1720-1-25         | 1.33                | 21.2              | 40   | 50                         | Flexible, resilient, good structure                 |
| 1720-1-20         | 0.835               | 13.4              | 25   | 45                         | Flexible, resilient, good structure                 |
| 1720-1-24         | 1.44                | 23.0              | 30   | 55                         | Flexible, resilient, medium cell size               |
| 1720-1-21         | 0.845               | 13.5              | 22   | 70                         | Flexible, resilient, medium cell size               |
| 1720-1-23         | 0.565               | 9.04              | 23   | 65                         | Flexible, resilient, good structure                 |
| 1720-1-22         | --                  | --                | --   | --                         | Brittle, very large cell size, collapsed on heating |
| <u>Group 5</u>    |                     |                   |  |                            |   |
| 1720-1-26         | 1.15                | 18.3              | 31   | 50                         | Flexible, resilient, good structure                 |
| 1720-1-27         | 0.399               | 6.36              | 7  | 55                         | Flexible, resilient, highly reticulated             |
| <u>Group 6</u>    |                     |                   |  |                            |   |
| 1720-1-28         | 1.17                | 18.7              | 44   | --                         | Flexible, resilient, good structure, voids          |
| <u>Group 7</u>    |                     |                   |  |                            |   |
| 1720-1-29         | 1.08                | 17.3              | 31   | --                         | Flexible, resilient, good structure, voids          |

The Jeffamines 400 and 2000 yielded poor foams. However, the Jeffamine D-230 gave useable foams with excellent compression set values, but when these foams were scaled up to a large size the quality of the cell structure worsened. Based on these results Jeffamine D-400 and D-2000 were excluded from future work.

In Group 2 the precursors were prepared at a diamine ratio of 0.2. This series failed to improve to a significant degree the mechanical characteristics of the foams. Jeffamine D-230 produced foams which exhibited poor characteristics and was eliminated from further study.

In Group 3 the amount of aliphatic diamine was further increased to 0.3 mole. All samples of this series exhibited poor mechanical properties and poor flame resistance. The foams of Group 3 produced some smoke and continued to burn for 5-15 seconds after removal from the flame. Therefore, the study of this system was discontinued.

In Group 4 the heterocyclic diamine was kept constant at 0.3 mole and the precursors were prepared at an aliphatic diamine ratio of 0.2. The foams obtained from this series had the most homogeneous cellular structure with the exception of foams made with Jeffamine D-230 (Resin 1720-1-22). A significant contribution of the foams derived from the precursors of Group 4 was the improved values for compression set. In addition, the density of these foams was considerably higher than that obtained with conventional copolyimide foams derived from 1702-1 system. Although low density is a desirable property for aircraft applications, we found that this property is responsible for early failure of foams tested for fatigue since the shearing effect is much more damaging. The fatigue resistance of these foams is illustrated in Figure 24 which shows a sample of a foam made from 1720-1-24 powder resin after being fatigued for 20,000 cycles. The resiliency of the foam remained within specification during the fatigue cycle and the change of thickness was not measureable. However, the compression set properties of the foams of Group 4 did not meet the minimum requirements.

Group 5 followed naturally in progression from Group 4 as the resins were prepared with a ratio of 0.3 mole of heterocyclic diamine. The precursors were prepared at an aliphatic diamine ratio of 0.3. The foams obtained had good structure and in one case excellent compression set properties. However, these foams were found to lose the characteristic fire resistance of polyimide resins. Therefore, the study of terpolyimide resins at molar ratios of aliphatic diamine higher than 0.3 was not attempted, and the investigation ended at this stage.

From the data obtained from this study, two candidates were selected for further evaluation. These precursors were 1720-1-20 and 1720-1-24. Scale-up studies of these two candidate precursors resulted in the selection of 1720-1-24 as the most promising candidate.

Polyimide foams prepared from this candidate terpolyimide system have homogeneous cellular structure, excellent fatigue resistance, good flexibility, good resiliency, and good mechanical properties. Previous work (Ref. 2) on the development of polyimide technology was mainly concentrated on copolyimide

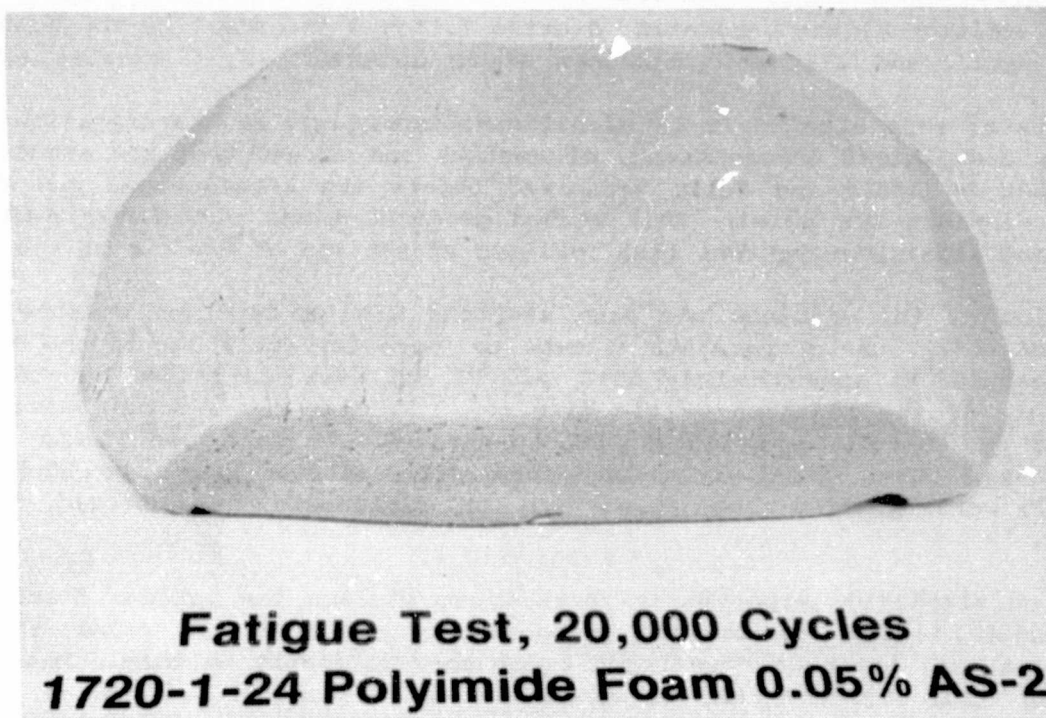


Figure 24. Fatigue Test; Terpolyimide Foam at the End of 20,000 Cycles. Foam 1720-1-24

systems. This being the first time that a terpolyimide system was selected as a candidate material for use in seating applications, studies were initiated to investigate the effect of DAH concentration and reaction parameters on foam properties.

Further modification of the aliphatic terpolyimide systems was carried out by the synthesis of resins 1720-1-28 (Group 6) and 1720-1-29 (Group 7). These two resins were made to study the effect of the aliphatic diamine concentration on foam properties. Results of this study have shown that the flame resistance of the foam decreases considerably at concentrations of aliphatic diamine greater than 0.2 mole. Due to this fact, the optimum concentration was selected at 0.2 mole although higher concentration produces foams with improved compression set values.

The most relevant process parameters, in addition to those already evaluated with the other resin systems, were studied to define optimum conditions. These parameters studied were the order of addition of the diamines and reaction temperature.

The study of order of addition of the diamines was carried out by:

- a) addition of the heterocyclic diamine followed in order by the aromatic and aliphatic diamines at an interval of 15 minutes each



- b) addition of the aromatic diamine followed in order by the heterocyclic and aliphatic diamines at an interval of 15 minutes each

The results of this study were of significant importance in clarification of previously unexplained inconsistency of results and showed that the aromatic diamine must be added and fully dissolved before the heterocyclic and the aliphatic diamines are added. This method produced foams with lower number of flaws and significantly less foam collapse at the end of the curing cycle.

The addition of the diamines was done starting with a reaction mixture of 30-35°C (86-95°F), the temperature allowed to increase freely due to the exothermic reaction to approximately 50°C (122°F) and then controlled by reducing the rate of the addition of the diamines. Finally the reaction mixture was heated to 60-65°C (140-149°F) and maintained at these conditions for five minutes. Lower final reaction temperature in the range of 50-55°C (122-131°F) were studied but found not to contribute to improved foam qualities.

The work on aliphatic terpolyimide systems has yielded the optimum flexible foam candidate. This system has shown to out-perform all other foams in seating tests, but have been found to be more difficult to foam. Foaming studies for this system will be described in Section 4.1.2 and 4.1.3.

#### Effect of Molecular Ratio of Heterocyclic Diamine on Compression Set Properties

The copolyimide resins belonging to the 1702 resin system have been the subject of extensive study in earlier work on polyimide technology. These foams possess good hydrolytic stability and have homogeneous cellular structure with some degree of reticulation. Reticulation present in the foam is known to upgrade important foam properties such as compression set loss values. Therefore, a study was initiated in an attempt to increase the degree of reticulation.

In the first stage of this study, four advanced copolyimide foam precursors were synthesized varying the concentrations of the heterocyclic diamine. Table 5 presents the properties of foams and compression set data derived from these systems. These foams were produced at a concentration of surface active agent of 0.05 percent AS-2 and were cured at 287°C (550°F). The data show that 1701-1 and 1702-1 produce foams with lowest compression set loss values and highest resiliency and have some degree of reticulation. This formed the basis for tentative selection of these systems for further modification. Figure 25 shows a sample of the polyimide foam produced from 1701-1 precursor.

Table 5

Properties of Advanced Copolyimide Systems

| Copolyimide System | Mole Ratio | Density           |                     | Resiliency | % Loss After 30 Minutes Recovery | Type of Foam                                 |
|--------------------|------------|-------------------|---------------------|------------|----------------------------------|--|
|                    |            | kg/m <sup>3</sup> | lbs/ft <sup>3</sup> |            |                                  |  |
| 1701-1             | 1:0.4:0.6  | 14.7              | 0.92                | 85         | 21.0                             | Flexible, resilient, fine cellular structure |
| 1702-2             | 1:0.3:0.7  | 8.2               | 0.51                | 70         | 28.5                             | Flexible, resilient, fine cellular structure |
| 1703-1             | 1:0.2:0.8  | 6.7               | 0.42                | 60         | 41.3                             | Flexible, resilient, fine cellular structure |
| 1704-1             | 1:0.1:0.9  | 8.5               | 0.53                | 50         | 33.7                             | Flexible, resilient, fine cellular structure |

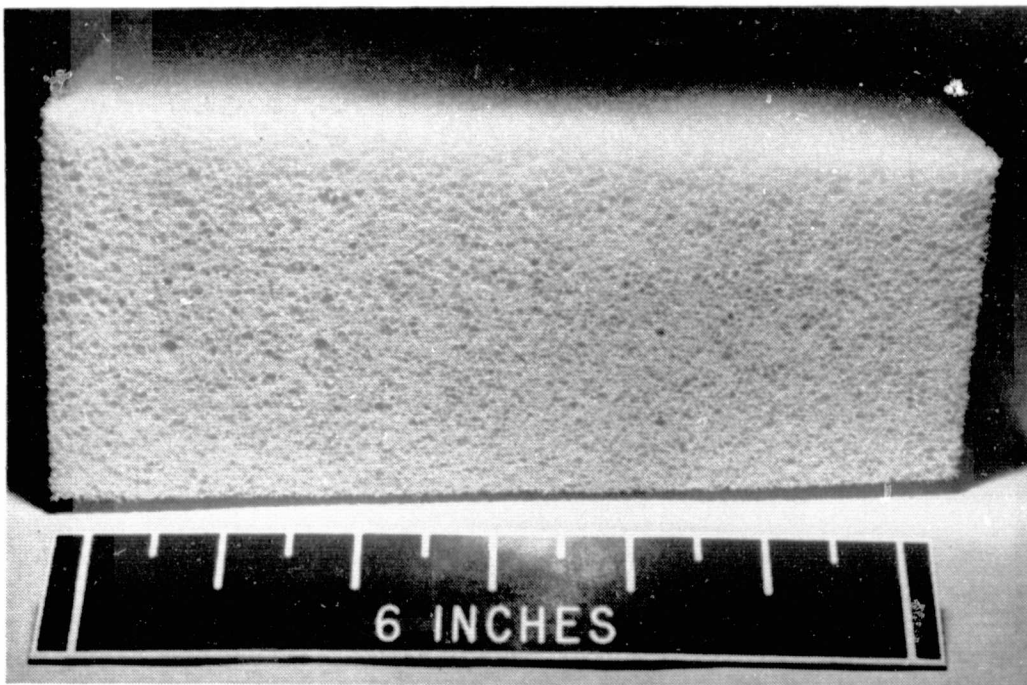


Figure 25. Reticulated Foam Derived From 1701-1 Precursor

From the data obtained in this preliminary study it was concluded that higher molar concentrations of the heterocyclic diamine favors improved compression set loss values. This objective was further pursued by synthesizing a total of three advanced polyimide precursors made at 0.42, 0.44 and 0.5 molar concentrations of the heterocyclic diamine respectively, and at a concentration of AS-2 of 0.0125 percent. A partial summary of this study is given in Table 6. During the course of this study it was found that microwave radiation produced good reticulation in polyimide foams at around 0.4-0.42 molar concentrations of the heterocyclic diamine. Below this concentration, little or no reticulation was observed. Above this concentration, cell walls disappear almost completely and were replaced by lamellae strands. This effect is most pronounced at a molar concentration of 0.5 where the foam produced was a hollow shell with a thick integral skin. This behavior was completely unexpected since the data obtained from the study of thermal foaming supported the fact that higher molar ratio of the heterocyclic diamine produced more flexible and resilient foams. The study carried out in this task has shown the critical effects of compositional changes and the narrow limit of the concentration of the heterocyclic diamine to achieve effective microwave foaming.

Table 6

Flexible, Resilient, Polyimide Foams; Effect of Molar Concentration of 2,6DAP on Compression Set Loss Values

| Foam Resin Number | Molar Ratio | Concentration of Surfactant AS-2 (%) | % Loss After 30 Minutes Recovery | Type of Foam   |
|-------------------|-------------|--------------------------------------|----------------------------------|--|
| 1702-1-62         | 1:0.3:0.7   | 0.0125                               | 40.0                             | Fine, homogeneous cellular structure   |
| 1701-1-5          | 1:0.4:0.6   | 0.0125                               | 19.6                             | Medium-large homogeneous cellular structure  |
| 1701-1-7          | 1:0.42:0.58 | 0.0125                               | 12.1                             | Reticulated foam with medium size cellular structure                                 |
| 1701-1-8          | 1:0.44:0.56 | 0.0125                               | --                               | Highly reticulated foam with large and weak cellular structure                       |
| 1701-1-10         | 1:0.5:0.5   | 0.0125                               | --                               | Highly reticulated foam with chopped strands like cell structure. Poor - hollow foam |

At the beginning of this study, reticulation was regarded to be a desirable foam property since it improved very significantly the compression set property of the foams. In subsequent testing, it was found that reticulation adversely affects the fatigue resistance of the foams causing early failure by a

mechanism of cell fracture and shredding. Therefore, the two systems specifically the 1701-1 and 1702-1 made at a ratio of 0.4 and 0.3 moles of heterocyclic diamine respectively, were selected for further evaluation as reported in the following sections.

### Hydrolytic Stability

Foam precursors belonging to the systems 1701-1 and 1702-1 were evaluated for hydrolytic stability along with the most promising candidate (1720-1) derived from the study of terpolyimide aliphatic systems. The samples were tested in a condensing humidity chamber at 74°C (165°F) and 90 percent relative humidity for a period of seven days. The summary of results is given in Table 7. The data indicate that none of the promising candidates show any sign of degradation, brittleness or adverse effects under high humidity environments.

Table 7

Hydrolytic Stability of Flexible, Resilient Polyimide Foams  
at 74°C and 90% Relative Humidity

| Resin Number | Surfactant (AS-2)<br>Concentration<br>(%) | Modification   | Initial Properties |            | Final Properties<br>(After 7 Days) |            |
|--------------|---|----------------|--------------------|------------|------------------------------------|------------|
|              |   |                | Weight, gr         | Resiliency | Weight, gr                         | Resiliency |
| 1702-1       | 0.025                                     | --             | 6,2350             | 70-80      | 6.2413                             | 70-80      |
| 1702-1       | 0.025                                     | --             | 4,4936             | 50-60      | 4,4987                             | 60-70      |
| 1720-1-24-7  | 0.05                                      | diamino hexane | 2,9771             | 50-60      | 2,9838                             | 60-70      |

To uncover differences in hydrolytic stability of various candidates not noticeable with shorter higher temperature tests, a new and much more realistic test was carried out. This test was conducted in a Controlled Temperature Humidity Chamber (Blue M) for a period of 30 days at 60°C (140°F) and 100 percent relative humidity. Data obtained from this test are shown in Table 8. The results indicate that both 1701-1 and 1720-1-24 survive the testing period without embrittlement of cellular structure. Series 1701-1 showed little change in flexibility and resiliency at the end of testing period. Series 1720-1-24 showed no change in flexibility and a loss of resiliency from 60 to 45. Figure 26 shows the foam sample of 1720-1 at the end of the humidity test (30 days).

Table 8

Hydrolytic Stability of Flexible Resilient Polyimide Foams  
at 60°C and 100 Percent Relative Humidity

| Resin No. | Surfactant (AS-2)<br>Concentration<br>(%) | Modification  | Initial Properties |                     |            | Final Properties<br>(After 30 Days) |                  |
|-----------|---|---------------|--------------------|---------------------|------------|-------------------------------------|------------------|
|           |   |               | Kg/m <sup>3</sup>  | lbs/ft <sup>3</sup> | Resiliency | Resiliency                          | Remarks          |
| 1701-1    | 0.05                                      | -             | 25.6               | 1.6                 | 50         | 45                                  | Almost no change |
| 1702-1    | 0.05                                      | -             | 16.0               | 1.0                 | 60         | 25                                  | Brittle          |
| 1720-1-24 | 0.05                                      | Diaminohexane | 16.0               | 1.0                 | 60         | 45                                  | Almost no change |

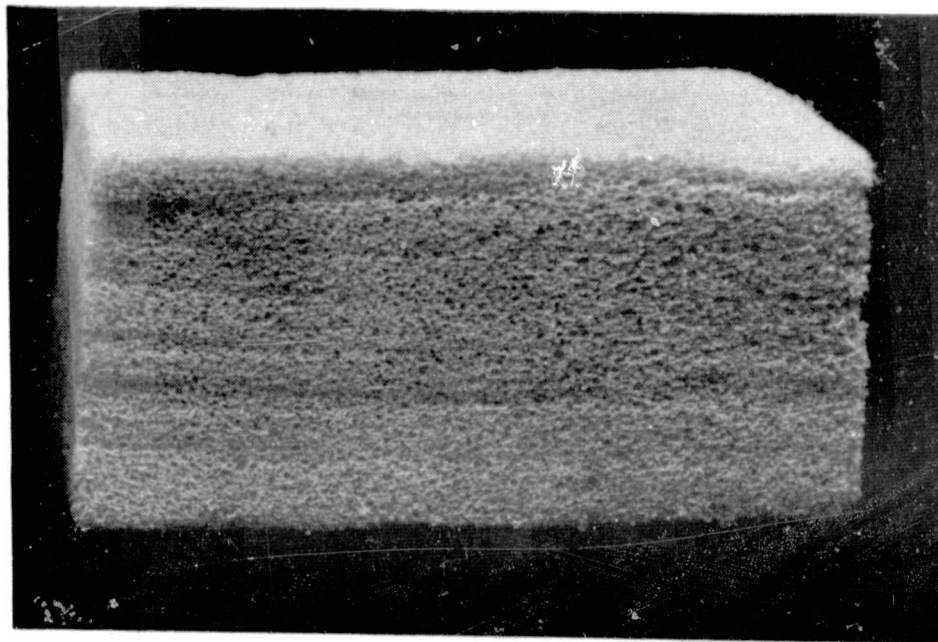


Figure 26. Polyimide Foam (1720-1) at the End of Humidity  
Test (30 Days)

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## Additive Studies

The polyimide compositions belonging to the 1702 and 1701 resin systems have been the subject of extensive study in earlier work on polyimide technology.

Foams derived from these precursors have a reticulated, homogeneous cellular structure with a cell size larger than that of any other system evaluated. This characteristic is known to contribute to improved compression set. To evaluate this parameter studies were initiated by modification of these precursors with additives, starting with the study of surface active agents.

A total of 37 copolyimide foam precursors, derived from 1702-1 system, were synthesized in the first phase of this work. The precursors were modified with three different types of surface active agents at a concentration ranging from 0.05 to one percent based on polyimide solids. Foams were prepared from each of the precursors and evaluated for density, resiliency, compression set and fatigue resistance. Polyimide precursors prepared at high surfactant concentration produced foams with very homogeneous cellular structure and little or no reticulation. The point of no reticulation generally coincided with the best fatigue properties of the foams as shown in Table 9. On the other hand, the foams which possessed a significant degree of reticulation were considerably less resistant to cyclic fatigue loading and failed by a mechanism of cell fracture and shredding.

Because fatigue properties are the most important requirements of seating foams, the effort to achieve reticulation was no longer pursued.

In subsequent studies, which will be reported in Section 4.1.3, efforts were actually expended to eliminate small reticulated areas present in foams produced in large size since they caused failure by shearing in seating tests.

A significant contribution resulting from the evaluation of surface active agents is the exceptional fatigue resistance of systems modified with specific surfactants. This effect is shown in Figure 27 for polyimide foams modified with 0.1 percent FSB, X-3-6, X-3 and AS-2 surfactants respectively. After a total of 10,000 cycles the foams modified with 0.1 percent AS-2 show little or no loss of thickness or resiliency. When the concentration of the surfactants was increased the fatigue resistance of the foams was adversely affected as is shown in Figures 28, 29 and 30. The 90 percent compression set values of the foams reported in Table 9 are still below standard. The data have been reported at 30 minutes and 60 minutes recovery. This has been done to demonstrate that the cellular structure of the foams is not damaged during the test as proved by the additional recovery. The data shown in Table 9 indicate that foams made with 1702-1 precursors modified with 0.1 percent AS-2 surfactant possess fatigue properties approaching the goal of this program. At the conclusion of this study, AS-2 surfactant was selected for further evaluation.

Table 9

1702-1 Resin Systems - Foam Properties

| % Surfactant | Density<br>kg/m <sup>3</sup> | Resiliency<br>Ball Rebound | 90% Compression Set<br>& Loss After |                        | % Thickness<br>Loss After<br>10,000 Fatigue Cycles |
|--------------|------------------------------|----------------------------|-------------------------------------|------------------------|--|
|              |                              |                            | 30 Minutes<br>Recovery              | 60 Minutes<br>Recovery |  |
| <b>X-3</b>   |                              |                            |                                     |                        |  |
| 0.05         | 7.0                          | 70                         | 45                                  | 27                     | 55   |
| 0.1          | 7.0                          | 65                         | 35                                  | 35                     | 24   |
| 0.2          | 6.7                          | 60                         | 50                                  | 40                     | 33   |
| 0.4          | 0.52                         | 50                         | 40                                  | 40                     | 40   |
| <b>X-3-6</b> |                              |                            |                                     |                        |  |
| 0.1          | 10.5                         | 65                         | 50                                  | 45                     | 22   |
| 0.5          | 7.0                          | 40                         | 35                                  | 35                     | 13   |
| 1.0          | 16.0                         | 45                         | 30                                  | 22                     | 36   |
| <b>AS-2</b>  |                              |                            |                                     |                        |  |
| 0.05         | 9.0                          | 70                         | 32                                  | 25                     | 0  |
| 0.1          | 8.3                          | 50                         | 31                                  | 22                     | 0  |
| 0.5          | 5.6                          | 60                         | 45                                  | 40                     | 16   |
| 1.0          | 4.8                          | 25                         | 55                                  | 45                     | 50   |

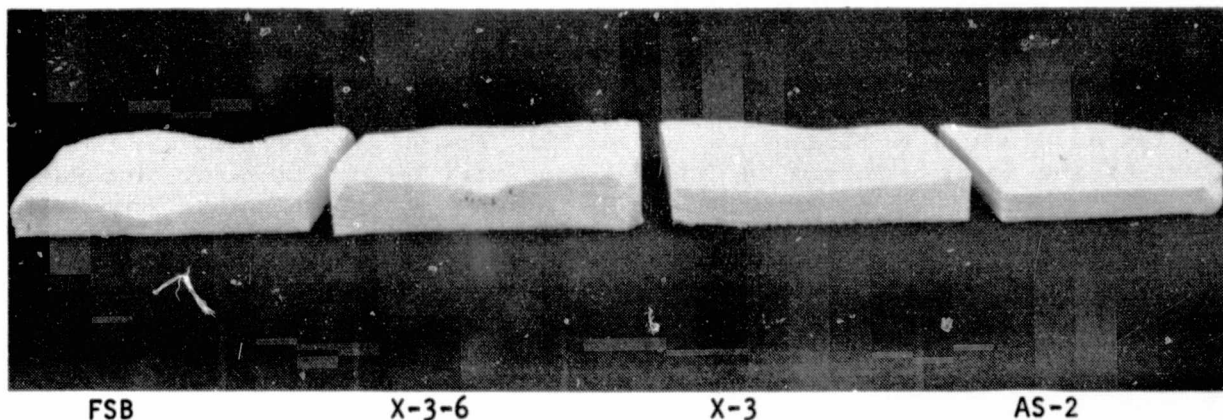
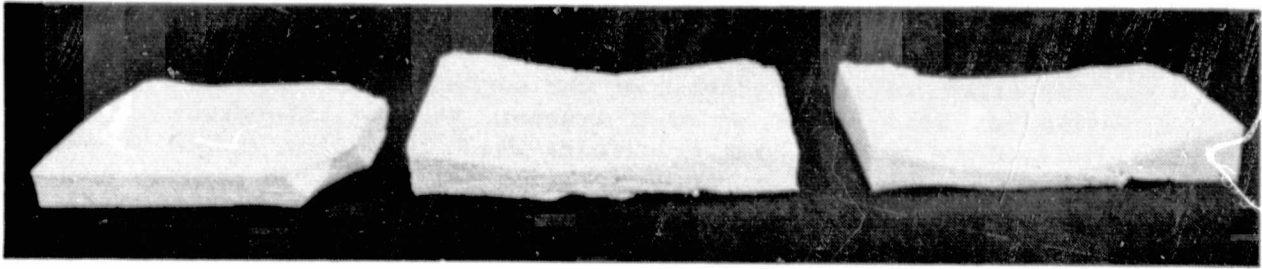


Figure 27. Fatigue Resistance of Foams Derived From 1702-1 Precursors Modified With Various Surfactants

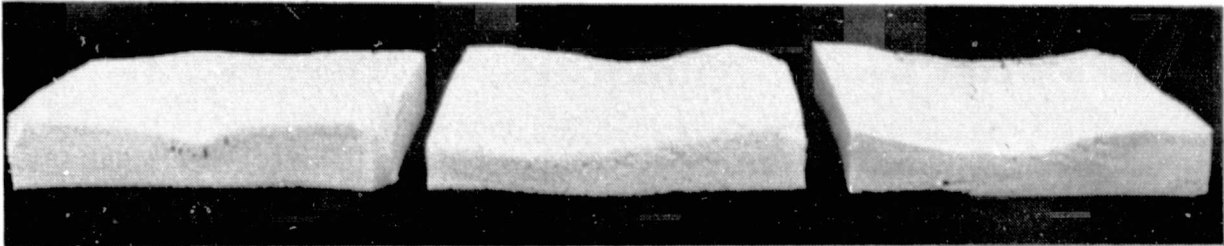


0.1%

0.5%

1.0%

Figure 28. AS-2 Surfactant Concentration Effect on Fatigue Resistance

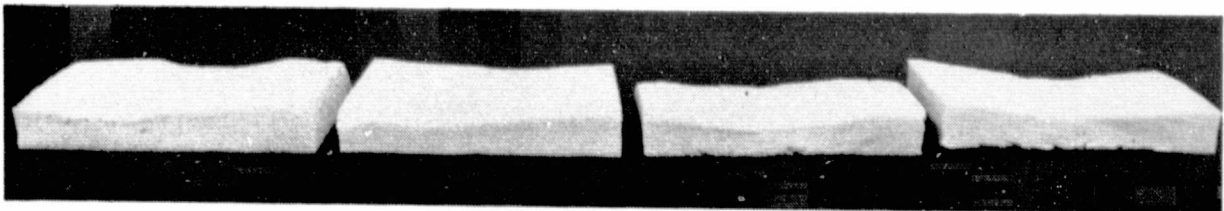


0.1%

0.5%

1.0%

Figure 29. X-3-6 Surfactant Concentration; Effect on Fatigue Resistance



0.05%

0.1%

0.2%

0.4%

Figure 30. X-3 Surfactant Concentration; Effect on Fatigue Resistance



After establishing optimum conditions to achieve best fatigue properties, the foam precursors belonging to the systems 1701-1 and 1702-1 were then studied to evaluate the effect of concentration of the surface active agent (AS-2) on the compression set loss values of each system. Varying concentrations of AS-2 were employed to produce foam precursors which were then foamed in the 5 kW microwave oven. The summary of compression set values at varying concentrations of AS-2 is given in Table 10. Figure 31 gives the graphical presentation of these same values. The data show that, for all concentrations of AS-2 surfactant, the compression set values of the 1701-1 system are significantly better than those of the 1702-1 system. By expanding this concept we can also conclude that higher ratio of the heterocyclic diamine favors better compression set characteristics. This improvement is significant especially at higher concentrations of AS-2 surfactant at which the 1701-1 system meets the compression set goal established for this program (15% maximum). Another important consideration is shown by the fact that the compression set properties of 1701-1 and 1702-1 foams are almost independent of the concentration of the surfactant. This wide range of concentrations permits fabrication of foams with specific properties, including fine cellular structure, lower density and high burnthrough resistance. This technology was utilized in the study of thermal acoustical foams, as will be discussed in Section 4.4.

On the basis of these results, the 1701-1 and 1702-1 systems were tentatively selected for continuing studies in preparation for scale-up processes of large size foams.

The effect of AS-2 surfactant on 1703-1 and 1704-1 candidates has also been evaluated. This surfactant has produced significant improvement of the foaming behavior of these precursors as is demonstrated in Figure 32, where the effect of surfactant on the cellular structure of foams derived from 1703-1 precursors modified with 0, 0.00625 and 0.05 percent AS-2 is clearly demonstrated.

The results of this evaluation were directly applied to the study of effect of surfactants on terpolyimide systems modified with aliphatic diamines (1720-1). Data derived from this study are graphically shown in Figure 33. The minimum of the curve corresponds to the optimum concentration of AS-2 for this terpolyimide system. The data show that modification of the 1702-1 system with aliphatic diamine does not contribute to improved compression set values although these same foams have shown to possess superior fatigue resistance as reported previously.

The improved fatigue property of the 1720 system is clearly a result of improved elasticity and flexibility of the foam structure and makes these foams viable candidates for further study of optimization as will be discussed in Sections 4.1.2 and 4.1.3.

Table 10

Flexible, Resilient Polyimide Foams; Effect of Surfactant Concentration on Compression Set Loss of 1701-1 and 1702-1 Systems

| Concentration AS-2 (%) | % Loss After 30 Minutes Recovery |        |
|------------------------|----------------------------------|--------|
|                        | 1701-1                           | 1702-1 |
| 0                      | 23.0                             | 19.0   |
| 0.005                  | 23.9                             | --     |
| 0.00625                | 23.0                             | 35.0   |
| 0.010                  | 26.3                             | --     |
| 0.0125                 | 17.5                             | 32.5   |
| 0.015                  | 24.2                             | --     |
| 0.020                  | 16.1                             | --     |
| 0.025                  | 15.0                             | 42.5   |
| 0.035                  | 13.7                             | --     |
| 0.050                  | 21.0                             | 32.0   |

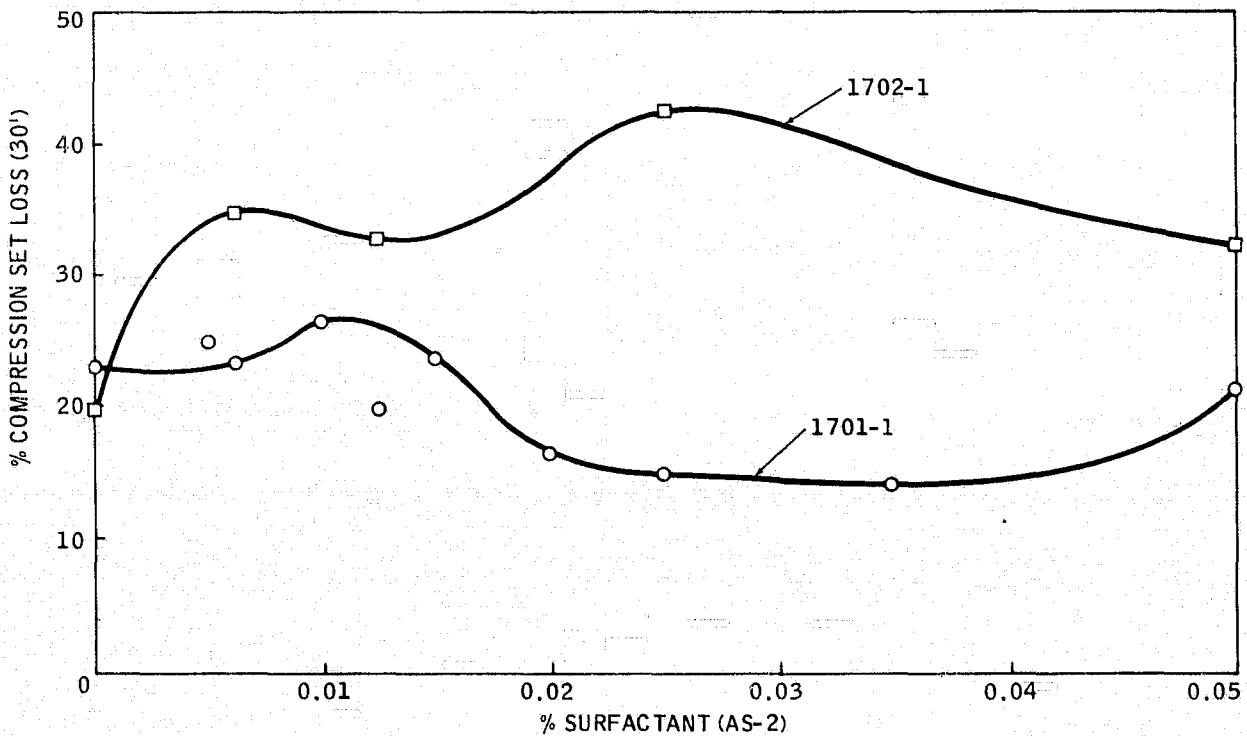


Figure 31. Flexible, Resilient Polyimide Foams; Effect of Surfactant Concentration (AS-2) on Compression Set Loss

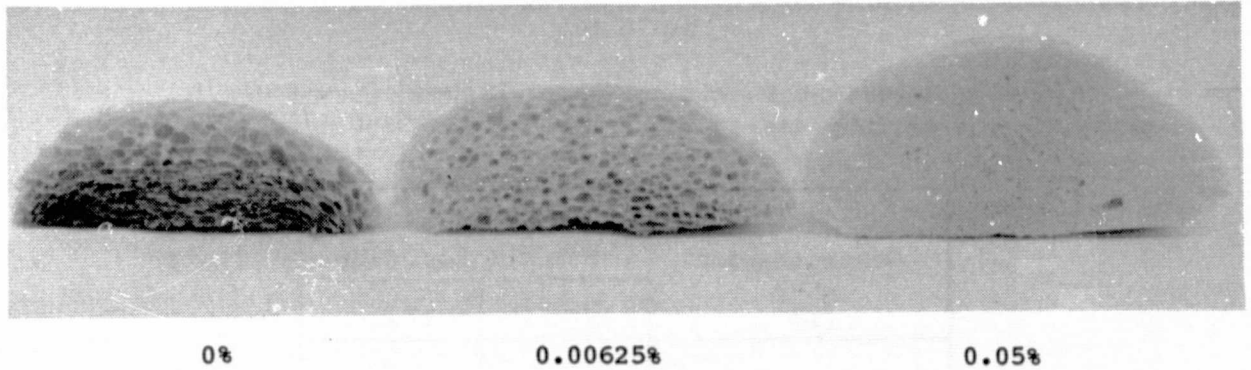


Figure 32. Effect of AS-2 Surfactant on Cellular Structure of Flexible, Resilient Polyimide Foams (1703-1)

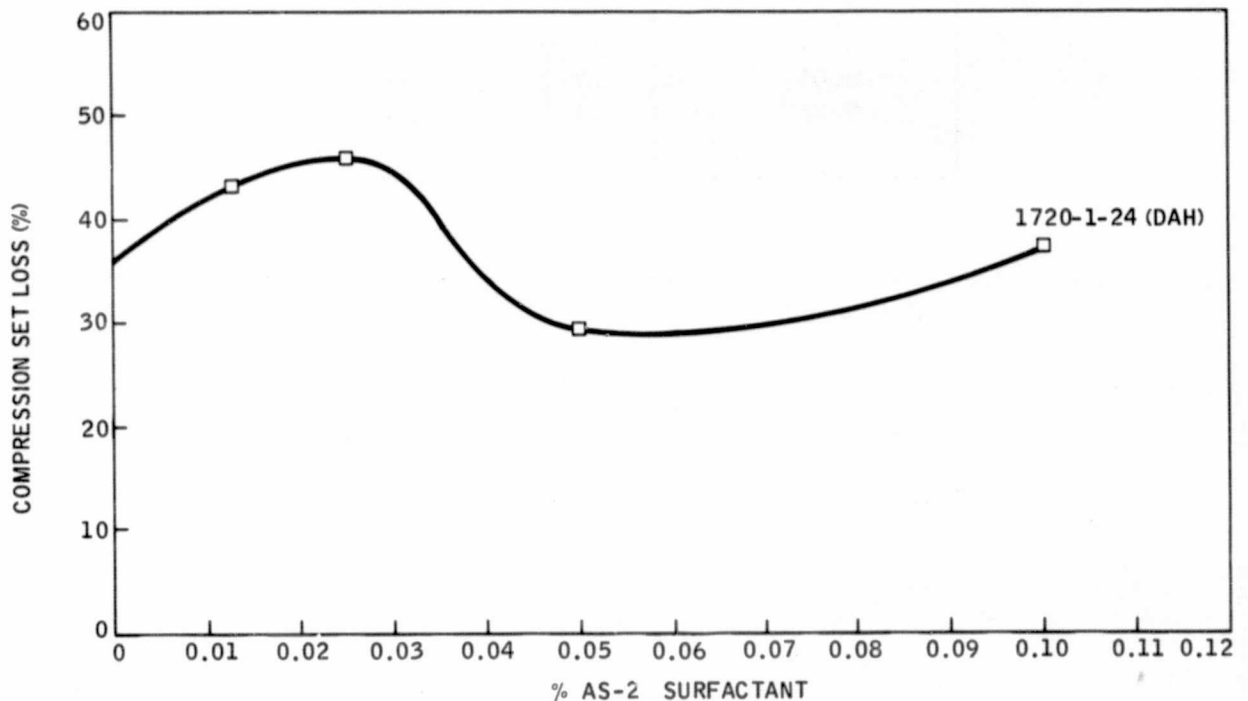


Figure 33. Effect of Surfactant Concentration on Compression Set Loss of Aliphatic Diamines Modified Polyimide Precursors (1720-1)

#### Modification of the Polymer Structure With Fatty Acids

The objective of this task was to achieve improved flexibility and elasticity of foams using long chain fatty acids in the molecular structure of the polyimides. The modification was effected by varying the concentration of the BTDA to accommodate the inclusion of a second dicarboxylic acid. Modification with dimethyl sebacate (DMS) was attempted at a ratio of DMS:BTDA of 0.2:0.8.

Powder precursors were obtained which decomposed during the foaming process and no foaming was possible. Modifications with other long chain acids such as rosin esters and dimerized fatty acid produced the same thermal decomposition. These results were not surprising since long chain acids are known to undergo oxidative degradation. Further work on this subtask was not warranted and therefore discontinued.

#### Advanced Polyimide Synthesis - Summary

The following brief review describes the major developments resulting from the experimental work carried out in Task I, Advanced Polyimide Synthesis.

1. Modification of precursors with aromatic diamines did not produce improved candidates for scale-up studies. Therefore, work on these systems was discontinued.
2. A candidate terpolyimide system modified with aliphatic diamine was selected for further study.
3. The study of the effect of molecular ratio of the heterocyclic diamine on copolyimide systems has shown that higher molar concentration of 2,6DAP favors improved compression set values. On the basis of data obtained, 1701-1 and 1702-1 were selected as viable candidates for scale-up processes.
4. The selected candidates show no detectable degradation under high humidity environments.
5. Additive studies have shown that surfactant AS-2 yields flexible and resilient foams with the most homogeneous cellular structure and compression set values meeting the program goal. Incorporation of this additive for the synthesis of polyimide foam precursors has become a standard procedure for all resin systems.

#### 4.1.2 Task II - Foaming Studies

The work carried out in this phase of the program is divided into four parts. The first part outlines the studies dealing with spray drying processing of liquid resins, the second part covers the development of a new process which permits foaming and curing polyimide resins in a one-step process followed by selection of substrates, evaluation of microwave process parameters and foam cutting techniques.

## Spray Drying Processes

The technique of spray drying converts a liquid into a dry powder in a continuous one step operation. Spray drying involves three fundamental unit processes:

1. Liquid atomization
2. Gas-droplet mixing
3. Drying

The basic principles involved concern the atomization of the feed liquid into a spray of very small droplets by means of a vaned wheel rotating at high speed. These droplets have a very large surface area and evaporation is completed rapidly. During the evaporation stage there is an accompanying cooling effect on the droplets and with the residence time in the chamber of short duration, heat damage of the product is prevented.

The liquid resin is fed to the atomizer under gravity or by a small capacity feed pump and atomized into a fine spray or droplets. The spray is contacted with hot air entering the chamber through a ceiling air disperser. The air disperser is positioned in the center of the chamber roof and is designed to create a swirling air flow directly around the vaned atomizer wheel. Removal of the solvent from the droplets is accomplished virtually instantaneously. Powder and air pass to a small highly efficient cyclone where the powder is separated out and collected in a glass jar.

The initial experimental work reported here was conducted with 1702-1 liquid resins modified with 0.1 percent X-3 surfactant, however the process was found to be applicable to all other precursors.

In order to determine the best operating conditions to dry the liquid resin, the effect of inlet and outlet temperature was studied at various flow rates of liquid resin. It is important to note here that outlet temperature is controlled by varying the flow rate of the feed.

Four different inlet temperatures were selected at various flow rates. These were 100, 110, 120 and 130°C (212, 230, 248 and 266°F). The results of this study are summarized in Table 11. At a flow rate capable of producing complete drying, the lowest possible inlet temperature (100-110°C) has shown to yield powder precursors with good foaming characteristics.

By far, the most critical parameter of the spray drying process is the outlet temperature. The outlet temperature determines the volatile content of powder resins and can cause excessive drying, thus producing prepolymerization. During the course of this study, the outlet temperature was varied by decreasing or increasing the feed rate.

With reference to Table 11, powder precursors obtained at an outlet temperature in excess of 80°C (176°F) produced powder resins with low bulk density and foams with poor cellular structure.

When the outlet temperature was reduced to 76°C (168.8°F) or below by means of higher feed rate, the powder precursors produced foams with good cellular structure. [Run #22 (80-74), #23 (80-70), #25 (80-75), #29 (80-74), #30 (80-74), #31 (80-70).]

This process was scaled up to establish performance for the unit and to gather more experimental data.

As pointed out previously, the foaming characteristics of powder precursors depend heavily on the outlet temperature. In spray drying technique, the outlet temperature was maintained within desired limits by decreasing or increasing the feed rate. Table 12 summarizes the results of scale-up study carried out in the last phase of the program during which narrow ranges of outlet temperatures were obtained by varying the feed rate of the liquid resin. This study was carried out with 1720-1 foam modified with 0.75 percent surfactant. The foam yield estimated from rough cut foam slabs was found to improve dramatically with a decrease of the outlet temperature. Figure 34 shows a rough cut 1720-1 foam. The experiments which produced the highest yield also possessed the best cellular structure and homogeneity.

Table 11

Summary of Spray Dryer Study

| Run Number | Inlet °C | Outlet °C | Δt, °C  | Average Flow Rate ml/min | Total g | Jar g | Wall g | Jar % | Powder Bulk Density |                     | Foam Properties |                     |                   |              |
|------------|----------|-----------|---------|--------------------------|---------|-------|--------|-------|---------------------|---------------------|-----------------|---------------------|-------------------|--------------|
|            |          |           |         |                          |         |       |        |       | g/cc                | lbs/ft <sup>3</sup> | Resiliency      | Density             |                   | Foam Quality |
|            |          |           |         |                          |         |       |        |       |                     |                     |                 | lbs/ft <sup>3</sup> | kg/m <sup>3</sup> |              |
| 21         | 110      | 80-86     | 30-24   | 22                       | 712     | 568   | 144    | 80    | 0.238               | 14.9                | 60-70           | 1.21                | 19.4              | Poor         |
| 22         | 110      | 80-74     | 30-36   | 54                       | 784     | 317   | 467    | 40    | 0.352               | 22.0                | 60-70           | 0.86                | 13.8              | Good         |
| 23         | 110      | 80-70     | 30-40   | 107                      | 747     | 131   | 617    | 17.5  | 0.414               | 25.8                | 50-60           | 0.75                | 12.0              | Good         |
| 24         | 120      | 80-86.5   | 40-33.5 | 335                      | 704     | 631   | 73     | 89.6  | 0.200               | 12.5                | 50              | 1.38                | 22.1              | Poor         |
| 25         | 120      | 80-75     | 40-45   | 80.8                     | 769     | 259   | 510    | 33.7  | 0.368               | 23.0                | 50-60           | 0.67                | 10.7              | Good         |
| 26-R       | 120      | 80-76     | 40-44   | 58.4                     | 767     | 594   | 173    | 77.4  | 0.329               | 20.5                | 50              | 0.66                | 10.6              | Poor         |
| 27         | 130      | 80-88     | 50-42   | 48                       | 749     | 558   | 191    | 74.5  | 0.198               | 12.4                | 50-60           | 1.52                | 24.3              | Poor         |
| 28         | 130      | 80-77     | 50-53   | 83.3                     | 714     | 250   | 464    | 35    | 0.241               | 15.0                | 50-60           | 1.06                | 17.0              | Poor         |
| 29         | 130      | 80-74     | 50-56   | 90.4                     | 646     | 197   | 449    | 30.5  | 0.343               | 21.4                | 60-70           | 0.59                | 9.5               | Good         |
| 30         | 100      | 80-74     | 20-26   | 35.8                     | 700     | 606   | 94     | 86.6  | 0.326               | 20.3                | 60-70           | 0.88                | 14.1              | Good         |
| 31         | 100      | 80-70     | 20-30   | 60.9                     | 687     | 250   | 437    | 36.4  | 0.413               | 25.8                | 60-70           | 0.95                | 15.2              | Fair-Good    |
| 32         | 100      | 80-79     | 20-21   | 23.8                     | 796     | 681   | 115    | 85.6  | 0.241               | 15.0                | 50              | 0.88                | 14.1              | Poor         |

Table 12

Effect of Outlet Temperature

| Foam Number | Inlet Temperature (°C) | Outlet Temperature (°C) | Powder Yield |       | Powder Precursor Volatile Content % | Foam Yield Rough Cut % | Density           |                     | Type of Foam                |
|-------------|------------------------|-------------------------|--------------|-------|-------------------------------------|------------------------|-------------------|---------------------|-----------------------------|
|             |                        |                         | kg/h         | lbs/h |                                     |                        | kg/m <sup>3</sup> | lbs/ft <sup>3</sup> |                             |
| 45-62       | 100                    | 58-63                   | wet powder   |       | -                                   | 10                     | 7.2               | 0.45                | Excessive Reticulation      |
| 68-78       | 100                    | 63-67                   | 2.9          | 6.4   | 21.4                                | 82                     | 10.2              | 0.64                | Good. Moderate Reticulation |
| 77-87       | 100                    | 67-70                   | 2.3          | 5.0   | 20.7                                | 65                     | 20.0              | 1.25                | Good. Some reticulation     |
| 70-80       | 100                    | 70-75                   | 1.7          | 3.8   | 19.2                                | 47                     | 22.2              | 1.39                | Fair. Striations present    |
| 46-63       | 100                    | 75-80                   | 0.64         | 1.4   | 19.0                                | 35                     | 25.6              | 1.60                | Poor. Full of voids         |

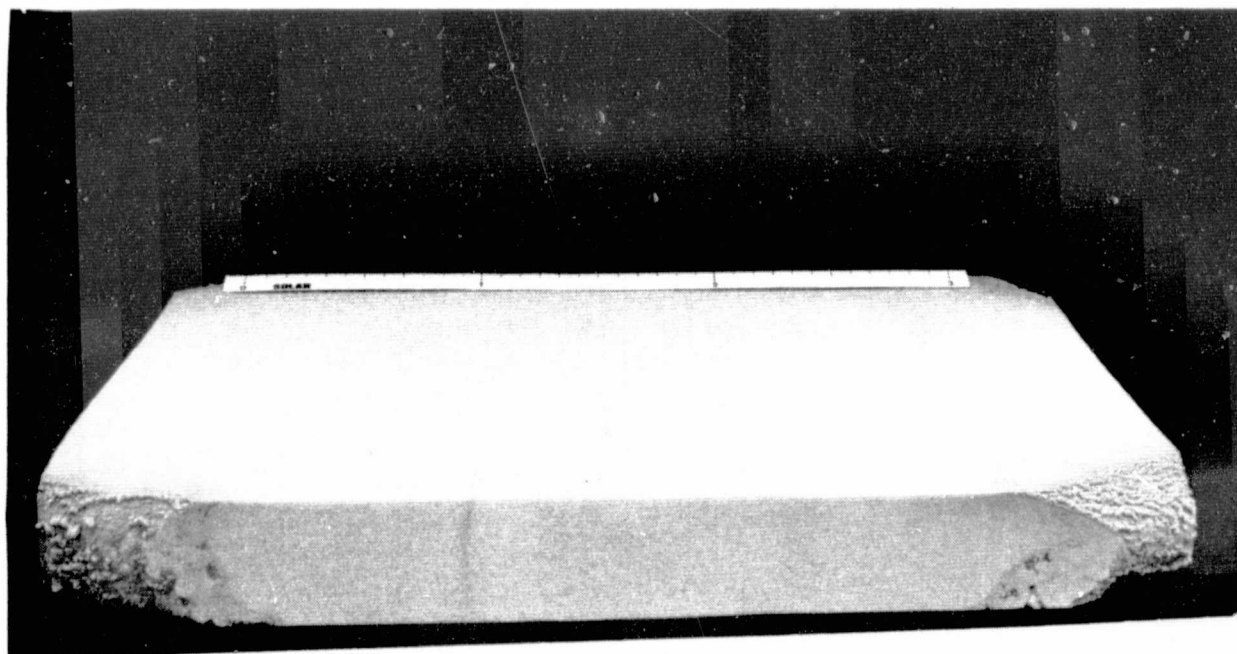


Figure 34. 1720-1 Foam - Rough Cut

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At these feed and inlet temperatures, the optimum outlet temperature was found to be in the range of 63-70°C (145.4-158°F). Figure 35 shows foam samples produced from 1720-1 system and spray dried at these conditions. Figure 36 shows a section of the 1720-1 foams after fatigue testing for 20,000 cycles.

On the basis of this experimental work, the feasibility of spray drying polyimide resins was established. This method has replaced the original vacuum process for the production of powder resins in large lots.

This experimental work was continued to refine the operating procedure and optimize the process parameters. A study was initiated to correlate the atomizer speed with foam quality. The results of this study indicate that low atomizer speed (24,000 rpm) yields powder precursors with high volatile content which give highly reticulated foams. At high speed the particle size of the powder precursors is very small, the volatile content low and the respective foams are semi-rigid. The optimum atomizer speed was found to be in the range of 30,000-32,000 rpm.

Since the atomizer speed is so critical for the satisfactory operation of the spray dryer, an electronic stroboscope, Gen Rad 1538-A Strobotac was used to keep weekly records of the atomizer speed. Also, fluctuations of the air pressure can cause variations in the turbine wheel speed. This problem was solved by the installation of a 60 cubic feet air reservoir coupled with booster pump (Teledyne-Sprague Engineering). This assembly delivers air to the atomizer at a constant pressure. The spray dryer was equipped with a feed pump (Sigmamotor Pumps) which delivers the liquid resin to the spray dryer at constant rate at any desired setting.

To further improve the operation of the spray dryer, the powder collection system at the point of discharge from the cyclone was modified as shown in Figure 37 and a timed-impact vibrator installed by mounting it on a channel plate located at the base of the dryer. This assembly is shown in Figure 38. These accessories have greatly facilitated the collection of powder resin directly into five gallon containers instead of laboratory size glass jars. The modifications discussed earlier have produced remarkable improvements of the spray dryer which make it possible to operate the unit continuously and practically unattended.

#### Microwave Foaming-Curing Process

The effort of this task involved the study of fillers capable of interacting with the microwave field and produce sufficient thermal energy to cause foaming and curing of polyimide precursors in a one-step process.

Exploratory experiments were carried out by modification of the precursors with conductive fillers followed by foaming in the 5 kW microwave oven. Immediately after foaming, the temperature rise of the foams was measured by means of thermocouples inserted into the center of the mass. The feasibility of this method was first attempted by modification of 1702-1 precursors with



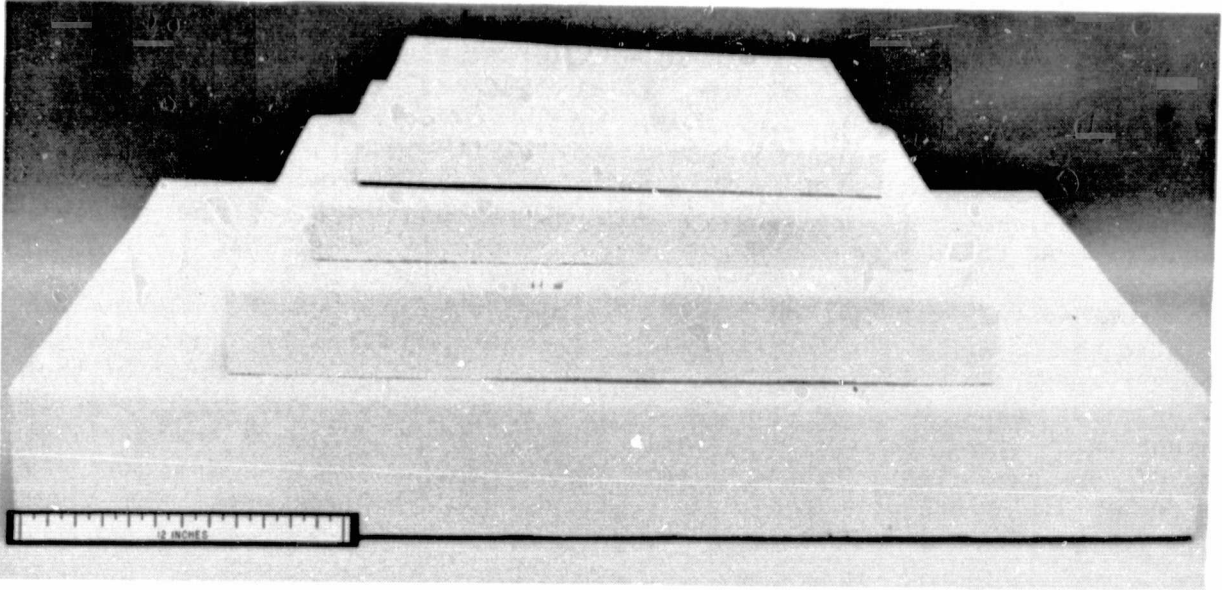


Figure 35. Polyimide Foam (1720-1) Produced at Spray Dryer Outlet Temperature (63-70°C)

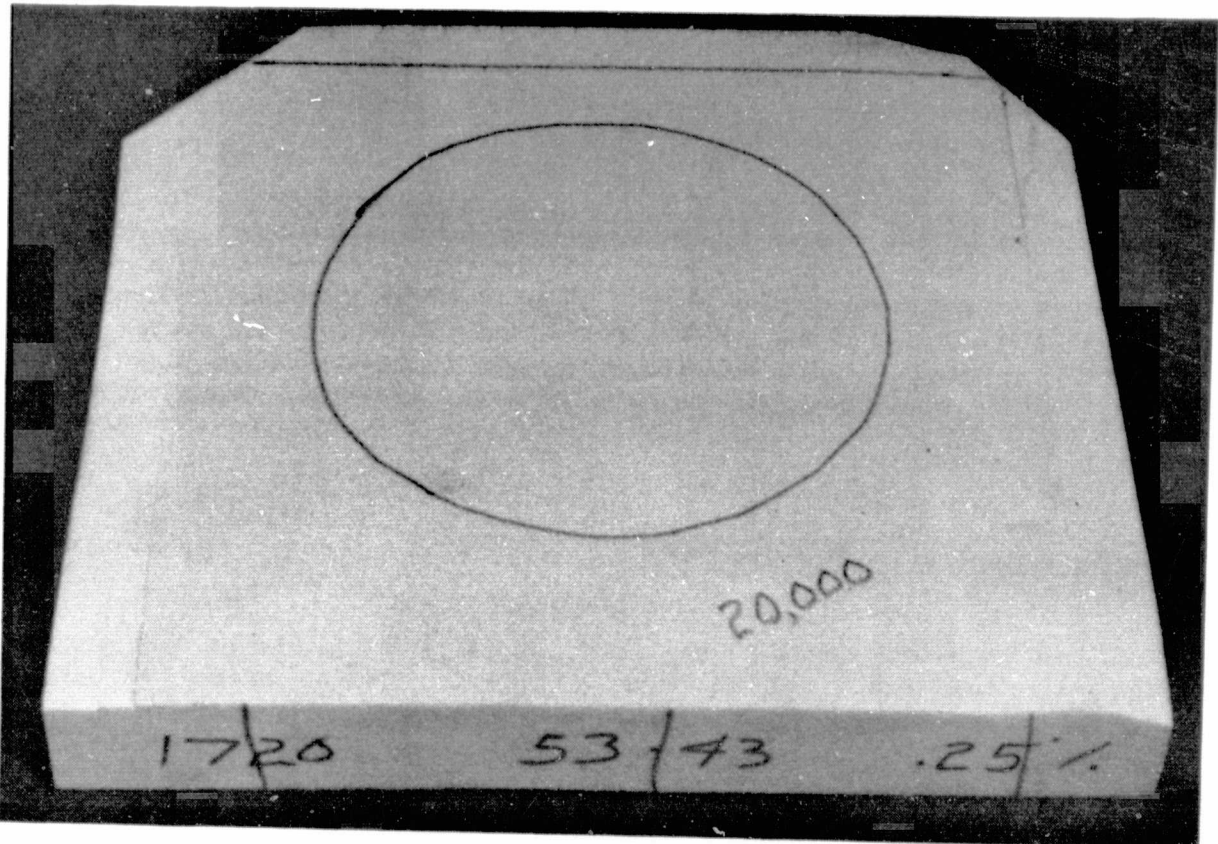


Figure 36. Foam Produced From Spray Dired 1720-1 Precursors After 20,000 Cycles Fatigue

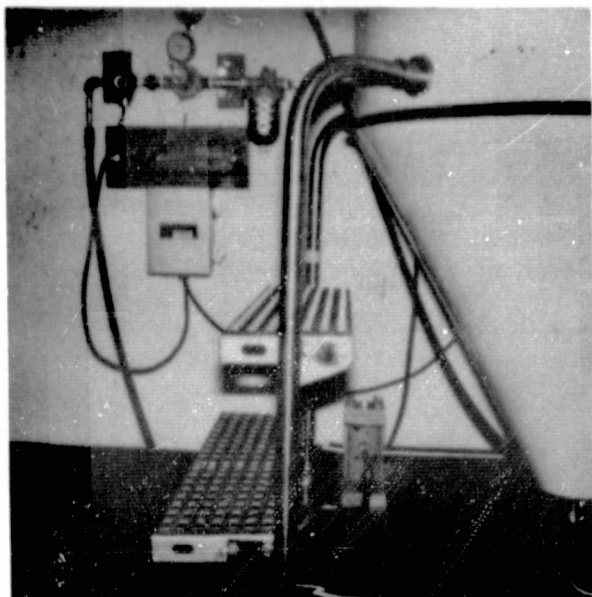
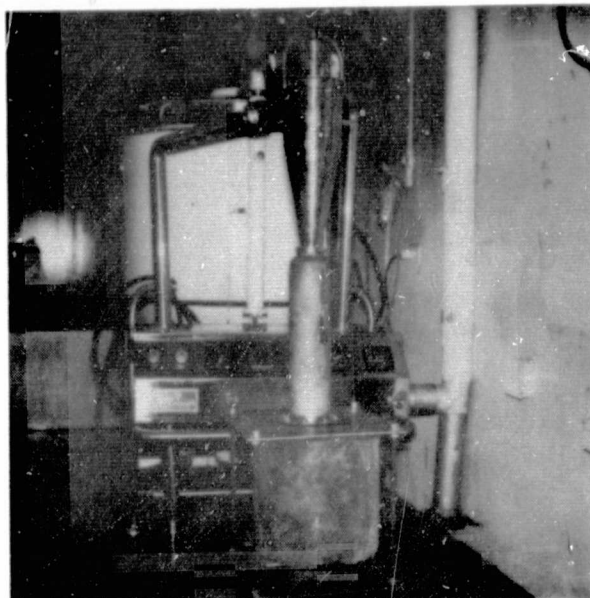


Figure 37.

Spray Dried Powder Resin Collection System

Figure 38.

Timed-Impact Vibrator for the Spray Dryer



various concentrations of micromesh aluminum powder (Alcoa MD105). Data derived from this study are shown in Table 13. Although none of the compositions produced fully cured foams in the microwave field, the energy liberated at increasing concentration of aluminum powder proved the feasibility of this concept.

A second series of experiments was then carried out by foaming compositions prepared by compounding 20 percent by weight of selected conductive fillers in 1702-1 precursors. The fillers are:

Micromesh Graphite Powder  
Activated Carbon Powder

Table 13

Effect of Conductive Filler on Foaming  
Temperature of 1702-1 Precursors

| % Aluminum Powder<br>in Precursors | Temperature Rise<br>at End of Foaming Cycle<br>(°C) |
|------------------------------------|---|
| 0                                  | 106   |
| 10                                 | 149   |
| 20                                 | 165   |
| 30                                 | 176   |

Titanium Dioxide  
Hydrated Alumina  
Boron Nitride  
Wood Resin  
Pelargonic Acid

The data derived from these experiments showed that the addition of graphite is capable of producing a temperature increase of 191°C (375°F) and partial curing of the foams. For activated carbon the temperature increase was in excess of 315°C (600°F) and possibly higher because the foams began to char. None of the other additives produced any significant thermal effect.

On the basis of these findings, activated carbon was selected for further study. Precursors derived from 1702-1 resins were modified by the addition of various amounts of activated carbon and foamed by the same method reported above. The results of these experiments are reported in Table 14. As shown, the compositions obtained by modification with 10 percent activated carbon started to foam in 40 seconds, but more importantly, the foams became fully cured and exhibited good resiliency and flexibility.

The energy absorbed during the foaming process was found to be dependent on the size of the powder charge. This was proved by the fact that when large size foams were prepared by this process (600 g of powder precursors) foaming and curing occurred at a filler concentration of four to five percent. It was also determined that higher surfactant concentration (0.3-1.0%) was required to produce homogeneous foams by this method in order to minimize cavities and other imperfections present when large size foams were produced. A study was then initiated to determine optimum conditions of powder loading in combination with microwave power output.

Table 14

Effect of Carbon Concentration on Foaming Behavior  
of 1702-1 Precursors

| % Activated Carbon<br>in Precursors | Time to Incipient Foaming<br>(Seconds) | Foam Characteristics                     |
|-------------------------------------|--|--|
| 2                                   | 120                                    | Good cellular structure, no curing       |
| 4                                   | 60                                     | Good cellular structure, no curing       |
| 10                                  | 40                                     | Good cellular structure, complete curing |
| 20                                  | 15                                     | Good cellular structure, charring        |

The effect of microwave power output was carried out by foaming 1702-1 precursors modified with 0.5 percent AS-2 containing five percent activated carbon at power output of 1.25 to 5.0 kW for 12 minutes. The results of this study are reported in Table 15. The data show that high power output is required to produce total curing of the foaming mass. Due to the limitation of the power output of the 4115 Model microwave oven, this study was terminated at this point.

The interaction of the microwave energy was also found to be dependent on powder thickness (Ref. 2). This study was repeated with 1702-1 precursors modified with 0.5 percent AS-2 and five percent carbon to determine the extent of curing obtainable when 100 g of powder was loaded at different thicknesses. Foaming was carried out on a Teflon sheet for 12 minutes at a power output of 5 kW. Data derived from this study are shown in Table 16. The data show that higher powder thickness contributes to total curing of polyimide foams. Incipient charring in the center of the foam was visible in several of the experimental foams.

A new graphite was evaluated during the last part of this effort and found to produce more homogeneous cellular structure than that obtained with activated carbon. Larger foam samples (600 g of powder) were prepared using 1702-1 precursors modified with 0.5 percent AS-2 and five percent graphite. Foaming at 2.5 kW for four minutes followed by curing at full power for eight additional minutes in the 5 kW microwave oven produced total curing and homogeneous foam structure. A sample of this foam is shown in Figure 39.

In subsequent studies it was established that microwave curing can also be achieved by using high power outputs only. This was proven in a 10 kW experimental microwave oven, as will be discussed later in this section, and achieved in the 15 kW NASA owned microwave oven as reported in Section 4.1.3, Scale-up Processes.

Table 15

Effect of Microwave Power on Foaming and Curing Behavior of 1702-1 Precursors (5% Activated Carbon; 0.5% AS-2)

| Power Output (kW) | Foaming Behavior                       | Compression Set Loss (%) |
|-------------------|--|--------------------------|
| 1.25              | No curing; poor structure              | -                        |
| 2.5               | No curing; good structure              | -                        |
| 3.75              | Partial curing; good structure         | -                        |
| 5.0               | Almost complete curing; good structure | 70                       |

Table 16

Effect of Powder Loading on Foaming and Curing Behavior of 1702-1 Precursor (5% Activated Carbon; 0.5% AS-2)

| Polyimide Powder Thickness (cm) | Foam Behavior                       | Rise (cm) | Compression Set Loss (%) |
|---------------------------------|-------------------------------------|-----------|--------------------------|
| 3.8                             | Total curing, good structure        | 14        | 10                       |
| 1.5                             | Considerable curing, good structure | 15        | 70                       |
| 0.5                             | Partial curing, flaws               | 7.5       | -                        |
| 0.35                            | No curing, flaws                    | 7.5       | -                        |

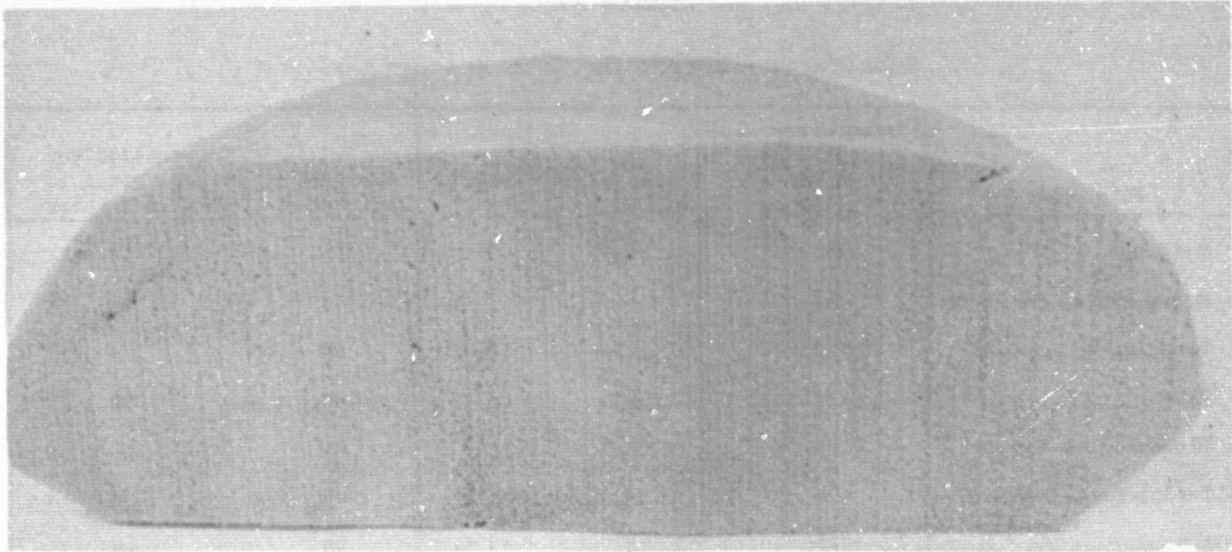


Figure 39. Polyimide Foam Produced by Microwave in a One-Step Process

#### Microwave Processing; Selection of Substrates

The microwave foaming process consists of placing the polyimide powder precursor on a substrate followed by application of electromagnetic radiation. To avoid local overheating and arcing the substrate must be compatible with the energy field. A number of substrates compatible with the microwave field were tested. These are:

- Glass filled polyimide (Solar)
- Glass filled Teflon (Fluorocarbon Corp)
- Kapton film (DuPont)
- Polypropylene (Ridout Plastics)
- Pyrex (Corning Glass)
- Pyroceram (Corning Glass)
- Teflon (DuPont)
- Teflon coated glass (Taconic)

Screening tests were carried out by placing 300 g of 1702-1 powder precursor modified with 0.1 percent X-3-6 surfactant on each substrate followed by foaming in the 5 kW microwave oven at full power for six minutes. Immediately after foaming the temperature of the expanded mass was measured by means of thermocouples inserted in the mass. Thereafter the foams were cured at 288°C (550°F) for 30 minutes and inspected for flaws and visual imperfections. The foam rise, cellular structure, resiliency, density and compression set were determined to screen the most promising substrate material. A summary of the results is shown in Table 17.

Table 17

## Substrates; Effect on Foam Properties

| Substrate              | Temperature Rise at End of Foaming Cycle (°C) | Foam Volume cm <sup>3</sup> x 10 <sup>3</sup> | Density kg/m <sup>3</sup> | Resiliency Ball Rebound | Compression Set % Loss After 30 Minutes Recovery |
|------------------------|---|---|---------------------------|-------------------------|--|
| Teflon                 | 141   | 15.9  | 9.0                       | 75                      | 40   |
| Glass Filled Polyimide | 143   | 9.6   | 8.6                       | 55                      | 35   |
| Pyroceram              | 176   | 11.6  | 10.4                      | 60                      | 30   |
| Pyrex                  | 154   | 8.5   | 10.1                      | 50                      | 30   |
| Glass Filled Teflon    | 158   | 10.8  | 10.7                      | 65                      | 25   |
| Teflon Coated Glass    | 145   | 9.3   | 13.6                      | 70                      | 20   |
| Kapton                 | 148   | 10.1  | 13.1                      | 70                      | 25   |
| Polypropylene          | 121   | 11.0  | 10.1                      | 65                      | 31   |

Kapton produced foams with very good rise and homogeneous cellular structure but the film was found to embrittle and to fall apart when the foam slab was removed from the substrate. From the data collected, Teflon, Pyroceram, polypropylene, glass filled Teflon and Teflon coated glass appeared to be the best candidates. Pyrex and glass filled polyimides produced less usable foam (returning volumes of 8.5 and 9.6 x 10<sup>3</sup> cm<sup>3</sup> respectively) because of increased number of flaws and sticking problems.

The substrates selected in this study possess a wide range of flexibility and rigidity. These properties allow the use of these substrates in a variety of microwave applications, including fabrication of foams in shaped molds and rigid foams in a one-step microwave process.

#### Microwave Processing; Selection of Process Parameters

This task involves evaluation and selection of process parameters for producing foams by microwave methods.

The process variables studied in this task include:

- Microwave frequency and power output
- Powder precursors loading
- Pre-heat temperature and time
- Microwave cavity - temperature and foaming time
- Microwave cavity - pressure
- Foam cutting techniques



Screening and selection of the optimum process conditions for each variable was made on the basis of best compression set loss, cellular structure and foaming behavior.

A summary of the significant accomplishments generated during the course of this study is reported below for each of the parameters evaluated.

#### Microwave Frequency and Power Output

Tests to evaluate effect of frequency and power output on foaming behavior of 1702-1 precursors were carried out at Gerling Moore in Santa Clara, CA.

The study of effect of frequency was done using microwave ovens operating at a frequency of 915 MHz and 2450 MHz. The 915 MHz unit had a rotating turntable 91.5 cm (3 ft.) in diameter. This turntable was used to prevent the foam from seeing a continuous wave pattern. The 2450 MHz unit was identical to the one used in this and previous programs funded by NASA-JSC except for the addition of two or more power units whose wave guides entered at the rear of the cavity. These two power units had their own on/off controls and had to be manned independently. Due to the small size of the loads used, problems with arcing were frequently experienced. In general, the power was run up to the point where severe arcing took place, then backed down and run up again to just under that point. All foaming experiments were done on a Pyrocera sheet with dimensions approximately 30.5 x 47.7 x 0.635 cm (12 in. x 18 in. x 1/4 in.) using 100 g of the 1702-1 powder precursor. The 915 MHz unit produced little or no foaming below a power output of 5 kW; foaming started at a power of 10 kW with highest foam rise at 15 to 20 kW, but arcing took place at these high outputs. The testing indicates that the 915 MHz frequency will foam polyimide resin precursors but the interaction of the precursors at this frequency is not as rapid as that obtained with the 2450 MHz frequency and more dependent on size effect. Therefore, the 2450 MHz frequency was selected for the study of power output as reported below.

The study of effect of power output was carried out by using a microwave oven operating at a frequency of 2450 MHz by varying the power output from 2.5 to 10 kW. A summary of the results are shown in Table 18. The data show that high field strength can provide sufficient energy to cause foaming and curing polyimide precursors in a one-step microwave process. Approximately 50 percent of the foam sample produced at a power of 10 kW was cured. When the same experiment was repeated with higher loading of powder precursor (400 g), the time to foam and total foaming cycle remained unchanged but the foam cured almost completely, leaving approximately 1.25 cm (0.5 in.) of uncured foams on the outer surface.

These experiments have proven the concept of microwave foaming and curing in a one-step process. These and other innovations have been successfully used to foam polyimide resins in a new GFE 15 kW microwave oven which will be discussed in Section 4.1.3.



Table 18

Foaming Behavior of 1702-1 Precursors  
at Various Power Outputs

| Power Output<br>(kW) | Time to Foam<br>(Seconds) | Total Foaming Cycle<br>(Seconds) | Foaming Quality  |
|----------------------|---------------------------|----------------------------------|--|
| 2.5                  | 120                       | 240                              | fine cellular structure  |
| 5.0                  | 75                        | 210                              | fine cellular structure  |
| 10                   | 60                        | 180                              | fine cellular structure<br>large portion of foam<br>cured in microwave |

#### Powder Precursor Loading

The effect of powder loading on the foaming behavior of polyimide resins was evaluated using a Gerling Moore Batch Cavity Model 4115 operating at a frequency of 2450 MHz and a power of 5 kW. This unit, shown in Section 3, Figure 12, was purchased after the selection of the optimum frequency and power requirements.

The thickness of the powder precursor has a considerable effect on the foaming behavior of polyimide precursors. Table 19 presents the properties of polyimide foams produced from 100 g of 1702-1 foam precursors modified with 0.05 percent AS-2 made at various powder loadings/unit area. The effect of loading on rise is shown in Figure 40.

The data show that below a powder loading of 1.6 kg/m<sup>2</sup> (0.32 lb/ft<sup>2</sup>) the cellular structure becomes irregular and the foam rise is low and uneven. Loadings higher than 5 kg/m<sup>2</sup> (1.05 lbs/ft<sup>2</sup>) produces foam rise that is too high (63 cm, 25 in.) to be handled with present process equipment. High thickness does not appear to affect cellular structure, however, the foam density is lower. These data also indicate that an increase in the powder loading adversely affects the compression set properties. Optimum conditions have been found to be those employing a powder loading of approximately 4.3 kg/m<sup>2</sup> (0.80 lbs/ft<sup>2</sup>) corresponding to approximately 2 cm (0.8 in.) thickness.

The study of effects of powder loadings on the aliphatic terpolyimide resins was carried out using foams derived from 1720-1 precursors modified with 0.05 percent AS-2. Data are shown in Figure 41. Optimum conditions have been found to be those employing a powder loading of approximately 7.7 kg/m<sup>2</sup> (1.5 lbs/ft<sup>2</sup>).

Table 19

Effect of Powder Loading on Properties of Polyimide  
Foams Derived From 1702-1 Precursors

| Powder Loading |     |                   |                     | Compression Set Loss<br>% | Foaming Behavior                 |
|----------------|-----|-------------------|---------------------|---------------------------|----------------------------------|
| Thickness      |     | Mass              |                     |                           |                                  |
| cms            | in. | kg/m <sup>2</sup> | lbs/ft <sup>2</sup> |                           |                                  |
| 0.51           | 0.2 | 1.6               | 0.32                | 40                        | Medium cellular structure, flaws |
| 1.02           | 0.4 | 2.4               | 0.49                | 45                        | Medium cellular structure        |
| 1.52           | 0.6 | 4.0               | 0.81                | 47                        | Good cellular structure          |
| 2.79           | 1.1 | 6.5               | 1.33                | 57                        | Good cellular structure          |

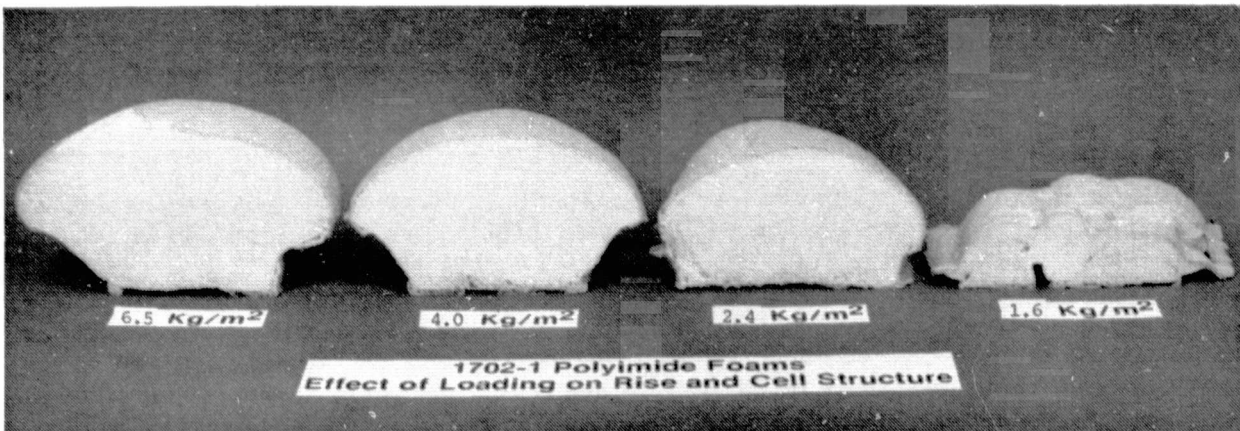


Figure 40. Effects of Powder Loading on Properties of Polyimide Foams

Pre-Heat Temperature and Time

This task covers the effects of preheating the powder precursors before the microwave foaming process. The first part of this study was conducted by keeping the preheat time constant and varying the preheat temperature. In the second part, the preheat temperature was kept constant and the time was varied.

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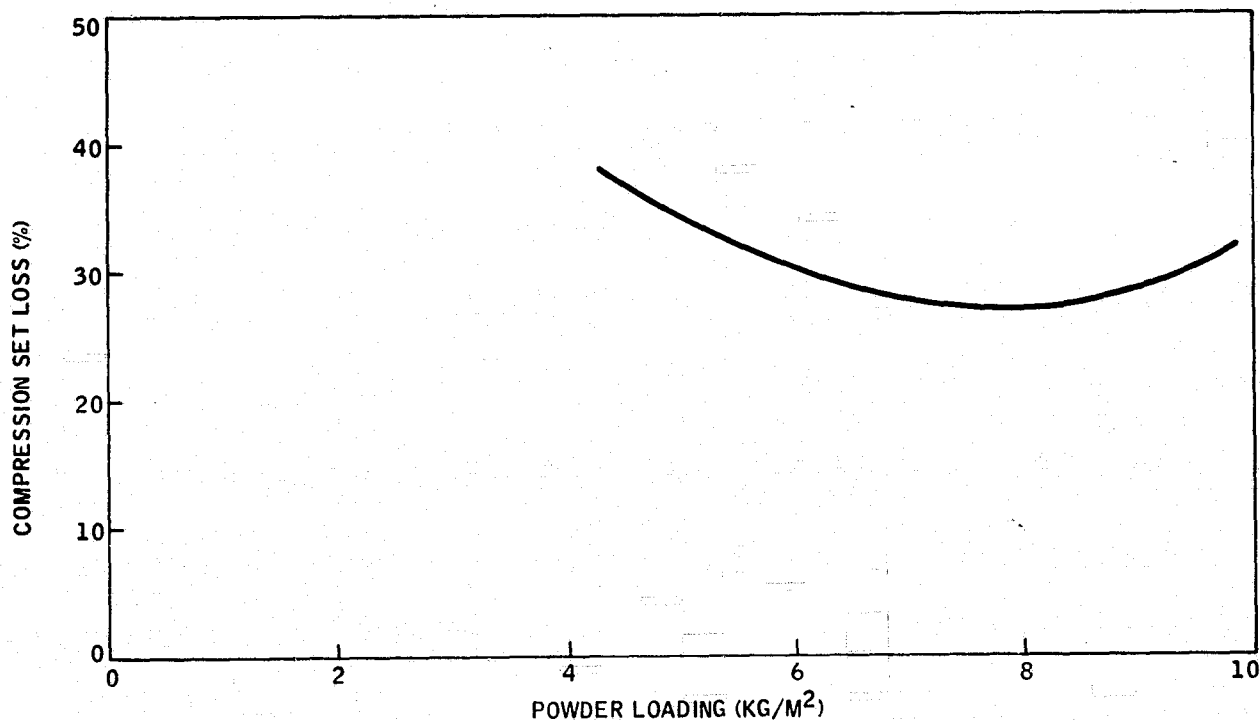


Figure 41. Effect of Powder Loading on Aliphatic Terpolyimide Foams (1720-1)

The effect of preheat temperature at constant preheat time was evaluated at four different temperatures using 1701-1 precursors modified with 0.015 percent AS-2. These were 121.1°C (250°F), 176.7°C (350°F), 232.2°C (450°F), and 287.8°C (550°F). The time of preheat was kept constant at 2 minutes for all experiments. Figure 42 shows the data obtained from this study. Table 20 presents a summary of the properties of polyimide foams derived from 1701-1 precursors modified with 0.015 and 0.05 percent AS-2 respectively.

The data show that pre-heating the polyimide powder at 121°C (250°F) for two minutes, prior to microwave foaming, contributes to higher foam rise, lower scrap rate and more homogeneous cellular structure. When the microwave foaming process was carried out by preheating the powder at 149°C (300°F) and higher, the foam rise was found to be erratic and the effects of thermal foaming was clearly evidenced by the presence of cavities, large flaws, and striations. The same data also indicate that the compression set properties

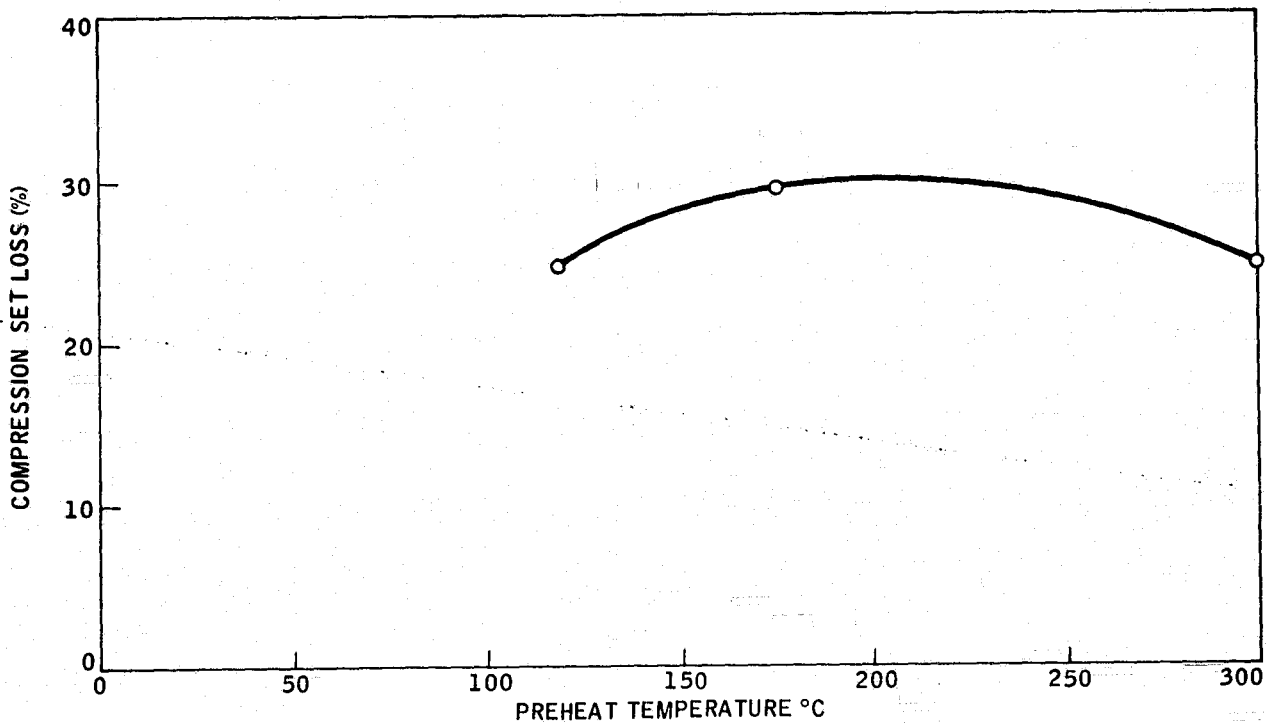


Figure 42. Effect of Preheat Temperature (2 Min.) on Compression Set Loss of 1701-1 Polyimide Foams Modified With 0.015 Percent AS-2

Table 20

Effect of Preheat Temperature on Properties of Polyimide Foams Derived From 1701-1 Precursors

| Foam Precursor | Surfactant Concentration AS-2 (%) | Preheat Time (Minutes) | Preheat Temperature |      | Density           |                     | Resiliency | Compression Set Loss (%) | Type of Foam                                      |
|----------------|-----------------------------------|------------------------|---------------------|------|-------------------|---------------------|------------|--------------------------|---|
|                |                                   |                        | (°C)                | (°F) | kg/m <sup>3</sup> | lbs/ft <sup>3</sup> |            |                          |   |
| 1701-1         | 0.015                             | 2                      | 121.1               | 250  | 11.7              | 0.73                | 80         | 26.6                     | Good cellular structure; highly reticulated       |
| 1701-1         | 0.015                             | 2                      | 176.7               | 350  | 10.7              | 0.67                | 80         | 28.5                     | Good cellular structure; moderate reticulation    |
| 1701-1         | 0.015                             | 2                      | 323.2               | 450  | 12.2              | 0.76                | 70         | 27.8                     | Fair cellular structure with flaws and striations |
| 1701-1         | 0.015                             | 2                      | 287.8               | 550  | 14.1              | 0.88                | 75         | 26.9                     | Poor cellular structure                           |
| 1701-1         | 0.015                             | 1                      | 287.8               | 550  | 14.1              | 0.88                | 75         | 26.0                     | Good cellular structure, densified layer          |
| 1701-1         | 0.015                             | 0.25                   | 287.8               | 550  | 12.3              | 0.77                | 50         | 24.5                     | Good cellular structure                           |
| 1701-1         | 0.05                              | 2                      | 121.1               | 250  | 15.2              | 0.95                | 70         | 16.3                     | Fine cellular structure                           |
| 1701-1         | 0.05                              | 2                      | 176.7               | 350  | 15.9              | 0.59                | 90         | 19.0                     | Good reticulation, flaws                          |
| 1701-1         | 0.05                              | 1                      | 232.2               | 450  | 17.5              | 1.09                | 45         | 22.9                     | Good cellular structure. Increasing flaws         |
| 1701-1         | 0.05                              | 1                      | 287.8               | 550  | 16.5              | 1.03                | 45         | 16.0                     | Poor cellular structure                           |

are independent of pre-heat temperature when the time is kept constant. Figure 43 shows the front view of polyimide foams produced at three different preheat temperatures. Figure 44 shows the effect of preheating 1701-1 precursors modified with 0.015 percent AS-2 at 121.1°C (250°F) for two minutes.

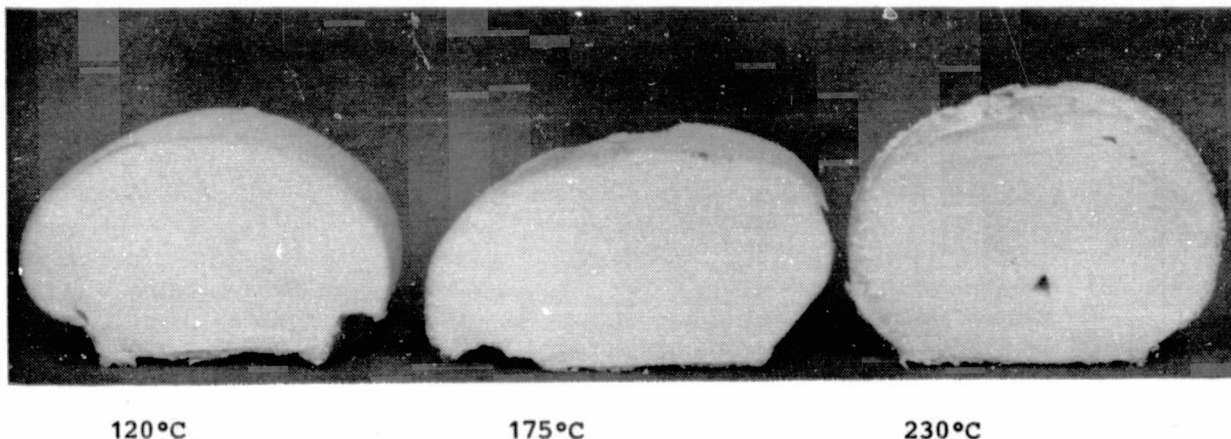


Figure 43. Effect of Preheat Temperature on Rise of Polyimide Foams Derived From 1701-1 Precursors

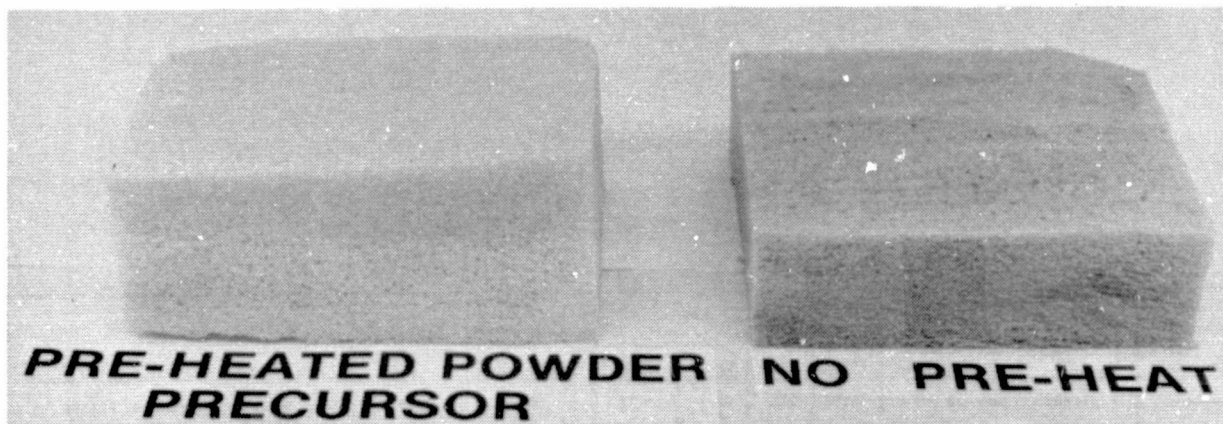


Figure 44. Effect of Preheating Powder Precursor on the Cellular Structure of Polyimide Foams

The second part of this study followed in sequence after selection of the optimum preheat temperature. The effect of preheat time was evaluated at various time intervals. The data from this study are shown graphically in Figure 45. The optimum preheat time has been found to be six minutes.

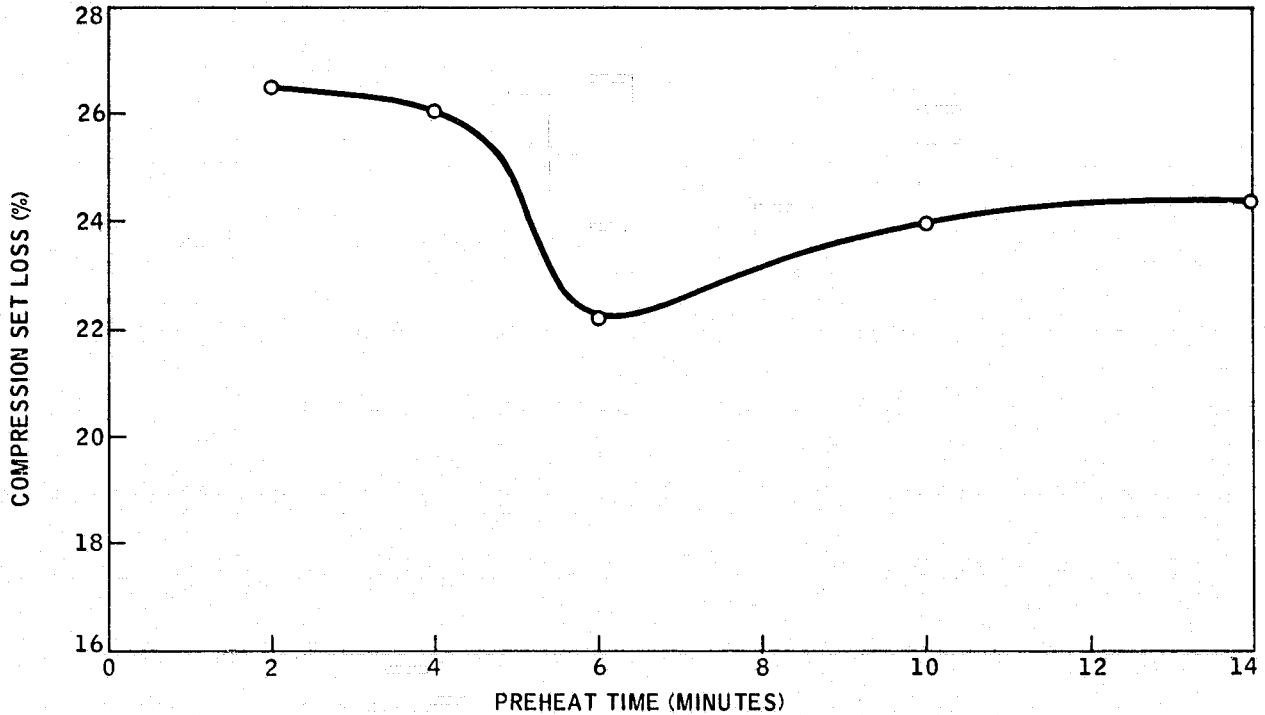


Figure 45. Effect of Preheat Time on Compression Set Loss (250°F) of 1701-1 Polyimide Foams

The results presented in this section have been found to apply directly to all the three promising candidates that emerged from the Advanced Polyimide Synthesis, namely the copolyimide 1701-1 and 1702-1 precursors, and the 1720-1 terpolyimide precursors modified with aliphatic diamines.

Preheating the powder polyimide precursors was found to be an essential step of the microwave foaming process developed in the early phases of this program utilizing a microwave oven of relatively low power output. In subsequent tasks dealing with scale-up of candidate polyimide precursors in the 15 kW GFE microwave oven it was found that preheating the powder was not any longer a necessary requirement since it did not produce improved foam quality.

#### Microwave Cavity - Temperature and Foaming Time

This section covers the work dealing with the effect of the temperature of the microwave cavity and foaming time on foaming behavior of polyimide precursors.

Direct heating of the microwave cavity was not possible since the Gerling Moore Batch Cavity Model 4115 is not equipped with hot air heating although such a modification could be attained with an electric heater and an air blower mounted outside the microwave cavity.

In the course of this study the heated cavity conditions were duplicated by using a preheated, heavy wall pyrex bell jar 38 cm diameter, 30 cm high (15 x 12 in.) which was placed upside down on the preheated Teflon substrate. This produced a heated cavity within the microwave cavity itself. All experiments were carried out by spreading 40 g of 1702-1 powder precursors on a substrate followed by placing the bell jar on top of the substrate so that the powder precursor was contained within the cavity of the jar. Microwave power was then applied to foam the powder precursor at a predetermined cavity temperature. It was found that when the bell jar was not preheated the foam rise was very low and erratic. When foaming was done by preheating the bell jar and the substrate at 121°C (250°F) the foam rise was very high, the cellular structure very uniform and the foam possessed a thin glazed skin. The scrap rate of this foam was very low. The same experiments repeated with a polypropylene jar produced the same results. When the temperature of the cavity was increased above 231.2°C (450°F) thermal foaming and microwave foaming occurred simultaneously and the foam structure became very poor.

These preliminary data indicate that moderate heating of the microwave cavity will result in improved microwave foaming processing and higher foam yield which will lower the cost of the finished product. Cavity heating has not been included in the 15 kW GFE microwave oven because more pertinent data from large scale experiments would be required to justify this modification.

The study of effects of foaming time on foam properties was carried out using 1720-1 terpolyimide precursors modified with aliphatic diamines containing 0.05 percent AS-2. The data obtained are graphically shown in Figure 46. Foaming was done at different power outputs of 2.5, 3.75 and 5.0 kW. The data show that, for all power outputs, increased foaming time produces foams with better compression set. Foaming time of six minutes at a microwave power output of 3.75 kW appears to offer the best conditions for processing the terpolyimide system under this study as shown by the compression set values. Foams derived from 1720-1 terpolyimide precursors foamed at these conditions were flexible, resilient and possessed fine homogeneous cellular structure with the best compression set. This type of foam met the fatigue requirements of 20,000 cycles without failure.

### Foaming Pressure

This section covers the work dealing with the effect of pressure on the foaming behavior of polyimide foams. This task was undertaken in view of the data previously reported (Ref. 2) showing the benefits of thermal foaming at reduced pressure. In the present effort, reduced pressure conditions were obtained by using a pyrex vessel connected to a vacuum pump located outside the oven cavity by means of a Teflon tubing. All tests were carried out under reduced pressures of 1726.5 and 3453 kg/m<sup>2</sup> (5 and 10 in. of mercury) respectively. It was found that the use of reduced pressure associated with microwave foaming causes non-homogeneous cellular structure. These findings although in distinct contrast to those found during the studies of thermal processes, were evident enough to discourage additional investigations.

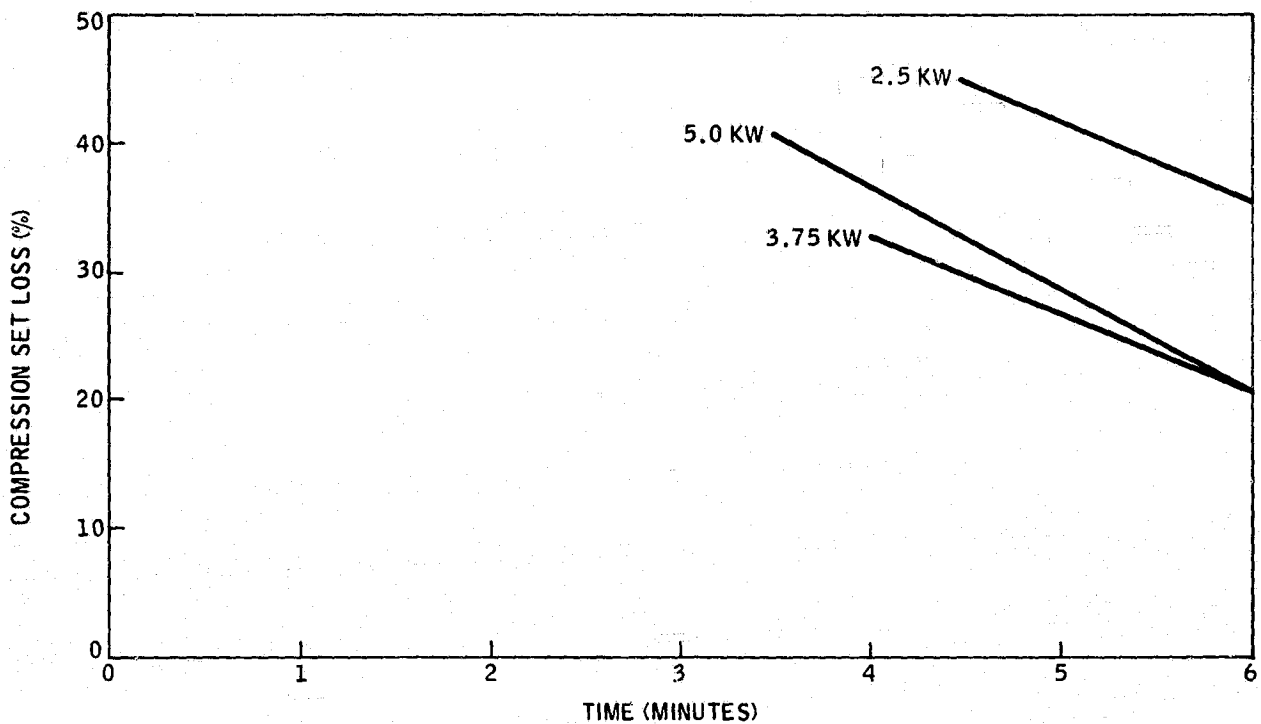


Figure 46. Effect of Foaming Time on Compression Set Loss of Aliphatic-Terpolyimide System (1720-1)

#### Foam Cutting Techniques

The first technique used to trim large size foams to the desired thickness was hot wire cutting. This process has previously been used to cut small size foams with good results (Ref. 2). A large hot-wire cutting tool was constructed but found to be ineffective in trimming large size foams. This difficulty was due to a layer of charred polyimide resin which formed around the wire and prevented its penetration in the foam. Therefore, the conventional mechanical cutting using a friction or band saw was used as the optimum method to cut flexible and rigid polyimide foams to the desired shape and size.

With this last effort, the most important and essential process parameters for producing and foaming the powder precursors were clearly defined to permit the scale-up of these formulations and foams to larger size.

#### Foaming Studies - Summary

The following brief review describes the major developments resulting from the experimental work carried out in Task II - Foaming Studies. All data relating to foaming were obtained from studies carried out in the 5 kW microwave oven.



1. The feasibility of spray drying polyimide resins was established. The continuous spray drying process has now completely replaced the original vacuum process for the production of powder resins in large lots.
2. The feasibility of microwave foaming and curing in a one-step process was established. The data show that high power output is required to produce total curing of polyimide foams by microwave techniques.
3. From the data collected, Teflon, Pyroceram, Polypropylene, glass filled Teflon, and Teflon coated glass cloth appear to be the best substrates for microwave foaming.
4. The data show that pre-heating the polyimide powder at 121°C (250°F) for two minutes contributes to higher foam rise, lower scrap rate, and more homogeneous cellular structure.
5. The process parameters for all three promising candidates (1701-1, 1702-1, and 1720-1) have been optimized.
6. Hot-wire cutting techniques have been found ineffective in trimming large size polyimide foams.

#### 4.1.3 Task III - Scale-Up Processes

The major objective of this task was to screen and scale-up two or more polyimide foam precursors to define parameters for an economically viable foaming method capable of producing samples as large as 61 x 61 x 7.6 cm (2 ft x 2 ft x 3 in.). The initial phase of this task was carried out using the Gerling Moore 5 kW microwave oven, Model 4115 which was only capable of yielding foams having approximate dimensions of 51 x 51 cm (20 x 20 in.) since the larger GFE 15 kW microwave oven became available in the final phase of this work due to a seven months delay in the delivery of the unit. The experimental work carried out for the accomplishment of this task is described in the following sequence:

- . Foaming by free rise techniques
- . Foaming by constrained rise in an open mold
- . Foaming by constrained rise in a closed mold
- . Selection and installation of NASA 15 kW microwave oven (GFE)
- . Prototype production foam samples

## Foaming by Free Rise Technique

The initial effort of this task involved scaling-up all three candidate polyimide precursors selected on the basis of best compression values and fatigue resistance using the Gerling Moore 5 kW microwave oven, Model 4115. The candidate precursors were 1701-1, 1702-1, and 1720-1. Large size foam samples were produced from these candidates using free-rise microwave techniques and the foams cut to a circular shape (51 cm diameter, 12.7 cm thick) and tested for seating applications, compression set properties and fatigue resistance. Seating tests were made by replacing the polyurethane foams of office chairs with upholstered polyimide foams using aircraft approved covering and liners. The foams derived from 1720-1 have undergone more than one year of use with little sagging, foams derived from 1701-1 have shown significant sagging after six months and foams derived from 1702-1 degraded in less than two months of use. Figure 47 shows a sample of 1720-1 foam and seat cushion. The fatigue properties and the cellular structure of the foams derived from the three polyimide precursors were found to be comparable to those obtained from foaming small samples, however, the compression set loss of the foams were appreciably worse indicating a size effect.

One of the factor which was found to be dependent on size was curing temperature. This finding was the result of preliminary experiments made with foams derived from 1701-1 precursors cured at two different temperature levels; 260°C and 288°C (500 and 550°F). The foams obtained displayed compression

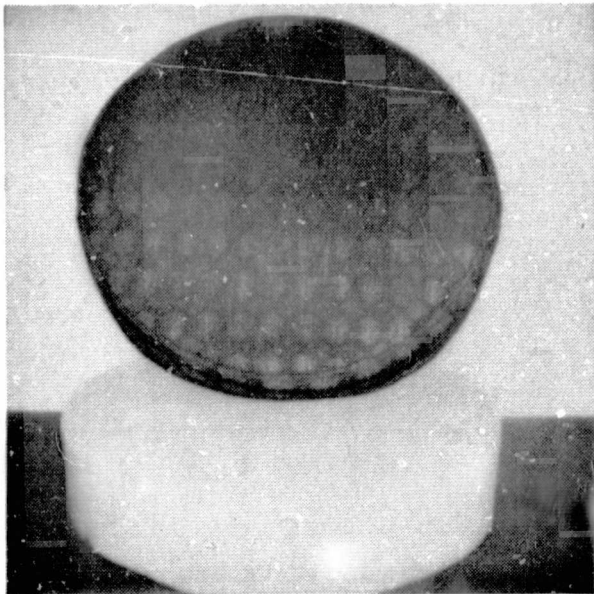


Figure 47.

Seat Cushion and Foam Derived From  
1720-1 Precursor

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set loss of 40 percent and 10 percent respectively. Foams derived from 1702-1 precursors cured at the same conditions displayed compression set loss of 45 and 23 percent respectively. Therefore, a study of effect of postcuring conditions on compression set was carried out to define optimum parameters. Precursors derived from 1701-1 resins were selected for this study.

Effect of Curing Temperature on Compression Set Properties of Foams Derived From 1701-1 Precursors

The initial effort of this task involved preparation of large batches (5 kg, 13.2 lbs) of 1701-1 powder precursors modified with 0.015, 0.02, 0.025, 0.035 and 0.05 percent AS-2 respectively. Foams were then produced by foaming 600 g of the powder precursor on Teflon substrates in the 5 kW microwave oven by free rise technique. The foams were finally cured at 260, 288, 325 and 330°C (500, 550, 600 and 625°F), respectively. The curing time used at each temperature condition was 30, 60 and 90 minutes respectively.

The data resulting from this evaluation are reported in Figure 48 for 1701-1 precursors modified with 0.015 and 0.02 percent AS-2 respectively and in

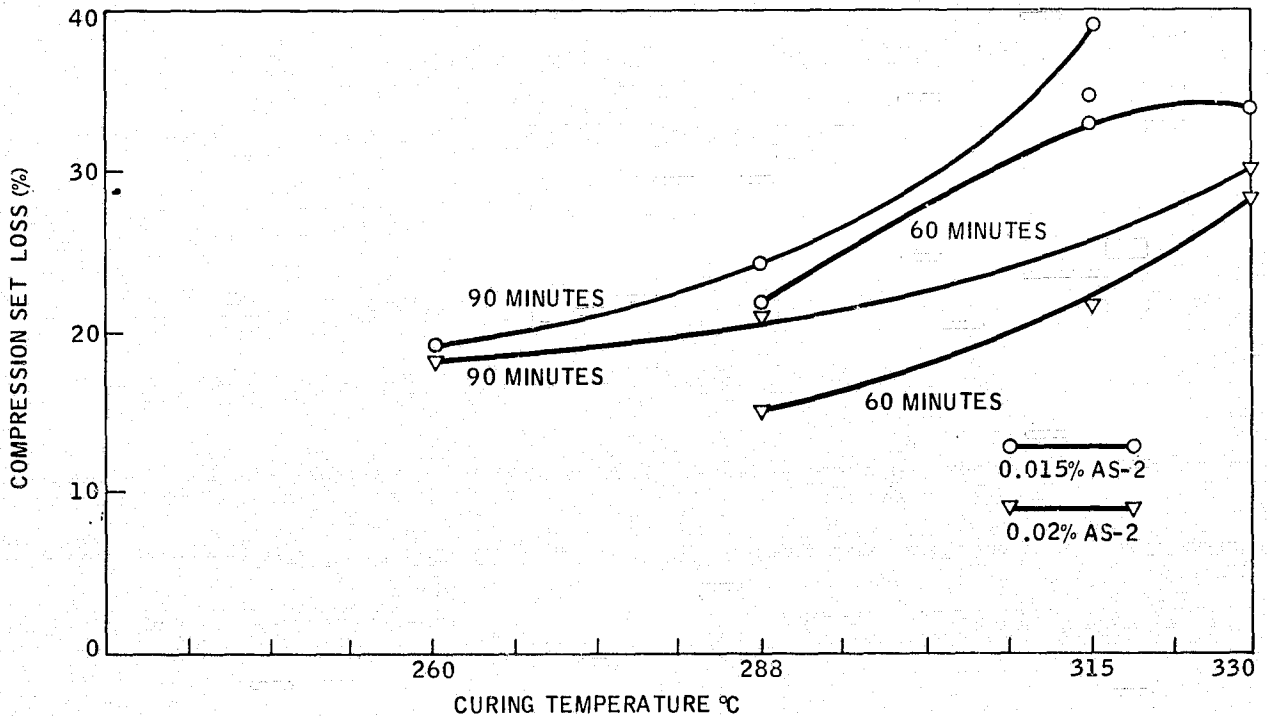


Figure 48. Effect of Curing Temperature on 90% Compression Set Values of Foams Derived From 1701-1 Precursors Modified with 0.015% and 0.02% AS-2 Respectively

Figure 49 for 1701-1 precursors modified with 0.035 and 0.05 percent AS-2 respectively. The data show that, at a curing time of 60 and 90 minutes, the foams produced at higher curing temperature possess poorer compression set properties. The data also show that longer postcure cycles yield foams with worse compression set properties. This is particularly evident for foams produced at low concentration of AS-2. The 30 minute curing time was not sufficiently longer to fully cure the foams.

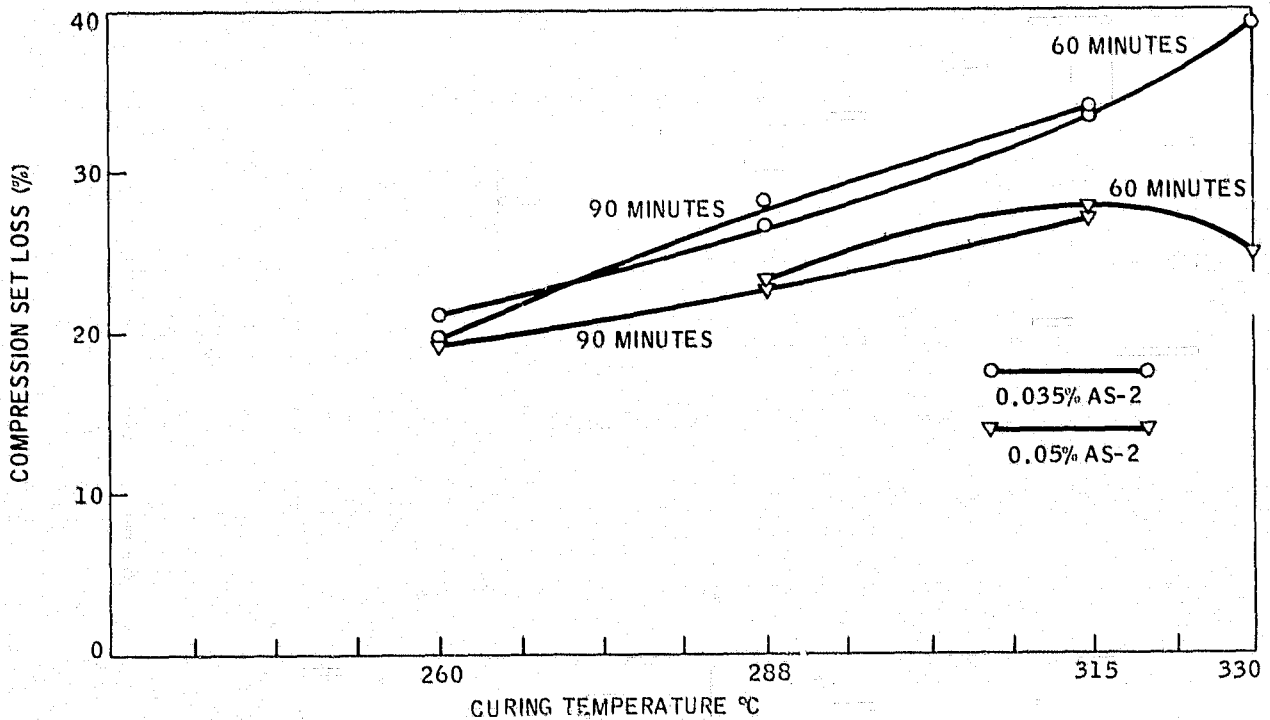


Figure 49. Effect of Curing Temperature on 90% Compression Set Values of Foams Derived From 1701-1 Precursors Modified With 0.35% and 0.05% AS-2 Respectively

The results of these tests show the extreme sensitivity of the compression set properties of polyimide foams to changes of process conditions and explain the wide scatter of data obtained.

By combining the best microwave foaming parameters discussed in Section 4.1.2 with the optimum time and temperature conditions defined in the present study, optimized foam properties have been obtained by free rise foaming techniques using the 5 kW microwave oven. These selected process parameters are presented in Table 21 for all three candidate precursors. Using these optimized conditions, foams have been produced with compression set loss values of 8-14 percent (1701-1), 20-35 percent (1702-1), and 25-30 percent (1720-1-24) at a density of 8.0-11.2, 11.2-16.0, and 9.1-13.1 kg/m<sup>3</sup> respectively.

Table 21

Selection of Optimum Process Parameters for Flexible,  
Resilient Polyimide Foams

| Process Classification | Parameter                           | Copolyimide System |                    | Terpolyimide System |
|------------------------|-------------------------------------|--------------------|--------------------|---------------------|
|                        |                                     | 1701-1             | 1702-1             | 1720-1-24           |
| Synthesis              | Reaction Temperature (°C)           | 60-65              | 60-5               | 60-65               |
|                        | Reaction Time (minutes)             | 5                  | 5                  | 5                   |
|                        | Additive                            | AS-2               | AS-2               | AS-2                |
|                        | Additive Concentration (%)          | 0.02               | 0.02               | 0.02                |
| Spray Drying           | Inlet Temperature (°C)              | 100                | 100                | 100                 |
|                        | Outlet Temperature (°C)             | 70                 | 70                 | 70                  |
|                        | Dilution Ratio (phr)                | 20                 | 20                 | 30                  |
| Microwave Foaming      | Substrate                           | Pyroceram, Teflon® | Pyroceram, Teflon® | Pyroceram, Teflon®  |
|                        | Powder Loading (kg/m <sup>2</sup> ) | 4.3                | 4.3                | 7.7                 |
|                        | Preheat Temperature (°C)            | 121                | 121                | 121                 |
|                        | Preheat Time (minutes)              | 2-6                | 2                  | 2                   |
|                        | Microwave Frequency (MHz)           | 2450               | 2450               | 2450                |
|                        | Microwave Power (kW)                | 5                  | 5                  | 3.75                |
|                        | Microwave Foaming Time (min.)       | 3-6                | 6                  | 6                   |
| Curing                 | Curing Temperature (°C)             | 228                | 228                | 121-226             |
|                        | Curing Time (minutes)               | 45                 | 45                 | 120                 |

#### Foaming By Constrained Rise in an Open Mold

The major objective of this study was to provide a more economical process for large scale production of foam cushion materials by constraining the foam rise to the desired thickness, thus reducing the rate of scrap.

With this technique, microwave foaming was achieved by placing the powder between two rigid substrates while the thickness of the final foam slab was controlled by means of spacers. The first effort of the task involved evaluation of materials compatible with the high frequency radiation.

The following substrate sheet materials were evaluated using the Gerling Moore 5 kW microwave oven, Model 4115:

- Polypropylene (Ridout Plastics)
- Glass filled polyimide (Solar)
- Pyroceram (Corning Glass)
- Pyrex (Corning Glass)
- Teflon® (DuPont)
- Perforated polypropylene (Ridout Plastics)
- Glass filled Teflon® (Fluorocarbon Corp)
- Teflon® coated glass cloth (Taconic)

The results of this study proved that Teflon®, glass filled Teflon®, and Teflon® coated glass were too flexible and bulged severely during foaming, while Pyrex overheated to the point of producing thermal foaming. The best foams by constrained rise were obtained using polypropylene, Pyroceram and glass filled polyimide sheets. The problem encountered with polypropylene was sticking of the foam to the surface of the substrate. This problem was overcome by lining the polypropylene sheets with Teflon® coated glass which facilitated removal of the uncured foam slab from the polypropylene sheets for the subsequent curing step.

Several factors were found to effect the foaming behavior of polyimide foams produced by constrained techniques. The most relevant are powder thickness, ease of vapor escape through the constrained foam, surfactant concentration, and thermal effects due to overheating of the substrates. This last effect was overcome by selecting polypropylene substrates which are almost completely transparent to the microwave radiation and do not heat up. The removal of the volatiles formed during foaming was facilitated and the problem overcome by using more than one layer of highly permeable Teflon® coated glass (Taconic 7278).

An evaluation of the effect of powder loading was then undertaken to provide means to control the density of the foam. Best conditions were found to be those employing a powder loading of 12.2-12.7 kg/m<sup>2</sup> (2.5-2.6 lbs/ft<sup>2</sup>) using a foaming area of approximately 61 x 61 cm (2 x 2 ft).

Since the foaming behavior and cellular structure of polyimide foams is governed by the concentration of the surface active agent, new precursors made at high surfactant concentration of AS-2 from 1.0 to 1.5 percent were tested. These precursors produced foams by constrained rise which possessed the best cellular structures as shown in Table 22.

The selected process for foaming polyimide resins by the constraining technique consisted of placing the powder precursors between two 1.25 cm (1/2 in.) thick polypropylene sheets covered with Teflon coated glass, Taconic 7278, at a powder loading of 12.2-12.7 kg/m<sup>2</sup> (2.5-2.6 lbs/ft<sup>2</sup>). The final thickness of the foam was controlled by placing polypropylene spacers between the sheets. The entire assembly was inserted in the 5 kW microwave oven and the precursor foamed for six minutes at a power output of 3.75 to 5.0 kW. The uncured foam was removed from the microwave oven and cured by thermal processes. Pyroceram was also used with good results, however, signs of thermal heating was evidenced by the presence of flaws. The disappointing conclusion of this study was that the compression set properties of foams produced by constrained rise in an open mold were considerably inferior to those produced by free rise techniques reported in the previous subsection. A summary of the data is reported in Table 22.

#### Foaming by Constrained Rise in a Closed Mold

The major objective of this study was to provide a more economical process for large scale production of foam cushion materials by foaming and constraining

Table 22

## Properties of Polyimide Foams Produced in an Open Mold

| Foam Resin Number | Surfactant Concentration AS-2 (%) | Density           |                     | Resiliency Ball Rebound | % Loss After 30 min. Recovery | Type of Foam  |
|-------------------|-----------------------------------|-------------------|---------------------|-------------------------|-------------------------------|---|
|                   |                                   | Kg/m <sup>3</sup> | Lbs/ft <sup>3</sup> |                         |                               |   |
| 1701-1            | 0.10                              | 12.82             | 0.80                | 40-45                   | 49                            | Good cellular structure with some reticulation.                   |
| 1701-1            | 0.25                              | 16.98             | 1.06                | 45                      | 33                            | Good cellular structure - some striation present                  |
| 1701-1            | 0.50                              | 15.22             | 0.95                | 55                      | 46                            | Good cellular structure - some large voids present at the bottom. |
| 1701-1            | 0.75                              | 13.62             | 0.85                | 40-45                   | 29                            | Good cellular structure.  |
| 1701-1            | 1.00                              | 9.61              | 0.60                | 35                      | 30                            | Very good cellular structure.                                     |
| 1701-1            | 1.50                              | 12.82             | 0.80                | 45-50                   | 30                            | Very good cellular structure.                                     |
| 1702-1            | 0.10                              | 14.42             | 0.90                | 45-50                   | 54                            | Fine cellular structure with no voids.                            |
| 1702-1            | 0.25                              | 14.42             | 0.90                | 45                      | 40                            | Fine cellular structure with no voids.                            |
| 1702-1            | 0.50                              | 13.78             | 0.86                | 60                      | 43                            | Fine cellular structure with few voids.                           |
| 1702-1            | 0.75                              | 12.82             | 0.80                | 40-45                   | 40                            | Fine cellular structure with no voids.                            |
| 1702-1            | 1.00                              | 9.77              | 0.61                | 40                      | 52                            | Very good cellular structure - some striations present.           |
| 1702-1            | 1.50                              | 10.89             | 0.68                | 45-50                   | 43                            | Very good cellular structure - no flaws.                          |
| 1720-1            | 0.10                              | 24.03             | 1.5                 | 50                      | 49                            | Striation and flaws present.                                      |
| 1720-1            | 0.25                              | 25.63             | 1.6                 | 45                      | 37                            | Good cellular structure - some striations present.                |
| 1720-1            | 0.50                              | 22.43             | 1.4                 | 40-45                   | 35                            | Very good cellular structure - some striation present.            |
| 1720-1            | 0.75                              | 22.43             | 1.4                 | 40                      | 34                            | Very good cellular structure - some striation present.            |
| 1720-1            | 1.0                               | 18.42             | 1.15                | 45                      | 27                            | Very good cellular structure - some striation present.            |
| 1720-1            | 1.5                               | 16.98             | 1.06                | 35-40                   | 27                            | Very good cellular structure - some striation present.            |

the foam rise to the desired configuration. This process would have further reduced the scrap rate.

The first effort of this task involved the fabrication of a mold compatible with the high frequency radiation. Molds were produced using Teflon coated glass, glass filled polyimide molded sheets, Pyrex glass and polypropylene respectively. A perforated mold produced from polypropylene is shown in Figure 50. The process involved placing the powder in the mold followed by foaming in a 5 kW microwave oven. The mold was lined with high porosity Teflon coated glass (Taconic, 7278) to permit escape of the volatiles formed during foaming. The mold was closed to produce foams to exact configurations. The foams were removed from the mold after foaming and postcured at 288°C (550°F) for one hour.

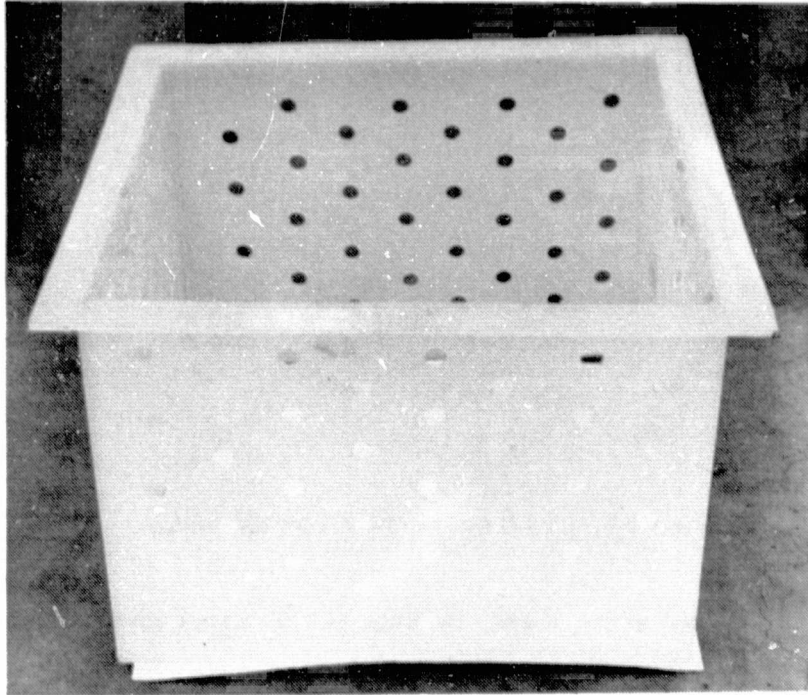


Figure 50. Polypropylene Mold for Use in Foaming Polyimide Precursors to a Shape

Figure 51 shows foams produced from 1701-1 precursors by free rise, open mold, and closed mold techniques respectively. The mold configuration had dimensions of 25 x 25 x 25 cm (10 x 10 x 10 in.) and was made by joining Taconic Teflon® coated glass, Type 7278 with RTV 102 silicon adhesive. The largest finished foam samples were obtained by using a polypropylene mold 61 x 61 x 43.18 cm (24 x 24 x 17 in.) high. The foams obtained with this mold possessed the best cellular structure. Molds were also produced by joining polyimide molded sheets with RTV 102 silicon adhesive but the foams obtained possessed poor cellular structure.

Each of the three foaming processes described in this subsection, specifically free rise, constrained free rise and foaming in a mold produced foams with different properties. This work also provided evidence of some of the limitations of these processes.

The free rise technique appears to be the most readily adaptable process, although the scrap rate is higher than expected. The constrained free rise technique offers no advantages in scrap rate, but provides means to adjust the density of the foam to any desired value. Finally, foaming in a closed mold has shown to be the most difficult process to scale-up due to limitations in the escape of the vapors formed during the foaming process.

Although all three processes could be further improved from the present level of development, the free rise technique has been found the most readily adaptable to larger scale processing and was selected as the optimum method



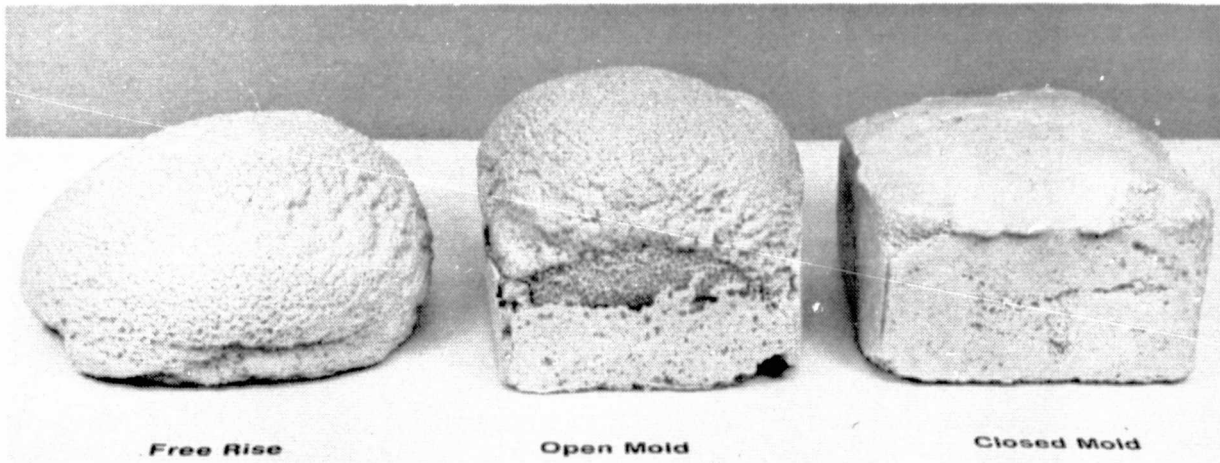


Figure 51. Microwave Foaming Methods

for fabrication of large size foams in the 15 kW microwave oven as will be discussed in the following subsections.

#### Selection and Installation of the NASA 15 kW Microwave Oven (GFE)

Solar Turbines International initiated competitive bidding, in accordance with accepted bidding rules, for a microwave oven having a power output of 15 kW and dimensions of 1.83 x 1.83 x 3.66 m (6 x 6 x 12 ft). These requirements were mutually agreed upon with the program monitor and NASA-JSC technical personnel.

Five suppliers responded and two were selected for further evaluation. A one-day lease was contracted with one of the suppliers to carry out a series of tests dealing with foaming polyimide resins in order to demonstrate performance. The results of the tests were compared with those obtained in a Gerling Moore microwave oven which was used for early development of the process. On the basis of the results obtained, the oven recommended by Gerling Moore was selected. The microwave unit has a power output of 15 kW and operates at a frequency of 2450 MHz. The cavity size of the unit is 1.83 x 1.83 x 3.66 m (6 x 6 x 12 ft). The width of the access door is 1.52 m (5 ft) minimum and will permit fabrication of large size samples for fabrication of aircraft hardware. The order for this microwave oven was placed in early June 1978 for delivery in October 1978.

The unit was delivered to Solar in April 1979, seven months behind schedule, and installed in the Research Pilot Plant in May 1979. The unit met all the requirements of this contract. This unit is shown in Figure 16. The delay of the unit forced a rescheduling of most of the tasks, particularly the characterization phase which was to be carried out with fully scaled-up candidate foams.

## Prototype Production Foam Samples

The major objective of this subtask was to develop scale-up processes and establish optimum process parameters, for the fabrication of prototype production foam samples in the NASA 15 kW microwave oven.

This parametric study was carried out in accordance with following sequence:

- Scale-up of 1702-1 foam precursors
- Scale-up of 1701-1 foam precursors
- Scale-up of 1720-1 foam precursors

### Scale-Up of 1702-1 Foam Precursors

The optimum process parameters summarized in Table 21 under the heading 1702-1 precursors were used as the starting point for the scale-up. This effort was carried out in accordance with the following scheme:

- increase powder loading in increments of 2.2 kg (4.8 lbs) to achieve largest possible foam size at a given power output
- increase power output to evaluate the level of microwave energy necessary to produce effective foaming
- variation of the power output and power sources distribution to produce homogeneous cellular structure
- Microwave curing of foam samples

The results of all these studies are summarized in Table 23 and illustrated in Figures 52 and 53. Figure 52 illustrates finished polyimide foams obtained from experiment numbers 3, 5 and 7. These foams were produced by constrained rise open mold technique using the 15 kW microwave oven and cured in a large size thermal oven at 288°C (550°F). Figure 53 illustrates an uncut polyimide foam obtained from experiment number 11. This foam was produced by using the free rise technique and was cured in the microwave oven at full power (15 kW). The foam possesses homogeneous cellular structure and met the size requirements of the program.

The foams obtained from experiment numbers 10, 11, 12 and 13 were produced by the microwave foaming and curing process. As discussed in Section 4.1.2, microwave foaming and curing processes offer the benefits of short processing time and eliminate the need of handling the uncured foam slabs which would be necessary if thermal curing was used. This is significant because these large uncured foam slabs are very fragile and too bulky to handle without the risk of cracking.

Table 23

Summary of Scale-Up Study in NASA 15 kW Microwave Oven  
(1702-1 Resin)

| Experimental Number | Foaming   |            |            | Curing |          |            | Powder Charges |      | Finished Foam Sizes |               | Foam Characteristics                              |
|---------------------|-----------|------------|------------|--------|----------|------------|----------------|------|---------------------|---------------|---|
|                     | Technique | Power (KW) | Time (Min) | Method | °C Or kW | Time (Min) | Kg             | Lbs  | Centimeter          | Inches        |   |
| 3                   | CR        | 5.0        | 8          | TH     | 288°C    | 120        | 2.2            | 4.8  | 64 dia x 7.6        | 25 dia x 3    | Homogeneous cellular structure-bottom striations. |
| 5                   | CR        | 5.0        | 12         | TH     | 288°C    | 120        | 4.4            | 9.7  | 79 x 51 x 7.6       | 31 x 20 x 3   | Homogenous cellular structure-bottom striations.  |
| 6                   | CR        | 5.0        | 20         | TH     | 288°C    | 150        | 6.6            | 14.5 | 116 x 84 x 13       | 45.5 x 33 x 5 | Homogeneous cellular structure-bottom striations. |
| 7                   | CR        | 5.0        | 30         | TH     | 288°C    | 200        | 8.8            | 19.4 | 160 x 89 x 18       | 63 x 35 x 7   | Homogeneous cellular structure - some striations  |
| 10                  | CR        | 10.0       | 15         | MW     | 15.0     | 40         | 8.8            | 19.4 | 183 x 87 x 10       | 72 x 34 x 4   | Homogeneous cellular structure - some striations  |
| 11                  | FR        | 10.0       | 15         | MW     | 15.0     | 30         | 8.8            | 19.4 | 165 x 65 x 20       | 65 x 25.5 x 8 | Homogeneous cellular structure - one striation    |
| 12                  | FR        | 10.0       | 15         | MW     | 15.0     | 23         | 11.0           | 24.2 | 183 x 84 x 20       | 72 x 33 x 8   | Homogeneous cellular structure                    |
| 13                  | FR        | 10.0       | 15         | MW     | 13.9     | 25         | 15.0           | 33.0 | 183 x 66 x 25       | 72 x 26 x 10  | Homogeneous cellular structure                    |

CR = Constrain Rise Open Mold  
FR = Free Rise  
TH = Thermal  
MW = Microwave

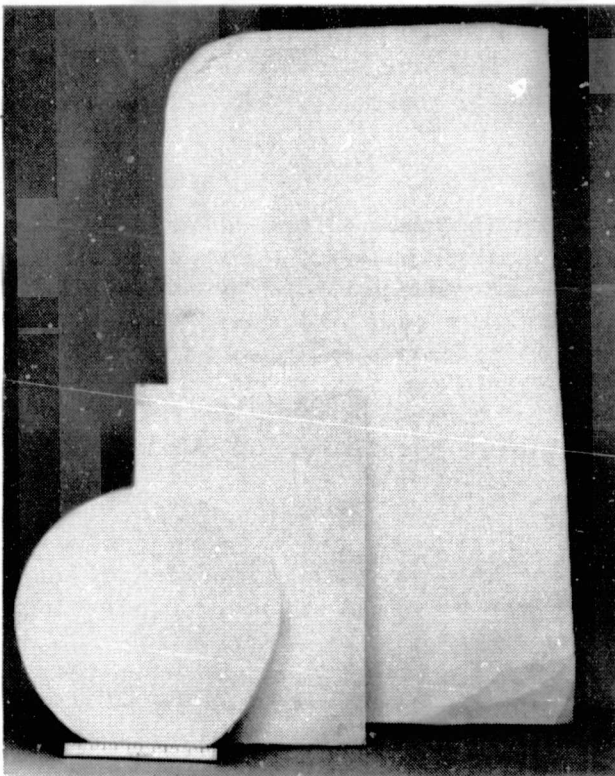


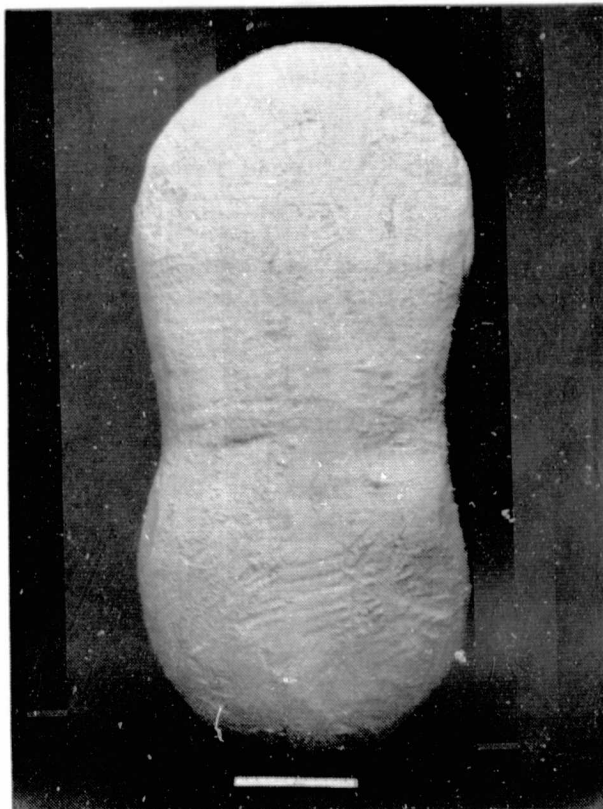
Figure 52.

Comparison of Finished Foams From  
2.2, 4.4, and 8.8 kg Powder Charge  
(1702-1)

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Figure 53.

Foam Samples by Microwave Curing  
at 8.8 kg of Powder Charge  
(1702-1)



Microwave curing was carried out by extending the foaming time and increasing the power output to 15 kW. The effect of microwave time on cellular structure was carried out by varying the curing time between 20 and 40 minutes. The data reported in Table 23 show that the lower time was sufficient to produce cured foams without burned spots due to overheating, although in all cases the outer 2.5 cm (1 in.) of the foam remained uncured. All foams were further postcured in a thermal oven at 288°C (550°F) for 1-2 hours.

This process made it possible to foam and cure large amounts of powder 1702-1 precursors (15.0 kg, 33.0 lbs) in the microwave oven in less than 40 minutes without the risk of cracking the foam slab due to handling. This compares favorably with the time required to thermally cure foam slabs of the same size.

During this scale-up study, it was found that preheating the powder precursor caused over-drying. This problem was solved by preheating the powder precursor in the microwave oven at low power output. However, preheating was eliminated later because it did not contribute to better foam quality.

The program objective of producing foam samples having dimensions of 61 x 61 x 7.6 cm (24 x 24 x 3 in.) has been accomplished for 1702-1 foam precursors. The foaming techniques successfully evaluated with the 15 kW microwave

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oven included free rise and constrained rise in an open mold using thermal and microwave curing.

#### Scale-Up of 1701-1 Foam Precursors

The work carried out in this phase of the program involves transfer of applicable information and data from the study of scale-up of 1702-1 foam precursors.

The scale-up of 1701-1 to prototype production foam samples was successfully carried out employing the optimum process parameters developed for 1702-1 foam precursors. This involved free rise technique in conjunction with microwave preheating for two minutes at 2.0 kW. The preheated powder precursor was foamed for 15 minutes at 10.0 kW followed by microwave curing for 20 minutes at 15 kW. It was further post-cured in the thermal oven at 232-288°C (450-550°F) for 1-2 hours. This foam had homogeneous cellular structure and was free of imperfections. Even for the 1701-1 candidate, the preheating step was later abandoned because it did not contribute to better foam quality.

Using the 15 kW microwave oven, the program objective of producing foam samples having dimensions of 61 x 61 x 7.6 cm (24 x 24 x 3 in.) has been accomplished for 1701-1 foam precursors using free rise techniques only. This type of foam is shown in Figure 54.

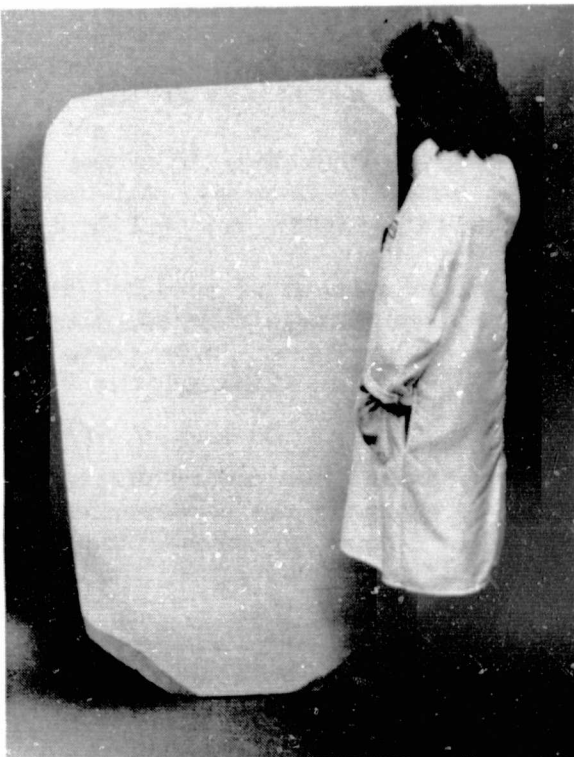


Figure 54.

1701-1 Foam Produced From 10 kg of Powder Precursor in 15 kW Microwave Oven

## Scale-up of 1720-1 Foam Precursors

The optimum process parameters summarized in Table 21 under the heading 1720-1 precursors were used as the starting point for this scale-up. These foams, which were at best adequate when produced in the 5 kW microwave oven, proved to be much more difficult to scale-up in the 15 kW oven than the previous two candidates.

These difficulties were further complicated by the seven months delay in the delivery of the microwave oven and repeated malfunctions of the spray dryer which left little time for development work. All this forced a shift of the activities toward the re-evaluation, in part, of the process parameters for foaming the 1720-1 candidate. These activities were carried out in accordance with the following scheme.

- Analysis of particle size distribution of the powdered precursor
- Study of the effect of preheating
- Study of the effect of porosity of Teflon® coated glass cloth substrate
- The geometrical configuration of the powder bed
- Study of the effect of powder thickness, powder load and power output
- Study of the effect of outlet temperature of the spray dryer
- Study of the effect of pulsing the microwave radiation

All these parameters were studied using free rise foaming techniques. Screening and selection of the optimum process parameters was made by evaluation of the foams for foaming behavior, foam yield, and visual inspection for flaws and imperfections.

### • Effect of Particle Size

Analysis of particle size distribution of the powdered precursor was initiated to evaluate the effect of this parameter on foam properties. Various particle sizes were obtained by either sieving through a Tyler mesh screen or grinding in a Pulvette bench model grinder. Table 24 summarizes the results from this study. All foams were produced on Teflon® coated glass type 7267/114 using a powder loading of 15 kg (33 lbs) at a thickness of 6.35 cm (2.5 in.).

Table 24

Scale-Up of 1720-1  
Effect of Particle Size on Foam Properties

| Particle Size | Indentation Load Deflection |       |      |       | Foam Quality                 |
|---------------|-----------------------------|-------|------|-------|------------------------------|
|               | 25%                         |       | 65%  |       |                              |
|               | N                           | (lbf) | N    | (lbf) |                              |
| #25           | 138                         | 39    | 534  | 120   | Good cellular structure      |
| #50           | 245                         | 55    | 1076 | 242   | Rigid structure              |
| Pulverized    | 267                         | 60    | 1054 | 237   | Rigid structure, large flaws |

The data developed to date show that larger particle size yields more useable foam and more homogeneous cellular structure with fewer imperfections than foams prepared at particle size of 50 microns and lower. These results were corroborated when the powder precursors were produced in the Niro Mobile Spray Dryer with atomizer running at speeds of between 37,000 and 40,000 rpm. At this speed, the powder precursors produced during the spray drying process possessed small particle size which in turn yield foams with flaws and rigid cellular structure. Atomizer speed lower than 30,000 rpm was not sufficient to produce complete atomization of the liquid resin. Best conditions were found to be those employing a speed between 32,000 and 35,000 rpm which produced a powder having a particle size distribution shown in Figure 55.

This atomizer speed and screening through a Tyler mesh screen #25 to eliminate lumpy particles were selected as the optimum conditions to prepare the 1720-1 powder for the subsequent foaming process.

#### Effect of Substrate

A number of substrates compatible with the microwave field were tested previously as described in Section 4.1.2. That study showed TCG (Teflon® Coated Glass Cloth, Taconic) to be one of the best candidates for microwave foaming along with polypropylene sheet as a rigid support for the powder.

To facilitate the escape of volatile during the foaming process and eliminate the excessive number of flaws occurring in the 1720-1 foams, the following TCG of different porosity, weave and surface smoothness were evaluated: Taconic 7276/91, 7276/114, 7356, 7278, 7308 and 7159. The 7276/114 candidate with the highest porosity and plain weave allowed the volatile to escape more freely from the rising mass and produced foams with more homogeneous cellular structure and minimum numbers of voids. This substrate material was used for all subsequent foaming studies dealing with the scale-up of the 1720-1 system.

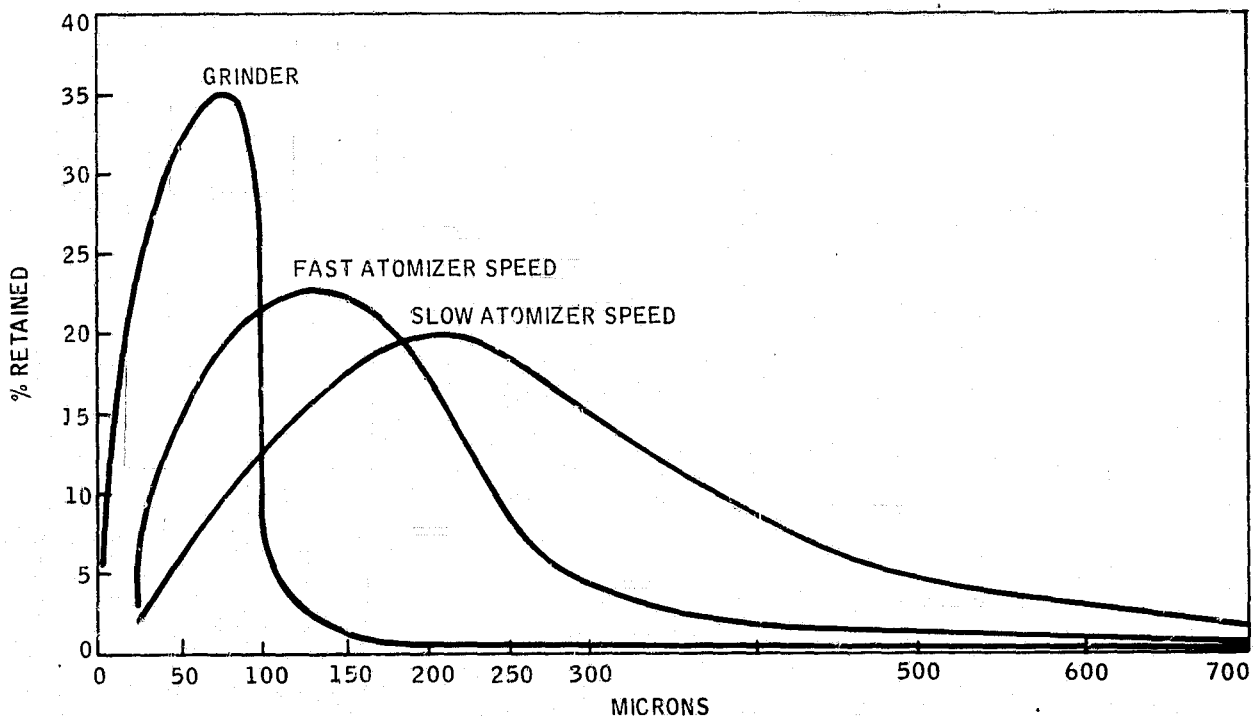


Figure 55. Particle Size Distribution of 1720-1 Precursors

#### Effect of Preheating

The effect of preheating on the 1720-1 system was studied during the course of the scale-up phase in the 5 kW microwave oven and discussed in Section 4.1.2. To re-establish the validity of this step, additional work was carried out in the 15 kW microwave oven by preheating the 1720-1 powder precursors using thermal processes, low power (2.5 kW) microwave process, and no preheating at all.

Surprisingly, foams produced without the preheating step possessed a more uniform structure and lower number of flaws. This finding, although unexpected, was significant and might be related to the higher absorption properties of the 1720-1 precursors in the microwave field which results in 30-50 percent faster foaming time at the same power output than that obtained with the other two candidates. The high rate of foam rise has been found to be always associated with high number of flaws, therefore, the step of preheating was eliminated from the standard procedure of foaming the 1720-1 candidates.



Effect of Powder Thickness, Geometrical Configuration, and Powder Load

The scale-up of the 1720-1 precursors was continued with studies of the processing conditions which have been previously found to affect foaming behavior in large foam size. These parameters include powder thickness, shape of the powder bed, powder loading, and microwave power output.

The polyimide powder precursors were foamed by placing the powder on a substrate followed by application of high frequency radiation. The effect of the powder thickness was found to be more critical for the 1720-1 candidate than for the two previous candidates. This study was carried out by evaluating powder thickness from 2.5 cm (1 in.) to 17.7 cm (7 in.) and measuring the rough cut yield of each foam. All other foaming parameters were kept constant. The data obtained are shown in Table 25.

Table 25

Effect of Thickness on Foaming Behavior of 1720-1 Precursors

| Powder Thickness |      | Rough Cut Yield |                 |
|------------------|------|-----------------|-----------------|
| cm               | Inch | m <sup>2</sup>  | ft <sup>2</sup> |
| 3.2              | 1.25 | 0               | 0               |
| 6.3              | 2.5  | 8.5             | 92              |
| 10.2             | 4    | 12.4            | 135             |
| 12.6             | 5.0  | 11.3            | 123             |
| 17.7             | 7.0  | 2.7             | 29.1            |

The results indicate that the useable foam obtained from the 1720-1 precursor is very dependent on powder thickness. The optimum powder thickness for all experimental work to follow was selected to be 10.2 cm (4 in.).

In the early phases of this effort, the powder precursors were placed on the substrate without consideration to the shape of the powder beds. After a substantial number of experiments (30) it appeared that square shaped powder beds (as opposed to elongated shaped powder beds) favored better quality foams. Therefore all subsequent work has followed this technique. This conclusion was based on visual observations only and does not represent a final process condition.

C 2

. Effect of Spray Drying Temperature

The work carried out on this subject was succinctly reported in Section 4.1.2, Foaming Studies in the task dealing with spray drying techniques. The relationships between rough cut yield and outlet temperature was reported in Table 12 which show the dependence of foam properties on spray drying parameters.

The work carried out to refine the operating procedure was outlined earlier in this section with studies of atomizer speed and precursor particle size. This work was carried out in the last phase of the contract. At the conclusion of this work, the optimizations reported in the preparation of the powder precursors, and the improved foaming process resulting from this same study, made it possible to produce foam samples having dimensions in excess of 61 x 61 x 7.6 cm (24 x 24 x 3 in.). With this development the program objective was met. Samples of 1720-1 foams having dimensions of 53.3 x 61 x 7.6 (21 x 24 x 3 in.) and 51 x 51 x 10 cm (20 x 20 x 4 in.) are shown in Figure 56 and 57 respectively.

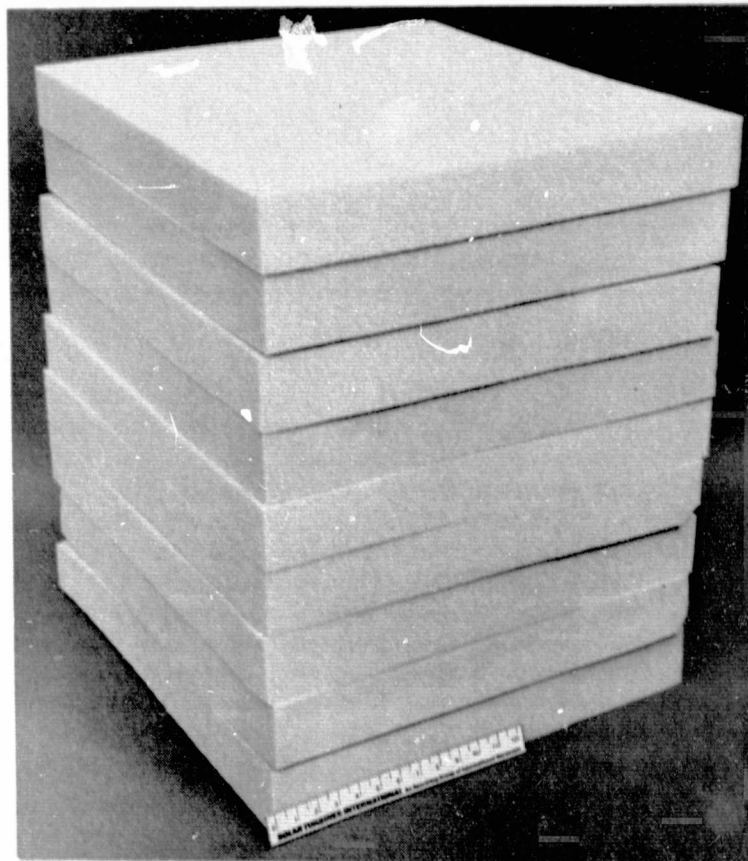


Figure 56. Final Prototype Production Samples, 1720-1

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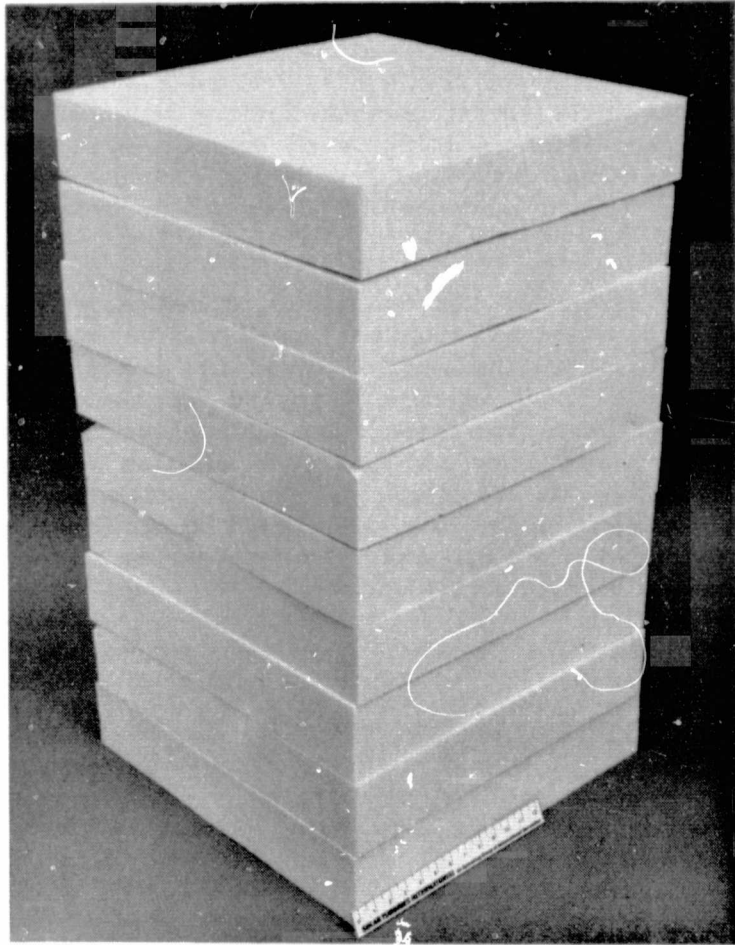


Figure 57. Final Prototype Production Samples, 1720-1

The foam samples were relatively free of visible flaws and imperfections and possessed a homogeneous cellular structure. The foam produced at this stage of the development were deficient in compression set and elongation properties, as was the case for the same foams scaled-up in the 5 kW oven, but met most other properties. A type of imperfection which was recognized to be critical during the execution of this task made it mandatory to carry out additional work on the scale-up of the 1720-1 candidate. This imperfection was foam reticulaton. As reported in the early development work, reticulation was considered a desirable property because it improved the compression set properties of the foams, but later recognized as being the weakest part of the foam in fatigue testing.

The degree of reticulation of the foams shown in Figures 56 and 57 was very low and detectable only by tactile and not by visual inspection. When these foams were tested for fatigue, the reticulated area having a lower density level than the surrounding foam, deflected under the shear-compressive load of the fatigue roller and produced a valley in the area of reticulation.

It goes without saying that shredding in the heavily deflected reticulated areas occurred and propagated through the cell walls in less than 10,000 cycles causing fatigue failure. The work on further optimization was then continued to overcome this deficiency and this effort carried out as described in the next subtask.

#### . Effect of Microwave Power Output and Power Pulsing

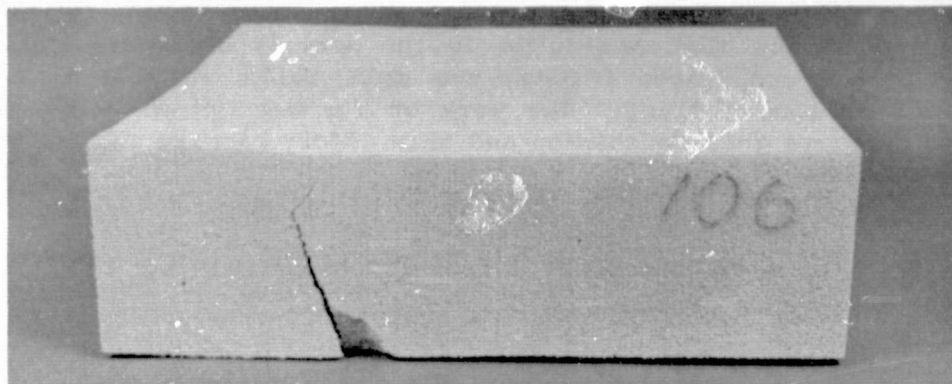
The activities described in this task were carried out during an extension of the program. This extension was necessary to compensate for delays in the delivery of the microwave oven and malfunctions of some of the equipment used to prepare the powder precursors.

The effort started with an evaluation of the ratio between powder loading and power output. The ultimate objective of this work was to generate data relating kW of power to unit weight of powder precursor (kW/kg).

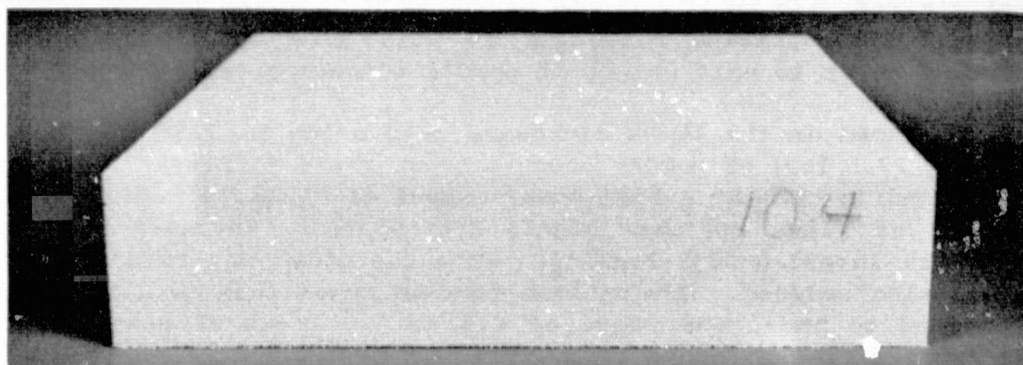
Foams were produced in the 15 kW microwave oven using 5, 7.5, 10 and 12.5 kg (11, 16.5, 22, 27.5 lbs) of powder precursors at three different power levels: 5 kW, 8.4 kW and 15 kW. At a high power output of 15 kW, all foams possessed a high number of flaws and were highly reticulated. Reticulation was most pronounced with lowest powder loading. When the power was reduced the reticulation was also reduced. The optimum foaming conditions to avoid reticulation were found to be in the range of 0.6 to 1.0 kW/kg of powder precursor with best results at the lowest level (12.5 kg at 8.4 kW).

These findings were based on visual inspection only since reticulation was very difficult to measure by any available means. Figure 58 shows structure of foams produced at various kW/kg. The evaluation of this parameter was terminated at a 12.5 kg loading, due to time limitations, but continuing work will be planned to expand the data to the maximum loading permitted. During the very last phase of this program a timer device was installed in the 15 kW microwave oven which permitted pulsing the power ON and OFF during the foaming and curing process. Due to time limitations only three experiments were completed.

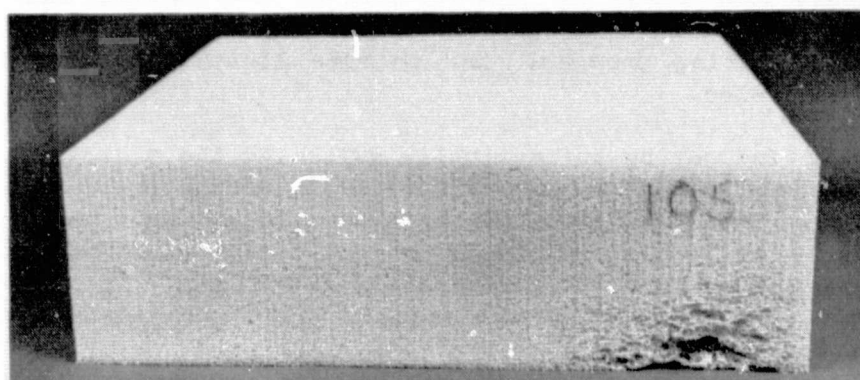
Pulsing was carried out by automatically switching the microwave power ON and OFF for 60 seconds and 20 seconds respectively during the entire foaming and curing process. The foams obtained by this pulsing technique at a power of 8.4 kW using 10 kg loading possessed a very homogeneous cellular structure and were practically free of reticulation and flaws. Foams obtained with this technique were selected as the optimum 1720-1 candidate for the preparation of samples for submittal to NASA-JSC.



(a) Fine unreticulated cellular structure obtained at 0.66 kW/kg



(b) Visible level of reticulated cellular structure obtained at 0.89 kW/kg



(c) High level of reticulated cellular structure obtained at 2.0 kW/kg

Figure 58. Effect of Microwave Power, kW/kg, on Cellular Structure of 1720-1 Foams

## Scale-Up Processes - Summary

- Using optimized conditions summarized in Table 21, foams have been produced in the 5 kW microwave oven with compression set values of 8-14 percent (1701-1), 20-35 percent (1702-1), and 25-30 percent (1720-1) at a density of 8.0-11.2, 11.2-16.0, and 9.2-13.1 kg/m<sup>3</sup> respectively.
- A NASA microwave oven (GFE) having dimensions of 1.83 x 1.83 x 3.66 meters (6 x 6 x 12 ft) and a power output of 15 kW has been selected and installed in Solar Research Pilot Plant. This microwave oven meets all the contractual requirements.
- Foaming techniques evaluated with the 15 kW microwave oven included free rise and constrained rise. Thermal curing and microwave curing were also tested. All these techniques were successfully proven with the 15 kW microwave oven.
- Using the 15 kW microwave oven (GFE) and optimized conditions summarized in Table 26, the program objective of producing foam samples having the dimensions of 61 x 61 x 7.6 cm (24 x 24 x 3 in.) has been accomplished for 1720-1 foam precursors.

### 4.1.4 Task IV - Characterization and Selection of Polyimide Foam Compositions

The effort of this task involved characterization of the candidate polyimide foam compositions and the selection of the optimum candidate for final fabrication of samples to be submitted to NASA-JSC for seating applications.

Because of the seven month delay in the delivery of the 15 kW microwave unit, the characterization effort was organized to proceed in two distinct steps.

In the first step, compositions were developed, process variables studied, and viable candidates optimized in the 5 kW microwave oven. These optimum candidates were characterized for mechanical, physical, and thermal properties. This resulted in the selection of a final candidate for scale-up.

In the second step the optimum candidate was re-evaluated and the work carried out in the 15 kW microwave oven, where final process parameters were developed to fabricate samples for final characterization and submittal to NASA-JSC.

The testing effort was organized to proceed in three steps which includes mechanical, physical, and flammability testing.

Table 26

Selection of Optimum Process Parameters for Flexible,  
Resilient Polyimide Foams (15 kW Microwave Oven)

| Process Classification | Parameter                    | Copolyimide System |               | Terpolyimide System  |
|------------------------|------------------------------|--------------------|---------------|----------------------|
|                        |                              | 1701-1             | 1702-1        | 1720-1               |
| Synthesis              | Reaction Temp. (°C)          | 60-65              | 60-65         | 60-65                |
|                        | Reaction Time (Min.)         | 5                  | 5             | 5                    |
|                        | Additive                     | AS-2               | AS-2          | AS-2                 |
|                        | Additive Conc. (%)           | 1.0                | 1.0           | 0.75                 |
| Spray Drying           | Inlet Temp. (°C)             | 100                | 100           | 100                  |
|                        | Outlet Temp. (°C)            | 70-74              | 70-74         | 63-70                |
|                        | Dilution Ratio (phr)         | 20                 | 20            | 30                   |
| Microwave Foaming      | Substrate                    | TCG, 7276/114      | TCG, 7276/114 | TCG, 7276/114        |
|                        | Powder Charge (kg)           | 15                 | 15            | 15                   |
|                        | Preheat                      | None               | None          | None                 |
|                        | MW Frequency (MHz)           | 2450               | 2450          | 2450                 |
|                        | Microwave Foaming Power (kW) | 10                 | 10            | 8.4                  |
|                        | Microwave Pulsing            | -                  | -             | ON/OFF = 60/20 Secs. |
|                        | Microwave Foaming Time       | 15                 | 15            | 15                   |
|                        | Microwave Curing Power (kW)  | 15                 | 15            | 10                   |
|                        | Microwave Pulsing            | -                  | -             | ON/OFF = 60/20 Secs. |
|                        | Microwave Curing Time (Min.) | 20-40              | 20-40         | 20-40                |
| Curing                 | Curing Temp. (°C)            | 232-288            | 232-288       | 232-260              |
|                        | Curing Time (hrs)            | 1-2                | 1-2           | 1-2                  |

The testing of mechanical properties started with the most critical properties which included evaluation of:

- fatigue
- compression set at 90 percent compression
- indentation load deflection

All characterizations were performed in accordance with ASTM Designation D-1564 as specified in the operating plan of the program. The characterization phases of the foams produced in the 5 kW and 15 kW microwave ovens is reported below.



## Characterization of Foams Produced in the 5 kW Microwave Oven

The three candidate foam precursors 1701-1, 1702-1 and 1720-1 were produced at a AS-2 surfactant concentration of 0.1, 0.25, 0.5, 0.75, 1.0 and 1.5 percent respectively. This wide range of concentration was selected based on the data developed for these three candidates and discussed in Section 4.1.3.

The test data derived for each of the following property, fatigue, indentation load deflection, compression set resiliency and density are reported in Table 27 for 1701-1, Table 28 for 1702-1, and Table 29 for 1720-1 foams.

Of all the materials subjected to fatigue, only four samples survived the 10,000 cycles and met the requirement of maximum loss of thickness (or ILD) of 20 percent. These candidates belong to the 1720-1 series and were produced at a AS-2 surfactant concentration of 0.1, 0.25, 0.5 and 0.75 percent respectively. All other samples tested for fatigue were either severely damaged or did not meet the minimum requirements.

Figure 59 shows the effect of fatigue for foams derived from the three candidate precursors 1701-1, 1702-1 and 1720-1 prepared at the same AS-2 surfactant concentration of 0.5 percent. The 1720-1 candidate survived the test without signs of any damage while the other two candidates were severely degraded.

At higher surfactant concentration, the damage was more severe especially for the candidates 1720-1 and 1702-1. This damage was characterized by shredding and foam collapse. This is shown in Figure 60 for a foam sample derived from 1702-1 made at 1.0 percent AS-2 and fatigued for 10,000 cycles. The surviving four 1720-1 candidates were retested for an additional 10,000 cycles in accordance with the recommended procedure and survived the test without visible foam damage at the end of 20,000 cycles.

The data reported in Table 27, 28 and 29 show some deficiencies in compression set and ILD for the three candidates 1701-1, 1702-1 and 1720-1. The 90 percent compression set loss of these foam candidates does not meet the 15 percent maximum requirement, although the 1720-1 foams, which are the only ones to survive the fatigue test, show best results.

The indentation load deflection of the 1701-1 and 1702-1 foams meet or approach the program requirement, but the foams derived from the 1720-1 candidate possess higher indentation load deflection values especially at 65 percent indentation. When higher AS-2 concentration was used the foams approached the program requirements.

The density and resiliency of the foams before and after fatigue testing generally meet the requirements for the program.

The results of the humidity test were discussed and presented in a previous section. From these results, 1720-1 system emerged as the most resistant to humid environments.



Table 27

## Mechanical Properties of 1701-1 Polyimide Foams

| Foam Number | Surfactant (AS-2) Concentration % | Density           |                     | Indentation Load Deflection (ILD) |       |      |     | Compression Set Loss (%) | Resiliency Before Fatigue | After Fatigue (10,000 Cycles) |               |
|-------------|-----------------------------------|-------------------|---------------------|-----------------------------------|-------|------|-----|--------------------------|---------------------------|-------------------------------|---------------|
|             |                                   | Kg/m <sup>3</sup> | Lbs/ft <sup>3</sup> | N                                 |       | Lbs  |     |                          |                           | Resiliency                    | Height Loss % |
|             |                                   |                   |                     | 25%                               | 65%   | 25%  | 65% |                          |                           |                               |               |
| 7           | 0.1                               | 12.8              | 0.8                 |                                   |       |      |     | 49                       | 42                        | *                             | *             |
| 8           | 0.25                              | 17.0              | 1.06                | 120.1                             | 400.3 | 27   | 90  | 33                       | 45                        | *                             | *             |
| 9           | 0.5                               | 15.2              | 0.95                | 177.9                             | 631.6 | 40   | 142 | 46                       | 55                        | 40                            | 60            |
| 10          | 0.75                              | 13.6              | 0.85                | 122.3                             | 386.9 | 27.5 | 87  | 29                       | 45                        | 30                            | 41.1          |
| 11          | 1.0                               | 9.6               | 0.6                 | 133.4                             | 542.6 | 30   | 122 | 30                       | 35                        | 20                            | 58.2          |
| 12          | 1.5                               | 12.8              | 0.8                 | 151.2                             | 556.0 | 34   | 125 | 30                       | 45                        | 20                            | 54.9          |

\* Cellular structure collapsed during fatigue.

Table 28

## Mechanical Properties of 1702-1 Polyimide Foams

| Foam Number | Surfactant (AS-2) Concentration % | Density           |                     | Indentation Load Deflection (ILD) |       |     |       | Compression Set Loss (%) | Resiliency Before Fatigue | After Fatigue (10,000 Cycles) |               |
|-------------|-----------------------------------|-------------------|---------------------|-----------------------------------|-------|-----|-------|--------------------------|---------------------------|-------------------------------|---------------|
|             |                                   | Kg/m <sup>3</sup> | Lbs/ft <sup>3</sup> | N                                 |       | Lbs |       |                          |                           | Resiliency                    | Height Loss % |
|             |                                   |                   |                     | 25%                               | 65%   | 25% | 65%   |                          |                           |                               |               |
| 13          | 0.1                               | 14.4              | 0.9                 | 133.4                             | 489.3 | 30  | 110   | 54                       | 47                        | 50                            | 36.0          |
| 14          | 0.25                              | 14.4              | 0.9                 | 142.3                             | 515.9 | 32  | 116   | 40                       | 45                        | 50                            | 34.0          |
| 15          | 0.5                               | 13.8              | 0.86                | 146.8                             | 515.9 | 33  | 116   | 43                       | 60                        | 50                            | 30.4          |
| 16          | 0.75                              | 12.8              | 0.8                 | 133.4                             | 471.5 | 30  | 106   | 40                       | 42                        | 45                            | 33.7          |
| 17          | 1.0                               | 9.8               | 0.61                | 146.8                             | 502.6 | 33  | 113   | 52                       | 40                        | *                             | *             |
| 18          | 1.5                               | 10.9              | 0.68                | 142.3                             | 544.8 | 32  | 122.5 | 43                       | 47                        | *                             | *             |

\* Cellular structure collapsed during fatigue.

Table 29

## Mechanical Properties of 1720-1 Polyimide Foams

| Foam Number | Surfactant (AS-2) Concentration % | Density           |                     | Indentation Load Deflection (ILD) |        |     |     | Compression Set Loss (%) | Resiliency Before Fatigue | After Fatigue (10,000 Cycles) |               |
|-------------|-----------------------------------|-------------------|---------------------|-----------------------------------|--------|-----|-----|--------------------------|---------------------------|-------------------------------|---------------|
|             |                                   | Kg/m <sup>3</sup> | Lbs/ft <sup>3</sup> | N                                 |        | Lbs |     |                          |                           | Resiliency                    | Height Loss % |
|             |                                   |                   |                     | 25%                               | 65%    | 25% | 65% |                          |                           |                               |               |
| 1           | 0.1                               | 24.0              | 1.5                 | 293.6                             | 1427.8 | 66  | 321 | 49                       | 50                        | 55                            | +3.9          |
| 2           | 0.25                              | 25.6              | 1.6                 | 266.9                             | 1352.2 | 60  | 304 | 37                       | 45                        | 47                            | +5.3          |
| 3           | 0.5                               | 22.4              | 1.4                 | 266.9                             | 1165.4 | 60  | 262 | 35                       | 40                        | 37                            | +2.0          |
| 4           | 0.75                              | 22.4              | 1.4                 | 195.7                             | 1009.7 | 44  | 227 | 34                       | 40                        | 43                            | -2.9          |
| 5           | 1.0                               | 18.4              | 1.15                | 155.7                             | 800.7  | 35  | 180 | 27                       | 45                        | *                             | *             |
| 6           | 1.5                               | 17.0              | 1.06                | 155.7                             | 809.5  | 35  | 182 | 27                       | 50                        | *                             | *             |

\* Cellular structure collapsed during fatigue.

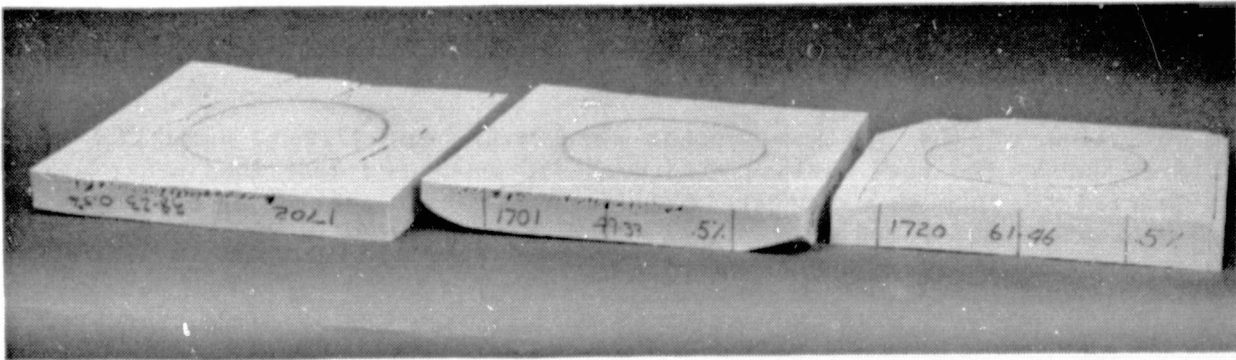


Figure 59. Fatigue Damage of Polyimide Foams After 10,000 Cycles - 1701-1, 1702-1 and 1720-1

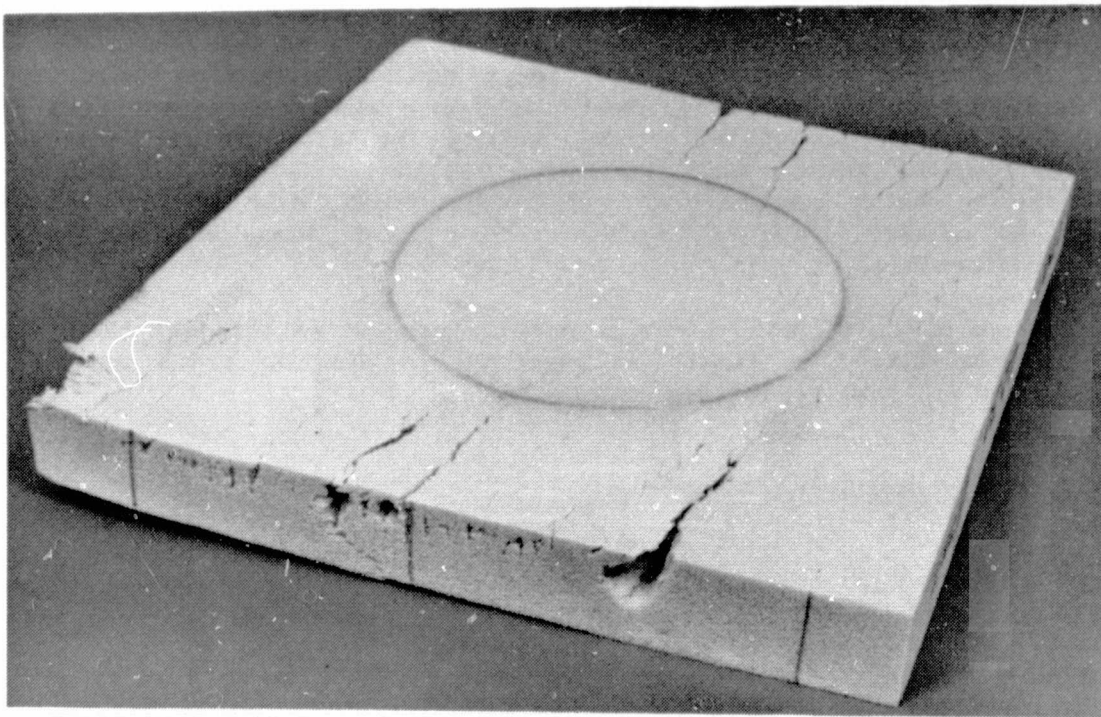


Figure 60. Fatigue Damage of 1701-1 Foam at High Surfactant Concentration

By far, the most critical properties for seating applications include fatigue resistance, compression set, and hydrolytic stability. The data derived from the characterization study of this first phase have shown that 1720-1 foams exhibit properties which meet or exceed the program requirements for seating applications more thoroughly than the other two candidates.

On the basis of these data the 1720-1 was selected as final candidate for scale-up processes in the 15 kW GFE microwave oven.

## Characterization of 1720-1 Produced in the 15 kW GFE Microwave Oven

The selection of the optimum process parameters for 1720-1 summarized in Table 26 during the task dealing with scale-up processes described previously was carried out through a concurrent study of process variables in conjunction with characterization and testing. This section deals with the testing data produced from that study and shown in Table 30. A brief explanation follows.

Foams number 41, 42 and 43 were produced to study the effect of particle size during foaming. Test data show that the particle size of foam precursors influences the indentation load deflection values. These values vary from 122.3 to 267 N (27.5 to 60 lbf) at 25 percent deflection and 489 to 1054 N (110 to 237.0 lbf) at 65 percent deflection as the particle size decreases from mesh screen #25 to finely ground powder.

Foams #51, 52 and 54 were produced to study the effect of the outlet temperature of the spray dryer. These foams were produced at a temperature of 70-75, 67-70 and 63-67°C respectively. Test data show that the indentation load values at 25 and 65 percent deflection change markedly as the outlet temperature is decreased. These values vary from 365 to 156 N (80 to 35 lbf) at 65 percent as the outlet temperature is decreased from a high of 75°C to a low of 63°C. In summary, lower outlet temperature yields foams which are softer and more comfortable.

Foams prepared under the conditions of pulsing process selected as the optimum method to foam 1720-1 candidate as reported in Section 4.1.3 were fully characterized and data reported in Table 31.

### Characterization and Selection Summary

1. 1720-1 was selected as final candidate for use in sample preparation for submittal to NASA-JSC.
2. This final candidate meets or exceeds the program requirement for fatigue resistance, hydrolytic stability, thermal properties, and mechanical properties.
3. This final candidate is slightly deficient in compression set and elongation characteristics.
4. The indentation load deflection values of the 1720-1 foams have been found to vary over a wide range depending upon particle size of the powder precursors and spray drying conditions.

Table 30

**Scale-Up Processes: Flexible Resilient Foams  
1720-1 Resin Test Data**

| Foam No.<br>Identification                       | #43<br>PL-5-12-28-43   | #42<br>PL-5-12-27-42 | #41<br>PL-5-12-26-41  | #51<br>FL-5-12-37-51       | #52<br>PL-5-12-38-52   | #54<br>PL-5-12-40-54       |
|--|------------------------|----------------------|-----------------------|----------------------------|------------------------|----------------------------|
| DRYER TEMP., (°C)                                | 70-75                  | 70-75                | 70-75                 | 70-75                      | 67-70                  | 63-67                      |
| RESIN  | 1720-1                 | 1720-1               | 1720-1                | 1720-1                     | 1720-1                 | 1720-1                     |
| AS-2   | 0.75                   | 0.75                 | 0.75                  | 0.75                       | 0.75                   | 0.75                       |
| SIEVE SIZE                                       | Ground                 | 1/3-2/3              | #25                   | #25                        | #25                    | #25                        |
| POWDER THICKNESS                                 | 10.1 cm (4")           | 10.1 cm (4")         | 10.1 cm (4")          | 10.1 cm (4")<br>Not Rolled | 10.1 cm (4")           | 10.1 cm (4")<br>Not Rolled |
| SIZE (lbs)<br>(kg)                               | 33<br>15               | 33<br>15             | 33<br>15              | 33<br>15                   | 33<br>15               | 33<br>15                   |
| PREHEAT  | No                     | No                   | No                    | No                         | No                     | No                         |
| Time (Min)                                       | -                      | -                    | -                     | -                          | -                      | -                          |
| Power (kW)                                       | -                      | -                    | -                     | -                          | -                      | -                          |
| FOAMING  |                        |                      |                       |                            |                        |                            |
| Time (Min)                                       | 8-1/2                  | 10                   | 9                     | 8                          | 8                      | 8                          |
| Power (kW)                                       | 15                     | 15                   | 15                    | 15                         | 15                     | 15                         |
| CURING-MICROWAVE                                 | Yes                    | Yes                  | Yes                   | Yes                        | Yes                    | Yes                        |
| Time (Min)                                       | 30                     | 30                   | 30                    | 30                         | 30                     | 30                         |
| Power (kW)                                       | 10                     | 10                   | 10                    | 10                         | 10                     | 10                         |
| CURING-THERMAL                                   | Yes                    | Yes                  | Yes                   | Yes                        | Yes                    | Yes                        |
| Temp. (°F)                                       | 450                    | 450                  | 450                   | 450                        | 450                    | 450                        |
| (°C)   | 232                    | 232                  | 232                   | 232                        | 232                    | 232                        |
| Time (Hrs)                                       | 1                      | 1                    | 1                     | 1                          | 1                      | 1                          |
| POST-CURE THERMAL                                | Yes                    | Yes                  | Yes                   | Yes                        | Yes                    | Yes                        |
| Temp. (°F)                                       | 490                    | 490                  | 490                   | 490                        | 490                    | 490                        |
| (°C)   | 254                    | 254                  | 254                   | 254                        | 254                    | 254                        |
| Time (Hr)  | 1/2                    | 1/2                  | 1/2                   | 1/2                        | 1/2                    | 1/2                        |
| DENSITY Lbs/ft <sup>3</sup><br>kg/m <sup>3</sup> | 1.0<br>16.0            | 1.04<br>16.7         | 0.81<br>13.04         | 1.39<br>22.2               | 1.25<br>20             | 0.64<br>10.2               |
| RESILIENCY                                       | 75                     | 70                   | 70                    | 45-50                      | 40-45                  | 55-60                      |
| ILD 25% lbs N<br>65%                             | 60.0 262<br>237.0 1054 | 30 133<br>90 400     | 27.5 122<br>110.0 489 | 80.0 356<br>277.0 1232     | 66.0 293<br>240.0 1068 | 35.0 155<br>122.0 542      |
| TEAR, lbs  | 1.15                   | 0.95                 | 0.45                  | 0.79                       | 0.68                   | 0.43                       |
| TENSILE STRENGTH, PSI                            | 28.5                   | 32                   | 29.6                  | 24.5                       | 10.1                   | 16.3                       |
| ELONGATION %                                     | 32.0                   | 22.5                 | 23.0                  | 23.4                       | 25.9                   | 22.7                       |
| COMPRESSION 30%<br>50%                           | 34.9<br>12.2           | 48.2<br>9.4          | 26.1<br>10.9          |                            |                        |                            |

#### 4.1.5 Task VI - Sample Preparation

These samples were prepared from 1720-1 precursors modified with 0.75 percent AS-2 using microwave foaming. A pulsing cycle of 60 second ON and 20 seconds OFF at a power of 8.4 kW was used for foaming. The power was increased to 15 kW for the curing process. A final thermal curing at 243°C (470°F) was used to ensure complete polymerization. Approximately 2.5 m<sup>2</sup> (3 sq. yards) of the foam having a thickness of 7.6 cm (3 in.) was prepared for shipment to NASA-JSC.

Table 31

Scale-up Processes: Flexible Resilient Foams  
1720-1 Resin

| Property                             | ASTM Method                | Units  | Goal                           | Actual                          |
|--------------------------------------|----------------------------|--|--------------------------------|---------------------------------|
| Density                              | D-1564                     | Kg/m <sup>3</sup><br>lbs/ft <sup>3</sup>             | 40.0<br>2.5                    | 25.8<br>1.6                     |
| Tensile Strength                     | D-1564                     | N/m <sup>2</sup><br>psi                              | 82.7 x 10 <sup>3</sup><br>12.0 | 246.0 x 10 <sup>3</sup><br>35.7 |
| Elongation                           | D-1564                     | %  | 30-50                          | 26.8                            |
| Tear Resistance                      | D-1564                     | N/m<br>lbs/inch                                      | 175.1<br>1.0                   | 205.7<br>1.17                   |
| Indentation Load Deflection          | D-1564                     |  |                                |                                 |
| 25%                                  |                            | N/3.2 dm <sup>2</sup><br>lb-force/50 in <sup>2</sup> | 111.2-155.6<br>25-35           | 442.5<br>99.5                   |
| 65%                                  |                            | N/3.2 dm <sup>2</sup><br>lb-force/50 in <sup>2</sup> | 667-1112.0<br>150-250          | 1968.2<br>442.5                 |
| Compression Set                      | D-1564                     | % Loss   |                                |                                 |
| 90%                                  |                            |  | 12-15                          | 49.9                            |
| 50%                                  |                            |  | 7-10                           | 12.85                           |
| Corrosion                            | FTMS No. 151               |  | None                           | No evidence                     |
| Resilience Rebound Value             | D-1564                     | %  | 50 min.                        | 58                              |
| Dry Heat                             | D-1564                     | % Loss Tensile Strength                              | 20 max.                        | 5.0                             |
| Humidity<br>73.9°C (165°F) 100% R.H. | D-1565                     | % Loss ILD   | 20 max.                        | 7.9                             |
| Fatigue                              | D-1564                     | % Loss ILD   |                                |                                 |
| 10,000 cycles                        |                            |  | 20 max.                        | 7.8                             |
| 20,000 cycles                        |                            |  | 20 max.                        | 15.5                            |
| Odor                                 |                            |  | None                           | Not detectable                  |
| Oxygen Index                         | D-2863                     | % Oxygen   | 40 min.                        | 38                              |
| Smoke Density<br>DS uncorrected      | NBS                        | Optical density                                      | 30-50 max.                     | 3                               |
| Thermostability                      | Thermogravimetric Analysis | Loss 204°C (400°F)                                   | None                           | No Loss                         |

## 4.2 PRODUCT II - LOW DENSITY WALL PANELS

The effort of this task starts with optimization of rigid panel configurations previously developed (Ref. 2), and development of techniques to produce low density core and high density skin panels in a one-step operation, followed by optimization studies, evaluation of new configurations, selection of candidates and final testing.

The work carried out in this phase of the program involves transfer of applicable information and data from Section 4.1.1, advanced polyimide synthesis and Section 4.1.2 dealing with foaming studies of precursor compositions by microwave methods.

### 4.2.1 Task 1 - Optimization of Rigid Polyimide Foam Panels

This task deals with the optimization of the low density rigid foam technology through the investigation of resin precursors and modifying agents, using a wide array of reinforcing materials and adjustment of process variables.

The first objective of this task was to evaluate an entire array of reinforcing materials with respect to use in low density rigid foam panel cores. This information was then used in the development of high density floor panels which is reported in the following section.

The complete list of these reinforcing materials is given in Table 32. The screening study of these fillers was conducted by fabricating a series of panels using 1702-0 liquid resin filled with each of the listed materials. The panels were fabricated using the free-rise technique followed by compressing the panel to a flat configuration. These panels were then evaluated on the basis of ease of lay-up, final foam structure, strength, and filler distribution. The table gives a summary of the results. With respect to use in low density rigid foams, 48 to 80 kg/m<sup>3</sup> (3 to 5 pcf), the following reinforcing materials proved the most promising: carbon mat (Union Carbide, VMA grade), chopped carbon mat (Union Carbide VMC grade), chopped glass rovings and chopped glass strands (Owens Corning Fiberglas). Candidate low density cores produced from carbon mat and glass strands are shown in Figure 61. The carbon mat will lend itself well to a large-scale automatic lay up process. These materials were found to give low density, fine cell, homogeneous foam when used at concentrations of 3 to 6 percent. Higher concentrations gave denser foam more suitable to floor panel applications. The target density of 48 to 80 kg/m<sup>3</sup> (3 to 5 pcf) at 0.635 cm (1/4 in.) has best been achieved with these two carbon reinforcements.

The two glass reinforcements, chopped strands and roving have been used at higher concentrations than the carbon reinforcements and still gave good foam rise. The glass strand reinforced resin mixtures tended to be more workable than chopped roving reinforced mixtures allowing slightly easier lay up and subsequently improved foam structure and reinforcement distribution. For both types of glass, however, lay up at the loading required to

Table 32

Summary of Rigid Panel Reinforcement Study

|                       |  |  |
|-----------------------|--|--|
| Carbon Mat            | VMA grade, Union Carbide                                     | Foam rise very uniform; foam structure fine, homogeneous; wide density range possible; suitable for sectioned foam panels.   |
| Chopped Carbon Mat    | VMC Grade, Union Carbide                                     | Foam rise good; structure fine, homogeneous wide density range possible; foams have higher compressive strength than with VMA grade.   |
| Chopped Carbon Mat    | VMD and VME grades, Union Carbide                            | Not suitable as primary filler, does not result in homogeneous foam.   |
| Chopped Glass Strands | 832, 405 and 419 of various lengths, Owens Corning Fiberglas | Dependent on fiber length and concentration. In general foam structure good and homogeneous; when used as primary filler strength inferior to carbon reinforced foams; compatible with microwave foaming techniques. |
| Chopped Glass Roving  | 449 AAS-2 of various lengths, Owens Corning Fiberglas        | Generally similar to strands; lay up more difficult.   |
| Milled Glass Fibers   | Type 739 Owens Corning Fiberglas                             | Not suitable as foam reinforcement   |
| Glass Microballoons   | C15-X, 3M & Company  | Generally same as milled fibers, may be suitable for use in high density applications.   |
| Glass Fiber Mat       | M720 C/S, Owens Corning Fiberglas                            | Foam structure good at low concentrations, layers tend to separate at high concentrations.   |
| Graphite Fiber        | Thornel, Union Carbide                                       | Foam structure poor, not homogeneous   |
| Graphite Powder       | POCO, Union 76 PXB-QS-325                                    | Suitable as auxiliary filler in small concentrations.  |
| Kevlar Fibers         | Dupont   | Foam structure good, similar to glass roving; shorter fibers lay up well and give better results; limited density range possible.  |
| Nomex Fibers          | Dupont   | Generally similar to Kevlar  |
| Fiberfrax             | Carborundum  | Foam structure poor, not homogeneous   |
| Phenolic Macrospheres | Type M20X to M14X Hollow macrospheres, 3M & Company          | Too heavy for use in small panel cores, have possible advantages for floor panel cores.  |

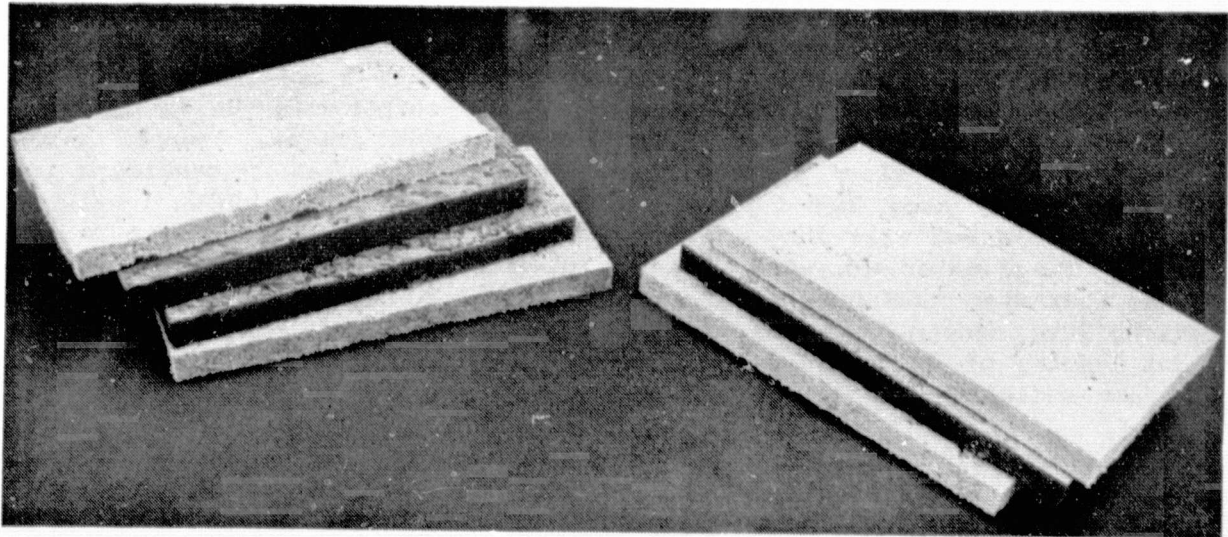


Figure 61. Foam Cores Made With Carbon Mats and Glass Strands



give low density foam at low panel thicknesses was more difficult than with the carbon reinforcements. When the reinforcements were compared at panel thicknesses of 1.27 cm (1/2 in.) the glass reinforced rigid foams did not have the rigidity of the carbon reinforced foams at comparable densities. The rigidity of glass reinforced foams was found to increase with addition of small percentages of carbon fiber reinforcement. This allowed the economic advantage of high glass content to be realized in a slightly more rigid foam.

As will be discussed in Section 4.3.1, the sizing of the glass strand reported in Table 49 has different effects on the final foam product due to interaction of the sizing with the resin system. The glass strands with the sizing most compatible with the polyimide resin (832 BC) are available in lengths of 0.635, 1.27 and 2.54 cm (1/4, 1/2 and 1 in.). At a given glass percentage, lay up was found to be easier with the shorter strands and subsequent foam rise was consistently higher than that obtained with the longer strands. The glass distribution in the finished foam was found to be good for all three lengths. Based on the results, the carbon reinforcements, VMA and VMC were selected for use in low density rigid foam panel cores produced by the free rise thermal foaming technique and the chopped glass strand reinforcement was selected for continued study because of its compatibility with microwave foaming techniques.

The second objective of this task involved studies of the resin precursors and modifying additives. This study started with the re-evaluation of surface active agents to determine their effects on foaming behavior of the 1702-1 liquid precursor which was selected as the optimum candidate based on cost and higher foam rigidity. This study consisted of recording the foam rise characteristics of medium density foam panels reinforced with chopped carbon mat. Of the surfactants tested, two giving the lowest density foam were Dow Corning L5410 and 3M Fluorocarbon FC431. These were selected for further use in rigid foams intended for low density applications. A summary of the results of this study is reported in Table 33.

In order to overcome the problem of laying up thin coatings of fiber filled resin mixtures to obtain low density foams, a study was undertaken to evaluate techniques of fabrication of uncompressed foam cores. This involved sectioning rather than compressing a foamed sheet to the desired thickness. The carbon mat (VMA grade) reinforced foam proved most adaptable to this process because of its fine cellular, homogeneous structure. A density of 48 kg/m<sup>3</sup> (3 pcf) has been achieved with this formulation at a thickness of 0.635 cm (1/4 in.). This type of core panel possessed a direct screw withdrawal of 57.4 N (12.9 lbf) and was tapered to feather edge with less than 0.08 cm (0.03125 in.) break-out. Figure 62 shows uncompressed and compressed wall panel cores made from this type of carbon mat reinforcement. Direct screw withdrawal tests have been conducted on foam cores made with this candidate reinforcing material. Results are in the 72-270 N (16-60 lb) range for panels having densities of 48 to 120 kg/m<sup>3</sup> (3 to 7.5 pcf). Table 34 presents data on screw withdrawal testing of 2.5 cm thick (1 in.) specimens made in accordance with ASTM D-1761 and prepared from different reinforcements.



Table 33

Results of Surfactant Addition to Carbon Reinforced Rigid Foams

|   |  |
|---|--|
| Surfactants giving significantly higher foam rise | DC L5410<br>DC L5340<br>DC 193<br>FC 431       |
| Surfactants giving slightly improved foam rise    | DC 190<br>DC 196<br>FSB<br>FSC                 |
| Surfactants showing no improvement in foam rise   | DC L520<br>DC L550<br>DC L5420<br>X-3<br>X-3-6 |

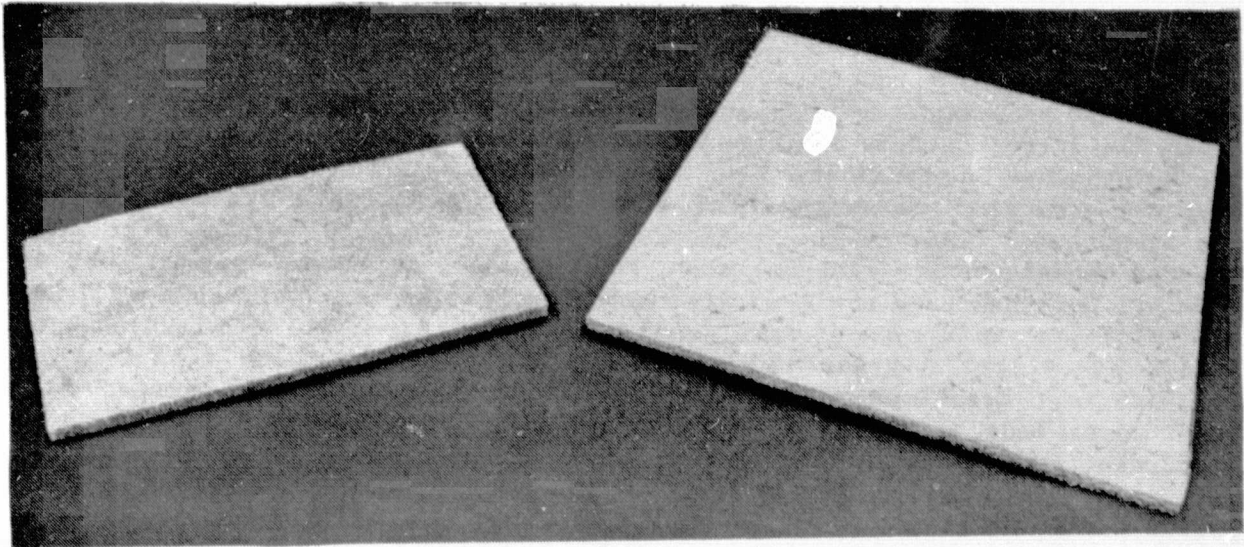


Figure 62. Wall Panels Produced From VMA Carbon Mat. Uncompressed Foam Core  $48 \text{ kg/m}^3$  at  $0.635 \text{ cm}$  (3 pcf at  $1/4 \text{ in.}$ ), Right. Compressed Foam Core  $80 \text{ kg/m}^3$  at  $0.635 \text{ cm}$  (5 pcf at  $1/4 \text{ in.}$ ), Left

Table 34

## Screw Withdrawal Testing of Low Density Rigid Panels

| Reinforcement                       | Panel Density     |                    | Withdrawal Force |      |
|-------------------------------------|-------------------|--------------------|------------------|------|
|                                     | kg/m <sup>3</sup> | lb/ft <sup>3</sup> | N                | lb   |
| Chopped Carbon Mat<br>(VMC Grade)   | 110.4             | 6.9                | 193.1            | 43.3 |
| Chopped Glass Roving<br>(449 AAS-2) | 100.8             | 6.3                | 197.0            | 44.3 |
| Graphite Fibers<br>(Thornel)        | 118.4             | 7.4                | 156.8            | 35.1 |
| Fiberfrax                           | 120.0             | 7.5                | 194.0            | 43.6 |
| Kevlar Fibers                       | 113.6             | 7.1                | 144.1            | 32.3 |

#### 4.2.2 Task II - Development of Techniques for Producing Rigid Panels With Low Core and High Density Skins

The initial efforts of this task involved re-evaluating both surface active agents and crosslinking agents to determine their effect on foam structure and to obtain cores with large cell and thick wall configuration. This involved transfer of technology from previous tasks dealing with flexible foams (Ref. 2). Initial studies showed that the most significant factor in achieving the desired cell structure was the concentration of the crosslinking agent. Addition of surface active agents to the resin did not significantly modify the structure obtained. The first phase of this task was conducted using thermal foaming techniques and foams made with powder precursor 1702-0 modified with a crosslinking agent in concentrations ranging from 0.5 to 2.0 percent. The foams obtained possessed large cell, thick wall structure and were rigid and hard. Microwave foaming of these compositions was also successfully demonstrated.

The processing of these foams to rigid panel configuration involved compressing the foams at 288°C (550°F) in a hot platen press to the desired thickness. This process resulted in partial densification of the panel surfaces but partial collapse of the core cell structure also occurred. This breakdown of the interior structure adversely affected the rigidity and surface hardness of the finished product. Therefore, a new technique was developed.

This technique yielded two processes both based on microwave foaming. The first process involved the use of the powder precursor and the second process involved the use of liquid precursors. The two processes are discussed below.

#### Powder Process

The process utilizing the powder precursor is based on a microwave foaming technique with constrained foam rise as shown in Figure 63. Additives were mixed with the powder resin in an Osterizer Blender for 1-2 minutes and the powder composition spread on a sheet of Teflon® coated glass at a loading of  $0.98 \text{ kg/m}^2$  ( $0.199 \text{ lbs/ft}^2$ ). The fabrication process for this type of rigid panel was discussed in Section 3.5 dealing with low density and high density panels.

Two additives, L-170 and Owens-Corning Fiberglas AA-10 unbonded glass fibers were studied to evaluate their contribution to the strength of the panels. Unbonded fibers produced the hardest product but the foam was brittle and had poor rise. As a result L-170 alone was selected for further study. The effect

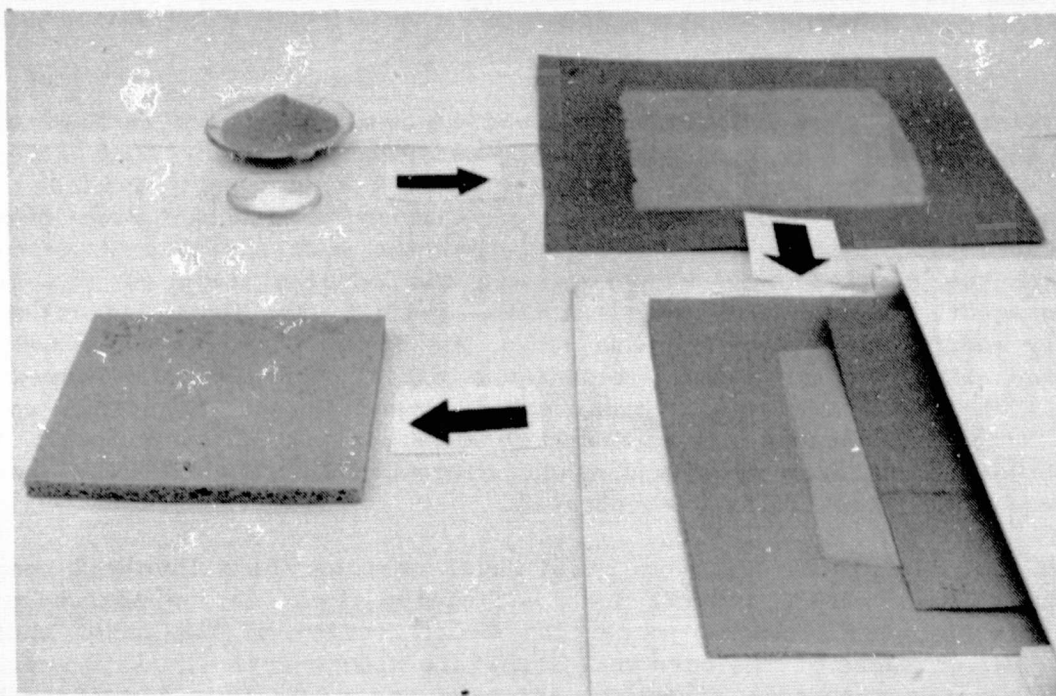


Figure 63. Fabrication of Rigid Low Density Panels From Powder Polyimide Precursors in a One-Step Microwave Process

of various concentrations of L-170 on the compressive strength of the rigid panels is illustrated in Figure 64. At concentrations of L-170 greater than 10.0 percent, the foams failed to cure.

Burn tests were performed to determine the burnthrough properties of panels made by this process. The test consisted of holding a two inch wide sample over a Meker burner [1290°C (2300°F)] for one minute. The amount of shrinkage for this type of panel was approximately 26 percent. This was considered unacceptable, so glass additives (strands, fibers, etc.) of varying concentrations were added to obtain improved fire resistance. The amount of improvement obtained was not significant due to the poor wetting characteristics of the glass. This consideration led to the second process which utilized liquid polyimide precursors.

This concluded the initial study for fabrication of rigid core panels by the powder process. The process parameters listed below are for a 413 cm<sup>2</sup> (64 in.<sup>2</sup>) panel:

|                    |   |
|--------------------|---|
| Resin              | 1702-1 no surfactant                                |
| Crosslinking agent | 1.5% L-170  |
| Loading            | 0.98 kg/m <sup>2</sup> (0.199 lbs/ft <sup>2</sup> ) |
| Microwave foaming  | 6 minutes at 5 kW                                   |
| Curing             | 30 minutes at 288°C (550°F)                         |

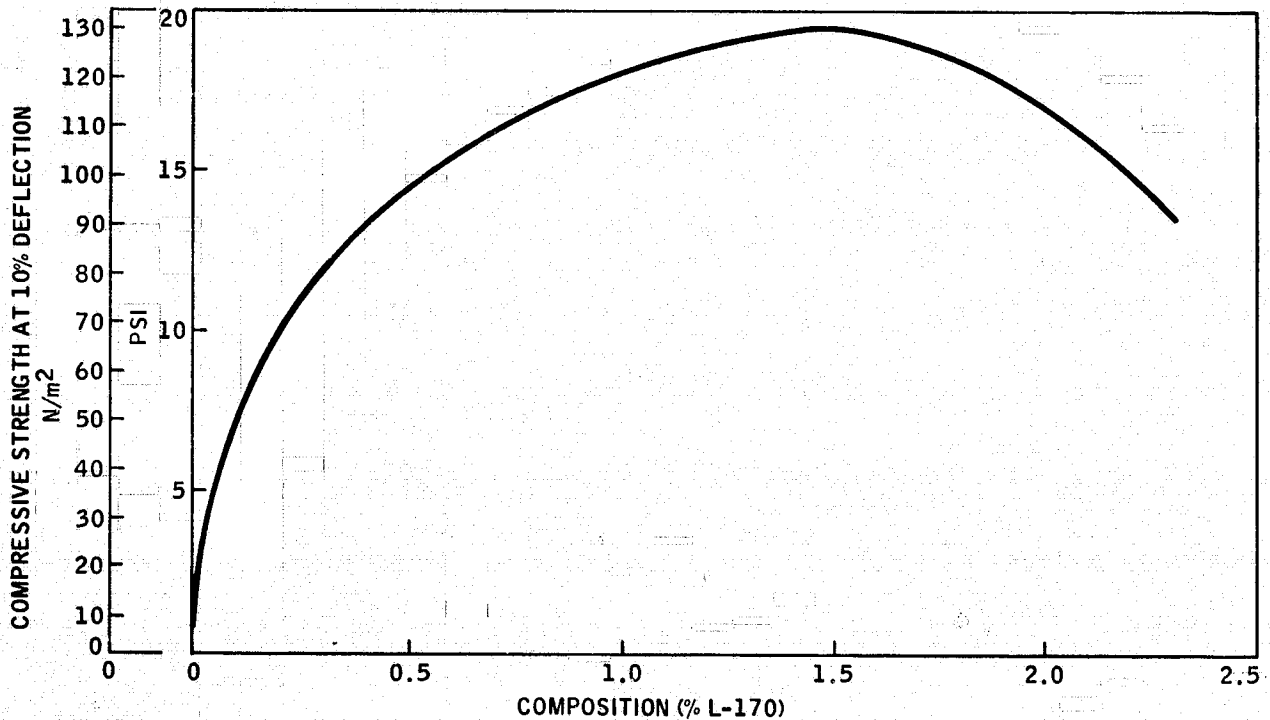


Figure 64. Effect of L-170 on Compressive Strength of Low Density Rigid Panels



## Liquid Process

Initial process parameters were taken directly from the glass filled powder process and adjusted to account for a slight change due to the presence of solvent. Therefore the initial study involved an evaluation of the drying conditions to obtain the desired foam structure. Fabrication of the panels for this study was done by a method similar to that used for the powder process and is shown in Figure 65. Foaming was carried out in the microwave oven at a power output of 5 kW followed by curing in a thermal oven at 287.7°C (550°F) for 30 minutes. The data derived from this study is listed in Table 35.

Initial drying conditions were selected by examining data taken during the study of other liquid processes. Panels #1 and #2 had a structure similar to a flexible foam, while Panel #2 failed to rise due to over-drying. Panel #3 possessed the best rise and structure, but was slightly soft. Since the combination of L-170 and unbonded glass fibers tested in the powder process yielded very hard panels, this same combination was tried in Panel #5. The panel produced by this composition and process was strong, hard and possessed an excellent structure. As a result it was selected for further studies.

This panel was produced by compounding 1702-1 liquid precursors with 2.2 percent L-170 and 1.0 percent AA-10 unbonded glass fibers (Owens Corning Fiberglas). During the drying and foaming process, a total of 40-41 percent volatiles were released which has been found to be critical to the quality

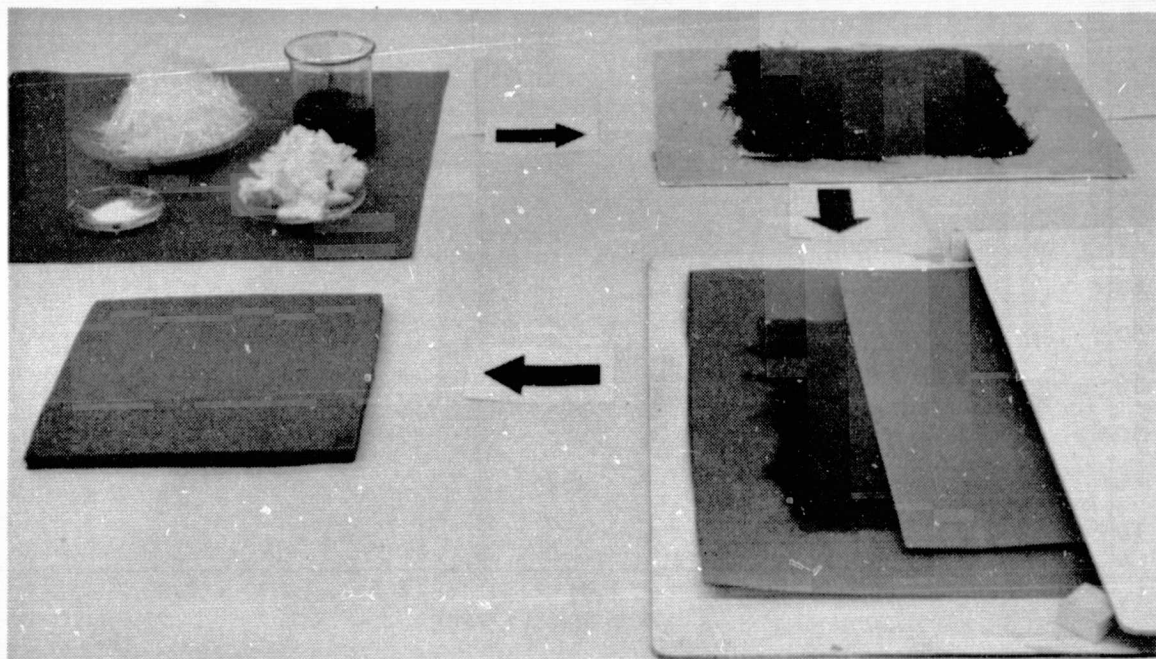


Figure 65. Fabrication of Rigid Low Density Panels From Liquid Polyimide Precursors in a One-Step Microwave Process

Table 35

Evaluation of Process Parameters for Fabrication of Low  
Density Wall Panels by the Liquid Process

| Number | Additive | (%) | Drying Temperature (°C) | Drying Time (hrs) | Foaming Behavior                   |
|--------|----------|-----|-------------------------|-------------------|------------------------------------|
| 1      | L-170    | 2.2 | 93                      | 2                 | Good rise, flexible                |
| 2      | L-170    | 2.2 | 93                      | 3                 | Low rise                           |
| 3      | L-170    | 2.2 | 82                      | 2                 | Good rise, slightly soft structure |
| 4      | L-170    | 2.2 | 71                      | 16                | Soft structure                     |
| 5      | L-170    | 2.2 |                         |                   |                                    |
|        | AA-10    | 1.0 | 82                      | 2                 | Good rise, strong structure        |

of the finished product. Best results were obtained when the evolution of volatiles during the drying process alone was in the range of 29-31 percent. After the proper drying conditions were established a study of various additives was then conducted. The results of this study are summarized in Table 36.

Table 36

Effect of Crosslinking Additives on Strength of Low Density  
Panels Made by the Liquid Process

| Additive                       | (%)        | Compressive Strength at 10% Deflection |       | Foaming Behavior          |
|--------------------------------|------------|--|-------|---------------------------|
|                                |            | N/m <sup>2</sup> x 10 <sup>3</sup>     | psi   |                           |
| None                           | 0          | 0.4                                    | 0.941 | Good rise, good structure |
| L-170                          | 2.2        | 86                                     | 12.6  | Good rise, good structure |
| AA-10 Glass Fiber              | 1.0        | 129                                    | 18.8  | Poor rise, hard structure |
| L-170 and<br>AA-10 Glass Fiber | 2.2<br>1.0 | 96                                     | 14.0  | Good rise, good structure |
| L-170 and<br>Milled Fibers     | 2.2<br>2.2 | 115                                    | 16.8  | Good rise, brittle foam   |

Selection of the best crosslinking additives was based on a combination of compressive strength, rise, and structure. Liquid polyimide precursors modified with 2.2 percent L-170 and 1.0 percent AA-10 glass fibers produced foams with the best properties.

This concluded the study of process parameters for fabrication of rigid core panels by the liquid process. The process parameters listed below are for a 413 cm<sup>2</sup> (64 in.<sup>2</sup>) panel.

|                    |   |
|--------------------|---|
| Resin              | 1702-1 no surfactant                                |
| Crosslinking agent | 2.2% L-170 and 1.0% AA-10 glass fiber               |
| Loading            | 0.98 kg/m <sup>2</sup> (0.199 lbs/ft <sup>2</sup> ) |
| Drying             | 2 hours at 82°C (180°F)                             |
| Microwave foaming  | 6 minutes at 5 kW                                   |
| Curing             | 30 minutes at 288°C (550°F)                         |

The process developed in this phase of the program represents an advancement in the art of foaming polyimide resins. With this work the task dealing with development of techniques for producing panels with low core and high density skins was completed. Optimization of this technology is reported in the next section.

#### 4.2.3 Task III - Optimization of Low Core, High Density Skin Technology

These optimization studies were carried out on both processes developed in the previous task and are discussed below.

##### Powder Process

Panels produced by the powder process made in the previous task exhibited poor flame resistance. Therefore, the study involving the use of selected reinforcing fillers was integrated with the study of process parameters. The fabrication process, used in this effort was reported in Section 4.2.2 and shown in Figure 63.

Initially milled glass fibers type 739 (Owens Corning Fiberglas) were tested at a loading of 1.21 kg/m<sup>2</sup> (0.247 lbs/ft<sup>2</sup>) and in concentrations ranging from 0 to 35 percent. Burnthrough data obtained on a Meker burner indicated that milled fibers increased the resistance to fire, however, the foam structure was brittle.

Next a study involving 0.375 cm (0.125 in.) chopped glass strands was conducted using concentrations of 10, 20 and 30 percent respectively, at a loading of 1.21 kg/m<sup>2</sup> (0.247 lbs/ft<sup>2</sup>). As the concentration of glass increased the amount of rise decreased, but the fire resistance of the foam improved.

Next a study of the effects of glass fiber length was conducted by compounding 0.3175 cm, 0.635 cm, 1.27 cm and 2.54 cm (0.125, 0.250, 0.500 and 1.00 in.) chopped glass strands with the powder resins at a concentration of 20 percent and a total loading of 1.21 kg/m<sup>2</sup> (0.247 lbs/ft<sup>2</sup>). The results are shown in Table 37.

Table 37

Effect of Glass Strand Length on Properties of Low Density Rigid Foams

| Glass Length        | Ease of Lay Up | Distribution of Glass    | Rise |
|---------------------|----------------|--------------------------|------|
| 1/8 in. (0.3175 cm) | Good           | Even                     | Good |
| 1/4 in. (0.635 cm)  | Hard           | Mostly on top            | Fair |
| 1/2 in. (1.27 cm)   | Very Difficult | Glass & powder separates | Poor |
| 1 in. (2.54 cm)     | Very Difficult | Glass & powder separates | Poor |

Due to the difficulties in working with chopped strands having a length of 1.27 cm (0.500 in.) and 2.54 cm (1.00 in.), they were abandoned from further studies. The contraction of foams obtained by compounding 0.3175 and 0.635 cm glass strands respectively with 1702-1 powder precursor modified with one percent L-170 at 0, 5, 10, 15 and 20 percent glass respectively, is shown in Figure 66.

The contraction of the foams modified with increasing loadings of 0.3175 cm (0.125 in.) glass strands failed to show any improvement. However, the contraction of foams modified with 0.635 cm (0.25 in.) glass strands decreased with increasing concentration of glass (percent contraction was 25, 25, 19, 15, and 12 at 0, 5, 10, 15 and 20 percent glass respectively) but failed to meet the expected goal of seven percent contraction obtained with carbon mat filled panels made by the conventional process described in Section 4.2.1.

It was expected that longer glass fibers would have produced the desired results, but, they had already been abandoned since they produced low foam rise and poor wetting, as shown in Table 37.

When scale-up to panels having dimensions of 81.3 x 121.9 cm (32 x 48 in.) was attempted, glass reinforcements were found to be detrimental to the amount of rise obtained during foaming. It was found that the use of any glass reinforcement (fibers, strands, milled or microballons) contributed to poor rise and densities in excess of program requirements. As a result



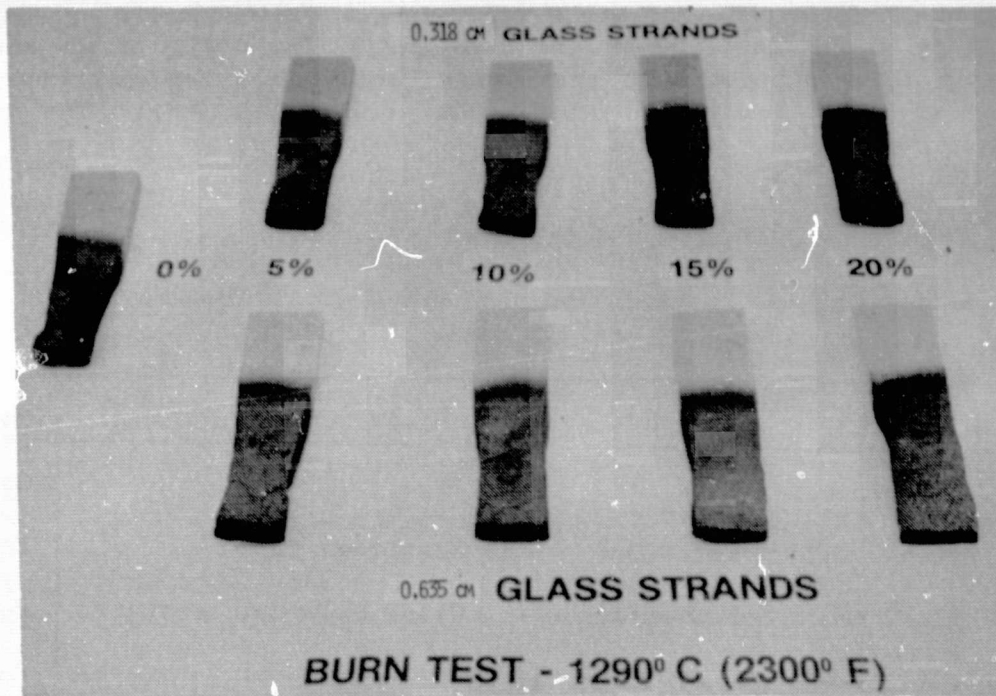


Figure 66. Wall Panels by Powder Microwave Process; Effect of Glass Strands Loading on Foam Contraction During Fire

the final core formulation for the powder process was modified to include 1702-1 (3% AS-2) powder resin and L-170 only.

To obtain a stronger product 120 style glass skins (coated with 1702-1 liquid resin) were added. An additional benefit of the glass skins was a panel with finished surfaces which is expected to require only a decorative skin for completion. In addition, the glass skins were bonded during foaming resulting in a one-step foaming bonding operation.

Fabrication of samples larger than 38.3 x 121.9 cm (32 x 48 in.) was not found to be possible at this time due to the limitation of available sizes of substrates compatible with both microwave fields and high temperatures [288°C (550°F)].

Panels having high density edges and low density cores were constructed using a two step process. The first step required the laying up of the high density edge material, described later in this section. This material was then microwave dried and flattened. The powder mixture used for the core was then added. This assembly was then foamed between two pyrex glass sheets in a microwave oven. Curing was carried out in a thermal oven at 288°C (550°F). All process parameters are summarized in Section 4.2.5, Task V.

## Liquid Process

The fabrication process used in this study was reported in Section 4.2.2 and shown in Figure 65. The procedure included blending fibers and additives into the liquid resins followed by drying and microwave foaming between two Pyrocera sheets using spacers to achieve the desired thickness.

Using this process the effects of chopped glass strand length and concentration were first investigated. The results of the studies dealing with the effect of glass fiber length on foam contraction and compressive strength are tabulated in Table 38 and illustrated in Figure 67. All panels were made at a chopped glass strand concentration of 25 percent at a loading of  $0.98 \text{ kg/m}^2$  ( $0.199 \text{ lbs/ft}^2$ ). The data show that longer glass strands contribute to decreased foam contraction during exposure to fire as was the case for the rigid panels made by the powder process. The panels made with the liquid process were easy to lay-up, and produced homogeneous foam with the glass fibers completely wetted and protected.

The results of the evaluation dealing with effect of glass fiber concentration on foam contraction and compressive strength are tabulated in Table 39 and illustrated in Figure 68. These panels were made using 2.54 cm (1 in.) chopped glass strands at a loading of  $1.03 \text{ kg/m}^2$  ( $0.213 \text{ lbs/ft}^2$ ). The foam contraction of the panels made at 30 and 40 percent chopped strands met the goal requirements.

Table 38

Wall Panels by Liquid Microwave Process; Effect of Glass Strand Length on Foam Contraction and Compressive Strength

| Glass Strands         | Compressive Strength at 10% Deflection |      | Foam Contraction (%) | Density           |                 |
|-----------------------|--|------|----------------------|-------------------|-----------------|
|                       | $\text{N/m}^2 \times 10^3$             | psi  |                      | $\text{lbs/ft}^3$ | $\text{kg/m}^3$ |
| 0.3175 cm (0.125 in.) | 90                                     | 13.2 | 25                   | 4.6               | 74              |
| 0.635 cm (0.250 in.)  | 142                                    | 20.7 | 12                   | 5.9               | 94              |
| 1.27 cm (0.50 in.)    | 111                                    | 16.2 | 10                   | 5.0               | 80              |
| 2.54 cm (1.0 in.)     | 81                                     | 11.8 | 10                   | 4.4               | 70              |

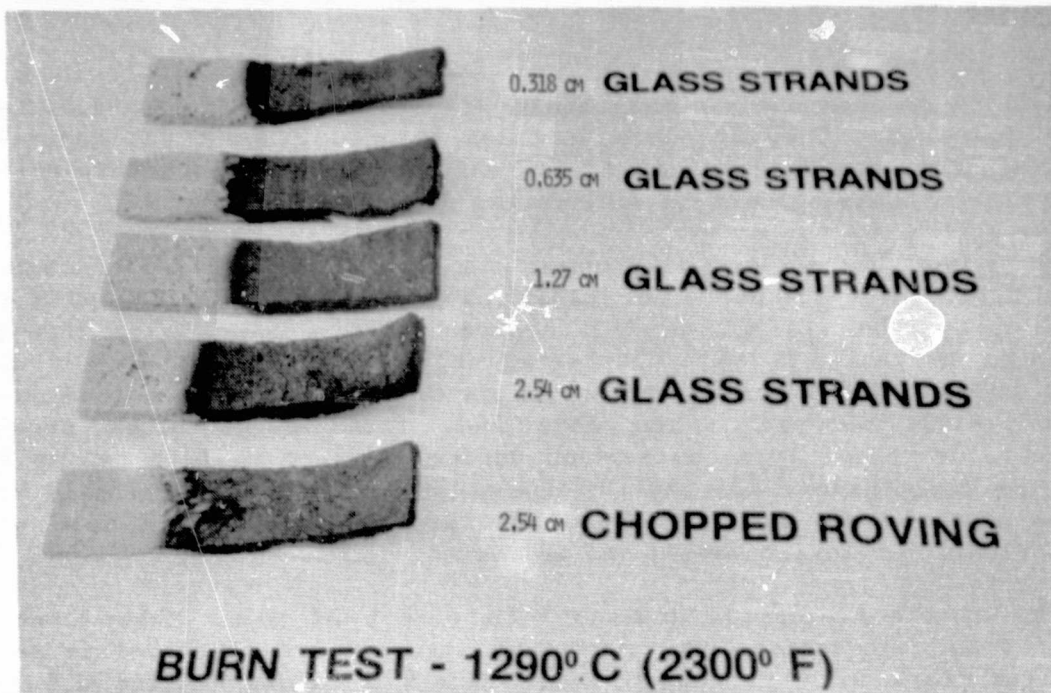


Figure 67. Wall Panels by Liquid Microwave Process; Effect of Fiber Length on Foam Contraction

Table 39

Wall Panels by Liquid Microwave Process; Effect of Glass Concentration on Foam Contraction and Compressive Strength

| Glass Concentration (%) | Compressive Strength at 10% Deflection |                                    | Foam Contraction (%) | Density             |                   |
|-------------------------|--|------------------------------------|----------------------|---------------------|-------------------|
|                         | psi                                    | N/m <sup>2</sup> x 10 <sup>3</sup> |                      | lbs/ft <sup>3</sup> | kg/m <sup>3</sup> |
| 10                      | 12.0                                   | 82                                 | 20                   | 3.6                 | 58                |
| 20                      | 14.0                                   | 96                                 | 15                   | 4.3                 | 69                |
| 30                      | 14.4                                   | 98                                 | 8                    | 5.6                 | 90                |
| 40                      | 14.1                                   | 96                                 | 5                    | 10.3                | 165               |



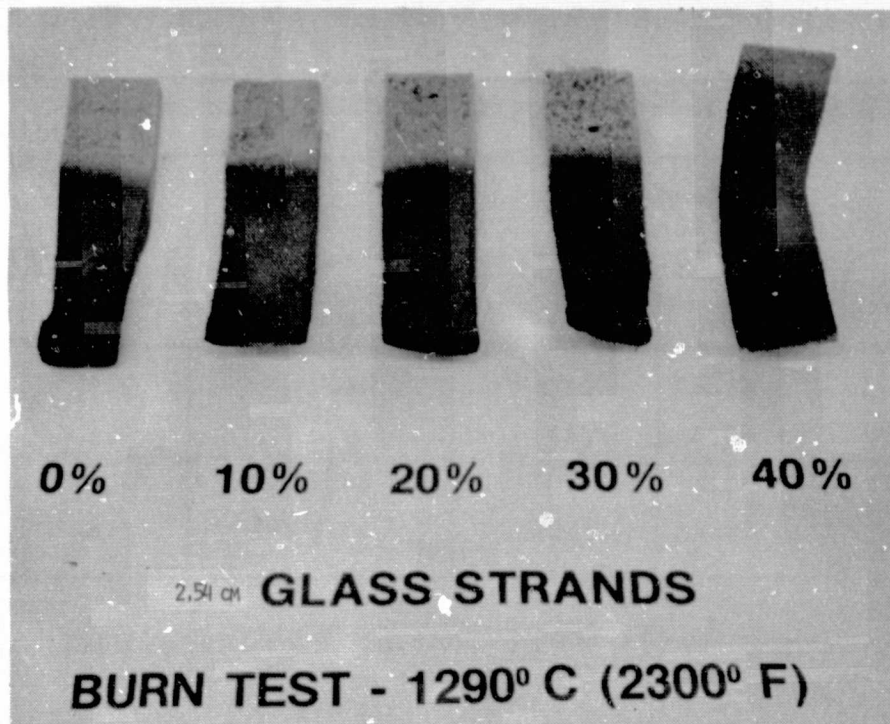


Figure 68. Wall Panels by Liquid Microwave Process; Effect of Fiber Concentrations on Foam Contraction

The results of the evaluation dealing with the effect of sizing at a constant glass strand concentration (25%) on foam contraction and compressive strength are reported in Table 40. These panels were made using 0.635 cm (0.25 in.) chopped glass strands at a loading of 0.98 kg/m<sup>2</sup> (0.199 lbs/ft<sup>2</sup>). The data show that the 405 sizing and the unsized or heat cleaned glass give the best results. Heat cleaned strands, when blended with a resin, tend to separate into individual small diameter fibers. This results in lower foam rise and a finer, higher density cellular structure as compared to a similar panel made by using 405 glass strands. Therefore to obtain a similar rise characteristic a lower concentration of heat cleaned strands was found to be necessary. In the course of these studies, some difficulty was experienced in obtaining reproducibility with the panels made using the 405 sized glass strands. This was attributed directly to a compatibility problem. A comparison of panels made with the 405 type sized strands and the unsized strands is given in Table 41 and illustrated in Figure 69. On the basis of these results and because of the incompatibility of the 405 sizing, the heat cleaned strands were selected for the candidate composition.

In an attempt to obtain improved fire resistance and higher panel strength a process was developed to bond integral woven glass fabrics on both surfaces of the rigid panels during the foaming process. The process involved coating the glass fabric with the liquid 1702-1 resin upon which was placed the resin composition reinforced with 30 percent 1.27 cm (0.5 in.) glass strands. A second sheet of coated glass fabric completed the lay-up. After drying at

Table 40

Wall Panels by Liquid Microwave Process; Effect of Glass Fiber Sizing on Foam Contraction and Compressive Strength

| Glass Fiber Sizing | Compressive Strength at 10% Deflection |                                    | Foam Contraction % | Density             |                   |
|--------------------|--|------------------------------------|--------------------|---------------------|-------------------|
|                    | psi                                    | N/m <sup>2</sup> x 10 <sup>3</sup> |                    | lbs/ft <sup>3</sup> | kg/m <sup>3</sup> |
| None               | 51.8                                   | 354                                | 6                  | 9.5                 | 152               |
| 405                | 63.6                                   | 434                                | 9                  | 9.4                 | 150               |
| 419                | 15.6                                   | 107                                | 19                 | 5.3                 | 85                |
| 832                | 18.4                                   | 126                                | 13                 | 5.6                 | 90                |

Table 41

Effect of Sizing on Properties of Wall Panels

| Glass Strand Sizing | % Glass Strands | Compressive Strength at 10% Deflection |                                    | Foam Contraction (%) | Density             |                   |
|---------------------|-----------------|--|------------------------------------|----------------------|---------------------|-------------------|
|                     |                 | psi                                    | N/m <sup>2</sup> x 10 <sup>3</sup> |                      | lbs/ft <sup>3</sup> | kg/m <sup>3</sup> |
| 405                 | 25              | 64                                     | 435                                | 9                    | 9.0                 | 144               |
| None (Heat Cleaned) | 10              | 55                                     | 374                                | 7                    | 9.0                 | 144               |

82°C (182°F) the composition was foamed in a microwave oven between Pyroceram sheets. Total loading of the system was 1.4 kg/m<sup>2</sup> (0.290 lbs/ft<sup>2</sup>) which is within the limit established for wall panels. The panels were tested for foam contraction and compressive strength and the data reported in Table 42.

The data show that the addition of woven glass fabric enhanced the shrinkage resistance and the compressive strength of the product. In addition, the burnthrough resistance of the foams subjected to a Mapp gas burner was found to meet the five minutes requirement. Failure occurred by cracking of the skin as shown in Figure 70.

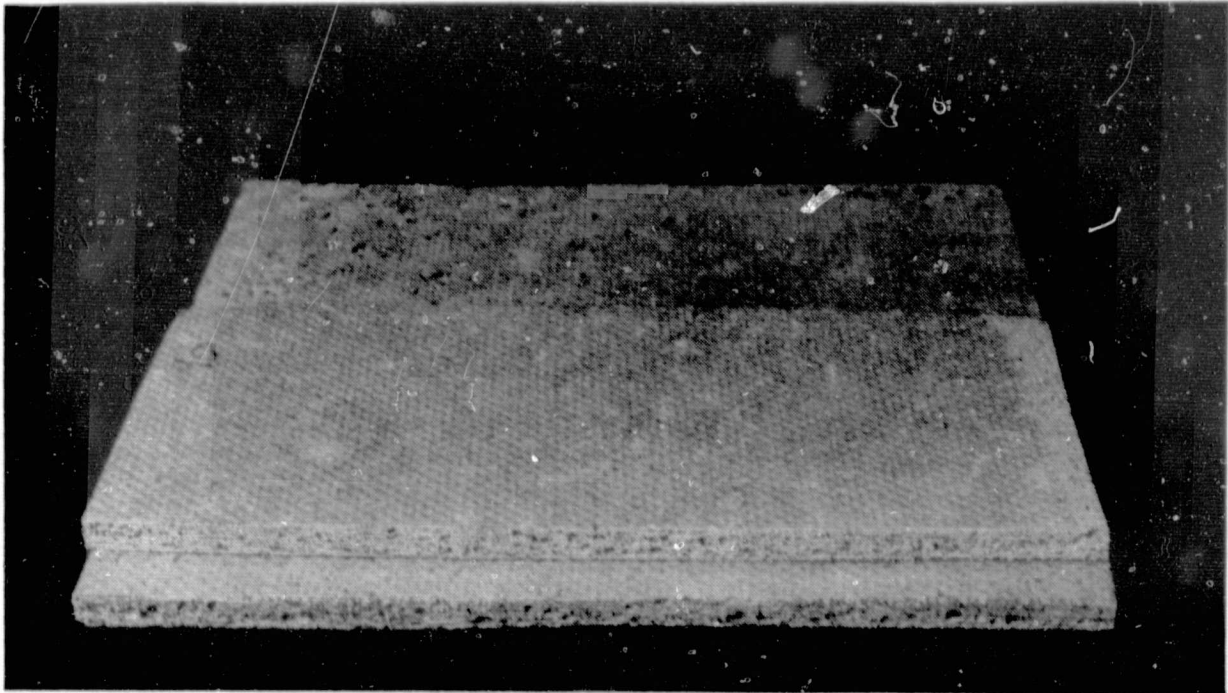


Figure 69. Comparison of Cellular Structure of Panels Made With Unsized Glass Strands (top) and Type 405 Sizing Glass Strands (bottom)

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Table 42

Wall Panels by Liquid Microwave Process; Effect of Woven Glass Skins on Foam Properties

| Panel Configuration | Density |                   | Compressive Strength at 10% Deflection |                                    | Foam Contraction (%) | Weight |                   |
|---------------------|---------|-------------------|--|------------------------------------|----------------------|--------|-------------------|
|                     | pcf     | kg/m <sup>3</sup> | psi                                    | N/m <sup>2</sup> x 10 <sup>3</sup> |                      | psf    | kg/m <sup>2</sup> |
| Woven glass skins   | 7.3     | 117               | 32.3                                   | 221                                | 5                    | 0.305  | 0.149             |
| Woven glass skins   | 7.1     | 114               | 21.5                                   | 147                                | 5                    | 0.293  | 0.143             |
| Foam only           | 5.6     | 90                | 14.4                                   | 98                                 | 8                    | 0.206  | 0.101             |

Additional optimization studies of the liquid process were carried out. These included an evaluation of pyrex glass for use as a substrate during the foaming process. Pyrex was found to be compatible with the high frequency radiation and to yield good rigid foams.

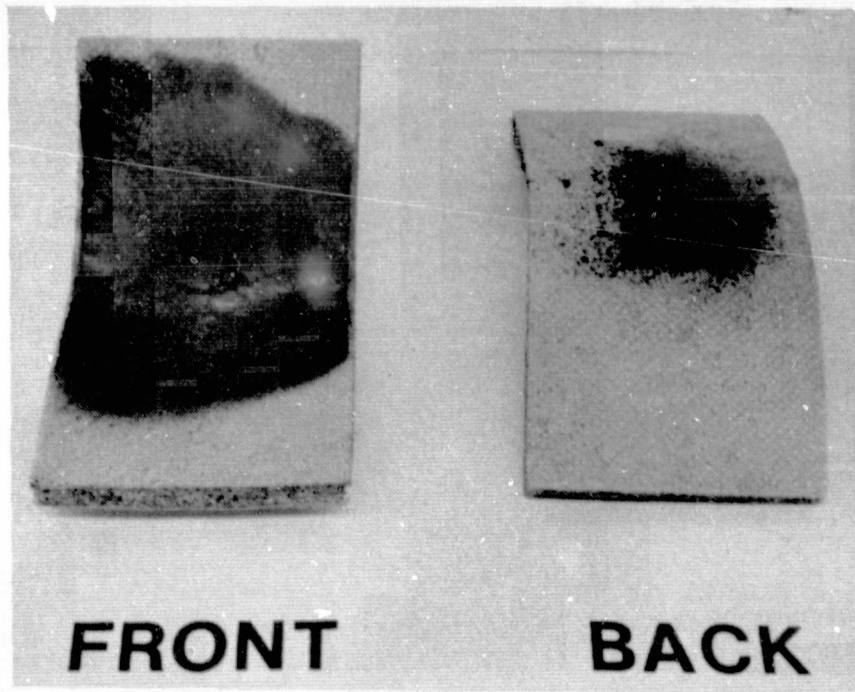


Figure 70. Burnthrough Resistance of Wall Panels With Integral Woven Glass Skin. Five Minutes Exposure to a Mapp Gas Burner

An improvement of the liquid microwave process involved the investigation of drying the panels in a microwave field as described in Section 3.5. This was a significant improvement over thermal drying because the heating occurs evenly throughout the mixture as opposed to thermal drying where the drying is uneven. The optimum time for drying of the panels was determined by the volatile loss (29-31% for a 20 phr resin dilution).

The advantage of microwave drying is shorter time and more even drying. This formed the basis for the selection of microwave drying process for all subsequent work.

The development of a microwave drying process and the use of heat cleaned glass strands led to the selection of a new series of process parameters. The parameters for a 413 cm<sup>2</sup> (64 in.<sup>2</sup>) panel are:

- . Resin System: 1702-1, no surfactant  
Additives: 2.2% L-170 crosslinking agent
- . Reinforcement: 10% 0.635 cm (0.25 in.) unsized chopped glass strands  
1% fiberglass batting (type PF-105-700, Owens-Corning)



- Skins: 120 style satin weave glass cloth impregnated with diluted resin mixture
- Charge Loading: 1.20 kg solids/m<sup>2</sup> (0.245 lbs/ft<sup>2</sup>)
- Microwave Drying Cycle: 2.25 minutes at 1.25 kW
- Substrates: Pyroceram or Pyrex
- Microwave Foaming Cycle: 6 minutes at 5 kW
- Curing: 30 minutes at 288°C (550°F)

Wall panel cores made at the conditions listed above exhibit densities and compressive strengths similar to those listed in Table 42 for heat cleaned glass. The densities of these panels were too high to meet program requirements, so studies were undertaken to reduce the densities.

The first study involved the modification of the parameters listed above by reducing the loading and concentration of glass strand fillers. A minimum density was reached at a glass fiber concentration of 5 percent and a loading of 0.62 kg/m<sup>2</sup> (0.127 lbs/ft<sup>2</sup>). Below this loading the panel exhibited inadequate rise. However, the density (96 kg/m<sup>3</sup>; 6 lbs/ft<sup>3</sup>) of this panel still exceeded the program requirement of 48-64 kg/m<sup>3</sup> (3-4 lbs/ft<sup>3</sup>) for a wall panel core.

The second study involved the replacement of glass strands with C-15X microballoons (3M & Company). At a minimum loading for adequate rise of 0.54 kg/m<sup>2</sup> (0.11 lbs/ft<sup>2</sup>) and 5 percent C-15X, a panel was obtained with a density of 78 kg/m<sup>3</sup> (4.9 lbs/ft<sup>3</sup>). This panel is shown in Figure 71. Physical testing of the panel gave a compressive strength at 10 percent deflection of 102 N/m<sup>2</sup> (15 lbs/ft<sup>2</sup>) and a burn contraction of 23 percent.



Figure 71. Wall Panel Core by Microwave Process Having Density Less Than 80 kg/m<sup>3</sup> (5 lbs/ft<sup>3</sup>)



Scaling up of this formulation to 81.3 x 121.9 cm (32 x 48 in.) resulted in a panel with numerous large holes and imperfections. Attempts to remedy this problem were not successful. Other deficiencies included spotty rise and inhomogeneous foaming. Due to these problems and the fact that the powder process had already been scaled-up successfully, the liquid process development was abandoned at this point.

The last effort of this task involved work dealing with development of multi-density panels.

Two processes were developed to produce a panel with an integral high density edge (blocking material). The first process involved layers of fiberglass cloth impregnated with liquid resin. This process was soon abandoned because of difficulties in fabrication.

The second process was carried out by compounding 30 percent C-15X (3M & Company) glass microballoons with 70 percent 1702-1 liquid resin (20 phr; no surfactant). This paste-like formulation was then spread out in the desired shape at a loading of 2.05 kg/m<sup>2</sup> (0.42 lbs/ft<sup>2</sup>) for a 0.635 cm (0.25 in.) thick panel. Drying, foaming and curing were carried out in the same manner as liquid microwave drying process for low density wall panels.

This material was tested for direct screw withdrawal in accordance with ASTM D-1761 and machinability as required. The results of the direct screw withdrawal testing are presented in Table 43. Figure 72 illustrates a panel and Figure 73 illustrates the results of the machinability testing.

Water absorption was tested in accordance with ASTM D 2842-69 (1975) except the underwater weighing rig was not used. As a criteria a major aircraft manufacturer specification was used. Initial results indicated that the blocking material absorbed excessive amounts of water. To remedy this problem L-170 was added. The results of this study are summarized in Table 44, the best candidate formulation being 25 percent microballons, 20 percent L-170 and 55 percent 1702-1 liquid resin.

Table 43

Screw Withdrawal Test of Blocking Material

|               | Density             |                   | Force |     |
|---------------|---------------------|-------------------|-------|-----|
|               | lbs/ft <sup>3</sup> | kg/m <sup>3</sup> | lbs   | N   |
| Actual        | 16                  | 256               | 196   | 872 |
| Specification | 16                  | 256               | 150   | 668 |

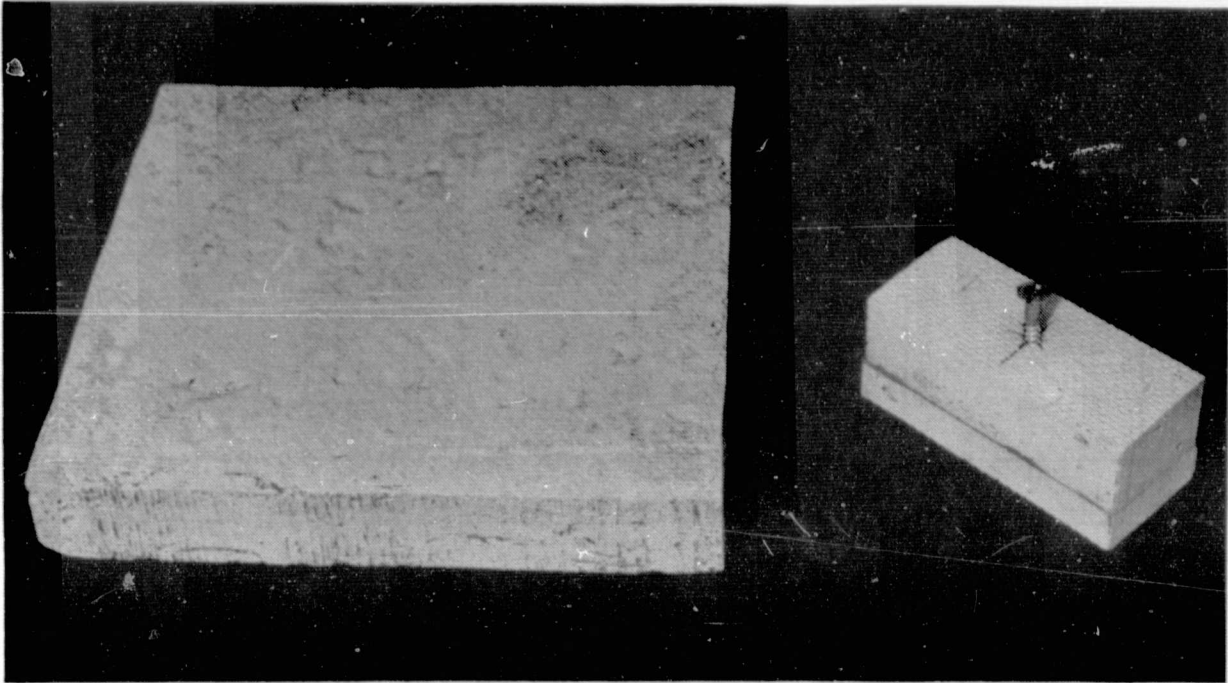


Figure 72. Example of Blocking Material (30% C-15X Microballoons) and Direct Screw Withdrawal Test Specimen

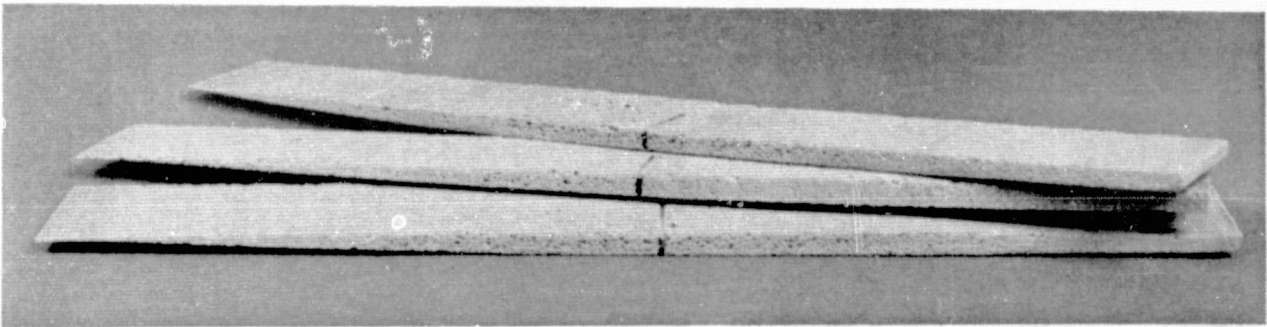


Figure 73. - Blocking Material Machined to a Feather Edge

A small panel has been made incorporating the blocking material into a wall panel made by the liquid process. This panel (Fig. 74) was constructed by, first, laying out the paste-like blocking material to the correct configuration. This was then dried in the microwave oven until 29-31 percent volatile loss had been achieved. The wet core was then added to complete the layout. This assembly was then microwave dried as previously described. The dried assembly was then foamed between two preheated pyrex sheets in the microwave oven. Curing was accomplished in a thermal oven at 287°C (550°F).

Table 44

Water Absorption Testing of Blocking Material

| Sample | Microballoons (%) | L-170 (%) | Water Absorption (%) |
|--------|-------------------|-----------|----------------------|
| 1      | 35                | --        | 37.4                 |
| 2      | 30                | 10        | 34.1                 |
| 3      | 30                | 15        | 31.0                 |
| 4      | 25                | 20        | 19.4                 |

Specification (at 18 lbs/ft<sup>3</sup>) approximately 8 percent

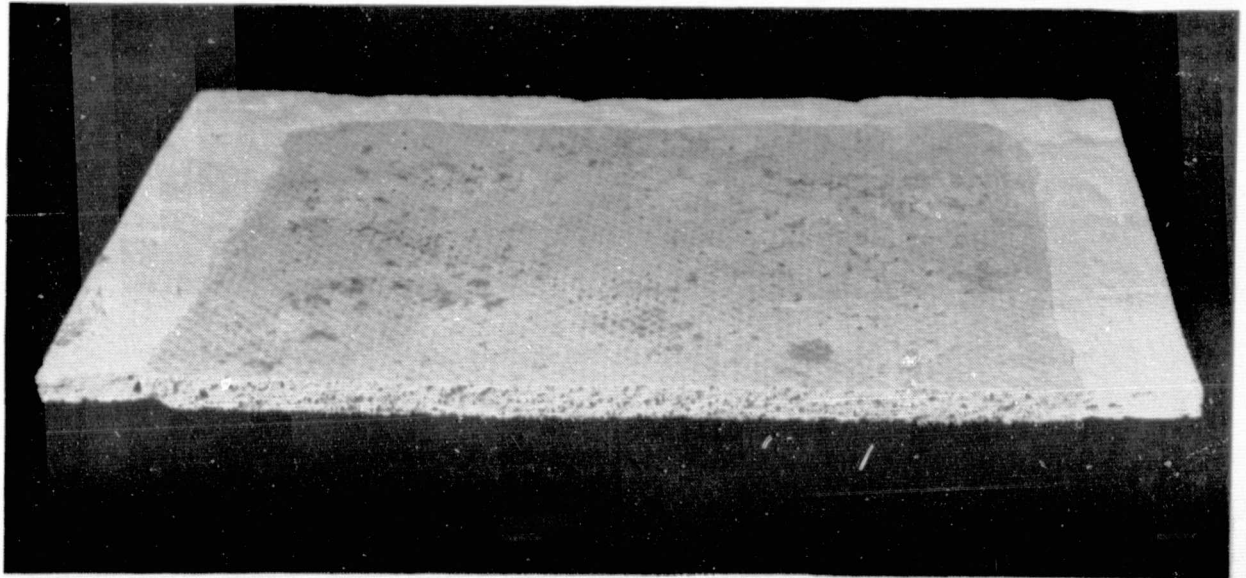


Figure 74. Wall Panel With Integral Blocking Material Edge

#### 4.2.4 Task IV - New Configurations and Reinforcements

The effort of this task which deals primarily with fabrication of low density wall panels by filling honeycomb structures, has been carried out in the task dealing with floor panels and reported in Section 4.3.2. This technology is completely applicable to fabrication of wall panels.

#### 4.2.5 Task V - Process Parameters and Screening of Candidates

This task deals with the evaluation of surface active agents, additives, B-staging parameters and selection of candidates for advanced testing by fabrication of large samples. The study of surface active agents has already been discussed in Section 4.2.1, Task I. The B-staging parameter study was discussed in Section 4.2.2, Task II and is summarized in Table 45 of this section for the microwave foaming method. The parametric study of additives was discussed in Section 4.2.2, Task II.

The most practical process as pointed out in Section 4.2.3, Task III, is the microwave drying process because of shorter time cycle, evenness of drying and a superior product. The largest panel core fabricated to date having dimensions of 53 x 79 x 1.27 cm (21 x 31 x 0.5 in.), is shown in Figure 75.

Table 45

B-Staging Parameters for One Step Wall Panels  
(Based on Panel Area of 413 cm<sup>2</sup>, 64 in.<sup>2</sup>)

| Panel Type     | B-Stage Method | Parameters  |
|----------------|----------------|---|
| Liquid Process | Microwave      | 1.25 kW for 2.25 minutes  |
|                | Thermal        | 82°C (180°F) for 120 minutes  |
| Powder Process | Spray Dry      | Inlet temperature 100°C (212°F)<br>Outlet temperature 70°C (158°F)<br>Time required: approx. 1 min. |

The parameters used in the fabrication of this panel are listed in Table 46 and compared to those used for a 20 x 20 cm (8 x 8 in.) panel.

In Table 46, pyrex has been selected as the foaming substrate. This was necessary due to the small size available for Pyrocera. Pyrex itself is also limited in size, the largest size available being 144 x 113 cm (57 x 44 in.). This limited the maximum size a wall panel could be made. The pyrex foaming rig installed in the 15 kW microwave is shown in Figure 76.

Table 46

**Process Parameters for the Fabrication of Large and Small  
Wall Panel Cores by the Liquid Process**

| Parameter     | Area of the Wall Panel Core                          |  |
|---------------|--|--|
|               | 4200 cm <sup>2</sup> (651 in <sup>2</sup> )          | 413 cm <sup>2</sup> (64 in <sup>2</sup> )            |
| Loading       | 0.119 kg/m <sup>2</sup> (0.245 lbs/ft <sup>2</sup> ) | 0.119 kg/m <sup>2</sup> (0.245 lbs/ft <sup>2</sup> ) |
| Thickness     | 1.27 cm (0.50 in.)                                   | 1.27 cm (0.50 in.)                                   |
| Substrate     | Pyrex  | Pyroceram  |
| Glass Strands | 25% 0.635 cm (0.25 in.)<br>Type 405                  | 30% 0.635 cm (0.25 in.)<br>Type 405                  |
| Drying        |  |  |
| Power         | 1.25 kW  | 1.25 kW  |
| Time          | 10 minutes   | 2.25 minutes   |
| Foaming       |  |  |
| Power         | 5.0 kW   | 5.0 kW   |
| Time          | 17 minutes   | 6 minutes  |
| Curing        |  |  |
| Temperature   | 288°C (550°F)  | 288°C (550°F)  |
| Time          | 45 minutes   | 30 minutes   |

During the course of the study involving the fabrication of large samples, it was found desirable to preheat the pyrex glass substrate prior to foaming. This preheat cycle resulted in higher rise giving a lower density product. The amount of time required to heat the sheets to the desired temperature [121-149°C (250-300°F)] was found to be dependent upon the mass of the sheets and the power level of the microwave energy.

Table 47 shows the process parameters used to fabricate samples of different sizes.



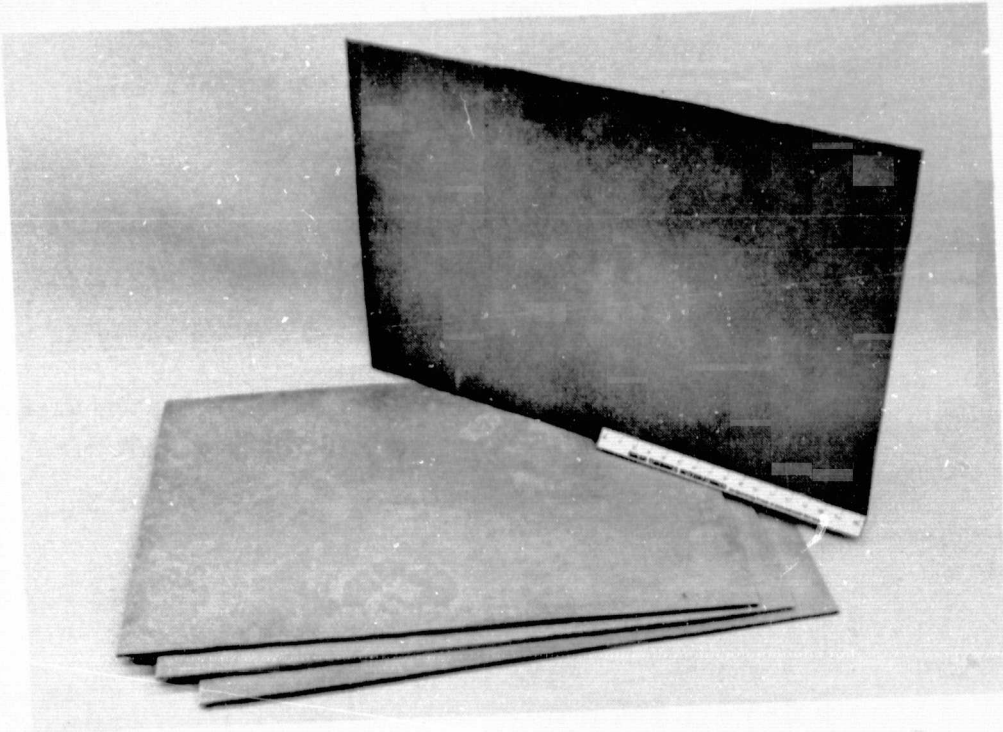


Figure 75. Scale-Up of Low Density Wall Panel Core

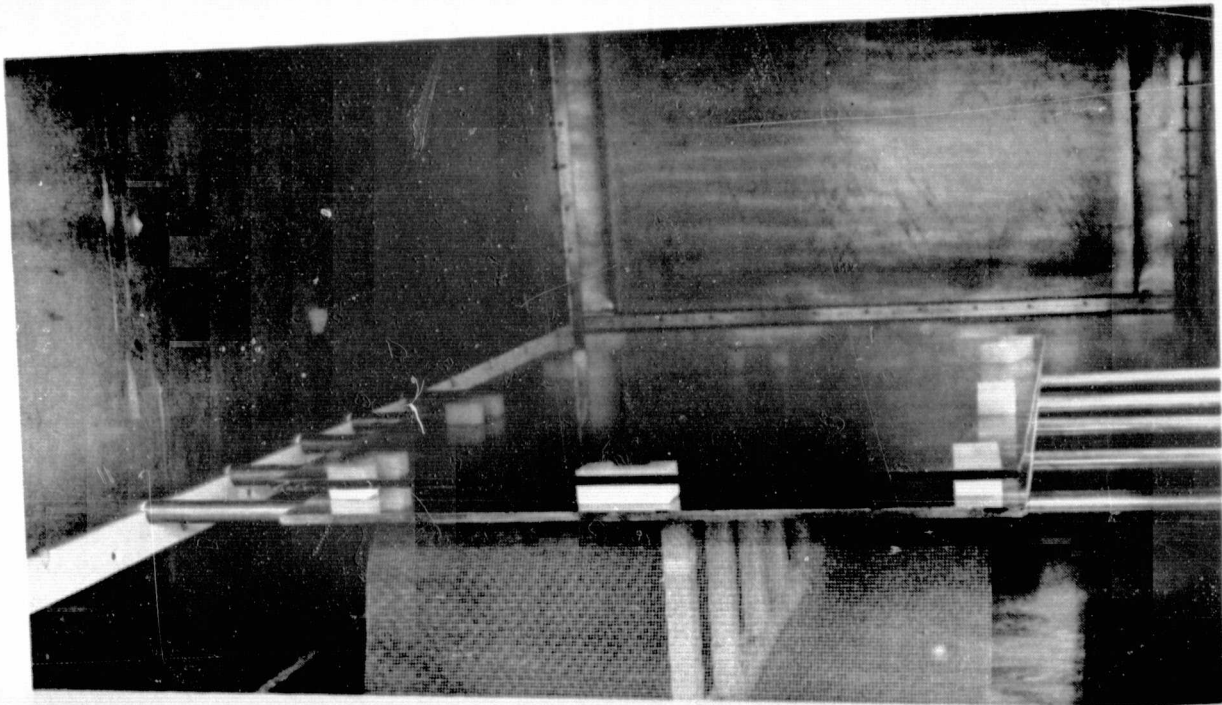


Figure 76. Pyrex Foaming Rig Installed in the 15 kW Microwave Oven

Table 47

**Process Parameters for the Fabrication of Wall Panel  
Cores by the Powder Process**

| Parameter                              | 0.991 m <sup>2</sup> (10.7 ft <sup>2</sup> )                     | 0.468 m <sup>2</sup> (5.04 ft <sup>2</sup> )                     |
|--|--|--|
| Loading                                | 0.070 kg/m <sup>2</sup> (0.143 lbs/ft <sup>2</sup> )             | 0.070 kg/m <sup>2</sup> (0.143 lbs/ft <sup>2</sup> )             |
| Thickness                              | 0.635 cm (0.25 in.)  | 0.635 cm (0.25 in.)  |
| Layup Substrate                        | Teflon® Coated Glass<br>(Taconic Plastics)                       | Teflon® Coated Glass<br>(Taconic Plastics)                       |
| Coating Thickness                      | 1.78 cm (0.70 in.)   | 1.22 cm (0.48 in.)   |
| Foaming<br>Substrate                   | Pyrex<br>(144 x 123 x 1.60 cm;<br>57 x 44 x 0.63 in.)            | Pyrex<br>81 x 112 x 1.60 cm;<br>32 x 44 x 0.63 in.)              |
| Reinforcement                          | 2 sheets 120 style satin<br>weave glass cloth<br>(Owens-Corning) | 2 sheets 120 style satin<br>weave glass cloth<br>(Owens-Corning) |
| Preheat<br>Model<br>Power<br>Time      | Custom 15 kW (GFE)<br>10 kW<br>15 minutes                        | 4115<br>5 kW<br>20 minutes                                       |
| Foaming<br>Power<br>Time               | 10 kW<br>20 minutes  | 5 kW<br>20 minutes   |
| Curing<br>Model<br>Temperature<br>Time | Despatch<br>288°C (550°F)<br>60 minutes                          | Blue M<br>288°C (550°F)<br>45 minutes                            |

Shown in Figure 77 are the full size wall panel cores with attached skins submitted to NASA-JSC. A finished wall panel, complete with skins is shown in Figure 78. A curved wall panel with high density edges is shown in Figure 79.

The low density core, high density edge wall panel was prepared as described in Section 4.2.3 - Task III. The process parameters used are the same as those listed for the 0.468 m<sup>2</sup> (5.04 ft<sup>2</sup>) wall panel in Table 47.

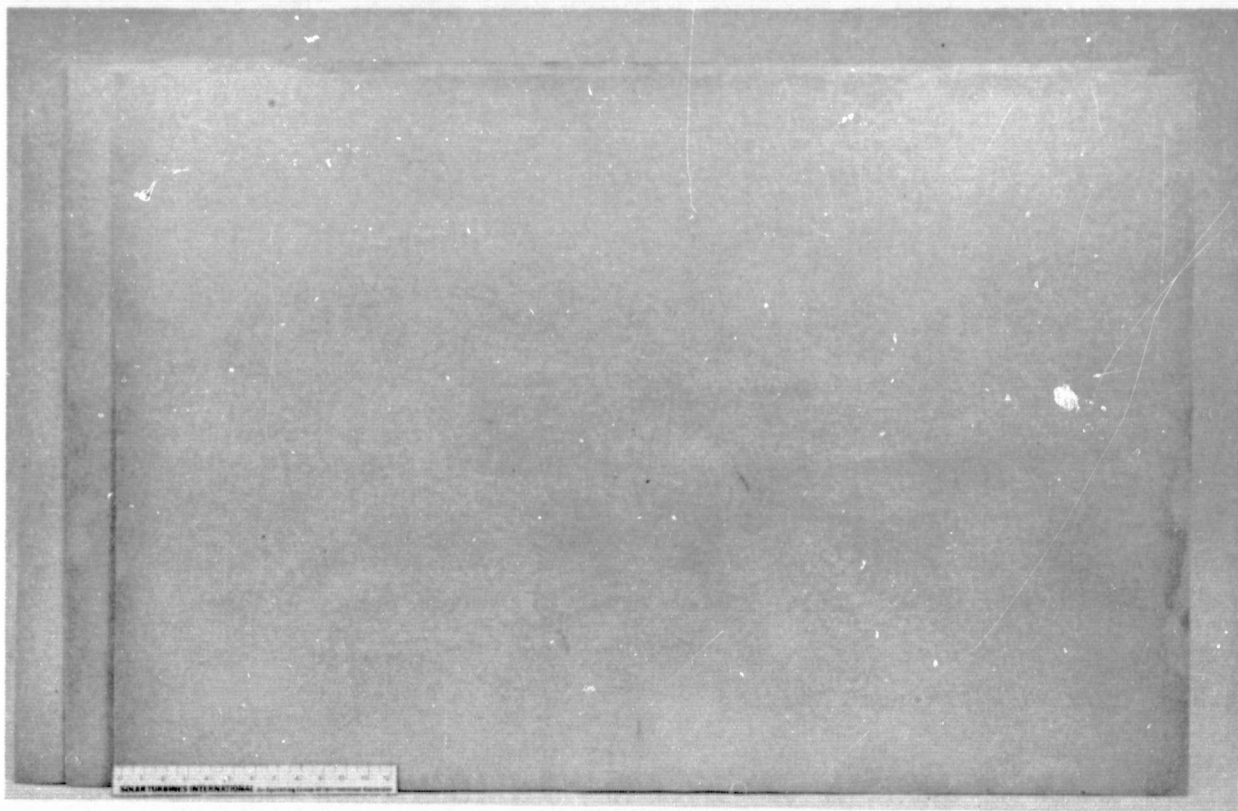


Figure 77. Full Size Wall Panel Cores [0.991 m<sup>2</sup> (10.7 ft<sup>2</sup>)]

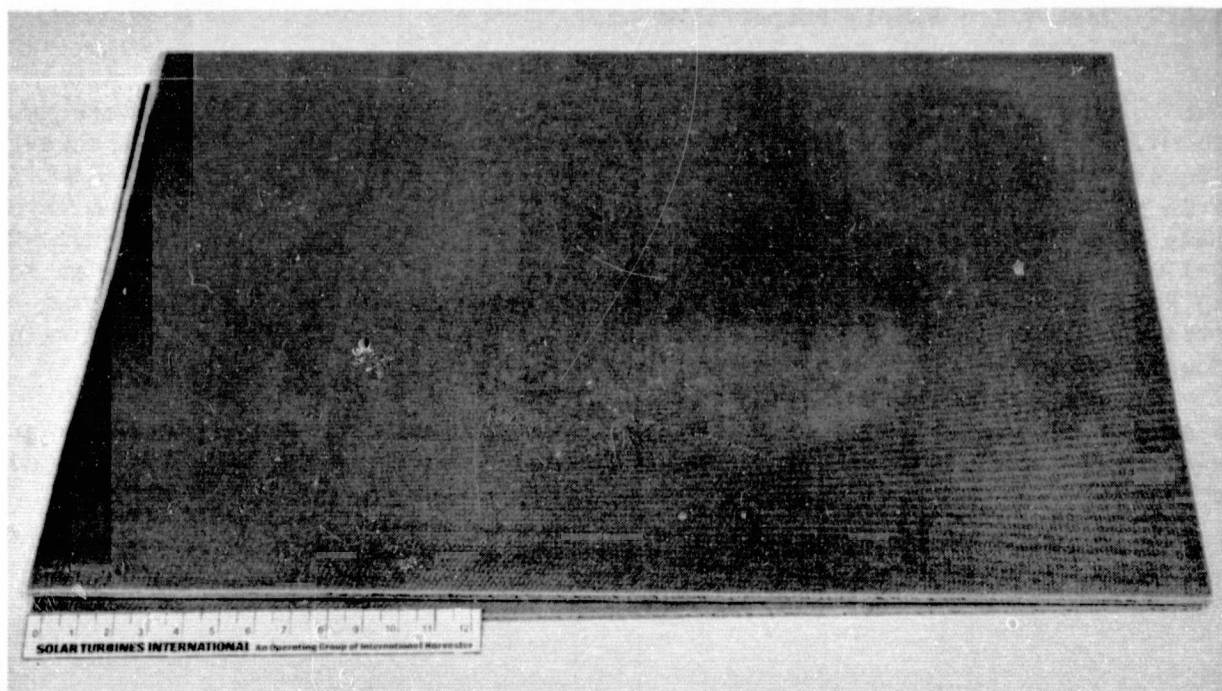


Figure 78. Finished Wall Panel

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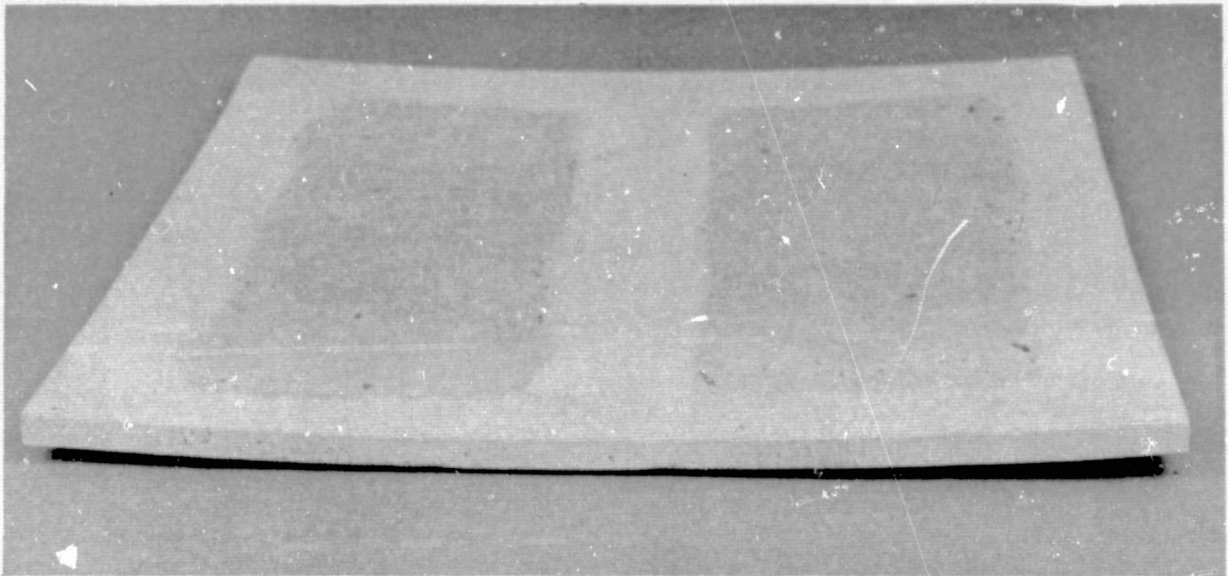


Figure 79. Curved Wall Panel With High Density Edge

#### 4.2.6 Task VI - Advanced Testing

The selection of the final candidate for characterization was made based on mechanical data, appearance and the ability to scale-up the panels to large size. The test samples were prepared as previously described in Sections 4.2.4 and 4.2.5. A summary of the results is given in Table 48.

#### 4.2.7 Task VII - Sample Preparation

Due to limitations in the size of commercially available glass substrates the 1.3 x 2.6 m (4 x 8 ft) panel could not be fabricated by the microwave process described previously. Three samples having dimensions of 0.81 x 1.22 m (32 x 48 in.) were produced instead (see Fig. 77). These panels were made from 1702-1 powder resin modified with 3 percent AS-2 and 1.5 percent L-170 and foamed between two coated 120 style satin weave glass fabric at 10 kW for 20 minutes followed by a thermal postcure at 288°C (550°F) for a period of one hour. The one-step microwave process produced a panel with facing skins bonded to the core.

A sample of a wall panel with multiple density characteristics shaped to an ellipse was also produced using a modification of the process and submitted to NASA-JSC.

Table 48

Summary of Results - Low Density Wall Panels

| PROPERTY                        | METHOD         | UNITS                                   | GOAL                             | ACTUAL                |
|---------------------------------|----------------|---|----------------------------------|-----------------------|
| Density                         | ASTM D 1622    | lb/ft <sup>3</sup><br>Kg/m <sup>3</sup> | 1.0 - 5.0 (1)<br>16 - 80         | 8.39 (2)<br>134.2 (2) |
| Weight                          |                | lb/ft <sup>2</sup><br>Kg/m <sup>2</sup> | 0.25 - 0.30 (3)<br>1.23 - 1.48   | 0.175 (2)<br>0.86     |
| Machinability                   | -              | in<br>cm                                | 0.0312 Maximum<br>0.029 Breakout | <0.0312<br><0.029     |
| Direct Screw<br>Withdrawal      | ASTM D 1761    | lbf<br>N                                | 150<br>668                       | 196<br>872            |
| Sandwich Peel<br>Strength       | 90° Peel       | lbf<br>N                                | 10<br>45                         | 13.2<br>59.4          |
| Water Absorption                | ASTM D 2842-69 | %                                       | 3 Maximum                        | 4.0                   |
| Oxygen Index                    | ASTM D 2863    | -                                       | 40 Minimum                       | 42                    |
| Smoke Density<br>DS Uncorrected | NBS            | -                                       | 30-50                            | 1                     |
| TGA                             | -              | °C<br>°F                                | Stable to 204.4<br>Stable to 400 | 400<br>750            |

(1) Core only  
 (2) Includes integral skin  
 (3) Finished panel

### 4.3 PRODUCT III - HIGH STRENGTH FLOOR PANELS

The work carried out in this phase of the program involved studies of optimization of the floor panels previously developed, transfer of technology from the task dealing with low density wall panels, and development of new floor panel core configurations, selection of candidates and final testing.

#### 4.3.1 Task I - Optimization of the Rigid Polyimide Foam Panel

This task deals with the optimization of the high density rigid foam technology through evaluation of resin precursors and reinforcements to achieve improved load bearing and fatigue characteristics. The first objective of the task included study of foam reinforcing materials, which were discussed in Section 4.2.1 in the task dealing with low density foam panels. Therefore, this effort represents a transfer of technology from work presented previously. This was followed by re-evaluation of the resin precursors for use in this application.

The results of the initial resin reinforcement study are given in Table 32 reported in section 4.2.1. From this work the following materials were selected for this application: chopped carbon mat (VMC grade, Union Carbide) and chopped glass strands of various sizings and lengths.

The carbon mat reinforcement gave foams with a homogeneous, fine cell structure which could be either compressed or sectioned to give desired foam density and thickness. For high strength applications, optimum carbon concentration was found to be in the range of 8 to 15 percent. The lower carbon concentration resulted in slightly higher foam rise but corresponding lower strength. Compression test data for chopped strands and chopped carbon mat reinforced cores are given in Table 49. A study was then undertaken to evaluate the effect of glass sizing on foaming. This study consisted of combining 1702-0 liquid resin precursor with chopped strands of different sizings supplied by Owens Corning Fiberglas. Figure 80 shows the effect of sizing on foaming behavior of 1702-0 filled with 20 percent chopped strands. It is evident that the 832BC and 419BB sizings allowed a significantly higher foam rise than did the 405AA sizing. Next, to determine the effect of glass concentration on the panel strength, studies were done using both 832BC and 405AA strands at 0.635 cm (1/4 in.) length. Panels were made at glass concentrations of 10, 20, 30, 40, 50 and 60 percent respectively for each of the two sizings and are shown in Figures 81 and 82. In both cases foam rise decreased with increased glass concentration. Foams were then compressed to rigid panel configuration and subsequently tested for compressive strength. This testing revealed that the strongest foams were those reinforced with 20 to 30 percent of the 405AA glass. Panels reinforced with the 832 glass exhibited lower strength at the same concentrations. However, in all cases, the glass reinforced rigid foams do not have the strength or the rigidity of the carbon reinforced foam at comparable densities. Combining small quantities of chopped carbon mat reinforcement with the chopped glass strands

Table 49

Mechanical Properties of Rigid Panels Made  
With Various Reinforcements

| Reinforcement                                       | Compressive Strength<br>Load at 0.3 Strain |     |
|---|--|-----|
|   | N/m <sup>2</sup> x 10 <sup>6</sup>         | psi |
| 20% 832 BC 0.635 cm (1/4 in.) chopped glass strands | 1.20                                       | 175 |
| 20% 405 AA 0.635 cm (1/4 in.) chopped glass strands | 1.60                                       | 235 |
| 40% 832 BC 0.635 cm (1/4 in.) chopped glass strands | 1.16                                       | 170 |
| 40% 405 AA 0.635 cm (1/4 in.) chopped glass strands | 1.40                                       | 205 |
| 20% 832 BC 0.635 cm strands + 5% VMC carbon mat     | 2.26                                       | 330 |
| 10% VMC carbon mat                                  | 3.18                                       | 465 |

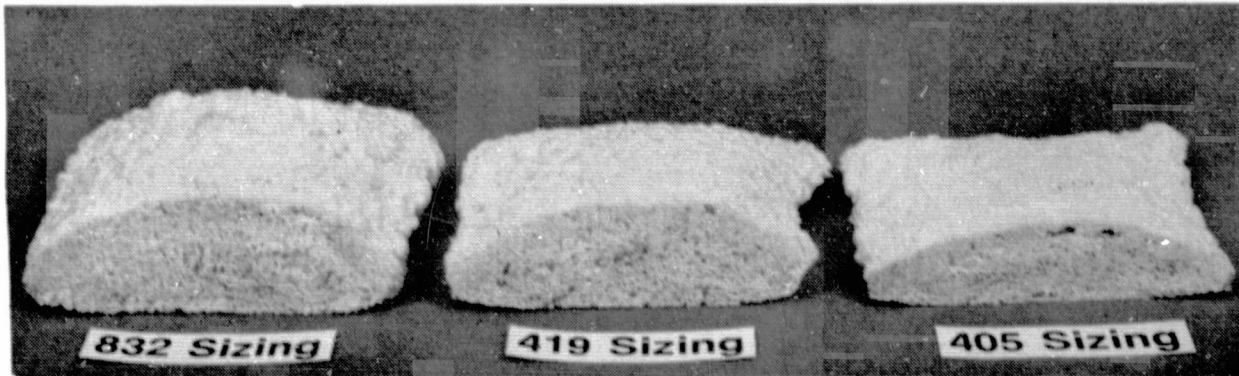


Figure 80. 1702-0 Glass Reinforced Rigid Foam; Effect of Sizing on Foam Properties

resulted in rigid foams with significantly improved strength, however, best results were still obtained with chopped carbon mat reinforcement alone. The data show that chopped carbon mat reinforced polyimide foam cores meet the minimum compressive strength requirements for use in underseat applications.

Process parameters have been defined for foaming the 1702-1 resin systems to rigid foam configurations and these are discussed in Section 4.2.1. One of the significant differences encountered between the two resin systems was the amount of foam rise at a given reinforcement concentration. Rigid foams made with 1702-1 possessed slightly lower rise characteristics than a similar

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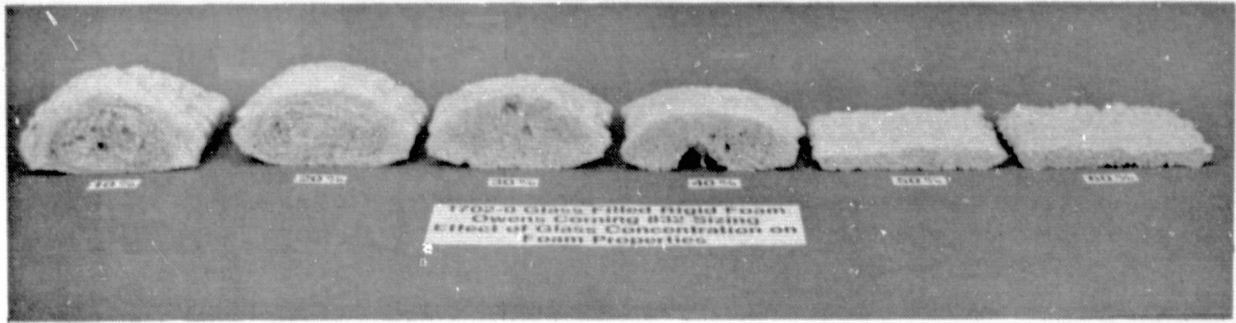


Figure 81. 1702-0 Glass Reinforced Rigid Foam Owens Corning 832 Sizing; Effect of Glass Concentration on Foam Properties

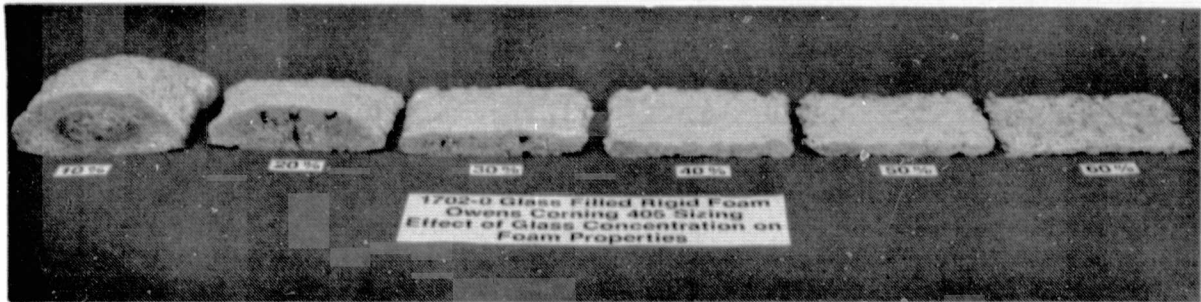


Figure 82. 1702-0 Glass Reinforced Rigid Foam Owens Corning 405 Sizing; Effect of Glass Concentration on Foam Properties

formulation using 1702-0 resin. This was a disadvantage in the task dealing with development of the wall panels because of the low density, high rise requirements. However, for higher density floor panel cores this characteristic resulted in an advantage because less compression is required to achieve panel configuration and therefore less foam structure deformation takes place. The compressive strength of foams made with 1702-0 and 1702-1 resins reinforced with the same level of chopped strands showed no detectable differences. Because the 1702-1 resin was used in wall panel applications this same system was selected also for use in the fabrication of polyimide foam floor panel cores.

#### 4.3.2 Task II - New Rigid Panel Configuration

The work carried out in this task is divided into two parts for clarity. The first part outlines the studies dealing with optimization of the process to produce polyimide foam filled honeycombs; the second part covers the development work carried out to fabricate polyimide core floor panels utilizing technology developed in the task dealing with preparation of low density wall panels, reported in Section 4.2.2.

## Polyimide Foam Filled Honeycombs

The major objective of this task is the development of rigid foam core panels possessing higher compressive strength for use in high traffic areas of interior aircraft.

The first phase of this task involved re-evaluating the foam filled honeycomb technology developed previously (Ref. 2) followed by optimization of the process to meet the specific requirements of low cost, high strength and improved flame resistance. For these studies, phenolic coated Nomex honeycomb panels identical to the type currently used in aircraft interior floor panel applications were used. These panels had a thickness of 0.95 cm (0.375 in.) and a cell size of 0.635 cm (0.25 in.)

The process involved dipping the honeycomb panels into a liquid resin mixture to fully coat the cells followed by a drying cycle to evolve the solvent. The panels were then foamed to completely fill the honeycomb cells. The panels were finished by curing followed by trimming the excess foam to flush with the panel surface.

The first step in the optimization of this product was the redefinition of the process parameters. This was carried out through a series of time-temperature studies using small scale samples. Typical results showed that a 929 cm<sup>2</sup> (1.0 ft<sup>2</sup>) coated with a dilute mixture of 1702-1 required a drying cycle of 3.0 hours at 104°C (220°F) to achieve optimum cell filling. Larger panels were found to require only slightly larger drying periods at the same temperature.

The flame resistance was improved by reinforcing the resin with graphite micromesh powder at a final solids concentration of 10 percent graphite/90 percent polyimide. The addition of this reinforcement resulted in a higher viscosity mixture which improved the cell coating during the dipping operation. No significant changes in the drying parameters were required with this mixture.

The second phase of this effort involved the fabrication of foam filled honeycombs starting with uncoated or nude Nomex honeycomb. These panels were prepared using the process described for the coated honeycomb panels.

Figure 83 shows both polyimide foam filled and unfilled samples of nude Nomex honeycomb. This process improved the fire resistance of the rigid panel, but, more important, the compressive strength of the material increased substantially from  $1.03 \times 10^6$  N/m<sup>2</sup> (150 psi) for the unfilled honeycomb to  $3.0 \times 10^6$  N/m<sup>2</sup> (440 psi) for the polyimide foam filled material. This type of panel meets the requirements for underseat floor panel applications.

In the last part of this study the feasibility of a coating-foaming process was investigated. This was achieved by preheating the honeycomb material at 288°C (550°F) followed by spray coating. It was found that the liquid sprayed resin dried immediately after coming into contact with the preheated honeycomb surface thus eliminating the need for the drying step. This process

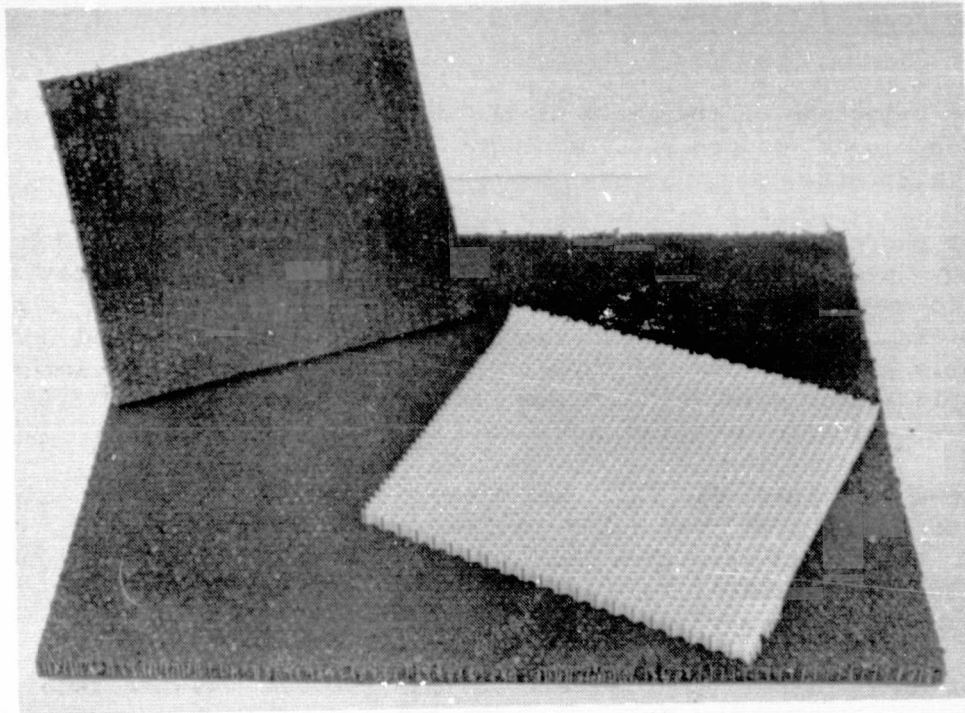


Figure 83. Polyimide Foam Filled Nude Nomex Honeycomb

permits immediate foaming of spray coated nude or phenolic coated honeycombs in a single step process. The compressive strength and foaming behavior of the panels produced with this process were comparable to those obtained with the more time consuming dipping and drying process used previously.

With the successful adaptation of the foam filling process to the uncoated honeycomb, it was not considered economically feasible to develop a honeycomb structure using polyimide impregnated glass strips as described in the proposal. By coating and reinforcing existing honeycomb structures, panels with superior burnthrough characteristics can be produced.

#### One-Step Microwave Foaming Process

This effort involved a transfer of technology from the one-step microwave technique developed for the low density wall panels. The concentration of additives and reinforcements and the microwave drying and foaming parameters were used as the basis for the higher density floor panel studies.

The first step involved increasing the loading sufficiently to give panels in the 144 to 240 kg/m<sup>3</sup> (9 to 15 pcf) density range. Microwave drying parameters were then established for these size parts. As was discussed in Section 4.2.1, drying parameters have been defined for 1702-1 resin systems using thermal processes. The optimum results were obtained when the percen-



tage of solvent lost was between 29 and 31 percent by weight of the original amount of resin at a dilution ratio of 20 phr. Using this optimum resin loss percentage, drying periods were established for the microwave cavity. With a power setting of 1.25 kW, drying times were found to be in the range of 2-1/2 minutes for 413 cm<sup>2</sup> (64 in.<sup>2</sup>) panels to 12 minutes for 1264 cm<sup>2</sup> (196 in.<sup>2</sup>) panels.

The next step involved substituting heat cleaned or unsized chopped glass strands for the 405AA. A series of rigid foam panels were made using these strands at concentrations that varied from 10 to 30 percent in five percent increments. These panels were prepared using the microwave drying and foaming techniques. The panel reinforced with 30 percent unsized strands had a slightly finer, denser structure than the panel reinforced with 30 percent 405AA sized glass strands.

Subsequent compression testing of the one step foam cores reinforced with 30 percent unsized strands showed them to be comparable, on a strength density basis, with the previously produced panels made using the free rise foam-compress to shape technique. Specifically, a 240 kg/m<sup>3</sup> (15.0 PCF) panel had a compressive strength of 1.64 x 10<sup>6</sup> N/m<sup>2</sup> (238 psi) at 0.3 strain.

To further improve the foam structure, glass microballoons were next evaluated as an auxiliary filler. A series of panels were made combining heat cleaned glass strands with 3M glass microballoons, Type C15X. These microballoons were selected on the basis of their low bulk density and their anticipated compatibility with the polyimide resin and the foaming process.

In these panels the concentration of microballoons was varied from 5 to 30 percent and the concentration of unsized glass strands was varied from 0 to 30 percent. The panels were prepared using microwave techniques and were evaluated on the basis of the following: ease of lay up of resin mixture, dimensional changes of laid up panel during drying and foaming, resulting panel surface, resulting foam structure and panel hardness and rigidity. The panels developed in this study exhibited the highest strength and rigidity of any glass reinforced foams produced thus far. On the basis of the criteria listed above, optimum results were obtained with a reinforcement consisting of 12.5-15.0 percent glass microballoons and 7.5 to 10 percent unsized 0.635 cm (1/4 in.) chopped glass strands. Panels with this composition had a compressive strength at 0.3 strain of 3.58 to 4.35 x 10<sup>6</sup> N/m<sup>2</sup> (520 to 630 psi) at a panel core density of 240 kg/m<sup>3</sup> (15.0 pcf). These test results show that this combination of glass strands and microballoons when used in conjunction with the one step microwave process, produces foams with higher strength than foams produced from carbon mat reinforced using the more involved free rise and compression technique. Also, high density foams of this panel composition possessed hard surfaces which would require a reinforcing skin on one side only or none at all. This property will be further studied in the next task. A 0.56 m<sup>2</sup> (6 ft<sup>2</sup>) size sample of this composition is shown in Figure 84.

In the course of the effort involving the studies of glass strands and glass microballoons, panels with high glass concentrations were evaluated. These

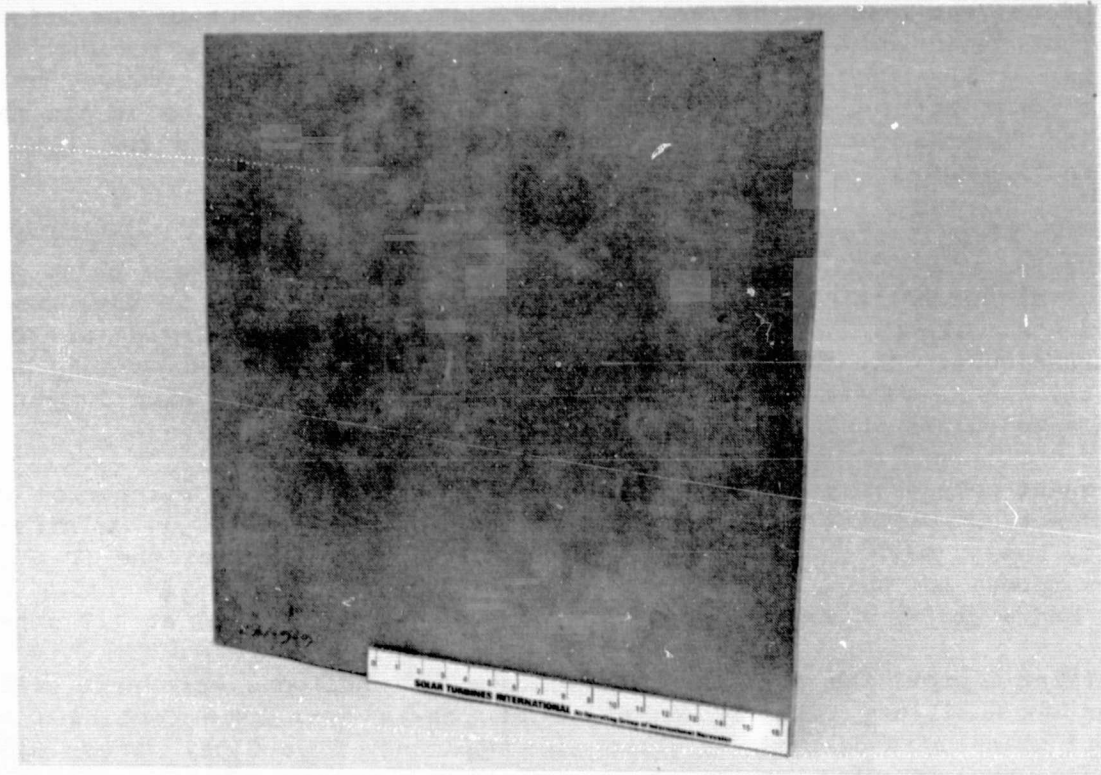


Figure 84. Floor Panel Core - One-Step Microwave Process  
Size 0.56 m<sup>2</sup>

panels had varying properties depending on the type and concentration of the reinforcement. Foams reinforced with 50-60 percent chopped strands lacked good surfaces due to resin starvation and difficulty of lay up. The maximum concentration of unsized chopped strands proved to be in the area of 30 to 40 percent, higher concentrations resulted in a very thick mixture which required significantly longer lay up time. Foams reinforced with 30 percent glass microballoons had a almost solid structure and were subsequently developed into panel edging or blocking material (see Section 4.2.4). For panel core applications, none of the high glass content compositions represented an improvement over the optimum strand/microballoon composition described above.

#### 4.3.3 Task III - Process Parameters and Screening of Candidates

This task covers the work dealing with the optimization of the microwave process to fabricate the rigid foam core candidate developed in the previous task. This effort was pursued through each of the following major stages of fabrication:

- a) compositional studies

- b) lay-up studies
- c) foaming studies

### Composition Studies

The first step was a re-evaluation of the contribution of the various additives and reinforcements to the properties of the finished panel core with respect to fabrication of large scale samples. The work reported in the previous section indicated that the combination of the unsized glass strands and microballoons had the most significant effect on panel strength; also the work done as part of the wall panel development revealed that a cross-linking agent concentration of 2.2 percent based on polyimide solids significantly improved foam rigidity. A study was therefore conducted to determine the effect of the unbonded glass batting in conjunction with the other reinforcements. Panels were made varying the unbonded glass batting/microballoon ratio. These preliminary experiments showed that the addition of the glass batting did not improve the strength, the cellular structure, or the rigidity of the panels when used in conjunction with the microballoons, therefore, the unbonded glass was deleted from the panel formulation.

Slight formulation changes were also found to be necessary during the scale-up efforts. During the task of preparation of larger size samples [0.56 to 1.11 m<sup>2</sup> (6-12 ft<sup>2</sup>)], surface uniformity became harder to achieve, therefore, the concentrations of the glass strands and glass microballoons were each dropped by two percent to improve the foam rise and subsequent panel surface. Also to facilitate lay up and achieve slightly more homogeneous mixture, the resin dilution was increased.

### Lay-up Studies

During scale-up, difficulties were encountered in achieving uniform solvent evolution from the larger area of the panels. Excess solvent usually is evidenced by darker foam color, coarser structure and more brittle foam. To improve panel drying a two stage lay up and dry process was initiated. This involved laying up half the resin mixture over the entire panel area followed by microwave drying. The remaining mixture was then laid up on top of this layer followed by second stage drying. This process resulted in uniform solvent evolution throughout the panel and improved panel surfaces. Typical drying cycles for a 1.11 m<sup>2</sup> (12 ft<sup>2</sup>) panel were found to be 15 minutes for the first stage followed by a 30 minute for the second stage using a power output of 10 kW.

## Foaming Studies

When the microwave method was used to develop the process parameters the development size panels [0.092 m<sup>2</sup> (1 ft<sup>2</sup>)] possessed good thickness and flatness uniformity, but during the scale up efforts, problems were encountered in maintaining these tolerances. Even in the fabrication of the 0.56 m<sup>2</sup> (6 ft<sup>2</sup>) panels, enough foaming pressure was generated to distort the 1.27 cm (0.50 in.) pyrex plate that formed the foaming mold. Therefore, for the larger size samples 1.11 m<sup>2</sup> (12 ft<sup>2</sup>), the thickness of the foaming plates was increased to 1.59 cm (0.625 in.). This tool was found to be the most suited for this application and produced panels within the required thickness tolerances. The apparatus was shown in Figure 76 as it was assembled in the 15 kW microwave oven.

The panel process parameters used for fabrication of the glass reinforced foam core panels by the one step microwave process is given below.

|                |  |
|----------------|--|
| Resin:         | 1702-1 modified with 2.2 percent crosslinking agent  |
| Reinforcement: | 10.5 percent glass microballoons, 3M type C15X<br>8.0 percent unsized chopped strands, 0.635 cm (1/4 in.)<br>Owens Corning |
| Dry:           | Two stage lay up and dry<br>Power 4 kW, time 35-45 minutes   |
| Foam:          | Open sided pyrex mold, thickness 1.59 cm (0.625 in.)<br>Power 15 kW  |
| Cure:          | Thermal oven at 288°C (550°F), time dependent on panel<br>area   |

Rigid foam core panels produced by this process are shown in Figure 85.

### 4.3.4 Task IV - Advanced Testing

The final characterization and testing of the candidate foam panel material was carried out in accordance with the specific test procedures given in the Work Statement.

For the tests which required completed panel specimens, several floor panel cores were laminated with 0.010 inch unidirectional glass joined using DMS 1911 epoxy film adhesive. The panels are shown in Figure 86. The flammability and smoke density tests were conducted on the core material alone to obtain an accurate indication of their performance in these areas. The complete results of the advanced testing of the candidate floor panel material are given in Table 50.

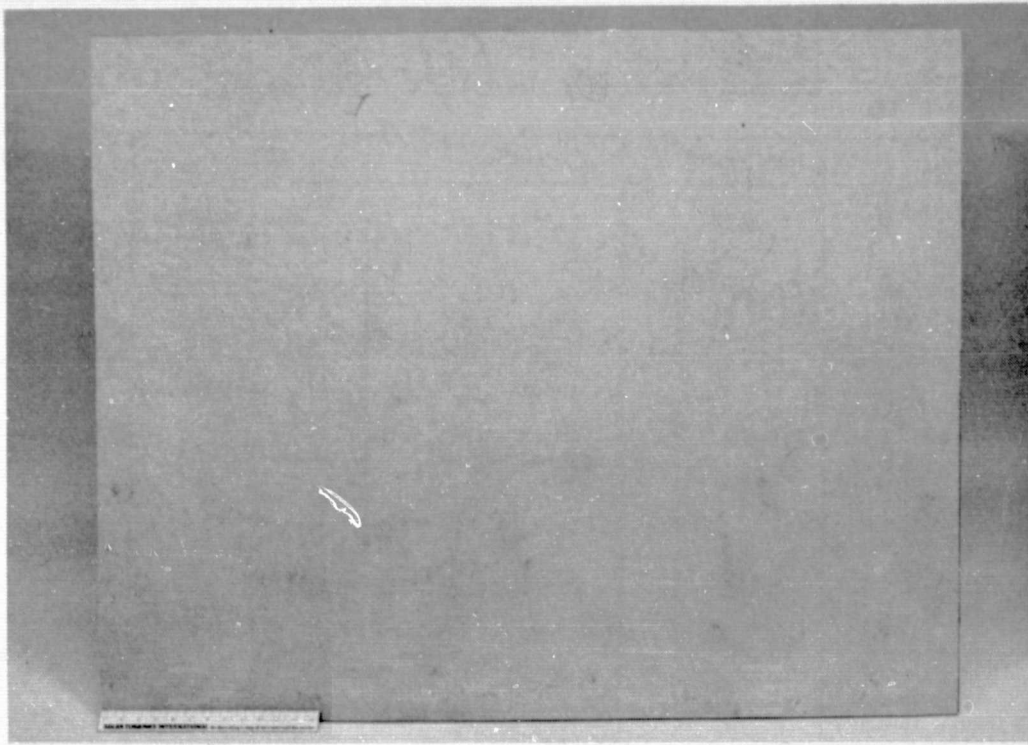


Figure 85. Floor Panel Core - One Step Microwave Process  
Size 1.2 m<sup>2</sup>

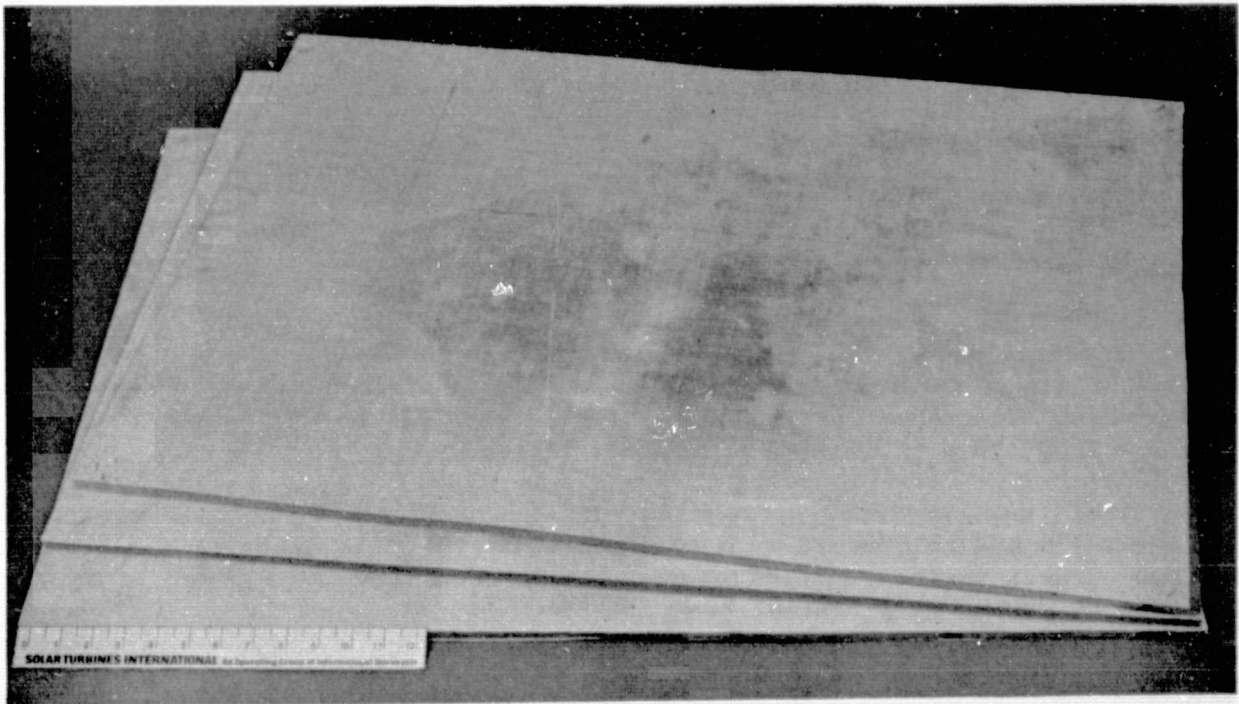


Figure 86. Floor Panel Cores With Unidirectional Glass Skins

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Table 50

## Advanced Testing Results - Floor Panel

| PROPERTY                            | TEST METHOD | UNITS                                   | GOAL   | ACTUAL                       |
|-------------------------------------|-------------|---|--|------------------------------|
| Weight                              | D 1622      | Kg/m <sup>2</sup><br>lb/ft <sup>2</sup> | 0.029 - 0.040<br>0.70 - 0.95                   | 0.043<br>1.03                |
| Thickness                           | C-366       | cm<br>in                                | 0.99 - 1.27<br>0.39 - 0.50                     | 1.27<br>0.50                 |
| Compressive Strength                | C-365       | N/m <sup>2</sup><br>lb/in <sup>2</sup>  | 11.7 x 10 <sup>6</sup> minimum<br>1700 minimum | 5.9 x 10 <sup>6</sup><br>855 |
| Warpage                             | (1)         | cm of warp/m<br>in of warp/ft           | 0.208<br>0.025                                 | 0.083<br>0.010               |
| Impact Strength                     | (1)         | Kg-cm<br>in-lb                          | 34.5 - 41.4<br>30-36                           | 34.5<br>30                   |
| Gain in Weight after Humidity Aging | (1)         | %                                       | 6.0 max  | 3.9                          |
| Core Shear Strength                 | C 393       | N<br>lbf                                | 1221<br>275                                    | 3046<br>686                  |
| Panel Flexure Strength              | C 393       | N<br>lbf                                | 1021<br>230                                    | 995<br>224                   |
| Long Beam Bending                   | (1)         | cm of deflection<br>in of deflection    | 2.03<br>0.80                                   | 1.02<br>0.40                 |
| Sandwich Peel Strength              | 90° Peel    | N/m<br>lbf/in                           | 1.12<br>10                                     | 1.30<br>11.5                 |
| Oxygen Index                        | D-2863      | -                                       | 40 min   | 42                           |
| Smoke Density                       | NBS         | -                                       | 30-50  | 0                            |

(1) Test method from Work Statement

## 4.3.5 Task V - Sample Preparation

Due to limitations in the size of commercially available glass substrates the 1.3 x 2.6 m (4 x 8 ft) panel could not be fabricated by the microwave process described previously. Three samples having dimensions of 0.91 x 1.22 m (36 x 48 in.) were produced instead.

These panels were produced by foaming 1702-1 liquid resin modified with 2.2 percent L-170 and reinforced with 10.5 percent type C15-X glass microballoons and 8.0 percent unsized chopped glass strands (0.25 in.) at a power of 10 kW followed by curing in a thermal oven at 288°C (550°F).

The samples were submitted to NASA-JSC.



#### 4.4 PRODUCT IV - THERMAL ACOUSTICAL INSULATION

The studies undertaken in this phase of the program start with advanced polyimide synthesis (Sec. 4.4.1), followed by foaming studies (Sec. 4.4.2), development of modified glass mat insulation materials (Sec. 4.4.3), prototype and selection (Sec. 4.4.4), final characterization (Sec. 4.4.5), and fabrication of final samples (Sec. 4.4.6).

##### 4.4.1 Task I - Advanced Polyimide Synthesis

The work dealing with advanced polyimide synthesis of flexible resilient foams including the studies of chemical alteration with aromatic diamines, aliphatic diamines, additives and the evaluation of the optimum concentration of the heterocyclic diamine to achieve low density, the desired mechanical and thermal properties, and minimize foam irregularities is completely applicable to the selection of candidate foam materials for use in thermal acoustical applications. Precursor compositions have been selected from these advanced polyimide system studies and have been used in the tasks reported in this section.

The selected precursors were the 1710-1, 1702-1 and 1701-1 candidates. The 1710-1 precursors made with Jeffamine AP-22 produced rigid, crosslinked, but low density cellular structures. These foams were further evaluated in the early phase of this work since they appeared to possess the best thermal resistance and burnthrough characteristics. The 1710-1 precursors were produced by replacing the aromatic diamine moiety with stoichiometric amounts of AP-22, a trifunctional amine. This development will be reported in Section 4.4.3. The work on the 1702-1 and 1701-1 precursors and the selection of the final candidate, will be reported in Sections 4.4.4 and 4.4.5, respectively.

The evaluation of short glass fibers, ceramic fibers, carbon, graphite and other additives and their effect on the acoustical and burnthrough properties of the polyimide foams was carried out by modification of the powder precursors and will be discussed in Sections 4.4.3, 4.4.4, and 4.4.5, respectively. This technology was transferred from the task dealing with microwave foaming of flexible, resilient foams.

The acoustical and burnthrough characteristics of the basic 1702-1 foams have been evaluated. The acoustical properties did not meet the requirements at all frequencies tested. Improvement in acoustical properties were achieved by laminating a layer of aluminum foil to the foam surface and to a lesser extent by joining layers of foam slab to achieve higher foam thickness. Table 51 shows values of acoustical attenuation of polyimide foam derived from 1702-1 precursors using reported test configurations. (Personal communication with NASA-JSC.)



Table 51

Acoustical Attenuation of Standard and Polyimide  
Foams Insulation

| Test Configurations  | Weight            |                     | Acoustical Attenuation, db |         |         |
|--|-------------------|---------------------|----------------------------|---------|---------|
|  | kg/m <sup>2</sup> | lbs/ft <sup>2</sup> | 1000 Hz                    | 2000 Hz | 4000 Hz |
| 6 Layers 1.25 cm thick (0.5 in.)<br>Standard Aircraft Fiberglass                       | 0.731             | 0.1500              | 10.5                       | 20.5    | 27      |
| 3 Layers 7.62 cm thick (3 in.)<br>Polyimide Foam                                       | 1.11              | 0.2280              | 9                          | 12      | 21      |
| 1 Layer 7.62 cm thick (3 in.)<br>Polyimide Foam  | 0.371             | 0.0760              | 6.0                        | 9.0     | 13      |
| 2 Layers 7.62 cm (3 in.) thick<br>Polyimide Foam, 1 layer (0.006 in.)<br>Aluminum Foil | 1.13              | 0.2320              | 11                         | 20.5    | 28.5    |

The burnthrough properties and foam shrinkage of 1702-1 foams modified with glass fibers and chopped strands exceeded requirements of 300 seconds in laboratory tests, but the samples failed in 15 seconds when tested in the NASA-JSC Fire Test Rig. The failure was due in part to a change of the heat flux of the NASA-JSC Lenox Burner from 16 watts (14 Btu/ft<sup>2</sup>/sec) to 23 watts (20 Btu/ft<sup>2</sup>/sec) since similar foam samples tested before this change approached the burnthrough requirements (300 seconds). The change of heat flux, however, was justified to obtain correlation with actual fuel fires. These findings made it necessary to place more emphasis on means to improve the burnthrough resistance of polyimide foams. This work will be reported in Sections 4.4.3 and 4.4.4 and finally in Section 4.4.5 where a final 1702-1 candidate was developed which met the stringent burnthrough requirements.

#### 4.4.2 Task II - Foaming Studies

The investigations dealing with development of spray drying and microwave processes, the selection of the 15 kW microwave oven, the study of substrates compatible with the high frequency radiation and selection of the process parameters and scale-up of the foam precursors were reported in Section 4.1.2. These data are completely applicable to the selection of spray drying and microwave foaming methods for preparation of foams for preliminary testing in thermal acoustical insulation applications and for fabrication of large size samples. This transfer of technology has resulted in significant benefit in the execution of this phase of the program.

#### 4.4.3 Task III - Development of Thermal Acoustical Insulation by Coating and Foaming a Polyimide Resin on Fiberglass or Mats

The primary objective of this task was to develop water dispersible polyimide resins for use as binders in preparation of standard aircraft fiberglass insulation. In order to expedite the development of candidate materials for use in the NASA-JSC Fire Test scheduled for fiscal year 1980, the work of this phase of the program was organized and carried out in accordance with the following major tasks.

- Evaluation of products and processes obtained by coating and foaming 1702 polyimide precursors on one or both surfaces of standard aircraft fiberglass insulation.
- Modification of the powder or liquid polyimide precursors for use as binders in the production of standard fiberglass insulation.
- Development of modified polyimide foams and selection of best candidates.
- Optimization of the foaming process and precursor compositions with additives, fibers, and microballoons to obtain foams with improved thermal resistance.

#### Coating and Foaming Polyimide Precursors on Fiberglass Insulation

The first objective of this task was to evaluate process parameters to cover one or both surfaces of standard aircraft fiberglass insulations with a liquid polyimide precursor followed by drying and foaming the resin to produce a protective layer of polyimide foam.

The process was carried out by spray coating the liquid resin over a Owens Corning PF105-700 fiberglass insulation (silicone binder) using a DeVilbiss spray gun with a fluid tip D. The resin was dried at 65.5°C (150°F) for 10 minutes and foamed at 287.7°C (550°F) for five minutes to yield a thin, low density foam layer with good adhesion to the fiberglass surfaces. Resin precursors with and without surfactants were used in the initial evaluation. The 1702-1 resin containing 0.2 percent X-3 surfactant appeared to wet and to distribute over the glass surfaces more uniformly and was selected for further study.

Samples of the same fiberglass insulation, 20 x 20 cm (8 x 8 in.), were then coated at various resin loading per unit area to evaluate the effects of loading on the burnthrough resistance of the material. The results of these tests are shown in Figure 87. The time to failure for the uncoated fiberglass insulation is relatively short (7 seconds) but it increases as the resin loading per unit area increases reaching a maximum of 590 seconds at the highest permissible material density. These tests were carried out using

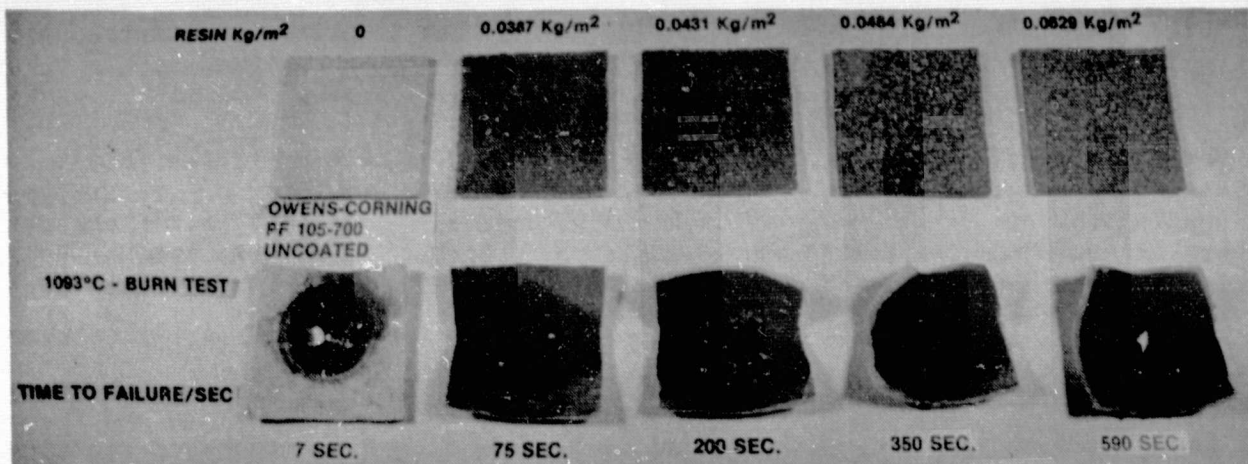


Figure 87. 1702-1 Polyimide Resin Spray Coated and Foamed on Owens Corning PF 105-700 Fiberglass 20 x 20 cm. Effects of Loading on Burn Test

a Meker burner having a flame temperature of approximately 1093°C (2000°F). The material exceeded the minimum burnthrough requirement of 300 seconds established as a goal for this program.

Large samples of the same material were then submitted to NASA-JSC for testing in the Fire Test Rig. These samples failed catastrophically. Failure was attributed to the autoignition of the silicone binder. These same results were later reproduced in the Solar Research Laboratories.

New specimens were then prepared using Owens Corning PF-105-500 fiberglass insulation (melamine binder) by coating and foaming 1702-1 liquid precursors at a loading of approximately 0.0629 kg/m<sup>2</sup>. In an effort to improve the burnthrough resistance of the foam layer the foaming time was extended, with no improvement as shown in Figure 88. Considerably better results were obtained in the laboratory when the burn tests were carried out with the flame impinging the uncoated side of the fiberglass insulation. The test samples are shown in Figure 89. These samples were later tested in the NASA Fire Test Rig and, although improved results were obtained and no autoignition was observed, the material did not meet the 300 seconds exposure time. Failure occurred in approximately 60 seconds. A double layer of coated fiberglass insulation failed in 100 seconds, a considerable improvement, but still far from meeting the expected requirements.

During the burn test carried out in the laboratory using a Meker burner, it was observed that, immediately after the flame impinged the uncoated side of the insulation, the glass melted leaving the foam as the only protection. This was followed by carbonization and cracking of the charred foam. Cracking appeared to be the result of stresses produced by differential thermal expansion which caused immediate flame breakthrough and failure of the insulation. Fiberglass insulation coated on both sides did not overcome this deficiency.

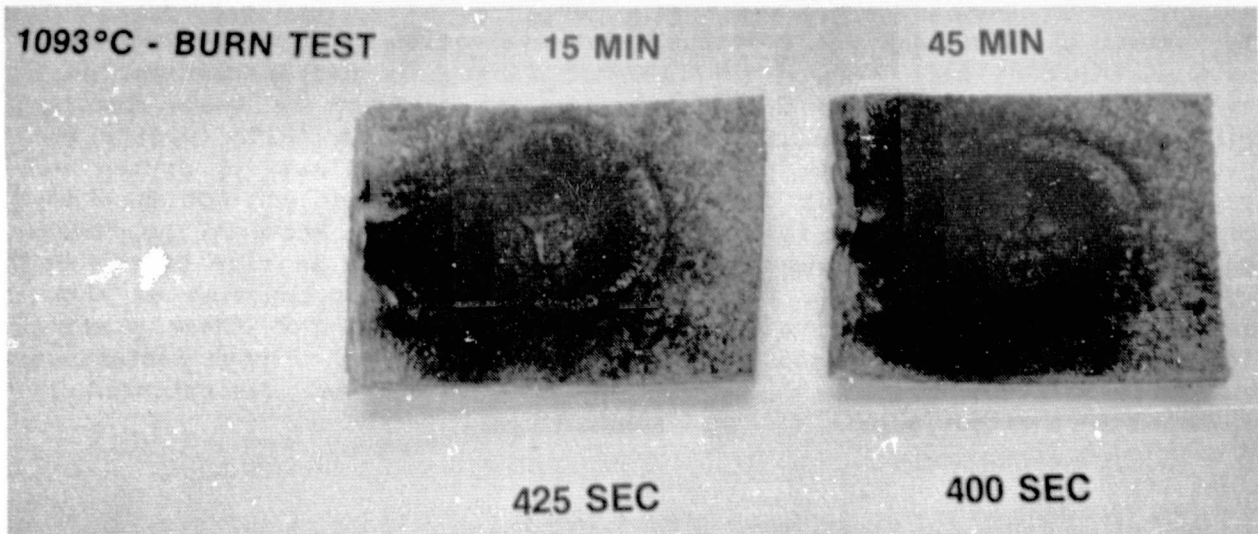


Figure 88. 1702-1 Polyimide Resin Spray Coated and Foamed on Owens Corning PF 105-500W Fiberglass. Effect of Foaming Time on Flame Resistance

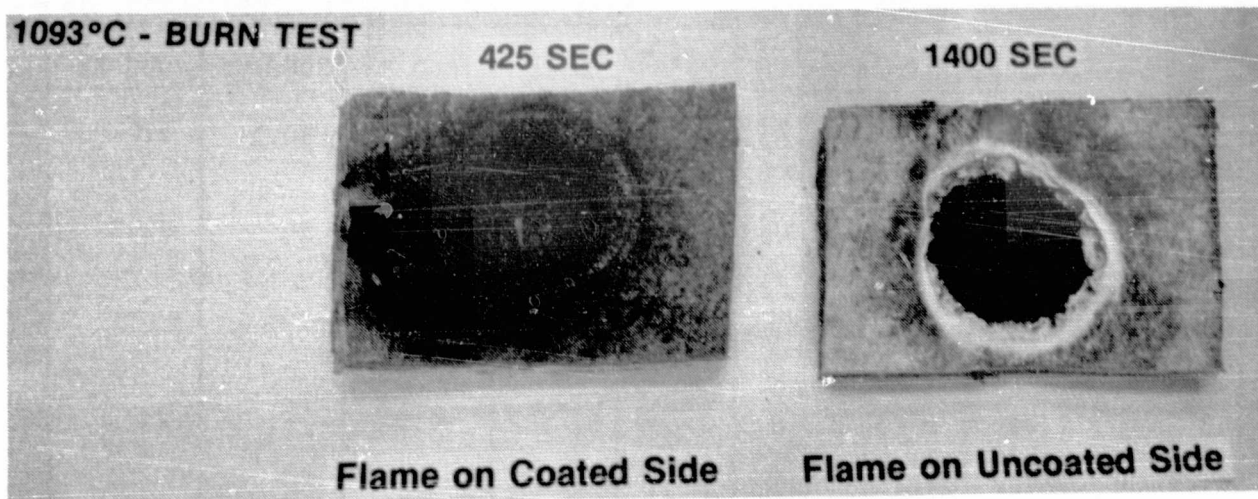


Figure 89. 1702-1 Polyimide Resin Spray Coated and Foamed on Owens Corning PF 105-500W Fiberglass. Difference Between Flame Impingement on Coated Side and Flame Impingement on Uncoated Side

To provide a better heat barrier, the fiberglass insulation was spliced into four layers [approximately 0.63 cm , (0.25 in.)], each layer was coated on both sides with 1702-1 resin, followed by drying and foaming. These samples were tested in the NASA-JSC Fire Test Rig but did not meet the exposure time requirements. In fact these samples appeared to delaminate under the effect of the heat at the interface between each foam layer producing burnthrough in less than 50 seconds.

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The effort of this task was continued with evaluation of Type 150 Aeroflex, 2.54 cm thick (1 in.) 27kg/m<sup>3</sup> (1.7 lb/ft<sup>3</sup>) fiberglass mat insulation, an E type glass product used as duct insulation and produced by Owens Corning Fiberglas. The Aeroflex insulation was heat cleaned at 492°C (900°F) and processed by coating it with 1702-1 liquid precursor followed by drying and foaming. The insulation was tested in a Meker burner but did not show improved burnthrough characteristics when compared with standard polyimide foam coated aircraft insulation. In addition to failing in fire tests, the coated fiberglass insulation failed to meet acoustical properties as shown in Table 52 (personal communication with NASA-JSC). Since these coating techniques did not provide the expected improvement in burnthrough resistance and acoustical properties, the work on this subtask was discontinued in favor of more direct approaches as discussed next.

Table 52

Acoustical Attenuation of Standard and Polyimide Resin Coated Fiberglass Insulation

| Test Configurations   | Weight            |                    | Acoustical Attenuation, db |         |         |
|---|-------------------|--------------------|----------------------------|---------|---------|
|   | kg/m <sup>2</sup> | lb/ft <sup>2</sup> | 1000 Hz                    | 2000 Hz | 4000 Hz |
| 6 Layers 1.250 cm (0.5 in.) Standard Aircraft Insulation  | 0.731             | 0.1500             | 10.5                       | 20.5    | 27      |
| 6 Layers 1.250 cm (0.5 in.) Standard Aircraft Insulation coated with polyimide resin on both sides (0.635 cm, 0.25 in. thick) | 1.388             | 0.2841             | 9.0                        | 16      | 22.5    |
| 3 Layers 1.25 cm (0.5 in.) Standard Insulation coated with polyimide resin on one side (0.635 cm, 0.25 in. thick)             | 0.780             | 0.1597             | 6.5                        | 16      | 25      |

Modification of the Powder and Liquid Polyimide Precursors for Use as Binders in the Production of Standard Fiberglass Insulation

This supposedly more direct approach to the problem of fire containment of fiberglass insulation was given immediate consideration in the early phases of the program. The effort involved replacing conventional binders with polyimide resins in the production of the fiberglass insulation. In large scale processing the binder is applied immediately after the glass fibers are spun, therefore this task was carried out in cooperation with Owens



Corning Fiberglas which agreed to participate in this effort with the studies reported below.

A plan of action was first devised with the major task being the adaptation of Owens Corning Fiberglas techniques to disperse the liquid or powder polyimide precursors in water in order to make nonflammable binder solutions since glass fibers manufacturing plants utilize exclusively open flame to provide process heat. The work carried out at the Owens Corning Technical Center is summarized below.

Liquid polyimide precursors were not readily emulsifiable in water. In this study it was found that the liquid polyimide resin separates as a heavy oil almost immediately and remained in this state even with the most effective emulsifiers. The powder precursors, however, produced water dispersions that were stable for a short period of time, approximately 30 minutes. This time was considered not sufficient for efficient processing of the glass insulation. Consideration was then given to the direct use of the powder polyimide precursors as binder by spreading the powder on the glass fibers immediately after they are spun, followed by a heat curing cycle to produce foaming and bonding into a low density mat. Because the foaming process is accompanied by a simultaneous release of alcohol, this concept was abandoned and considered unsafe for these types of manufacturing plants.

The method of using polyimide resins as binders in the manufacturing of fiberglass insulation would be feasible but it will require plant modification to overcome the difficulties reported above.

#### Optimization of the Foaming Process and Precursor Compositions With Additives, Fibers and Microballoons

The first effort of this task involved attempts to optimize the dimensional stability of polyimide foams derived from 1702-1 precursors. Dimensional stability is a deficiency that has been known to exist and occurs when the foams are exposed to high flux fire.

This study was carried out by first defining the effect of foaming time on foam contraction during fire. The results of these tests are shown in Figure 90 for a burn duration of one minute using a Meker burner. The data show that increased foaming time produces more dimensionally stable foams but this improvement alone (10%) was not enough to overcome the deficiency.

The next effort involved the evaluation of fibers and additives. Polyimide precursors were modified with CX-15 (3M & Co.) hollow glass microballoons at a concentration of 10, 15, and 20 percent and the compositions foamed in the Model 4115 microwave oven. Test specimens were then cut and evaluated for burnthrough characteristics on a Meker burner. These results are shown in Figure 91 where the effect of fillers on foam contraction is clearly demonstrated. Above a glass microballoon concentration of 10 percent, the foam contraction is reduced but the foams were relatively brittle and possessed poor cellular structure and high density. To overcome these deficiencies,

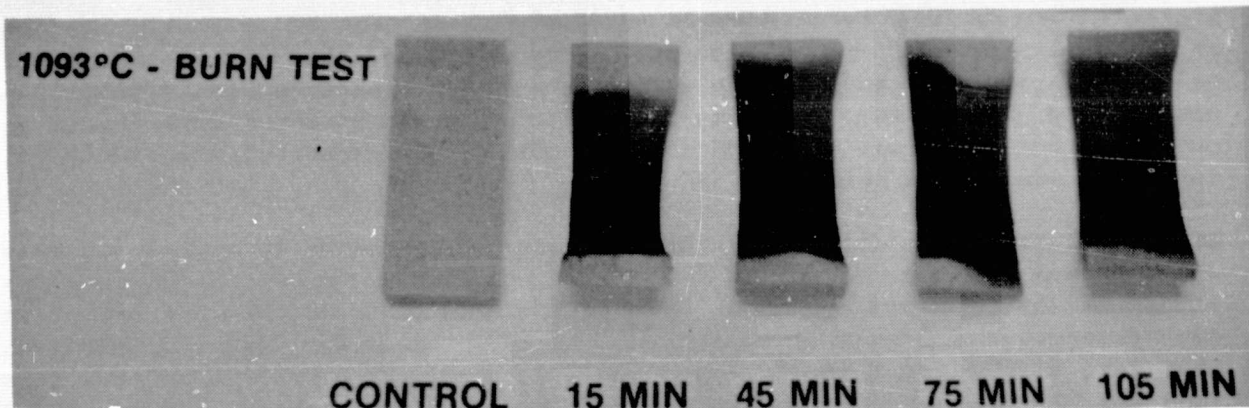


Figure 90. 1702-1 Polyimide Foam. Effect of Foaming Time on Contraction During Burn Test

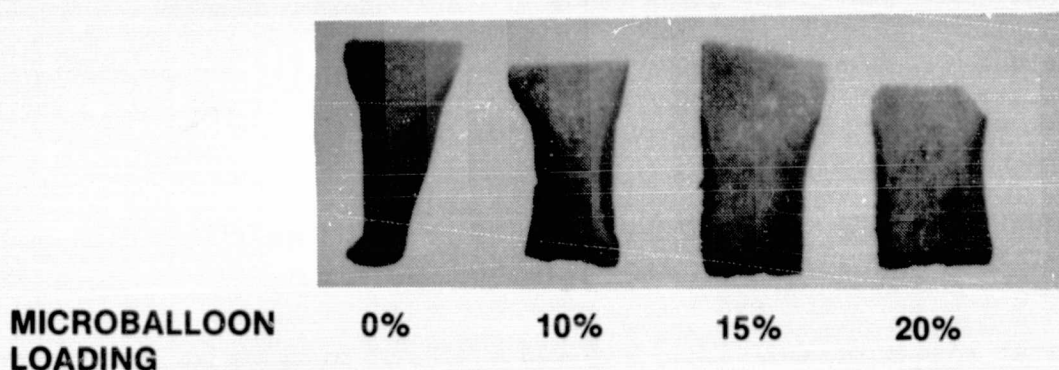


Figure 91. 1702-1 Polyimide Foam. Effect of Glass Microballoons on Contraction During Burn Test

blends of 405AA glass strands [(0.63 cm, (0.25 in.))] and CX-15 glass microballoons were evaluated. This was done by mixing the fillers with 1702-1 polyimide precursors modified with 0.1 percent AS-2 surfactant followed by microwave foaming. Foams derived from the various compositions and the respective one minute burn test are shown in Figure 92. The foam contraction was found to be directly related to the concentration of the microballoons; the higher the concentration the lower the foam contraction, but the density of the foam also increased. The data are shown in Table 53.

In order to further decrease the density, experiments were carried out with compositions containing the minimum concentration of microballoons (Experiment No. 5) but varying the concentration of the surface active agent. The data are reported in Table 53 (Compositions No. 6 and 7) for foams derived from



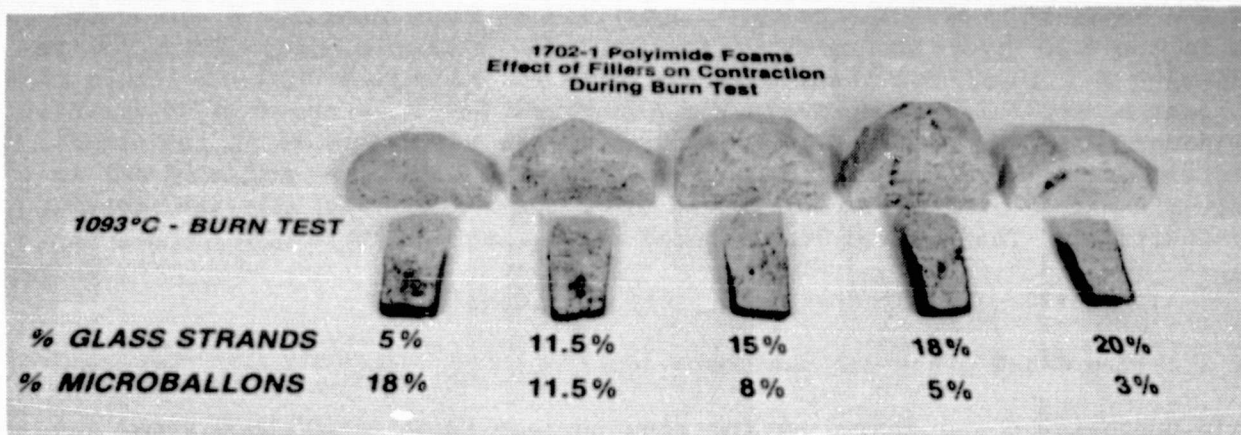


Figure 92. 1702-1 Polyimide Foams. Effect of Fillers on Contraction During Burn Test

Table 53

Effect of Glass Strands and Microballoons on Foam Contraction During Burn Test

| Experiment Number | % CX-15 Microballoons | % 405 AA Chopped Strands | Foam Contraction % | Density           |                     |
|-------------------|-----------------------|--------------------------|--------------------|-------------------|---------------------|
|                   |                       |                          |                    | kg/m <sup>3</sup> | lbs/ft <sup>3</sup> |
| 1                 | 18                    | 5                        | 16.6               | 35.2              | 2.2                 |
| 2                 | 11.5                  | 11.5                     | 19.4               | 22.4              | 1.4                 |
| 3                 | 8                     | 15                       | 25.0               | 22.4              | 1.4                 |
| 4                 | 5                     | 18                       | 25.0               | 16                | 1.0                 |
| 5                 | 3                     | 20                       | 33.0               | 14.4              | 0.9                 |
| 6                 | 3                     | 20                       | 28.0               | 10.4              | 0.65                |
| 7                 | 3                     | 20                       | 26.0               | 10.7              | 0.67                |

1702-1 resin precursors modified with 0.5 percent and 1.0 percent AS-2 respectively. At a concentration of 1.0 percent AS-2 surfactant, the foam rise was the highest and the cellular structure was very small and homogeneous. Therefore the composition of Experiment No. 7 was selected for further study. The effect of chopped strands (20%) and microballoons (3%) on the burnthrough properties of foams derived from 1702-1 precursors modified with one percent AS-2 is shown in Figure 93. These tests were carried out on a Meker burner for a duration of 10 minutes or until failure occurred. These filled foams exceeded the 10 minutes duration and met the goal requirements in laboratory tests.

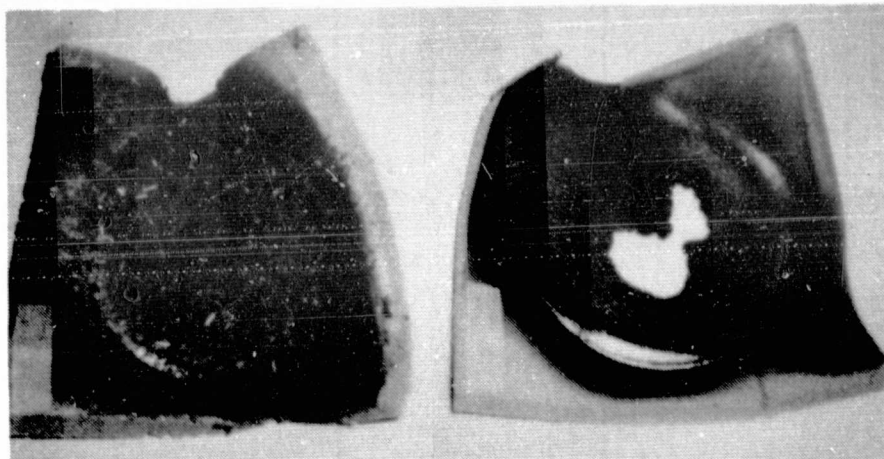
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On the basis of these results the composition of Experiment No. 7 was scaled-up in the 5 kW microwave oven to fabricate large samples [66 x 61 x 7.6 cm (26 x 24 x 3 in.)] for testing in the NASA-JSC Fire Test Rig. A sample of thermal acoustical foam derived from Experiment No. 7 is shown in Figure 94. Although this type of foam appeared to offer the best burnthrough resistance, additional work was carried out to improve this important property and involved coating both surfaces of the foam with specially selected coating compositions. The coating was prepared by milling a mixture of:

100 g 1702-1 diluted with 20 parts of alcohol

10 g C15-X glass microballoons

This composition was coated on the foam surface using a DeVilbiss spray gun, dried at 65.5°C (150°F) for 30 minutes and foamed at 287.7°C (550°F) for 15 minutes. This process produced a thick [(0.317 cm (0.125 in.))] homogeneous coating sealing the entire surface of the foam. The foam density increased considerably [density increased from 4.8 kg/m<sup>3</sup> to 9.9 kg/m<sup>3</sup> (0.3 lbs/ft<sup>3</sup> to 0.62 lbs/ft<sup>3</sup>)] but the foam exhibited a burnthrough time on a Meker burner in excess of 20 minutes. Therefore, a sample of each of the coated and uncoated foams derived from Experiment No. 7 (a 1702-1 precursor modified with one percent AS-2 and filled with three percent CX-15 glass microballoons and 20 percent 405A chopped glass strands) was submitted to NASA-JSC for



Glass & Microballoons

Unfilled

No failure after ten  
minutes exposure

Burnthrough 2.5 minutes

Figure 93. Effect of Fillers on Burnthrough Characteristics of Polyimide Foam: Left 1702-1, 1.0% AS-2, 20% Glass Strands, 3% Microballoons

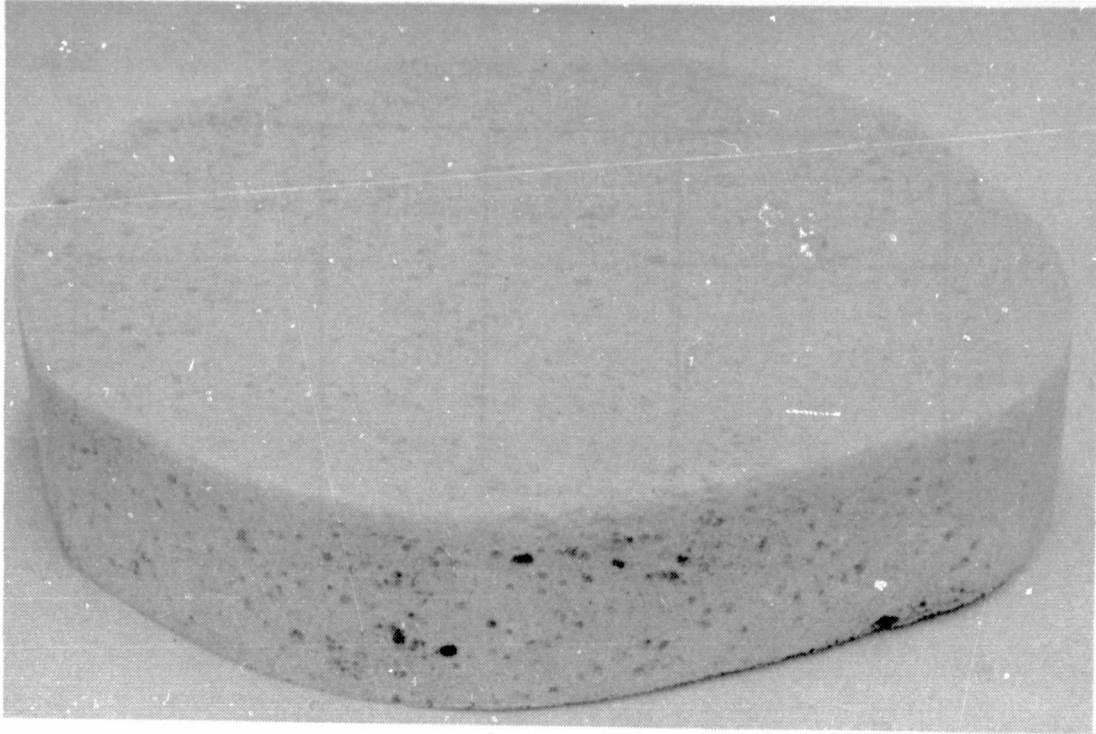


Figure 94. Thermal Acoustical Foam Derived From 1702-1 Precursors Modified With Glass Fibers and Microballoons

testing. Both samples failed catastrophically in 15-20 seconds. Cause of the failure appeared to be the high velocity of the flame which eroded the foam, and the higher heat flux used in the test. A contributing factor to the poor erosion resistance of these foams was the presence of microballoons which, as we have reported previously, adversely affects the mechanical properties of the foams.

A series of experiments were then initiated with the objective of finding a suitable substitute for glass microballoons capable to produce more durable and flame resistant foams. Milled fibers, type 739, a glass powder produced by Owens Corning Fiberglass was selected as a good candidate for this application. The effect of milled fibers on foam contraction of foams derived from 1702-1 precursors modified with 0.5 percent AS-2 is shown in Table 54. The addition of the chopped strands, Owens Corning 405A, 0.317 cm long (0.125 in.) produced further improvement of the foam contraction as shown in Table 55. Three of these foams met the density requirements (maximum  $10.8 \text{ kg/m}^3$ ) and possessed the best flame resistance to date, being in excess of 20 minutes when tested on a Meker burner. The composition containing 13 percent milled fibers and four percent glass strands was selected for scale-up studies and a sample was prepared for testing in the NASA-JSC Fire Test Rig. As in previous tests, this sample failed catastrophically in 15 seconds by erosion

Table 54

Effect of Milled Fibers on Foam Contraction During Burn Test

| Concentration Milled Fiber (%) | Foam Rise (cm) | Density kg/m <sup>3</sup> | Foam Contraction (%) |
|--------------------------------|----------------|---------------------------|----------------------|
| 0                              | 25.4           | 6.32                      | 37                   |
| 5                              | 20.3           | 7.10                      | 30                   |
| 10                             | 22.8           | 7.15                      | 29                   |
| 20                             | 19.0           | 11.9                      | 27                   |
| 40                             | 12.7           | 24.8                      | 18                   |

Table 55

Effect of Glass Strands and Milled Fibers on Foam Contraction During Burn Test

| Filler Concentration (%) |                 | Foam Rise (cm) | Density (kg/m <sup>3</sup> ) | Foam Contraction (%) |
|--------------------------|-----------------|----------------|------------------------------|----------------------|
| Milled Fibers            | Chopped Strands |                |                              |                      |
| 13                       | 2               | 21.5           | 8.0                          | 24                   |
| 13                       | 4               | 20.3           | 9.6                          | 12                   |
| 13                       | 8               | 19.0           | 10.8                         | 16                   |
| 13                       | 14              | 20.3           | 12.0                         | 19                   |

and burnthrough. A second sample [66 x 61 x 7.6 cm (26 x 24 x 3 in.)] tested in an aluminum aircraft structure also failed to produce improved burnthrough resistance in a comparative study against standard fiberglass insulation.

On the basis of these results, the laboratory fire test was changed to include a higher velocity flame. This was accomplished with the use of a Mapp gas burner having a flame temperature of 1593°C (2900°F). A test set up is shown in Figure 95.



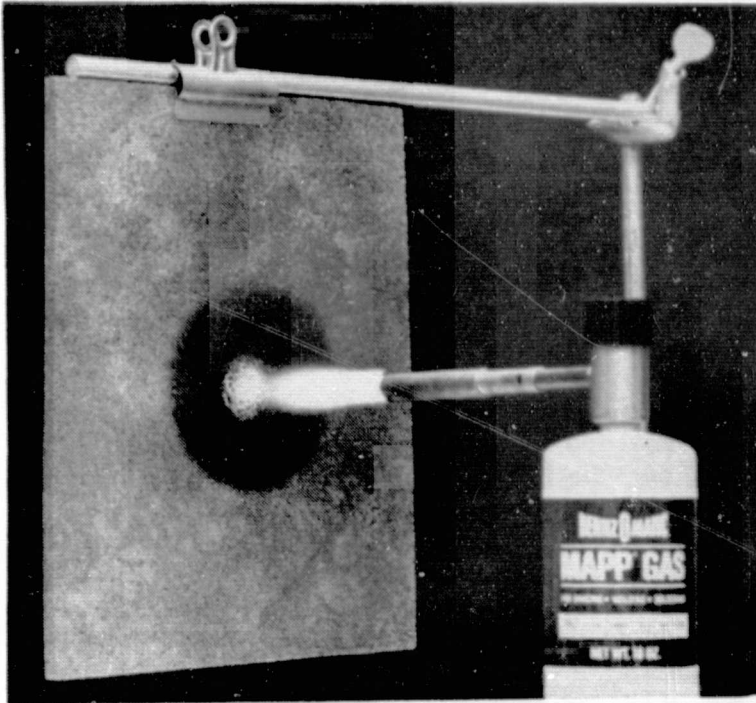


Figure 95.

Mapp Gas Burner Test  
Set-up

At the conclusion of this study it became evident that a reinforcement like glass strand was not effective in providing resistance to fire penetration and fire erosion since the multitude of fibers comprising the strands did not diffuse through the foam to produce a fire resistant network. Therefore, a series of experiments was initiated to find alternate means of reinforcing the foams. These experiments were of exploratory nature only and were carried out by modification of 1702-1 foams with surfacing mats, reinforcing mats, long glass fibers, ceramic fibers and by the use of a new crosslinked foam with and without a densified skin.

The crosslinked foams and foams reinforced with fiberfrax gave best results when tested for burnthrough resistance using the Mapp gas burner and were selected for further study as reported in the next section.

#### 4.4.4 Task IV - Preparation of Thermal-Acoustical Insulation Materials and Selection of Candidates

The primary objective of this task was to process the polyimide materials developed in the previous tasks and to screen suitable candidates for further characterization and selection. On the basis of the results obtained in Task III, two viable candidates were selected. These candidates were a cross-linked polyimide foam produced from a trifunctional amine and the fiberfrax filled 1702-1 foam. A discussion of the experimental work and the results derived will be presented in the following sequence:

- . Development of Crosslinked Polyimide Foams

- . Modification of Polyimide Foams With Inorganic Fillers
- . Modification of Polyimide Foams with Fiberfrax and Milled Fibers

### Development of Crosslinked Polyimide Foams

The work leading to this new family of polyimide foams was carried out in the task dealing with the development of flexible resilient foams and reported in Section 4.1.1.

Jeffamine AP-22, a trifunctional amine, was obtained commercially from Jefferson Chemical Co. The amine possesses an average functionality of 2.2, an equivalent weight of 103 (based on  $-NH_2$ ) and was used without purification. The process to produce the liquid and powder precursors and foams from this diamine is the same as that reported for the other polyimide precursors and is described in Sections 3.3.1 and 3.3.2 respectively.

The first effort of this task involved evaluation of inorganic, light weight substrates to improve the burnthrough resistance of the foams. To accomplish this, powder precursors made from Jeffamine AP-22 modified with 0.1 percent AS-2 surfactant (1710-1) were foamed in the 5 kW microwave oven supported respectively on 120 style woven glass fabric, M720 chopped strand mat and unsupported. In these series of experiments the resin foamed as expected and the foams met the density requirements. The adhesion of the foam to the fiberglass surface was good but the majority of the glass remained exposed, consequently the glass fabric and the glass mat failed immediately upon application of a flame. In addition, the glass fabric contracted into wrinkles during foaming producing an uneven surface. These foams, supported or unsupported, were tested for fire resistance in the Mapp burner. The burnthrough resistance of the foam itself, 7.62 cm (3 in.) thick, was in excess of five minutes with minimum shrinkage (10%) and distortion, but no contribution from the fabric or mat was noticeable.

Therefore, the concept of providing a protective layer of glass on one side of the foam was abandoned and the unsupported foam concept was further pursued by scaling up the crosslinked polyimide (1710-1) to large size samples for testing in the NASA-JSC Fire Test Rig. The samples were prepared using powder precursors derived from Jeffamine AP-22 filled with chopped glass strands (1710-1). Table 56 gives a summary of the data obtained by testing these foams in the NASA-JSC Fire Test Rig.

As shown, the polyimide foam prepared without the use of surfactants or fillers produced the best burnthrough resistance and was selected for testing in an aircraft section.

Table 56

## Burnthrough Resistance of Crosslinked Polyimide Foams (1710-1)

| AS-2<br>Surfactant<br>(%) | 0.317 cm<br>Chopped Strands<br>(%) | NASA-JSC Rig<br>Burnthrough Time<br>(Seconds) |
|---------------------------|------------------------------------|---|
| 0.1                       | 0                                  | 40  |
| 0.1                       | 25                                 | 56  |
| 0                         | 0                                  | 80  |

This test sample was a foam, 66 x 61 x 3.8 cm (26 x 24 x 1.5 in.) prepared by microwave foaming a 1710-1 precursor. The foam was densified by compressing it in a press to obtain a density of 24 kg/m<sup>3</sup> (1.5 lbs/ft<sup>3</sup>) and submitted to NASA-JSC for testing in an aircraft section. This foam failed to give improved results in comparison to conventional fiberglass batting insulation. Failure of the sample appeared to be caused by thermal stresses induced by flame impingement which produced foam cracking and early burnthrough.

Studies were continued to improve the resistance of the foam to thermal stresses and surface cracking. This was attempted by the use of light weight protective polyimide coatings applied on the surface of the foam. The coatings were prepared by milling fiberfrax in a liquid precursor (1702-1) at a concentration of five percent based on polyimide solids. The thick coating was then spread over the surface of the foam (1710-1) with a spatula and cured at 287.7°C (550°F) for 15 minutes. The coating configurations are shown in Figure 96. All samples exceeded the burnthrough requirements of five minutes in laboratory tests carried out with a Mapp Burner, but the sample which was coated on both sides exhibited a burnthrough resistance in excess of 20 minutes. However, even this last sample failed in less than 30 seconds when tested in the NASA-JSC Fire Test Rig. Failure was again caused by cracking due to thermal stresses induced by the flame impinging the foam.

Investigations were then continued and were directed toward increasing the thermal conductivity of the foams, in order to permit more homogeneous distribution of the thermal stresses over the entire surface of the foams. This task was attempted using additives and fillers as discussed below.



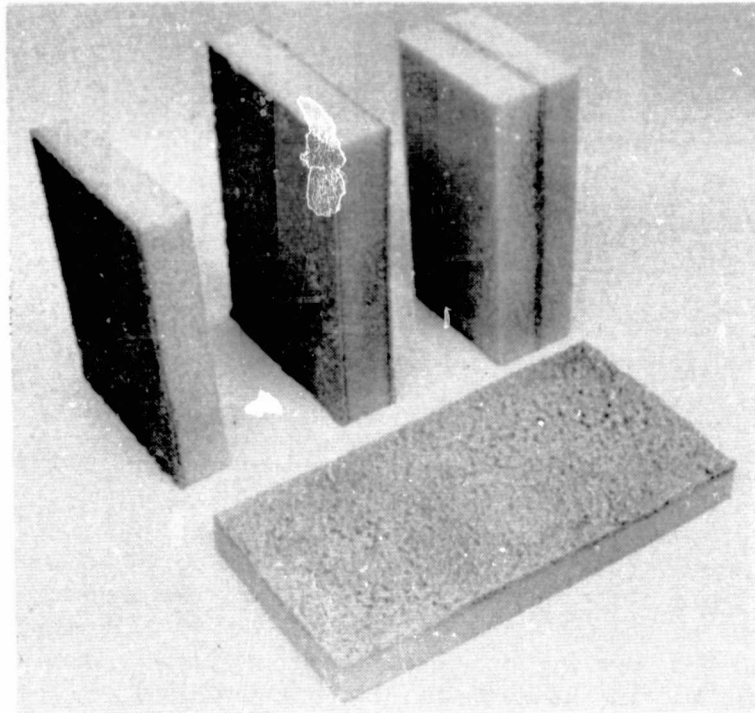


Figure 96. Polyimide Coating Configurations on Foams (1710-1)

#### Modification of Polyimide Foams With Fillers and Additives

The addition of specific additives such as fibers, mats, strands or powders to a resin composition produces significant and often predictable changes in the mechanical and thermal properties of the final product. This approach was used to modify the foam compositions to obtain improved burnthrough resistance.

The following fillers were tested alone and, in many instances, in combination with each other.

Glass hollow microballoon C15-X (3M Co.)

Glass rovings 2.54 cm (1 in.) long - S type

Milled glass fibers. Type 739 - Owens Corning Fiberglas

Chopped strands, Type 832 - Owens Corning Fiberglas

Graphite powder, Type PXB-QS-325 - Poco, Union 76

Fiberfrax bulk fiber (Carborundum)

Barium phosphate

Ammonium hydrogen phosphate

Chromium oxide

Silica flour

Aluminum hydroxide

Aluminum oxide

The concentration of each additive varied depending upon the nature of the additive. Glass fibers could not be used at concentrations higher than 25 percent based on polyimide solids since they produced low foam rise while powder additives could be used at concentrations as high as 75 percent without altering the foaming behavior.

These preliminary screening studies were carried out using precursors produced from AP-22 (1710-1). The foams were first inspected for cellular structure and those which met the minimum quality requirement were further tested for burnthrough resistance.

Fiberfrax and glass milled fibers produced foams with the most improved burnthrough resistance. From these preliminary tests, it was found that as little as five percent Fiberfrax bulk fibers improves the burnthrough resistance of the 1710-1 foams by minimizing warping and cracking. Therefore, a more extensive evaluation was undertaken as discussed below.

#### Optimization of Polyimide Foams With Fiberfrax and Milled Glass Fibers

The effort dealing with optimization of fiber filled polyimide resins was carried out in the following sequence:

- . Selection of the optimum resin system including best surfactant concentration.
- . Selection of optimum filler concentration.
- . Selection of optimum process parameters.

Four resin systems were first evaluated to screen optimum candidates; these were 1701-1, 1702-1, 1710-1 and 1720-1. The precursors were modified by the addition of 15 percent Fiberfrax bulk fibers and 25 percent milled glass fibers, and each foam was evaluated for burnthrough resistance using a Mapp burner. In this test, attention was paid to the ability of the foams to withstand a flame source without surface cracking since this was found to be the main cause of failure in previous tests. Foams prepared from 1702-1 precursors gave best results. These foams expanded in volume and appeared to flow thermoplastically when impinged by the high intensity flame source. This last characteristic was of significant importance. Samples of foams derived from these same 1702-1 precursors modified with the addition of 15 percent Fiberfrax and 25 percent milled glass fiber were then submitted to NASA-JSC for testing.

A sample, 7.62 cm thick (3 in.) having a density of approximately  $12.8 \text{ kg/m}^3$  ( $0.8 \text{ lbs/ft}^3$ ), exhibited a burnthrough resistance in excess of three minutes, thus approaching the five minutes goal requirement for the program. The foam expanded during this test as it was expected. Samples of the foam before and after the burn test are shown in Figure 97.

Although this foam exhibited improved burnthrough resistance, its cellular structure was characterized by large cells which often propagated through the foams. Therefore, studies were initiated to overcome this deficiency.

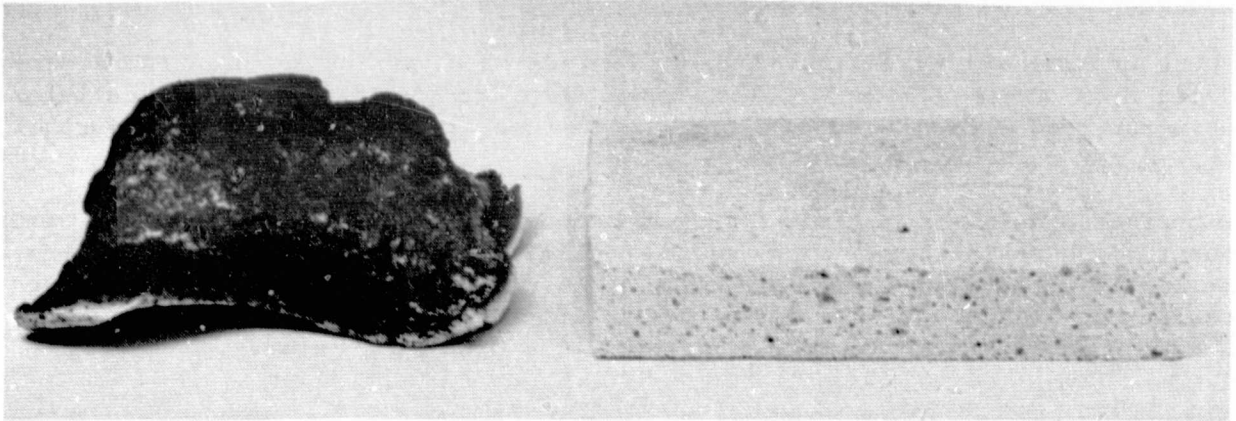


Figure 97. Thermal-Acoustical Insulating Foam - Before (Right) and After (Left) Burnthrough Test at NASA-JSC

This cellular deficiency was attributed to the presence of the Fiberfrax fibers still in the bulk state after being processed through a mechanical blender (Waring Blender). In the blending process Fiberfrax was reduced to small size chunks which during microwave foaming absorbed more electromagnetic radiation than the surrounding media thus causing local overheating. This condition produced a large cellular structure and flaws which extended throughout the mass of the foam. Since Fiberfrax fibers were not commercially available, attempts were made to prepare fibers from the Fiberfrax bulk material. This was achieved by passing the bulk fiber through a grinder and then blended with the powder precursors and milled again to a fine powder using a herring bone type screen  $0.058 \text{ cm}$  ( $0.023 \text{ in.}$ ) size. Precursor compositions produced from this process gave foams with very homogeneous cellular structure as shown in Figure 98. The two foams shown in Figure 98 were produced from the same precursor composition but the upper foam was made by grinding and the lower by blending.

Improvements in compositions were then attempted and carried out by evaluating the affect of AS-2 concentration and that of the fillers on the burnthrough resistance of the foams. Precursors derived from 1702-1 series

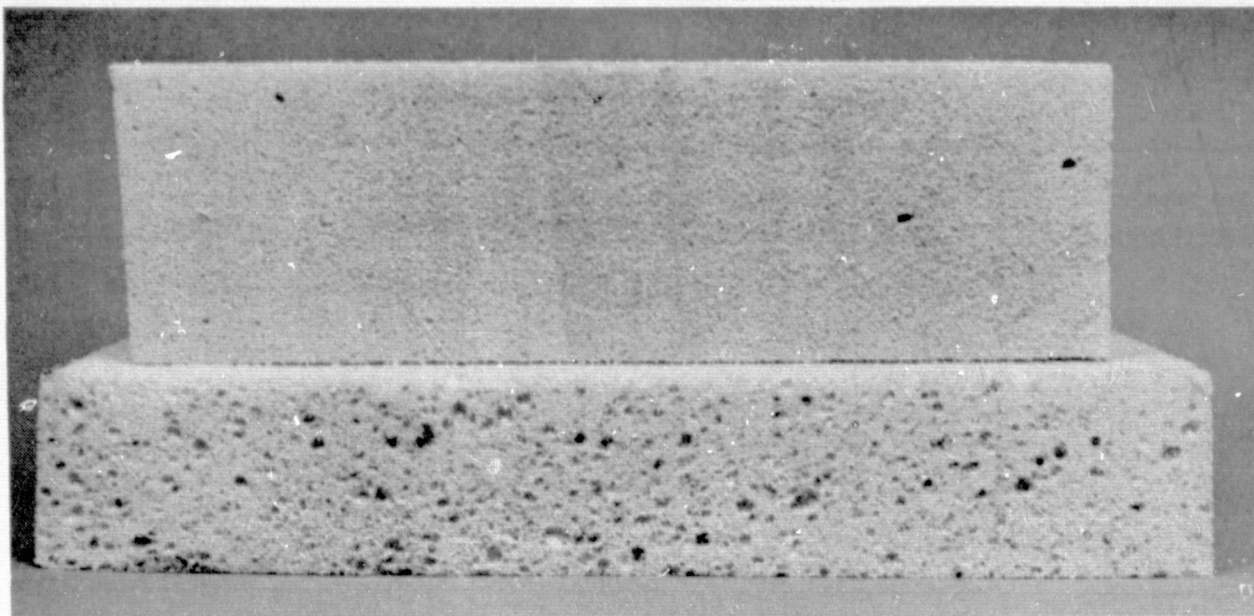


Figure 98. Effect of Grinding and Blending the Fiberfrax on Cellular Structure of Thermal-Acoustical Polyimide Foams

were prepared at an AS-2 concentration of 0.75, 1.0 and 1.5 percent respectively and modified by the addition of 15 percent fiberfrax and 25 percent glass milled fibers. The foams produced at a surfactant concentration of 1.5 percent showed improved flexibility and resiliency and were selected for the following studies of filler concentrations. These were carried out by evaluating the effect of fiberfrax concentration followed by the effect of glass milled fiber concentration on the burnthrough resistance of the foams. The first series of experiments was carried out by keeping the concentrations of the glass milled fibers at 10 percent and increasing the fiberfrax concentration in 5 percent increments. The data derived from testing these foams for burnthrough resistance using a Mapp burner are shown in Table 57. The data show that the burnthrough resistance of the foams is directly related to the concentration of the fiberfrax and that the density is not significantly affected by the increasing levels of the fiberfrax.

A second series of experiments was carried out by keeping the concentration of the fiberfrax at 10 percent and increasing the milled fiber concentration in five percent increments. The data derived from testing these foams for burnthrough resistance using a Mapp burner are shown in Table 58. None of the foam failed in the fire test although the sample made at 25 percent glass milled fibers was scorched more severely than other foams. The data also show that milled fibers decrease foam rise and therefore increase their density significantly. These two series of experiments have demonstrated that fiberfrax is contributing considerably more to the thermal and burnthrough resistance of these foams than glass milled fibers at no expense to the density. Therefore fiberfrax was selected as the only filler for the additional studies described below.

Table 57

Burnthrough Resistance of Polyimide Foams (1702-1) at Different Concentrations of Fiberfrax

| Percent Fiberfrax | Density           |                     | Time to Burnthrough (seconds)<br>(2.54 cm (1 in.) thick) | Mode of Failure       |
|-------------------|-------------------|---------------------|--|-----------------------|
|                   | kg/m <sup>3</sup> | lbs/ft <sup>3</sup> |  |                       |
| 25                | 15.6              | 0.98                | 335  | Through existing flaw |
| 15                | 17.6              | 1.1                 | 298  | By flame erosion      |
| 10                | 16.0              | 1.0                 | 250  | By flame erosion      |
| 5                 | 15.3              | 0.9                 | 50   | Through crack         |
| 0                 | 12.8              | 0.8                 | 15   | By burnthrough        |

Table 58

Burnthrough Resistance of Polyimide Foams (1702-1) at Different Concentrations of Glass Milled Fibers

| Percent Milled Fibers | Density           |                     | Time to Burnthrough Seconds |
|-----------------------|-------------------|---------------------|-----------------------------|
|                       | Kg/m <sup>3</sup> | lbs/ft <sup>3</sup> |                             |
| 25                    | 22.4              | 1.4                 | >300                        |
| 20                    | 22.4              | 1.4                 | >300                        |
| 15                    | 19.2              | 1.2                 | >300                        |
| 10                    | 16.0              | 1.0                 | >300                        |
| 0                     | 15.2              | 0.95                | 255                         |

The study dealing with the effect of fiberfrax as the only additive for thermal acoustical foams was done using the same precursor 1702-1 modified with 1.5 percent AS-2. These experiments were carried out using fiberfrax concentration of 10, 20 30 and 40 percent respectively. The fiberfrax bulk filler was first heat cleaned at 482°C (900°F) for one hour and ground to small fiber chunks. These were then blended with the powder precursors and the composition foamed at 3.75 kW in the Model 4115 microwave oven.



These foams possessed burnthrough time characteristics in excess of five minutes when tested in the laboratory using a Mapp gas burner. Foams produced from precursors modified with 20 percent fiberfrax were selected and tested in the NASA-JSC Fire Test Rig. This type of foam exceeded the burnthrough requirement of five minutes (failure occurred in five minutes and 30 seconds).

After this development compositional and process parameters were evaluated in attempts to improve the cellular structure and eliminate the blending step (Waring Blender). The first attempts involved re-evaluation of a high level of AS-2 surfactant since this modification is known to yield foams with much finer cellular structure. A series of experimental precursors were produced at an AS-2 surfactant concentration of 1.5 and 3.0 percent. The precursors were then modified with 20 percent fiberfrax and the compositions processed using the blending method. The foams produced at 3.0 percent AS-2 surfactant concentration had a finer cellular structure and were relatively more flexible than those produced at a concentration of 1.5 percent AS-2. A sample of the foam produced at 3 percent AS-2 was tested in the NASA-JSC Fire Test Rig and again met the requirement of the program.

The final effort involved improving the blending process using milling techniques. This was accomplished with the use of a Pulvette bench model grinder operating at a speed of approximately 2000 rpm. Blending was accomplished by passing the precursor compositions through the Pulvette grinder until the particle size of the fiberfrax bulk fiber was reduced to a size similar to that obtained with the Waring Blender (2-3 passes).

A new milled fiberfrax fiber having a mean length of 14 microns was obtained from Carborundum during the last phase of this program. This filler was also processed by the same blending method through the Pulvette grinder. The two foams obtained from these two fiberfrax materials possessed a fine cellular structure, good flexibility and were free of imperfections. These foams were tested in the NASA-JSC Fire Test Rig and both passed the five minutes burnthrough resistance. The foam produced from the fiberfrax milled fiber, however, showed considerably less shrinkage and more resistance to thermal stresses than foams produced from the fiberfrax bulk fibers. Therefore the foam derived from 1702-1 precursors modified with 3 percent AS-2 and 20 percent fiberfrax milled fibers was selected as the optimum candidate for characterization and fabrication of final sample as will be discussed in the next paragraphs.

#### 4.4.5 Task V - Final Characterization of Thermal Acoustical Materials

The characterization of the final candidate was conducted using samples produced by microwave foaming 1702-1 precursors modified with 3 percent AS-2 and 20 percent fiberfrax milled fibers. Summary of the results is given in Table 59.

Table 59

Summary of Results - Thermal Acoustical Insulation  
1702 Resin 3% AS-2

| Property                                 | ASTM Method     | Units  | Goal                        | Actual               |
|--|-----------------|--|-----------------------------|----------------------|
| Density                                  | D-1564          | Kg/m <sup>3</sup><br>lbs/ft <sup>3</sup>       | 9.6<br>0.6 max              | 9.6<br>0.6           |
| Breaking Strength                        | CCC-T-191       | N/m<br>lbs/in                                  | 175.1<br>1.0 min            | 893.0<br>5.1         |
| Wicking as received                      | Water immersion | cm<br>in<br>precipitate                        | 1.0 max<br>0.25 max<br>None | None<br>None<br>None |
| Wicking after oven drying 71.1°C (160°F) | Water immersion | cm<br>in<br>precipitate                        | 1.0 max<br>0.25 max<br>None | None<br>None<br>None |
| Flexibility                              |                 | deterioration after bending on one-foot radius | None                        | None                 |
| Corrosion (Aluminum)                     |                 | Pitting  | None                        | None                 |
| Elevated Temperature Resistance          |                 | Weight loss                                    | 15 mg max                   | 7 mg                 |
| Oxygen Index                             | D-2865          | % oxygen                                       | 40 min                      | 42                   |
| Smoke Density DS Uncorrected             | NBS             | Optical Density                                | 30-50 max                   | 2.0                  |
| Verticle Bunsen Burner Test, 60 seconds  |                 | Flame Time seconds                             | 10 max                      | 0                    |
|  |                 | Burn length cm                                 | 15 max.                     | 3.0                  |
|  |                 | in   | 6 max                       | 1.2                  |
|  |                 | Dripping                                       |                             | None detectable      |
| Vibration                                |                 | 1 Hr<br>30 Hz<br>5 cm amplitude                | No damage                   | None                 |
| Acoustical Properties                    |                 | Absorption Coefficient                         |                             |                      |
|  |                 | 1000 Hz  | 0.869*                      | 0.569                |
|  |                 | 2000 Hz  | 0.851*                      | 0.928                |
|  |                 | 4000 Hz  | 0.998*                      | 0.999                |

\* Owens Corning PL 105 500W

4.4.6 Task VI - Fabrication of Samples for Submittal to NASA-JSC

The foam specimens were prepared by microwave foaming a 10.1 cm thick (4 in.) layer of the 1702-1 precursor modified with 3 percent AS-2 and 20 percent fiberfrax using a power of 10 kW for foaming followed by 20 minutes at 15 kW



to cure the foam. Thermal curing at 287.7°C (550°F) was found to be necessary to complete the polymerization. The large foam was cut to size using a band saw. A total of 10 samples approximately 60 x 66 x 7.6 cm (24 x 26 x 3 in.) were delivered to NASA-JSC.

# 5

## RECOMMENDATIONS FOR FUTURE WORK

Pilot plant size processing and fabrication have been demonstrated for both flexible and rigid polyimide foams. These products have been produced in large size by microwave processes and their unique features have been discussed in this report.

At the present state of development the properties of the flexible resilient foams fall within a narrow range of values from which it has been difficult to select products meeting specific requirements. The recommended future work will involve characterization and classification of the flexible resilient foams into five groups of products according to established indentation load deflection values. The program will lead to the selection of these classes of polyimide foams which will be clearly identified on the basis of seating comfort.

The wall and floor panels produced by microwave processing have also been scaled up to large size. The only limitation now preventing these panels from being produced in the proposed size of 1.2 x 2.4 m (4 x 8 ft) are equipment limitations, specifically the microwave compatible mold plates. Because of the amount of effort designated for the rigid foam product in this program, a thorough mold material and design configuration study was not feasible. With additional effort a mold could be developed to produce rigid foams over a wide range of thicknesses at dimensions of 1.2 x 2.4 m (4 x 8 ft) or 1.2 x 3.6 m (4 x 12 ft) limited only by the microwave cavity size.

The rigid foams produced by this microwave process possess very good mechanical, physical and thermal properties. The only area where a significant deviation from the proposed material properties was noted was the compressive strength of the core material. However, this specification was derived from the compressive strength of the honeycomb material which the foam core was to replace rather than from the functional requirements that the material must exhibit when used in aircraft interior applications. For this the critical property requirements are weight, flexural strength, fatigue endurance and impact strength.

An area of further improvement will involve the use of fibers reinforced polyimide resins to replace the unidirectional glass skins. This will significantly improve flame resistance of the finished panels and not sacrifice any of the structural contribution of the face sheets. The microwave process is designed to accomplish bonding of the face sheets to the foam core in a single step operation.

The process to fabricate flat and elliptical foam core panels with multiple density characteristics has been established, but further improvement of this technology is required. This needed effort will be directed towards studies designed to match the thermal expansion coefficients of the various materials used in the multi-density structure. Improved fabrication techniques will also be evaluated to overcome the difficulties encountered in foaming materials with different density.

The blocking material formulated during this program has shown to be a versatile product. Further work of optimization will lead to a suitable replacement for filled high density polyurethane foam used as a primary structural component in overhead storage compartments.

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