NASA CR- [illegible]

NASA-CR-159129
19800007845

MANUFACTURING PROCESSES FOR FABRICATING GRAPHITE / PMR 15 POLYIMIDE STRUCTURAL ELEMENTS

C.H. Sheppard, J.T. Hoggatt and W.A. Symonds

BOEING AEROSPACE COMPANY
Seattle, Washington

Contract NAS 1-15009

NASA
National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23665
AC 804 827-3966

NASA CONTRACTOR FINAL REPORT

MANUFACTURING PROCESSES FOR FABRICATING GRAPHITE / PMR 15 POLYIMIDE STRUCTURAL ELEMENTS

C.H. Sheppard, J.T. Hoggatt and W.A. Symonds

BOEING AEROSPACE COMPANY
Seattle, Washington

Contract NAS 1-15009

NASA
National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23665
AC 804 827-3966

N80-16105#

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF TABLES (CONT.)

LIST OF TABLES (CONT.)

LIST OF FIGURES

LIST OF FIGURES (CONT.)

LIST OF FIGURES (CONT.)

LIST OF FIGURES (CONT.)

1.0 SUMMARY

This report documents work performed by BAC for the National Aeronautical and Space Administration, under NAS1-15009 Tasks A through H. The objective of this program was twofold: first, to develop processes and the required quality assurance methods and controls for fabricating Graphite/PMR-15 Polyimide Structural Elements; second, the demonstration of those processes and controls through the fabrication of major composite structural elements. The work was performed in eight separate tasks over a 17-month period.

The program was divided into two phases: (1) Process Development and (2) Demonstration Components. The Procescess Development phase consisted of Tasks A, B, and C, with the Demonstration Component phase Tasks D through H. The first phase of the work involved the Quality Assurance of the Graphite/ PMR-15 Prepreg (Task A), Process Studies (Task B) and Process Qualification (Task C). This effort resulted in the definition of the material controls, process parameters, and quality assurance methods required to produce quality graphite polyimide composites using PMR-15 polyimide matrix. Tasks A and B were conducted concurrently with the required chemical characterization and document preparations being accomplished in Task A and the autoclave process development conducted in Task B. Midway during the program a significant material variability problem was encountered causing problems with regard to selecting a suitable fabrication process for the Task C effort. Task C was therefore completed using processes that were dictated by the material lots used.

During Task A studies, materials were obtained from three separate sources and chemically characterized. Based on these data, Company A was selected as program supplier for materials required during the remainder of the program. The Material and the Process Specifications developed under Tasks A and B are based on Company A's material. The remaining two documents (Quality Assurance and Non-Destructive Test (NDI) documents) were based on graphite/PMR-15 polyimide composites and/or structural element data using the same materials. A series of components were fabricated and NDI inspected during the second phase as a means of demonstrating the adequacy of the processing methods established during the Development Phase of the program. The Material and Process Specifications, the Quality Assurance Plan, and the NDI Plan prepared and verified during phase one were utilized when possible in controlling component manufacture. All prepreg materials used in fabricating the components were procured and subjected to special quality control testing because of the material variability problem discovered in the Process Development Phase of the program. All manufacturing, in process inspection, and NDI test requirements were defined in the Process Specification, Quality Assurance Plan, and NDI Plan and were utilized in fabricating the components. Layup, bagging, and assembly operations were performed by experienced Engineering aides and manufacturing personnel in the BAC Materials Technology Laboratory.

As a result of the material variability problem discovered in the first phase of the contract, this contract was modified to add Task J (PMR-15 Variability Program) for additional studies of prepreg quality control Results from Task J are to be reported separately.

"Use of commercial products or names of manufacturers in this report does not constitute official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration."

2.0 INTRODUCTION

This report presents the work accomplished by Boeing Aerospace Company for the National Aeronautics and Space Administration, Langley Research Center, under Contract NAS1-15009, during the period of 26 July 1977 through 15 February 1979. This program consisted of experimental studies structured to develop a process specification for the manufacture of structural elements and to demonstrate the manufacturing feasibility of graphite/PMR-15 polyimide prepreg materials. The program was divided into eight separate tasks which consisted of:

- TASK A Quality Assurance Program
- TASK B Process Studies
- TASK C Process Qualification
- TASK D Flat Panels
- TASK E Skin-Stringer Panels
- TASK F Honeycomb Panels
- TASK G Chopped Fiber Moldings
- TASK H Aft Body Flap

This work was conducted under the technical direction of Mr. E. L. Hoffman of Langley Research Center, Hampton, Virginia. The Materials Technology Department of The Boeing Aerospace Company was responsible for the work performed on this program. Mr. W. A. Symonds was the Program Manager, Mr. J. T. Hoggatt was the Technical Leader and Mr. C. H. Sheppard was the Principal Investigator. Acknowledgement is made of the technical assistance provided during the program by the following BAC and Company A personnel:

Boeing Aerospace Company

- A. B. Hunter
- Sylvester Hill
- Frank Horan
- Evan House
- Bill Dumars
- Ralph Hodges
- Julie Jaquish
- Verla Monroe
- Oscar Davis

Company A

- Don Beckley, Technical Director
- Sidney Street, Research Manager

The objective of this program was the development of processes and the required quality assurance methods and controls for fabricating Graphite/PMR-15 Polyimide Structural Elements and the demonstration of those processes and controls through the fabrication of major composite structural elements. Consequently, during the first part of the program work was concentrated on preparing Material and Process documents that aided in the fabrication of quality structural elements. Four separate documents were prepared and are as follows:

Material Specification	D180-20545-4	(Appendix B2)
Process Specification	D180-20545-5	(Appendix B3)
Quality Assurance Plan	D180-20545-3	(Appendix B1)
NDI Plan	D180-20545-6	(Appendix B4)

The Material Specification controls the quality of the incoming graphite/polyimide prepreg. It includes controls on the resin, fiber, and the graphite prepreg. The Process Specification governs the fabrication of polyimide composite parts. The Quality Assurance Plan defines the specifications, inspection operations, and final accept/reject criteria and the NDI Plan defines the NDI equipment and procedures to be followed for composite inspection. Process development studies were performed simultaneously with Task A after preliminary quality control parameters had been established on the graphite/PMR-15 prepreg. The remaining tasks were then performed sequentially as described below.

Quality Assurance Program -- Task A

The objective of this task was to generate the documentation required to control the quality of polyimide composite components. During this task, input data was obtained for the critical processing steps from initial polymer synthesis through final part acceptance. Criteria were then established for the determination of the acceptance/rejection for each critical step and all required operations defined.

Process Studies -- Task B

The objectives of this task were to develop manufacturing processes for five different structural elements and obtain process control and inspection data required for specification preparation under Task A. The five structural elements studied under this task were as follows:

- Flat laminates
- Hat stiffeners
- "I" stiffeners
- Honeycomb sandwich panels
- Chopped fiber moldings

Process Qualifications -- Task C

The objectives of this task were to qualify the processes developed under Task B through the fabrication and test of selected demonstration elements. All materials, processes, and inspection procedures utilized for these elements were defined and controlled by the applicable documentation of Task A. This program was designed to provide assurance of the structural integrity of the graphite/PMR-15 composites through the acquisition of preliminary design data. The data obtained possessed sufficient depth so that a design engineer could assess the graphite/PMR-15 system and associated process for potential application to critical structural hardware.

Component Demonstrations -- Tasks D through H

The objective of these tasks were to fabricate designated structural elements using the established processes and inspection criteria and deliver them to NASA Langley for their testing. Under Task H a 30-inch simulated section of the aft body flap of the Space Shuttle, selected as representative of space hardware, was fabricated.

3.0 TASK A QUALITY ASSURANCE PROGRAM

This task of the program was devoted to establishing controls on the PMR-15 resin and/or prepreg to ensure a solid base for the subsequent process development task. Details of the Task A studies are presented below. Chemical testing procedures and a summary of the analytical data are given in Appendix A with the four documents presented in Appendix B.

3.1 EVALUATION OF GRAPHITE/PMR-15 PREPREGS

To meet the objective of preparing Quality Assurance Documents, samples of PMR-15 graphite prepreg were obtained from three potential prepreg vendors in order to obtain baseline material, chemical, and performance data. The testing consisted of working through a Chemical Characterization Schematic (Figure 1). In reviewing the analysis methods, each of the tests from the chemical characterization schematic (Figure 1) will be discussed in order, along with the representative test results and the test's validity with respect to the PMR-15 system. Following is a summary of the test methods, the analysis of each test method with regard to PMR-15 system and the results of the initial screening of vendors' materials.

1. Pyrolysis Gas Chromatography (PGC)

   This analysis method gives a complete fingerprint of the material in terms of a chromatogram and a pyrogram, the chromatogram showing solvents and volatile portion of the material below 573K, (572^{o}F) and the pyrogram showing the components of the pyrolyzed resin. It produces very fast and reproducible results. This method indicated considerable difference between suppliers but it does not appear sensitive enough to consistently detect some minor components that are quite critical. For an example of the data, see Figure 2.

2. Fourier Transform Spectroscopy (FTS)

The output is an infrared scan that identifies the functional groups present. Although this method can be quantitive, it is being used as a semiquantitative tool in this program. This method also is very fast and reproducible. It appears to be very sensitive in detecting imidization as noted by the appearance of the bond at 1770 cm^{-1} and changes taking place at 1380 cm^{-1} and 750 cm^{-1}. This was demonstrated using a series of IR scans on uncured PMR-15 resin which was heated so that the imidization would occur. The FTS method was chosen as a receiving inspection requirement in the D180-20545-4 material specification. For an example of the data, see Figure 3.

3. Calorimetry (DSC)

Differential Scanning Calorimetry was evaluated at ambient pressure and under 200 psig in both a nitrogen and an air atmosphere. The results are rather uneventful but they do show volatization taking place in two steps: the first from 372K (212°F) to 392K (248°F) and the next from 392K (248°F) to 437K (329°F). This volatization is followed by a broad exotherm. These results seem to be consistent with the known reactions of the norbornene end-capped addition-type polyimides. DSC under pressure had the same general scan but the outgassing was suppressed considerably and shifted slightly to higher temperatures. Even though DSC does follow the reaction, it would be extremely difficult to quantify the data for specification purposes. Therefore, it was not included as a receiving inspection requirement. For an example of the data, see Figure 4A through C.

4. Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) is very sensitive to the amount of solvent, reaction volatiles, resin, and graphite. It also gives some control over the graphite itself by characterizing the manner by which it decomposes. The TGA is used as a receiving inspection requirement. For an example of the data, see Figure 5.

5. Gas Chromatography/Mass Spectrometry (GC/MS)

Two different methods were evaluated with the GC/MS. The first method was to place the material into the mass spectrometer by the direct probe. The probe was then heated, driving off the volatile products which were immediately analyzed by the mass spectrometer. This method is suitable but does not adequately separate the volatile components.

The second method, and probably the best, was to pyrolize the material under vacuum using a controlled heat-up rate. A sample of the pyrolyzate was withdrawn and injected into the GC/MS. The components were then separated prior to being introduced into the mass spectrometer for identification. Identification was made by computer search of the mass spectrometer library. This method gives good identification of the pyrolyzed products as well as any solvents used in the manufacturing of PMR-15. For example, the normal solvent, methanol, is easily detected by this method. However, some samples analyzed during this phase of the program contained other solvents (i.e., Company B's sample contained butanol; Company D's sample contained methyl isobutyl ketone, ethyl acetate, isopropanol, and ethanol). For an example of the data, see Figures 6A and 6B.

6. Elemental Analysis

Elemental analysis performed during this study included energy dispersive X-ray techniques and emission spectroscopy. A typical analysis, for example, of Company A material should be:

Major (10%)	C
Minor (1 - 10%)	Si, Fe, Al
Lesser (0.1 - 1%)	Sn, Ag, Ni, Cr, Mo, Cu, Ca
Trace (0.1%)	Li, Mg, B, Na, Mn, Ti

It was not deemed essential through the primary effort of the program to quantitize these data. The main element of concern was traces of sodium (or other alkali metals) as it relates to the fiber and its thermal stability. However, we do not see the need to establish receiving inspection requirements on sodium at this time if the fiber vendor will certify the weight loss of his product.

7. Liquid Chromatography (LC)

Prior to the liquid chromatography test, the samples were submitted to thin layer chromatography (TLC) for solvent selection. Using circular development methods and similar plates, which correlate very well to the columns used in the LC, the solvent mixture and strengths are determined and optimized. The solvents selected were then utilized for the parallel modes on the LC. During this evaluation a determination was made that the PMR-15 contained a water-soluble portion. An infrared scan of the water-soluble portion showed that portion to be almost identical to the normal scan of PMR-15. In addition, the water-soluble portion dissolved in the normal organic solvents used with PMR-15. Therefore, the determination was made not to peform LC separations on the water-soluble portion.

a. Size Exclusion Chromatography

Molecular weight distribution was determined by Gel Permeation Chromatography (GPC) (for an example, see Figure 7). Considerable differences were noted between suppliers. Some suppliers' resin had two distinct bands, while others had one major band with some additional small bands. It was also noted that early in the chromatogram there was a small band that increased with the age of the material. GPC was selected as the primary receiving inspection test. (For more detailed discussion of procedures development, see Section 3.6.)

b. Partition Chromatography

The materials were evaluated by both reverse phase and normal phase chromatography. Reverse phase (Figure 8) results in good separation of the material into many bands. It did not appear to be as sensitive to differences in the material as was GPC. All of the samples analyzed gave essentially the same chromatogram. Although the test shows good separation, it appears to add nothing that is not contained in the GPC. Therefore, it was not selected as a receiving inspection test.

Normal phase chromatography was evaluated but not used. The polarity of PMR-15 and the types of solvent needed for normal phase chromatography presented problems with obtaining reproducibility with this analysis method.

c. Adsorption Chromatography

Adsorption Chromatography yields good separation of the material but when used alone it appeared to add nothing that is not contained in the GPC. However, during the evolution of the final HPLC test procedure Adsorption Chromatography proved to be a useful tool in obtaining a more detailed separation of the PMR-15 reaction products. Because Liquid Chromatography was selected as the primary chemical characterization test, the analytical techniques were constantly improved during the program. A more detailed description of the test improvement is given in Section 3.6.

8. Temperature Transition Measurements

This includes correlation of thermal analysis with the heated cell Fourier tranform spectroscopy and mass spectrometry data, Figures 10, 11A, 11B, 3A through 3D, 6A, and 6B. The data correlated quite well in following the reaction. It is interesting to note the dielectrometer (Figure 10) shows a double peak. The first peak appears to be from volatilization and the second peak from the beginning of imidization as detected by the heated cell FTS-IR (Figure 3). It was also noted that, as the material ages, the double peak reduces to a single peak. Dielectrometry was initially selected as a receiving inspection test, but as the program developed it was concluded that the major changes to the graphite/PMR-15 prepreg as detected by dielectric measurements didn't adversely affect the autoclave processing of the material. The test was therefore not included in the material specification.

During the discussion of the specific screening tests performed on the PMR-15 resin samples, an example of the results was included to demonstrate the technique. The procedures used in the comprehensive testing for the remainder of the program are included in Appendix A.

After evaluating the data obtained from the initial Chemical Characterization study, the following tests were selected for determining the chemical characteristics of the graphite/PMR-15 polyimide prepreg:

a. Gas Chromatograph/Mass Spectrometer (GC/MS)
b. Fourier Transform Spectrophotometer (FTS-IR)
c. Thermal Gravimetric Analysis (TGA)
d. High Pressure Liquid Chromatography (HPLC)

The data obtained from the evaluation of vendors materials were incorporated in tabular form (Table I) for comparison. Several conclusions were derived from Table I data and are summarized below:

a. Samples received from Company A and Company C were close to possessing the same chemical properties.
b. Company B material was significantly different than those received from other suppliers and contained the undesirable characteristic of containing a solvent other than methanol.
c. For some unexplained reason, the fractions isolated from Company B and Company C were different from those isolated from Company A materials.

Based on this information and results of an on site survey of the vendors manufacturing plants, additional material was obtained from Companies A and B prior to the selection of the program supplier.

3.2 EVALUATION OF COMPANIES A AND B GRAPHITE/PMR-15 PREPREG

This evaluation consisted of obtaining the chemical characteristics of materials received from Companies A and B. The materials received consisted of graphite/PMR-15 tape, PMR-15 resin, and the monomeric reactants. The chemical characterization of the PMR-15 resin extracted from the graphite prepreg, the PMR-15 resin, and the monomeric reactants revealed significant differences in the materials. Major emphasis was placed on the purity of the monomethyl ester of nadic anhydride and the diamine, methylene dianiline. In addition, the major analysis of both the extracted PMR-15 resin and the neat PMR-15 resin was conducted by the use of High Pressure Liquid Chromatography. Experimental details of these analyses are given below.

3.2.1 CHEMICAL CHARACTERIZATION OF COMPANIES A AND B PMR-15 MATERIALS

This work was centered on (1) analysis of the monomeric reactants, (2) analysis of PMR-15 resin, and (3) analysis of PMR-15 resin extracted from the graphite tape. The analysis was limited to the tests contained in the Material Specification (i.e., GC/MS, TGA, FTS-IR and HPLC) and the dielectric properties.

3.2.1.1 ANALYSIS OF COMPANIES A AND B MONOMERIC REACTANTS

Detailed analyses were conducted on the monomethyl ester of nadic anhydride (NE) and the amine, methylene dianiline (MDA). The analysis was limited to these ingredients since the dimethyl ester of benzophenone tetracarboxylic dianhydride (BTDE) was obtained from a single source. Analysis indicated that the monomeric reactants from the two suppliers were substantially different in quality. The NE received from Company B material was a uniform white powdery material, while the NE from Company A was a non-uniform off-white and was moist. Differential Scanning Calorimetry indicated a melting point of 371K (210°F) for Company A and 375K (217°F) for Company B (Figures 12 and 13). The Company B heat of fusion curve was a little sharper than the Company A (note that the quantities of NE differ). The Company A material undergoes thermal degradation at a lower temperature than the Company B. Thermal Gravimetric Analysis (Figures 14 and 15) indicated the Company B material started to outgas at 397K (258°F). Company A material outgassed at room temperature. The volatile portion of the Company A material was identified as methanol, acetone, toluene, and possibly tetrahydrofuran. Identification was made by gas chromatography-mass spectrometry.

The methylene dianiline material received from both suppliers was in flake form. The sample received from Company B was an off-white color, and Company A's sample was yellow. Differential Thermal Analysis (Figures 16 and 17) indicated a melting point of 364K (198°F) for Company B and 361K (192°F) for Company A. Once again the heat of fusion curve was much sharper for Company B than for Company A. Also the Company A material had a slight endotherm occurring about 346K (165°F), indicating the presence of some contaminant. Thermal Gravimetric Analysis (Figures 18) showed thermal decomposition beginning at 373K (214°F) for Company B and 461K (372°F) for Company A; the Company A material's stability in 473 (394) to 573K (574°F) range was also superior to Company B's. This apparent contradiction in chemical behavior cannot be explained at this time. The gas chromatograph - mass spectrometer did not detect any contaminants. However, it did indicate the Company A material was more prone to fragmentation than Company B's.

3.2.1.2 ANALYSIS OF COMPANIES A AND B PMR-15 RESIN AND GRAPHITE PREPREG

Investigation of the two sets of materials showed some differences in the material received from the two suppliers (Tables II through IV). Some minor differences were detected in the PMR-15 resin before and after the prepregging operation indicating little or no changes to the PMR-15 resin as a result of that operation. The major difference noted in the dielectric properties of the material was not clearly understood since it could not be related to processing and therefore disregarded.

3.2.1.3 CONCLUSIONS FROM THE ANALYSIS OF COMPANIES A AND B MATERIALS

The analysis of data obtained during this study established the following with regards to suppliers' materials:

1. Samples of the PMR-15 graphite received by BAC from Companies A and B showed extensive differences, primarily in purity of the monomers.

2. The monomers used in manufacture of PMR-15 resin by Company B were significantly different from those used by Company A with the materials received from Company B being of a higher purity than the materials received from Company A.
3. Significantly different processes would be required to fabricate laminates from material received from the two vendors. It appears that material received from Company B, possibly because of its higher purity, processes in a much narrower range than that received from Company A.

3.2.1.4 PROGRAM VENDOR SELECTION

Based on results of the evaluation of two lots of material received both from Companies A and B, and a survey of the vendors manufacturing facilities, Company A was selected as the program supplier. The two major reasons for this selection were the overall manufacturing capability with respect to technical competence and quality control and the performance of the graphite/PMR-15 in autoclave molded composites (see Section 4.1).

3.3 QUALITY CONTROL INSPECTION OF COMPANY A HTS/PMR-15 GRAPHITE PREPREG

During the course of the program, several lots of graphite/PMR-15 were received from Company A. With respect to the initial shipments, selected Chemical Characterization tests were conducted on the graphite prepreg. On analyzing these data two major problems were discovered. The first major problem was that the materials received varied significantly with respect to their chemical properties. The second major problem was deterioration in the quality of HTS-2 graphite fiber. These problems could best be explained through the evaluation of prepreg lots 2W4169 received directly from the vendor and 2W4170 received from the vendor through NASA Langley Research Center.

3.3.1 QUALITY CONTROL TESTING LOT 2W4169 AND 2W4170

The Chemical Characterization tests were conducted on prepreg Lots 2W4169 and 2W4170. The resin used on Lot 2W4169 rolls 1 through 3 (Lot 2W4170) and roll 1 was the same, with the remaining 4 rolls (Lot 2W4170) being made from a separate resin mix. The chemical characteristics using GC/MS, Thermal Gravimetric Analysis (TGA), and FTS-IR were closely related. However, the HPLC data showed some differences. Samples of both lots were obtained throughout the rolls of graphite prepreg. These samples were taken to determine uniformity within lots. A summary of these data are presented (Table V through VIII) along with the like data obtained from Lot 2W4083 (Standard Material). Due to the differences noted, new testing procedures were developed for the HPLC to improve efficiency and reliability. For detailed description of procedure development see Section 3.6. The method developed as a result of the development study was a combination of size exclusion chromatography and adsorption chromatography. An example of a chromatogram is given in Figure 19. The first part of the chromatogram with retention times up to 11.00 minutes represents size exclusion and the latter part adsorption chromatography. This method is much more sensitive than the original GPC method, because it provided better resolution of the PMR-15 resin system.

Material representing the 5 rolls of Lot 2W4170 received from NASA Langley were reevaluated using the new HPLC procedure (Tables VII and VIII). The data includes: (1) the retention times with their average and standard deviation, and (2) the area under the peak correlation, with their average and standard deviation. The asterisk indicates where the material (roll 5) is outside the standard deviation. Also notice that roll 5 has a component at retention time 16.30 which is not present in the other samples. That component is about 1 percent concentration and the chromatogram indicates it is a reaction product. This data would indicate that material contained on roll 5 Lot 2W4170 should process differently than the other rolls of material from the same lot. In order to compare HPLC data Lot 2W4169 was retested using the revised procedure and compared to Lot 2W4170 (Table IX). Again the data readily demonstrates the differences between the two lots of material and nonuniformity within a single lot.

3.3.2 QUALITY CONTROL TESTING LOT 2W4215

Material obtained in the second production lot (2W4215) was divided into five rolls in order to study the within lot variation observed in previous lots (i.e., 2W4169 and 2W4170). Chemical characterization was completed on all five rolls with the results indicating that Lot 2W4215 is again substantially different from previous lots of material. Using the revised HPLC procedure, considerable difference was observed. Lot 2W4215 possessed different solubility characteristics and molecular weight distribution. An extra component representing quantitatively about 10 percent of the resin was present.

3.4 QUALITY CONTROL INSPECTION OF COMPANY A CELION 6000/PMR-15 GRAPHITE PREPREG

The results of the Chemical Characterization and associated composite evaluation of lots 2W4169 and 4170 demonstrated that both the resin matrix and HTS graphite fiber were variable leading to multiple autoclave cycles for the production of quality graphite/PMR-15 composite panels. A change in graphite fiber reinforcement was requested and granted from NASA Langley Research Center. The new fiber (NR150B2 sized Celion 6000) then became the reinforcement for the remainder of the program which included Tasks B through H. From this point in time the only analytical method used to obtain the PMR-15 resin characteristics was the HPLC. Following is a brief discussion regarding the lots of material analyzed by the HPLC and the tasks in which the majority of the material was utilized. (See Table XI for summary of data.)

Task B Materials--Lots 2W4240 and 2W4251, Material lot 2W4240 was used in the cure and postcure study of Task B. It was also used to develop the NDI testing document. Material lot 2W4251 was utilized in obtaining flat panel and structural element data.

Task C Materials--Material lots 2W4280 and 2W4282 were utilized in obtaining flat panel and structural element data.

Task D Materials--Material lot 2W4282 was utilized in the 12 ply flat panel whereas lots 2W4716 and 2W4717 were used to make the 6 and 24 ply flat panels required in Task D.

Task E Materials--Lots 2W4301, 2W4345, and 2W4715 were utilized to fabricate the "I" stiffened stringer panels. Lots 2W4317, 2W4345, 2W4388, and 2W4917 were utilized to fabricate the small corrugation stiffened stringer panels. Lot 2W4448 was utilized in fabricating the large corrugation stiffened stringer panels.

Task F Materials--Lot 2W4345 was utilized to fabricate a large sandwich panel which was subsequently machined into 5 small deliverable panels; Lot 2W4364 was utilized to fabricate one small deliverable sandwich panel.

Task H Materials--Lot 2W4364 was utilized to make one sandwich rib and one skin for the demonstration hardware. Lot 2W4394 was utilized to make one sandwich rib and the other skin for the hardware. Lot 2W4448 was utilized to make the corrugations, spar, and angles on the demonstration hardware.

3.5 QUALITY CONTROL DOCUMENTATION FOR PROCESSING GRAPHITE/PMR-15 POLYIMIDE PREPREG

One of the major objectives of Task A was the preparation of the documentation to control the quality of the graphite polyimide components. To achieve this goal, input data was obtained for control processing steps from initial polymer synthesis through final part acceptance. Accept/reject criteria were established for each step and all the required inspection operations defined. Under this task Boeing prepared the following plans and specifications to meet this objective (Appendix B).

QUALITY ASSURANCE PLAN - D180-20545-3

This document defined the specifications and final accept/reject criteria for polyimide components.

MATERIAL SPECIFICATION - D180-20545-4

This document defined the chemical and physical quality of the incoming graphite/PMR-15 polyimide prepreg. This included controls on both the resin and fiber from which the prepreg was constituted and the accept/reject criteria. Since both molding and laminating materials were considered in this program, it was necessary for material specification to cover both types of composites.

PROCESSING DOCUMENT - D180-20545-5

This document governs the fabrication of graphite polyimide composite parts. It defines the handling, layup, bagging procedures, curing parameters, quality control procedures, and the precautions that must be used in the fabrication process. This document covers laminates, chopped fiber moldings, and honeycomb panels. It also contains accept/reject criteria for each process/engineering requirement.

NDI PLAN - D180-20545-6

This plan defines the NDI equipment and procedures to be followed during in-process and final composite inspection.

3.6 DEVELOPMENT OF HPLC TEST PROCEDURES

Initial development of GPC test procedures involved the use of thin layer chromatography to quickly screen solvent systems to be used as the mobile phase. The technique used was a circular development method that rapidly evaluates solvents and modes. Although size exclusion cannot be evaluated with this technique, adsorption and partition chromatography can. The major limitation to this method was that solutions of greater than 50% water strength cannot be tested, which in the case of PMR-15 was not necessary.

Using this technique, the optimum solvent strength is determined and then composition at that solvent strength is evaluated and optimized. The information developed using this technique was then transferred to the liquid chromatograph for further evaluation and optimization. The importance of this evaluation can be seen from the formula expressing liquid chromatography resolution.

$$R_S = 1/4\ (-1)\ N \quad \frac{K'}{1 + K'}$$

R_S = Resolution

a = Separation selectivity

N = Separation efficiency

K' = Solvent strength

From the formula it can be seen that resolution is dependent on the three variables α, N, and K'. Two of these variables are directly related to the solvent used. The composition of the moving and/or stationary phase efects α, while K' is varied by changing solvent strength.

The thin layer chromatography evaluation indicated reverse phase chromatography to be the best mode with a mixture of methyl acetate/pentane at a solvent strength of 0.50 of a 50% water/tetrahydrofuran mixture. The water/tetrahydrofuran mixture was chosen because of its better UV characteristics.

The information gathered from the thin layer chromatograph was evaluated using both reverse phase and gel permeation chromatography. The initial evaluations were conducted using a C_{18} column with water/tetrahydrofuran as the mobile phase. Additional evaluations were conducted using one 500 A^o and four 100 A^o gel permeation columns. This experimental arrangement gave good data. Because of the importance of molecular weight distribution and its effect on processing properties of the PMR-15 resin system, the gel permeation method was initially chosen as a receiving test with the reverse phase chromatography as a backup method. Gel Permeation evaluation continued with the reproducibility of the determinations being continuously monitored. During this monitoring, a variability was noted in the method, with apparent changes occurring in the column. Internal standards were developed to counter these changes. The internal standards consisted of a high molecular weight polystyrene and orthodichlorobenzene. These standards were sufficiently narrow in range to place upper and lower limits on the PMR-15 and proved very satisfactory. However, even with standards the columns still seemed to degrade causing unreliable data. Since the columns possessed the undesirable feature of rapid degradation and also were expensive, it was determined that the method would be uneconomical as a quality control procedure. However, the differences that had been noted in molecular weight distribution between "good" and "bad" batches by the gel permeation chromatography method indicated the concept of controlling the molecular weight distribution was a valid concept. Therefore, evaluation was conducted using DuPont SE 60 size exclusion columns. Initial work was done using tetrahydrofuran/water with 0.1% glutamic acid and 0.1% glycine mobile phase. After extensive evaluation of the glutamic acid/glycine mobile phase it was found that both the glutamic acid and glycine tended to precipitate out in the instrument causing problems. To alleviate this condition, the method was changed by using 33% tetrahydrofuran, 67% water, and 0.1% acetic acid. This modification proved satisfactory and yields a considerable amount of detailed separation. As an added benefit, the method was more economical than those previously evaluated. The SE 60 columns are fairly inexpensive when compared to other columns and have a longer life than the gel columns. The SE 60 columns give excellent separation and consist of a combination of size exclusion and adsorption chromatography. As previously mentioned, considerable detail (see Figure 19) is obtained with this method. The use of these columns does require a very detailed calibration method.

3.7 DEVELOPMENT OF NDI TEST PROCEDURE

Ultrasonic inspection of composite materials generally involves a scanning search for voids and delaminations having dimensions exceeding some established minimum. In most materials this is not difficult since the air gap present in a void or delamination results in a total blocking of the ultrasound beam. For detection of porosity, conditions must be ideal (absolutely uniform signal transmission through ideal material), since the presence of porosity introduces only a slight increase in sound path attenuation at the normal frequencies of operation. In most graphite/epoxy systems inspected to date, the response of solid, non-porous materials is generally uniform enough that porosity conditions could be detected using care and very close cut-off thresholds, using conventional ultrasonic equipment. During this program, two separate NDI procedures were developed; one for the HTS-2 graphite polyimide composites and the other Celion 6000 graphite polyimide composites. Both procedures were cross checked with the procedure used at NASA Langley Research Center with excellent correlation between the BAC and NASA procedures. Detailed discussions pertaining to the test procedures are given below.

3.7.1 HTS-2/PMR-15 GRAPHITE COMPOSITE NDI TEST DEVELOPMENT

During the initial procedure development using HTS-2/PMR-15 graphite composites, a standard composite was fabricated and determined to be essentially void free, by studying the photomicrographs. Various NDI testing conditions were evaluated and subsequently compared to NDI test data obtained from NASA Langley. The procedure accepted using HTS-2/PMR-15 possessed excellent correlation with the NASA Langley procedure (see Figures 20 and 21).

3.7.2 CELION 6000/PMR-15 GRAPHITE COMPOSITE NDI TEST DEVELOPMENT

During the NDI testing of Celion 6000/PMR-15 composites, a higher attenuation than previously experienced using HTS-2/PMR-15 composites was detected. As a cross check, photomicrographs of additional representative samples were obtained from composites containing the two different graphite reinforcements. (See Figures 22 through 25.) The photomicrographs of the Celion 6000/PMR-15 composite indicate essentially void free composites with exception of Lot 2W4240 and compare favorably with the HTS/PMR-15 composites. Based on these data a detailed test development effort was undertaken.

Celion 6000 graphite/polyimides presented a problem due to an apparent slight variation in modulus across the surface of the part. The cause of the modulus variation is possibly due to slightly non-uniform resin flow, cure, or some other unknown parameter. Nevertheless, the variation is there which produces a variable thickness resonance response to ultrasound energy. This response is illustrated in Figure 26 where the through transmission response curves of a uniform thickness sample were plotted at three closely spaced locations using a Holosonics Model 200 system with swept frequency drive. It can be seen that not only do the constructive and destructive peaks and valleys shift in frequency, the intervals between them also vary. The signal variation between the maxima and minima is in the 10 to 15 db range for this particular sample. If a conventional ultrasonic test instrument such as the Nortel 131, with bandpass responses shown in Figure 27, is used for inspection, then the maxima and minima of the composite response would be continually passing through the response peak of the instrument. To verify the variable resonance problem, a standard composite sample (i.e., lot 2W4251) was scanned with the Nortel 131 instrument at

1, 2, 2.5, and 5 MHZ, and broadband at a recording level to produce partial loss of recording. Each of the four recordings produced a unique pattern. If the system gain were increased sufficiently to produce recorded images in the minima areas, then detection of the presence of porosity would be completely lost in the maxima areas. Ideally, the ultrasonic inspection system must possess a flat response over a frequency range sufficient to include one or more of the thickness resonance harmonics of the composite material throughout the scan. This ideal inspection system should include the transducer assembly, the receive amplifier, and the energy source, making pulse sources questionable. In establishing a set-up procedure, using Model 200 with sweep frequency sinc burst drive, it was initially decided to use each panel separately as its own set-up standard. The part was manually searched for nominal maximum indications, using a 5 to 6 MHZ sweep frequency drive. Once a maximum transmission point was located the gain was adjusted to provide a 100% output reference signal. The recorder cut-off was adjusted for 60% of the reference, or approximately 4.5 db below maximum. Subsequent tests, however, indicated that not all porosity conditions were being detected using this technique since, in the case of parts with overall porosity, the set-up was being made on the porosity itself. As a result, the set-up procedure had to be changed to use the straight water path as the set-up standard and the recorder adjusted to cut out for signals under 4 db below this straight water path signal. (Note: This value was obtained experimentally by performing a series of NDI scans at different attentuation levels and matching with the photomicrographs of standard panels, Figures 28 and 29). For this, a Hewlett-Packard 355C attenuator was added to the inspection system. The 5 to 6 MHZ sweep range was chosen because of the upper frequency limitations of the transducer pair and the decreased sensitivity to porosity at the lower frequencies. The NDI testing Document D180-20545-6 was altered to incorporate the above information. The standard samples (i.e., panels from lot 2W4240 and lot 2W4251) were then submited to NASA Langley for a comparison (see Figures 28 and 29). Based on these results and the photomicrographs (Figures 24 and 25), the NDI test procedure was finalized as a quality control test through the remainder of the program.

4.0 TASK B PROCESS STUDIES

This task of the program was devoted to establishing the processes by which the graphite/PMR-15 polyimide prepreg is converted into useful structural elements. The effort was divided into subtasks which included evaluation of commercially available graphite/PMR-15 polyimides, detailed processing of Companies A and B material, and detailed process development of Company A prepreg with regard to fabrication of various structural elements. The processes developed included the fabrication of flat panels, hat sections, "I" sections, honeycomb sandwich panels, and chopped fiber molded panels. During process development studies numerous problems were encountered, which could be expected with new resin systems. The two major problem areas were the PMR-15 resin and/or graphite fiber variability, along with the normal problems associated with elevated temperature testing (e.g., adhesive induced specimen failures). Details of the Task B studies are presented below. Physical and mechanical property testing procedures and the different processes used to obtain the composite and/or structural elements are given in Appendix C.

4.1 PRELIMINARY PROCESSING OF PMR-15 GRAPHITE PREPREGS RECEIVED FROM COMPANIES A, B, AND C

To aid in the selection of a program supplier, a parallel study was conducted under this task to obtain structural properties from composites fabricated using the same materials evaluated in Task A. Toward this goal the material obtained from the three suppliers were molded into composites using the following curing conditions: the graphite prepreg was predried for 2 hours at 408K (275°F) in layers of four plies. The prepreg then was stacked to yield 12-ply laminates, vacuum bagged, and cured in an autoclave using the following cycle: raise temperature under vacuum pressure to 477K (400°F) at 2.9 - 3.4K/minute (5 - 6°F/minute) and apply 1380 KPa (200 psi) and hold for 60 minutes. Raise temperature to 589K (600°F) at 1.8 to 2.9 K/min (3 - 5°F/minute) and hold for 120 minutes, cool to ambient conditions and post-cure under pressure in a press for 16 hours at 589°K (600°F). Panels were NDI tested by through-transmission "C" scans (see Figures 30 through 32) using the initial NDI testing procedure, machined and tested both at ambient and 589K (600°F) (see Table XII).

These data readily show that the prepreg received from Company A produces better composites than from other suppliers. The flexural properties of the composites made from Company A prepreg are excellent when they are normalized to 60% fiber volume. The fiber volumes of all composites made in this initial screening were significantly lower than the desired 60% (i.e., Company A @ 51%, Company B @ 50%, and Company C @ 36%). This was caused by the initial BAC cure cycle which minimizes resin "bleed-off". This cycle would indeed cause some problems at the prepreg manufacturers' facilities in that, by lowering the prepregs' resin content requirement, it would in turn cause problems in obtaining uniform graphite prepreg. To initially demonstrate the shelf life capability of the graphite/PMR-15 system, composites were fabricated using 50 day old material aged at 255K (0°F) and upon testing yielded equivalent properties (Table XIII).

4.2 DETAILED PROCESSING OF COMPANIES A AND B

In conjunction with the chemical characterization of the second lot of prepreg materials received from the two suppliers (Section 3.2), a more extensive processing evaluation of the materials was conducted. The evaluation of the materials consisted of processing each system by four different cycles and fabricating (1) composites for mechanical properties testing, (2) hat sections with both systems, and (3) a honeycomb sandwich panel from the Company A material. The reason for the numerous processing cycles was to evaluate the processing limits of the two systems and, based on NDI testing and mechanical properties, select the most viable system. For base data, a press-cured panel was fabricated using both materials and the processing cycle developed by TRW Equipment Laboratory for the press molding of jet engine compressor blades. As previously indicated, all panels were subjected to NDI testing. Following is a brief description of the experimental data.

4.2.1 EVALUATION OF COMPANY B'S MATERIAL

Graphite composite panels were fabricated using the material furnished by Company B. The first series of panels were fabricated to obtain composite property data for comparison with like data obtained from Company A's material. After NDI testing (ultrasonic C-scans) showed the panels to be of poor quality, additional panels were fabricated using three additional processing/curing cycles (see Appendix C). The resulting composites were judged to be of poor quality except for a 1.5mm thick (0.060 inch) unidirectional panel 1A fabricated for tensile testing. Table XIV presents the data obtained from all the panels. The press-molded panel (No. 4) was fabricated using the well-known and optimized curing cycle developed for fabrication of jet engine compressor blades by TRW Equipment Laboratory under a NASA Lewis Research Center contract. The NDI testing indicated the panel to be of excellent quality (see Table XIV for property data).

4.2.2 EVALUATION OF COMPANY A MATERIAL

Graphite composite panels identical to the panels described in paragraph 4.2.1 were fabricated using materials received from Company A. The composites fabricated for mechanical property determination using previously developed curing cycles (refer to Section 4.1) were of a marginal quality as indicated by NDI testing. These data tended to confirm that a variability did exist in either the PMR-15 resin or the HTS-2 graphite fiber or both. However, one of the cycles used did produce a composite that met the NDI standards and yielded satisfactory mechanical properties (Table XV). Based on the results of these data as compared to Company B's data, Company A was selected as program supplier.

4.3 PROCESSING PROBLEMS WITH COMPANY A MATERIAL

Based on the results of the previous study (para. 4.2.2), additional prepreg was obtained from the program supplier in production quantities. Using the first lot of production material (lot 2W4169), a cure study was conducted, because the material possessed different chemical characteristics (para. 3.3) than the baseline system (lot 2W4083). This cure study used flat panels and was based on the concept of "energy-input". The "energy-input" was defined, for the purpose of the study, as the area under the curve as depicted on the time vs. temperature record obtained from each autoclave cycle before the full vacuum and pressure was applied to the assembly. All other variables such as vacuum levels, cure times, cure temperature, rate of temperature rise, and cure pressure were held constant. Appendix C lists the processing conditions. After the panels were postcured 16 hours at 589K (600^{o}F), they were NDI tested, machined into test coupons, and their mechanical properties determined (Table XVI). Upon analysis of the data, the trends were summarized and are as follows:

1. The curing parameters have definite effect on composite properties.
2. NDI testing indicates only the uniformity of the laminate but this uniformity is apparently not correlatable to mechanical properties.
3. When the general area under the time-temperature curve lies between 49 to 66X10^{6} mm secs (1.9 to 2.6X10^{6} in secs.), NDI testing generally indicates that a uniform panel is obtained.

4.3.1 VARIABILITY OF LOT 2W4169

After developing an acceptable autoclave cure cycle, panels were fabricated from prepreg obtained adjacent to or near the samples of prepreg used for the Chemical Characterization Study (Lot 2W4169 samples 1 and 2). Mechanical properties were obtained from the cured composites (see Table XVII). A comparison of these data indicates variation within the lot. This confirms the previously reported chemical characterization which indicated that sample 2 was indeed different than sample 1 (see Section 1.3).

4.3.2 EVALUATION OF LOT 2W4170

Due to difficulties encountered at NASA Langley, samples of their HTS-2/PMR-15 were submitted to BAC for evaluation. Five composite panels were fabricated, NDI tested, machined, and mechanical properties determined (see Table XVIII for results). The cure parameters used were those developed on Lot 2W4169 (see Appendix C) and were identical to the cycle used by NASA Langley. The mechanical and physical properties of the composites from roll 5 were not determined because of their extremely poor NDI test results.

4.3.3 EVALUATION OF LOT 2W4215

Composites were fabricated from Lot 2W4215 using both Process Specification cycles (Appendix B, D180-20545-5). NDI test results of the laminates indicated poor composites. Due to the poor NDI test results, mechanical properties were not obtained. An additional 11 cure cycles were evaluated with the same results. This work tends to verify the chemical characterization reported (Table X). No additional work was done using this material.

4.3.4 MULTIDIRECTIONAL COMPOSITES

With the analysis of three separate lots of HTS-2/PMR-15 graphite prepreg the first major problem of the program appeared: the variability of the materials received from the prepreg supplier. The cause of the problem was not readily apparent but was attributed to either the PMR-15 resin and/or the HTS-2 graphite fiber. In an attempt to isolate the problem multidirectional composites were fabricated using Lot 2W4169.

A process was developed using a $(0^{\circ},\pm45^{\circ})_{8T}$ balanced construction with a nominal thickness of 3.2 mm (0.125 inch). A 300 mm X 150 mm (12 inches X 6 inches) composite was fabricated, NDI tested, and cross sectioned across the width of the panel. The composite cross sections were polished and micrographs obtained. A portion of panel was supplied to NASA Langley for their evaluation with respect to NDI quality (for more detailed discussion see Section 3.7). The cure cycle used for the multidirectional composite was the revised cycle obtained from prepreg Lot 2W4169. The only difference in the cycle was limiting the cool down rate to 1.1K (2°F) per minute maximum.

4.3.5 SUMMARY OF DATA THRU LOT 2W4215

1. Two excellent multidirectional composites of greater than 2.5 mm (0.1 inch) thickness were fabricated from Lot 2W4169 prepreg and evaluated by both NDI testing methods and photomicrographs of cross sections from the composites. The orientations of the composites were $(0^{\circ},90^{\circ})_{4T}(90^{\circ},0^{\circ})_{4T}$ $_S$ and $(0^{\circ},\pm45^{\circ})_{4T}(\pm45^{\circ},0^{\circ})_{4T}$ S with balanced construction.
2. Verification of the BAC NDI test method was obtained using both unidirectional and multidirectional composites of 3.2mm (0.125 inch) nominal thickness.
3. The mechanical property data obtained in the program was good, but there were indications that the quality of HTS-2 graphite fiber had deteriorated and could possibly be a cause of the variability problem. The basis for this observation was the lower flexure properties on part of Lots 2W4169 and 2W4170.
4. Material Lots 2W4169 and 2W4170 (except roll 5) were processed successfully per D180-20545-5, as determined by NDI testing.

5. Attempts to fabricate graphite composites of greater than 2.5mm (0.1 inch) thickness using Lot 2W4215 were not successful based on NDI test results.

4.3.6 GRAPHITE FIBER ISOTHERMAL AGING STUDY

In reviewing the first quarterly report from General Dynamics Convair Division (Reference 1) it was noted that HTS graphite fiber showed a significant weight loss after isothermal aging at 589K (600°F). Prior to selection of the graphite fiber reinforcement and in an attempt to solve the variability problem, it was decided to perform a brief weight loss study of various commercial graphite fibers. The fibers selected to undergo isothermal aging were Hercules HMS and HTS, Morganite Modmor II and Celanese Celion 3000 and 6000. Samples were prepared, weighed, and placed in a 589K (600°F) environment. Periodically the samples were removed and cooled in a desiccator and reweighed. Results are shown in Table XIX. Preliminary indications were that the HTS graphite fiber didn't possess the necessary thermal stability for the program.

The data obtained using the Celanese Celion 3000 and 6000 graphite were poorer (i.e., weight loss was higher) than reported by the vendor or by General Dynamics (Reference 1). It was for this reason a second series of tests were conducted with the results showing the same trends (Table XIX). The repeat tests were terminated at 628 hours because of an oven controller failure.

Another series of experiments were conducted as a result of these data and verbal conversations with both the fiber and prepreg manufacturers.

The fibers evaluated in these tests were as follows:

1. Celion 3000, Lot HTA-7-7311 Package 41
2. Celion 3000, Lot HTA-7-7311 Package 207
3. High Purity T-300, Lot H.P.
4. Hercules HTS-2, Batch 76-8
5. Modmor II, Batch 0702

The data obtained in the experiment are presented in Table XX. The results of this test are slightly different than the previous test. The second test indicates that the Celion fiber does not lose as much weight at 589K (600°F) as previously indicated. It does, however, show the same trends that previous studies by BAC and other investigators showed. The cause for the different loss rates of Celion and HTS fiber was probably sampling, fiber variability, and/or testing conditions. Careful consideration was given in selecting a graphite fiber and it was the position of BAC that the fiber used on the program should be the most thermally stable of the high strength/intermediate modulus fibers presently on the market.

To further investigate the thermal stability of HTS-2 fiber, samples of the fiber were obtained from Companies A and B and subjected to isothermal aging. These fibers (i.e. the fibers received from Companies A and B) were prepared, placed into a covered, dried, tapered glass dish, weighed, and placed into a 589K (600°F) gravity oven. Periodically the samples were removed, cooled in a desiccator and reweighed. Results of the data are shown in Table XXA. In the initial portions of the study, the HTS-2 appeared to be more thermally stable than previous tested lots. However, after 600 hours of aging the weight loss rate increased so that at 1152 hours of exposure the total weight loss was approximately the same as HTS at 1152 hours. The overall conclusion of the fiber aging studies was that the

HTS-2 and the Celion graphite fibers were essentially the same with respect to weight loss and poorer than the Modmor II fibers. Based on the BAC obtained data, the fact that Modmor II fibers were no longer being produced, and the recommendation of NASA program monitor, Celion 6000 (NR150B2 sized) was selected for the remainder of the program.

4.4 TESTING PROBLEMS ASSOCIATED WITH COMPOSITE EVALUATION

During the course of the program numerous problems associated with obtaining mechanical properties of the graphite composites were encountered. Generally speaking, most of the problems were in obtaining 589K (600^{o}F) properties; however, with respect to the compressive properties, great difficulty was experienced at all temperatures. The major testing problems could be summarized as follows:

1. Sensitivity of flexural and shear properties to composite thickness.
2. Obtaining compressive properties on laminates, sandwich panels, and structural elements.
3. Obtaining 589K (600^{o}F) tensile and compressive properties on flat laminates, structural elements, and sandwich panels.

The testing problems were encountered throughout the program, but for the sake of simplicity the problems and their solution are discussed in this section.

4.4.1 SENSITIVITY OF FLEXURAL AND SHEAR PROPERTIES TO COMPOSITE THICKNESS

In evaluation of the graphite/PMR-15 graphite composites the mechanical properties were abnormally low, but initially, the low properties were attributed to the low fiber volume of the composites and the HTS-2 fibers used. When the graphite fiber reinforcement was changed to Celion 6000 the nominal per ply thickness was reduced from 0.190 mm (0.0075 inch) to 0.132 mm (0.0052 inch) and the fiber volumes were increased to approximately 60 percent. The flexural properties of a 24 ply (3.17 mm (0.125 in)) composite with a fiber orientation of zero degrees still were below 1378 MPa (200 ksi). To isolate the cause for the low values, a study was conducted to determine if the low flexural properties could possibly be caused by the testing method. The study included the parameters of composite thickness and the specimen loading method (i.e., bag side in tension or compression). Results of this study are given in Table XXI and Figure 33. Figure 33 readily shows a dramatic change in flexural properties of Celion 6000/PMR-15 graphite composites, hence a standard thickness of 2.0 mm (0.080 inch) was adopted for composites used in obtaining flexural and/or shear properties.

4.4.2 TENSILE PROPERTIES AT 589K (600^{o}F)

During the testing of unidirectional composites in this task it was found that obtaining the 589K (600^{o}F) tensile properties was more difficult than originally believed. Several different techniques were used in an attempt to obtain the 589K (600^{o}F) tensile strength and included using A7F bonded aluminum tabs, FM 34 and A7F bonded polyimide fiberglass tabs, FM 34 bonded polyimide fiberglass tabs with pin grips, and finally HT424 film adhesive bonded polyimide fiberglass tabs. With respect to the polyimide (A7F) bonded aluminum tabs, the wide differences in the coefficient of thermal expansion between aluminum and graphite composite cause specimen distortion and/or tab debonding. This problem was solved by using polyimide glass laminate tabs, but the two polyimide adhesives used (i.e., FM 34 and A7F) didn't produce acceptable bonds all the time. Further attempts to solve this problem included the use of pin grips, which were found to be unacceptable due to the low bearing strength of the polyimide glass laminate and/or the PMR-15 graphite composite. The final approach was to use HT424 film adhesive and the polyimide glass laminate tabs. This was not the most desirable approach due to the inability of the film to withstand the 589K (600°F) longer than approximately 15-20 minutes; however, it was the only system to produce reproducible tab bonds. This caused the testing to be more time consuming because the specimen had to be tested one at a time. This was caused by the requirement of holding the specimen at 589K (600°F) for a minimum of 10 minutes to obtain equilibrium with the test environment.

A similar study was also conducted in order to obtain a method for testing the sandwich panels in flatwise tension. The room temperature properties were easily obtained but the 589K (600°F) properties were more difficult to test.

Studies using steel flatwise tensile block and three adhesives (FM 34, A7F, and HT424 film adhesive) were conducted with FM 34 failing at the graphite/PMR-15 composite surface and the A7F failing at the steel block adhesive. The only adhesive surface to produce satisfactory bonds at both the steel and composite interfaces was the HT424 film. The performance of the bonded block was satisfactory at short times at 589K (600°F) producing the same testing inconvenience as experienced with the tensile specimens.

4.4.3 COMPRESSION PROPERTIES OF GRAPHITE COMPOSITES AND SANDWICH PANELS

The most difficult testing problem encountered on this program was obtaining the compressive properties of flat laminates, sandwich panels, and the structure elements at 589K (600°F). As in the case of tensile testing it was found that obtaining compressive properties was more difficult than previously anticipated. It was known that by using the Celanese compression specimen compressive properties could be obtained. To alleviate the testing time required of a Celanese coupon, various other coupon configurations and/or testing fixtures were evaluated with only marginal success. The first specimen evaluated was the ASTM D694 coupon with an improved testing fixture. The predominate failure mode of the coupons was end crushing. To alleviate this situation, the test coupon was modified to a straight side coupon and tested, using a special compression test fixture. With the new test fixture, some success was obtained but due to critical specimen machining and misalignment of the test fixture caused by subjecting the fixture to 589K (600°F), this test method was also discarded. Hence the majority of the compressive data obtained on flat panel coupons were obtained from Celanese test coupons using polyimide fiberglass tabs bonded with A7F adhesive film.

The next major problem was the testing of sandwich panels in edgewise compression. The specimen finally used was a modified ASTM specimen in which polyimide fiber glass tabs, similar to the ones used on the Celanese test coupon, were used to stabilize the ends of the graphite sandwich panel. These tabs, in conjunction with a potting compound at the ends of the test specimens, introduced the compressive loads during testing into the sandwich faces at the center of the specimen. Some minor difficulties were encountered in finding a suitable potting compound that could withstand the 589K (600°F) test temperatures and still perform the necessary stabilizing function. After unsuccessfully trying BR-34, HT424 paste adhesive was selected, but the same problem of single specimen testing as described in the discussion on tensile testing was experienced.

4.4.4 STRUCTURAL ELEMENT TESTING

The last testing problem to be solved was the compressive testing of structural elements (i.e., hat stiffened, multiple hat stiffened, and "I" stiffened panels) at both ambient and 589K (600°F). The major problem was to stabilize the ends of the specimens so that the loads could be introduced into the center portion of the specimen. This was accomplished by potting the ends of the specimens in a room temperature curing aluminum filled epoxy (see Figure 34). The room temperature properties were easily obtained using the specimen (see data from para. 4.5.2) but obtaining the 589K (600°F) properties was another matter. Unsuccessful attempts were made to use high temperature potting materials such as BR 34 and HT424 paste adhesives. It was then decided to design a test set-up in which only the center portion of the test specimen would be heated (see Figure 35). It was found that a black heat absorption paint was necessary for obtaining a uniform temperature across the center of the specimen when using quartz lamps as the heat source.

4.5 DETAILED PROCESS DEVELOPMENT

Due to the major problem of material variability, the process development phase of the program lacked continuity. A suitable process was developed using HTS-2/PMR-15 graphite prepreg. However, as the material variability problem surfaced, autoclave processes had to be developed based on the chemical characteristics of the specific lot of graphite prepreg. For the sake of simplicity the processes developed for flat laminates, hat section, multiple hat sections, sandwich panels, chopped fiber moldings will be discussed separately in this section. The major portion of process development effort used Celion 6000/PMR-15 graphite tape. As previously noted, some of the process development work used HTS-2/PMR-15 graphite tape. For the purposes of this section and report continuity, the processes developed either with the HTS-2/PMR-15 and Celion 6000/PMR-15 are assumed to be the same, but later studies should be conducted to demonstrate this fact. Details of the experimental studies are given below.

4.5.1 FLAT LAMINATES

In the process studies for flat laminates, laminates of three thicknesses and three fiber orientations were investigated. The laminates were nominally 0.76 mm (0.030 inch), 1.52 mm (0.060 inch), and 3.16 mm (0.125 inch) and each thickness was evaluated in 3 fiber orientations (0^o), $(0^o, 90^o)_S$, and $(0^o, \underline{+}45^o)_S$. The reason for the fiber orientation study was to investigate thermal stresses, load transfer, and microcracking tendencies associated with high temperature processing. The study determined that the process was amenable to the different configurations. Some difficulty was experienced in scaling up from the 1290 square mm (72 square in) size and with some of the lots of material with the thickness in excess of 2.03 mm (0.080 inch). For large area laminates special attention was necessary for the removal of the large volume of reaction products generated by the PMR-15 during the autoclave cure cycle. Also, special consideration was given to the warpage problem associated with graphite composites, in that all laminates used in a secondary bonding process had to have surface bleeders on both sides of the composite. More detailed discussion of the processes are given below by laminate thickness.

4.5.1.1 0.76 mm (0.030 inch) FLAT LAMINATES

No specific problems were encountered in fabricating any laminate of this thickness. The majority of the work was with Celion 6000/PMR-15 graphite tape. Properties determined are presented in Table XXII.

4.5.1.2 2.03 mm (0.080 inch) FLAT LAMINATES

The majority of the process development using Celion 6000/PMR-15 graphite composite used a thickness of 2.03 mm (0.080 inch) in place of 1.56 mm (0.060 inch) since it was at this thickness that all of the quality control panels were tested (see para. 4.4.1). It was assumed that if a 2.03 mm (0.080 inch) composite could be fabricated, all of the thinner composites could also be fabricated. (Note: The thicknesses were also a direct result of per ply thickness of Celion 6000/PMR-15 and not HTS-2/PMR-15 graphite prepreg.) No particular problems were encountered at this thickness except maybe the warpage problem often associated with graphite composite systems.

As with the case of 0.76 mm (0.030 inch) composites, special "bleeder" systems were developed for those parts used in secondary bonding, in order to prevent severe warpage problems. Also the same type "bleeder" systems were used in the large area composite fabrication. Properties determined for the different fiber orientations are given in Table XXIII.

4.5.1.3 3.18 mm (0.125 inch) FLAT LAMINATES

Most of the work with HTS-2/PMR-15 graphite was done with this thickness. Among the studies conducted using this thickness was the multidirectional laminate (0^o, $\pm 45^o$) with both HTS-2 and Celion 6000 fiber and the cure and postcure study. Details of these studies are described below.

Using HTS-2/PMR-15 graphite prepreg from Lot 2W4169 a process was developed using a $(0^o, \pm 45^o)_{8T}$ balanced construction with a nominal composite thickness of 3.2 mm (0.125 inch). A 300 mm X 150 mm (12 inch X 6 inch) composite was fabricated, NDI tested, and cross sectioned across the width of the panel (see Figure 20 for NDI scan). As a cross check on the NDI testing procedure and to demonstrate that Boeing could fabricate this panel thickness, a portion of the composite was submitted to NASA Langley Research Center for a comparison (see Figure 21). The process cycle used for its fabrication is described in the D180-20545-5 processing document. During this time period, indications of poor reproducibility of the HTS-2 graphite fiber became apparent (see Section 4.3) and the Celion 6000 fiber was substituted on the program. Due to the fiber change the multidirectional study was repeated with the Celion 6000 graphite tapes. Initial attempts to fabricate 24 ply 3.2 mm (0.125 inch) multidirectional composites were unsuccessful; however, using lots 2W4240 and 2W4251, 24 ply unidirectional composites were fabricated for and used as part of other studies (see detailed discussion below). At this time additional studies for the fabrication of multidirectional composites were conducted with prepreg Lot 2W4345 and consisted of evaluating different prestage cycles and "bleeder" systems. A successful process was developed for 93,000 square mm (144 square inches) composites using Lots 2W4345 and 2W4388. Because of the material variability problem, the process did not produce satisfactory composites using the other lots of material. From the viewpoint of Boeing personnel this was one of the most serious problems encountered during the program and as previously stated was the result of the material variability.

It was previously mentioned (Section 3.4) that 24 ply unidirectional composites were fabricated using prepreg Lots 2W4240 and 2W4251. The composites fabricated from Lot 2W4240 used in the cure and postcure study consisted of two 305 mm X 305 mm (12 inches X 12 inches) panels using the method described in D180-20545-5 process specification. These panels were also used in the NDI test development program (Section 3.7). The variable studied during the cure study was limited only to the final cure temperature. On one composite, the final cure temperature was 589K (600^{o}F) and the other composite was cured at 604K (625^{o}F). The two composites were then machined into four equal laminates and post cured using various post cure temperatures and times. The post cured composites were then machined into flexural and short beam shear specimens and their properties determined both before and after isothermal aging at 589K (600^{o}F) for 125 hours. There appeared to be little difference in the overall properties (Table XXIV) and so the lowest autoclaving temperature and shortest postcuring times were selected as processing conditions and incorporated into the processing documents. Subsequent NDI testing of these composites indicated that the Celion 6000/PMR-15 "C" scanned differently than the HTS-2/PMR-15 composites (for more detailed explanation see Section 3.7). This fact, in conjunction with the composite thickness, was the reason for the lower than expected mechanical properties obtained with this particular lot of material (2W4240).

4.5.2.1 SINGLE HAT SECTIONS

It should be emphasized at this point that all stiffener elements fabricated under this Task B were strictly designed to demonstrate the fabricability of the graphite/PMR-15 composite system. In order to demonstrate the versitility of these manufacturing techniques, the elements fabricated were significantly thicker and/or heavier than elements used in any proposed structure. The property data obtained should only be used in comparison with properties of similarly constructed elements.

Initially, seven hat sections were fabricated to evaluate the process, material handling characteristics, tool design, and vacuum bagging techniques. The first four hat sections were to evaluate two separate fiber orientations. Two of the hat sections were made with a balanced layup of $(0^{\circ},90^{\circ})_{4T}$ while the remaining two were made with a balanced $(\pm45^{\circ})_{4T}$ layup. All sections yielded good NDI scans and visually were acceptable with the exception of the bottom radii. It appeared that in all cases the "bleeder" systems bridged, causing a no pressure area along the bottom radii. See Figure 36 for an overall view of two hat sections. Flat panels were bonded to the hat sections and compressive strengths determined (Table XXV).

(Note: Due to testing limitations, panels were evaluated as stiffened panels.) Based on the results of the initial four hat sections, two additional sections were fabricated using a balanced layup $(\pm 45^{0})_{4T}$. The two variations used in processing these hat sections were 1) improve bagging procedures by prestaging the layup and cutting the top bleeder along the bottom radii, and 2) using an angle pressure plate on an unstaged layup. Results of these hat sections showed a definite improvement but fell short of the desired results. Consequently, the hat section tooling was modified by enlarging the tool radii to 3.2 mm (0.125 inch). Using the new tooling, a seventh hat section was fabricated using a balanced layup $(\pm 45^{0})_{4T}$. The process included the cut top bleeder, prestaged layup, and improved over the hat sections made on the previous tooling with 1.5 mm (0.060 inch) radii. However, due to a change in the material chemical properties, this process was not feasible. Consequently, the final process selected and described in the processing document includes a compromise consisting of a one stage autoclave cycle with a tool of not less than 3.2 mm (0.125 inch) bottom radii. The compressive properties of the secondary bonded hat sections were so promising that the next phase of the program studied the fabrication of cocured hat stiffened panels. Two separate cocured hat stiffened panels approximately 203 mm (8 inches) X 914 mm (36 inches) were fabricated using the same technique as described above. The only difference is that the "C" section tool was placed on a flat panel (i.e., 12 plies $(0^{0}, 90^{0})_{S}$) and the hat section placed on top of the tool (see Figure 37 for cocured hat stiffened panel). The panels were then tested in buckling with the results given in Table XXV. Again, the overall properties were equivalent to the secondary bond hat stiffened panels.

4.5.2.2 MULTIPLE HAT SECTIONS

With the success obtained with single hat sections the study was then expanded to demonstrate that the process would work equally well with multiple hat sections. The only variation studied here was the open mold versus the closed mold method of fabrication. Two multiple hat sections were fabricated using the "open" tool concept. The two sections were made from balanced layups: $(0^{o},90^{o})_{4T}$ and $(\underline{+}45^{o})_{4T}$. It was very difficult to vacuum bag the multiple hat section layup but the resulting structural elements were visually acceptable with the exception of the bottom radii. The $(0^{o},90^{o})_{4T}$ section possessed less "resin bridging" than the $(\underline{+}45^{o})_{4T}$ layup. In comparison, a process was developed where two multiple hat sections were fabricated using the closed mold concept (Figure 38). Hat sections fabricated using this technique presented a better visual appearance although they didn't show any differences with regard to NDI testing and mechanical properties when tested as a hat stiffened panel (see Table XXV).

4.5.3 FABRICATION OF "I" BEAM STRUCTURAL ELEMENTS

The "I" stiffener configuration developed under this phase consisted of two 102 mm (4 inch) X 25 mm (1 inch) "C" sections with two 50 mm (2 inch) cap strips. The size of the stiffener was sufficient to permit fabrication of large elements, since this only involves increasing the web height. The 102 mm (4 inch) web is also deep enough to minimize edge concentrations at the corner radii. The radii are not as important in the case of the "I" beam as was found in the hat section (para. 4.5.2.1) since a male mold was used in lieu of a female mold. The stiffeners had a nominal wall thickness of 3.2 mm (0.125 inch) which is the most difficult laminate construction to fabricate and showed a definite difference when subjected to both NDI and mechanical property testing.

Two separate concepts were studied for the fabrication of "I" beam structural elements. The first concept utilized secondary bonding of subcomponents (i.e., C sections and cap section) with the second being the cocuring of the assembly in one operation. The tooling used in both cases is shown in Figure 39. In the first concept (i.e., secondary bonding), two C channels were fabricated on the side portion of the mold using a balanced $(0^o,90^o)_{4T}$ layup and the cap section was fabricated as a flat laminate 100 mm (4 in) by 760 mm (30 in) using a balanced $(0^o,90^o)_{8T}$ layup. See Figure 40 for a photomicrograph of a cross-section of the cap section. The subcomponents were autoclave molded using Method 1 of D-180-20545-5. The subcomponents were machined to size, primed with a modified LARC 13 adhesive (A7F), assembled on the tool using A7F adhesive film 3 mm (0.012 inch) thick and bonded in the autoclave. Using the cocuring concept, identical layups were made as previously described on the tool, assembled, vacuum bagged, and the part again processed using the same curing schedule.

The secondary bonded "I" beam and its subcomponents were successfully NDI tested. Both panels were prepared for determination of compressive strength, as described in paragraph 4.4.4 and coupons taken from the excess were machined for determination of flexural and shear properties. In Figure 41, the secondary bonded "I" beam is #3 and the cocured beam is #4.

Three additional "I" beams were fabricated; one was cocured and was 864 mm (34 inches) in length while the other two were secondary bonded and were each 422 mm (17 inches) long. The secondary bonded "I" beams used A7F adhesive. Visually, the "I" beams were acceptable and compressive buckling strength was determined as described in paragraph 4.4.4. Results of the element testing (see Table XXV) definitely shows the preferred process to be the secondary bonding technique. However, the cocured process was indeed demonstrated as a viable route if thinner web and/or cap sections were required.

4.5.4 STRUCTURAL ELEMENT TESTING

Testing was completed on the structural elements fabricated in this phase of the program. The elements were tested at room temperature and included hat sections, multiple hat sections, cocured "I" beams, and secondary bonded "I" beams (Table XXV). Photographs were taken of some of the typical failures (Figures 42 through 44).

The failed specimens were evaluated by stress engineers regarding their failure mode and loads. Preliminary conclusions with regard to the secondary bond "I" beam elements were that they were equivalent to and probably better than similar "I" beam elements made from Hercules AS/3501-5 epoxy/graphite systems (Ref. 2). In addition, the preliminary indications were that the following manufacturing methods yield the best overall elements:

1. "I" Beams - C channel molding with secondary bonding.
2. Hat Sections - Open mold fabrication with secondary bonding.
3. Multiple Hat Sections - Matched mold fabrication with secondary bonding.

4.5.5 PROCESS DEVELOPMENT OF PMR-15 GRAPHITE/HONEYCOMB PANELS

In the development of processing techniques for honeycomb core panels, Boeing assessed cocuring versus secondary bonding and three types of core materials (glass-polyimide, stainless steel, and titanium). Table XXVI shows the type and number of panels and specimens fabricated with HRH-327 polyimide glass honeycomb core. Prior to the start of the sandwich process development study, a short adhesive study was conducted with FM-34 adhesive (American Cyanamid), LARC-13 (LaRC), and A7F (TRW). The results of these studies indicated that the LaRC 13 modified adhesive (i.e. A7F) was the best adhesive for large area bonding and provided acceptable properties. However, FM 34 adhesive was used as an alternative system on a random basis and also provided excellent properties as long as the panel size was relatively small (i.e., no more than 305 mm (12 inches) wide). The three secondary bonded sandwich panels used skins that had thicknesses of 0.76 mm (0.030 inch), 1.52 mm (0.060 inch), and 3.05 mm (0.125 inch) respectively. The second set of three sandwich panels were identical except that they were cocured. The last two panels consisted of 1.52 mm (0.060 inch) Celion 6000/PMR-15 graphite skins with stainless steel and titanium core. Details of adhesive evaluation and the sandwich panel fabrication and testing are given below.

4.5.5.1 ADHESIVE SELECTION FOR HONEYCOMB SANDWICH PANELS

The initial problem in honeycomb sandwich fabrication was the selection of an adhesive. Toward this end two studies were conducted on candidate adhesive systems. Following is a description of those studies.

Two HTS-2/PMR-15 sandwich panels using titanium core and two adhesives were fabricated. The two adhesives initially evaluated were BR34/FM34 and LARC-13 (Figure 45). The sandwich panel NDI evaluation indicated the FM34 adhesive to be slightly superior to the LARC-13 adhesive. The sandwich panels were tested in flatwise tension at 295K (RT) and 589K (600°F) and confirmed the NDI test results (i.e., the FM34 system yielded 4.18 MPa (606 psi) at 295K (RT) and 2.69 MPa (390 psi) at 489K (600°F), whereas the LARC-13 values were 2.33 MPa (338 psi) at 295K (RT) and 1.13 MPa (164 psi) at 589K (600°F). Using these data another study was conducted. The study consisted of making lap shear panels using HTS-2/PMR-15 graphite composites as the substrates and three polyimide adhesives (FM34 from American Cyanamide, LARC-13 from NASA's Langley Research Center, and A5F using P13N/AMOCO 1130L obtained from Ciba Geigy and AMOCO.) The test program included testing controls at ambient and 589K (600°F) with the remaining specimens being isothermally aged at 200 hours and 589K (600°F). (See Table XXVII for results.) Based on the analysis of these data the AMOCO modified P13N system appeared to possess slightly better properties after isothermal aging than the other two adhesives. However, the initial properties of the LARC 13 adhesive were slightly better than the A5F. Based on these data, the adhesive selection was a compromise, A7F (blend of LaRC-13 and AMOCO 1130L).

4.5.5.2 GRAPHITE/PMR-15 SANDWICH PANEL EVALUATION

The first series of sandwich panels evaluated were the secondary bonded panels. The secondarily bonded panels were fabricated using the following process:

1. The various thickness skins were fabricated using material from Lot 2W4251 and Method 1 process (D180-20545-5) except the postcure was omitted.
2. The precured skins were lightly abraided, primed with A7F paste, assembled onto primed 305 mm (12 inch) X 305 mm (12 inch) honeycomb core with A7F film adhesive, as specified in Table XXVI.
3. The sandwich was then autoclave cured using 689 kPa (100 psi) and the previously reported A7F cure schedule.
4. The sandwich panel was postcured 4 hours at 604K (625°F) under slight restraint.

The cocured sandwich panels were processed as follows:

1. The Celion 6000/PMR-15 skins were assembled with the A7F adhesive and A7F primed core.
2. Processing conditions were as described in the D180-20545-5 Document (see Appendix B).
3. The sandwich panels were then postcured 4 hours at 604K (625°F).

After completion of the postcuring cycle, the sandwich panels were machined and specimens prepared for testing (see Table XXVIII for results). Testing included flatwise tension and edgewise compression at both ambient and 589K (600°F). See Figure 46 as an example of sandwich panels. For a more detailed discussion of the testing problems associated with testing of sandwich panels, see paragraph 4.4.4. Results of these studies indicated that the preferred process was secondary bonding of precured skins. The main reason for this conclusion was that the relatively low pressures required during cocuring to prevent the HRH 327 low density core from crushing didn't provide quality PMR-15 graphite skins.

4.5.6 PROCESS DEVELOPMENT CHOPPED FIBER MOLDING COMPOUND

A chopped fiber molding process was developed in this phase of the program. During the course of the study, six different parameters were investigated: (1) resin content, (2) fiber length, (3) resin flow, (4) molding temperature, (5) pressure application temperature, and (6) dwell temperature. All the work in this phase of the program was performed on flat laminates. Each molded composite was tested for tensile and flexural strength and compressive properties were determined for the best compound. This was the most difficult of all tasks to accomplish because of the PMR-15 variability problem. Each of the different lots of molding compound required a separate process. The material supplier had great difficulty in making the material due to the dry boardy nature of the Celion 6000/PMR-15 graphite tape. The only manufacturing method that proved somewhat successful was to take conventionally made prepreg, dry it to a certain volatile content, and then chop it to the prescribed length by hand. By using this method, the end resin content could not be controlled since the devolatilized PMR-15 resin is a dry yellow powder. Special handling procedures were necessary when handling the material. Details of the process development phase and experimental results are given below.

4.5.6.1 PMR CHOPPED GRAPHITE MOLDING COMPOUND

Six separate batches of graphite/PMR-15 chopped fiber molding compound were received from the program vendor. Two of these batches were made from HTS-2 graphite fiber and the remaining four used Celion 6000 graphite fiber.

After developing processes that produced visually acceptable composites (Appendix C), panels were fabricated using two different molding compounds (i.e., resin contents were 30-36% and 40-46% respectively) and two different cure temperatures. The panels were machined into flexural, tensile, and compression specimens to obtain mechanical properties (see Table XXIX). The results of the tensile testing indicates the system to be extremely brittle. On a majority of panels, it was difficult to obtain tensile modulus and tensile strain data because of the apparent brittleness of the system. The data also demonstrated that the higher resin content molding compound possesses overall better properties. All molded panels were of excellent quality and uniform in fiber/resin distribution. Since the program fiber was changed to Celion 6000, the remaining evaluations were conducted on chopped fiber compounds using this fiber as the reinforcement. There were two variations studied with these compounds, with the first being the fiber length and the second being the resin content. Attempts to use the same process as the HTS-2 fiber compound composites were unsuccessful and another process was developed for these compounds. The panels were postcured, machined, and tested with the results being given in Table XXX. The results show that the high resin compounds with the longer fiber lengths yield the best overall properties. However, due to mold design on Task G, the high resin content 12.7 mm (0.5 inch) fiber length was selected for Task C studies.

5.0 TASK C PROCESS VERIFICATION

The purpose of this task was to qualify the processes developed under Task B by the fabrication and testing of selected demonstration elements. Since in Tasks A and B a material variability was discovered, separate autoclave cycles were evaluated for the lots of prepreg used in this task. Upon evaluation of the quality control composites by NDI and physical property tests the most promising cycle was selected. Using the appropriate cycle, laminates of various fiber orientations, hat stiffeners, "I" stiffeners and a graphite/fiberglass honeycomb sandwich panel were fabricated and tested. Details of the experimental activities and data are given below.

5.1 FLAT LAMINATES

The first structural parts fabricated under this task were flat laminates. The mechanical properties obtained were tension, compression, flexural and interlaminate shear at ambient, 589K (600°F) and at 589K (600°F) after 125 hours of aging at the same temperature. These properties were obtained on 0° orientation laminates along with flexural and shear properties between the two temperatures to determine if any structural deficiency exists in the basic laminate material. Tension, compression, and bearing properties were also obtained on ±45° laminates in the zero direction. See Tables XXXI and XXXII for the resulting data.

5.2 STIFFENER ELEMENTS

The next structural elements fabricated under this task were hat stiffened laminates and "I" beams. As previously stated in Section 4.6.2.1, it should be emphasized again that the stiffener elements fabricated under Tasks B and C were designed solely to demonstrate manufacturing techniques of that graphite/PMR-15 system. In order to demonstrate the versatility of the manufacturing technique, the elements fabricated were significantly thicker and/or heavier than elements used in any proposed structure. The property data is only relative unless compared against similarly constructed elements. The general processes used for fabrication of these elements are described in the processing document, D180-20545-5 (Appendix B). Mechanical property determinations were made using three different fabrication methods; the resulting data was analyzed by stress engineers and reported herein. Details of the fabrication, testing, data tabulation, and data analysis are given below.

5.2.1 HAT STIFFENED PANELS

Eighteen hat stiffened panels were fabricated for the purpose of demonstrating that the processes developed in Task B were viable and that the mechanical properties of these panels were comparable to the data obtained in Task B. The hat stiffeners were fabricated in 915mm (36 inch) lengths so that on machining a 305mm (12 inch) hat stiffened panel could be obtained. Four each hat sections 8 ply thick with the web being of $(\pm 45^\circ)_s$ orientation were made for the bonded and the mechanically fastened stiffened panels. The flat panels were 12 ply with a $(0^\circ,90^\circ)_s$ configuration. The bonded hat stiffened panels were autoclave cured using A7F adhesive while the mechanically fastened used hex head bolts on 19 mm (.75 inch) centers. Two 915mm (36-inch) cocured hat sections were fabricated using a 76mm (3 inch) wide by 25mm (1 inch) high aluminum tool to provide the hat portion of the panel (see Figure 37 for example). All hat stiffened panels (i.e., 18 total) 305mm (12 inches) in length were then postcured and the ends potted using a low temperature curing aluminum filled potting to stabilize the ends. The assembly ends were then machined parallel and the stiffened panels tested in compression to obtain the buckling loads.

5.2.2 "I" STIFFENERRS

Eighteen "I" stiffeners were fabricated for the purpose of demonstrating the processes developed in Task B were usable and that the mechanical properties of those stiffeners were comparable to the data obtained in Task B. Three of the "I" stiffeners were fabricated using the secondary bonding technique, three using the cocuring technique, and the remaining three using mechanical fasteners for assembly. Figure 47 is an example of a 915mm (36 inch) cocured beam with Figure 48 showing examples of the "I" stiffeners before potting. All of the stiffeners were fabricated 915mm (36 inches) in length, postcured, machined to length and then the ends were potted using a low temperature curing aluminum filled potting compound. After potting the specimen ends were machined parallel and the compressive buckling strength determined.

5.3 EVALUATION OF TEST DATA

See paragraph 4.4.4 for a more detailed discussion of testing procedures and Tables XXXIII and XXXIV for a summary of the data and Figures 49, 50, and 51 for examples of failed elements. The element test data were evaluated by BAC stress engineers with consideration of failure mode, testing method, and comparison of failures with state-of-the-art resin systems. This assessment, like the preliminary assessment described in paragraph 4.5.4, consisted of evaluating representative specimens after test for determination of compressive stress at failure. Visual inspection showed the control portion of the heated specimens to be coated with a black coating (see para. 4.4.4). This coating aided the absorption of applied radiant heat but could cause large temperature gradients at the coated/uncoated surface interface which in turn could cause large thermal stresses. The largest stresses in a specimen under heating and applied load would then occur at the edge of the coated portion and specimen failure could be expected at this location. The majority of heated specimens showed failure at the edge of the coating. Since the specimen temperature is lower at the edge of the coating than in the center of the coated area where the temperature was measured, the actual 589K (600°F) strength should be greater than the measured value. The hat sections which were fabricated by cocuring exhibited lower crippling loads at ambient conditions than either the fastened or the secondary bonded but were somewhat better than the bonded specimens at 589K (600°F). Since the predominate failure mode in the secondary bonded specimens was composite failure in the shear mode at ambient conditions and adhesive failure at 589K (600°F), it could be postulated that the A7F adhesive was not strong enough at 589K (600°F).

The "I" stiffened sections show that at ambient conditions there was no significant difference between the bonded and the cocured in crippling load but both manufacturing processes were better than the fastened configuration. However, due to the poor NDI test results of the cocured beams, elevated temperature data was not obtained on that process. With respect to the fastened "I" sections, the drastic drop off of the 589K (600°F) tested specimens suggests an initial imperfection in the specimens. These observations were confirmed when coupon data from the failed beams indicated high void content composites that went to make up the beams (see Table XXXIV).

As noted in Table XXXIII, the specimens are composed of (0°/90°) and (±45°) laminates. Compression failure occurred in the (0°/90°) laminate. This is expected since the (0°/90°) laminate has a lower strain to failure and will be loaded to ultimate stress before the (±45) laminate. A stronger section would be obtained if the (±45°) laminate was made stiffer with addition of some 0° plies. The quantity of 0° plies depends on the particular design objective but would result in a more efficient section (strength to weight ratio). This assumes that the adhesive system used is not the limiting parameter.

Using material allowables data for a typical intermediate strength graphite epoxy, the hat section and I-section specimens should fail at room temperature under loads of 26,620 kg (12,100 pounds) and 58,300 kg (26,500 pounds), respectively. The graphite/PMR-15 system (i.e., secondary bonded) failed at 34,270 (15,585) and 50,600 kg (23,000 pounds), respectively. The results of the stress evaluation could be summarized as follows:

1. Test specimens and test procedures used are adequate for making "quick-look" material evaluations.

2. Using intermediate strength design allowable data for a typical intermediate strength epoxy (i.e., collected from coupon data) crippling loads of fabricated elements could be predicted.
3. The graphite/PMR-15 elements yield equivalent properties to similar graphite/epoxy elements.

5.3.1 HONEYCOMB PANELS

Two honeycomb sandwich panels were fabricated using 12 ply $(\pm 45)_s$ skins, FM 34 and A7F adhesives and 48 kg/m^3 (3 lb/ft^3) density HRH 327 polyimide honeycomb core (see Figure 52). The panels were fabricated using the secondary bonding method described in D180-20545-5 process specification. After satisfactory passing of the NDI tests, the mechanical properties were determined. The properties obtained consisted of edgewise compression and flatwise tension at ambient, 589K (600^{o}F) and after 125 hours 589K (600^{o}F) at the same temperature for the A5F system (see Table XXXV for a summary of the data). The only data obtained for the FM 34 bonded panel was flatwise tension at ambient and 589K (600^{o}F).

5.3.2 CHOPPED FIBER MOLDINGS

The chopped fiber molding compound selected as a result of Task B studies was molded into flat panels 3.2mm (0.125 inch) thick using a process developed for this specific molding compound (see para. 2.5.5 for details). The panel was postcured 8 hours at 604K (625^{o}F), machined into tensile, bearing and flexural specimens and its properties determined at ambient, 589K (600^{o}F) and at 589K (600^{o}F) after 125 hours at 589K (600^{o}F) (see Table XXXVI for results).

6.0 COMPONENT DEMONSTRATION (TASKS D, E, F, G, H)

It was the purpose of this phase of the program to demonstrate that the processes developed and tested during the three previous tasks could be adapted to structural element and hardware fabrication. To accomplish this, a series of components were fabricated and NDI tested as a means of demonstrating the adequacy of the processing methods. Since a material variability problem was discovered midway through the program, the original objective of using one material, controlled by the Material Specification (D180-20545-4) and one process, controlled by the Processing Specification (D180-20545-5) was not accomplished. Celion 6000/PMR-15 graphite materials received for use in these tasks were chemically different (see Section 4.0 for details) although they were all autoclaved with the same cycle and varying degrees of success. Therefore, a special handling procedure was established and is shown in Figure 53. This procedure was in addition to the procedures described in the quality assurance plan and had to be used because of the variability problem. The lots of material used in the demonstration hardware are also given in Figure 53 with regard to the types of component fabricated using them. All manufacturing was accomplished in the Boeing Materials Technology laboratories using engineering technicians instead of regular manufacturing personnel. This again was mandated by the variability of the incoming prepreg. To the extent possible, all manufacturing operations, in-process inspection, and NDI test requirements defined in the graphite/polyimide Process Specification (D180-20545-5), Quality Assurance Plan (D180-20545-3) and NDI Plan (D180-20545-6) were used in fabricating the components.

All scale-up problems encountered during the fabrication of the demonstration components were resolved through appropriate modification to the process and all specialized techniques were subsequently incorporated into the process specifications. During the fabrication of the components, particular attention was given to the vacuum bagging technique, the resin bleeder systems, vacuum breather configuration, and vacuum/temperature/pressure profile control during the autoclave cycle. It was found during the manufacturing operation that the release film, tooling type and configuration, bagging technique, layup thickness, and layup area were all critical factors in obtaining quality components. It was found that the proper release film, resin bleeder system, and vacuum breather configuration were indeed important in fabricating polyimide composites. Indeed, the component size and thickness appeared to be very critical with regards to the removal of all the methanol and water from the layup during the autoclave cycle. It was also found that some of the TFE release fabric adhered to the component if autoclave temperatures reach 604K (625°F). This fact, along with the desire to produce high quality polyimide laminates and to control resin flow, led to the use of multiple thermocouples during each autoclave cycle. Detail discussion of the manufacture of each type of deliverable component is given below along with a picture of the same components.

6.1 FABRICATION OF FLAT PANELS - TASK D

The objective of this task was to fabricate three large area panels 610mm X 1220mm (24 inches X 48 inches). The three panels used the same orientation of $(0^o,+45^o,-45^o)_{4T}$ and the third panel was 24 ply balanced construction $(0^o,+45^o,-45^o)_{8T}$. The panels were fabricated 660mm X 1270mm (26 inches X 50 inches) and trimmed to 610mm X 1220mm (24 inches X 48 inches) for delivery.

The panels were fabricated on a steel tool with six vacuum ports evenly spaced in bottom of tool. A 1.3mm (0.050 inch) perforated titanium sheet was on top of the tool to eliminate mark off on panels from the vacuum ports. For each panel fabricated a 23,200 square mm (36 square inches), 14 ply, 0^o process control panel was fabricated on the same tool. These panels were tested for physical properties to ensure quality of part (see Table XXXVIII).

The three panels were layed up in basically the same manner from Company A Lots 2W4282, 2W4516, and 2W4517. The 152mm (6 inch) prepreg tape was pre-cut and layed up into two ply "kits" with the aid of methanol. The layups were then vacuum bagged for 10 to 15 minutes to compact the plies and remove entrapped air. The completed 6, 12, or 24 ply part was then vacuum bagged to compact the kits together.

PANEL ONE - 6 ply

The six ply (Figure 54) panel was bagged for cure and cured per D180-20545-5 Method 1. It was bled from one side with an aluminum caul sheet on top to act as a pressure plate. Panel was warped in the longitudinal direction.

PANEL TWO - 12 ply

Due to the warpage obtained in the 6 ply panel, the 12 ply panel was bled on both sides per D180-20545-5.

PANEL THREE - 24 ply

The procedures developed in Task B for making 24 ply panels that is described in D180-20545-5, was used to make the panels (see para. 2.5.1). This procedure was slightly different than the process used for Task E thick panels. In that process two 12 ply layups were made and staged separately with Celgard microporous release film at 308K (95°F) for 16 hours. The layups were then mated together and cured per document D180-20545-5 with one layer of 120 and 6 layers of 181 glass fabric on both sides of panel. Additional vacuum ports were used for curing of the 24 ply panel to ensure the complete removal of reaction products.

The three panels were postcured under slight weight for 6 hours at 604K (625°F) with heat up rate of 2.8K (5°F) per minute and cool down rate of 0.8K (1.5°F) per minute maximum (see D180-20545-5).

6.2 STRINGER PANELS - TASK E

A total of 21 skin stringer panels were fabricated and inspected to demonstrate processing methods for configured hardware of this type. Eighteen of the panels were approximately 229mm (9 inches) by 305mm (12 inches) in size, nine multiple hat stiffened and nine "I" stiffened. Within each group of nine panels, three contained secondary bonded stiffeners, three contained mechanically attached stiffeners, and the remaining three were cocured. The other three skin stringer panels consisted of a multiple hat stiffened panel approximately 330mm (13 inches) X 1270mm (50 inches).

This configuration was selected because the elements yielded the best strength to weight data in Task B and C. In addition, the tooling required to fabricate stringer panels of these dimensions could also be utilized in parts needed in the manufacture of the simulated aft body flap (Task H Demonstration Component). A separate discussion on the manufacture of each type of stringer panel is given below.

"I" BEAM STIFFENED PANELS Bonded Panel (Figure 55)

The bonded "I" beam stiffened panels were fabricated from the following component parts: Two C shaped web panels, 12 ply $(\pm 45^{\circ})_{6T}$; two cap strips, 12 ply $(0^{\circ},90^{\circ})_{6T}$; and one 24 ply $(0^{\circ},\pm 45^{\circ},90^{\circ})_{6T}$ panel.

The "C" shaped web panels were fabricated from two ply kits 165mm X 914mm (6.5in x 36in) which had been compacted under vacuum to remove entrapped air. The two ply kits were then formed over the tool (Figure 39) with vacuum and heat 315K (110°F) and the procedure repeated until 12 plies had been obtained. The parts were then bagged for cure per D180-20545-5 with no top pressure plates.

The cap strips were layed up and cured per D180-20545-5. The 12 ply $(0^{\circ},90^{\circ})_{6T}$ 305mm X 915mm (12 inches X 36 inches) panel was then cut into 48mm X 915mm (1.9 inches X 36 inches) cap strips.

The 24 ply $(0^{\circ},\pm 45^{\circ},90^{\circ})_{6T}$ flat panels were fabricated individually 254mm X 305mm (10 inches X 12 inches). The flat panels were assembled and cured per D180-20545-5 with the following modifications: Two 12 ply kits were layed up and staged with Celgard microporous release film under vacuum for 16 hours at 308K (95°F). The two kits were then mated and cured on a tool with four vacuum ports evenly spaced in center of panel. The panels were bled on both sides with one ply 120 and 6 plies of 181 glass bleeder. A 9.5mm (3/8 inch) perforated aluminum caul was placed on top of the layup.

The bonding of the component parts together was done in two stages. All bonding surfaces were prepared by sand blasting and solvent cleaning. The cleaned faying surfaces were then primed with dilute A7F liquid adhesive and then baked for 30 minutes at 394K (250°F). In the first stage the two C shaped web panels were placed back on the tools and mated together with a layer of 0.3mm (0.012 inch) A7F modified polyimide adhesive between them. A paste form of A7F was used to fill the area where the radii came together. Film adhesive was also used to bond the cap strips to the top and bottom of the "I" beam assembly. The assembly was then bagged and cured at 604K (625°F) with 1380 kPa (200 psi) pressure and vacuum. This completed the bonding of the "I" beams. (See D180-20545-5 for additional details.)

The second stage consisted of bonding three "I" beams to the 24 ply flat panel. To accomplish this the 915mm (36 inch) "I" beam and two 915mm (36 inch) tools were cut into 305mm (12 inch) sections and lined up on the flat panel with a 12.7mm (0.5 inch) caul sheet under the flat panel. A7F film adhesive was also used for this bond. The assembly was bagged and cured same as above.

The same bagging procedure was used for postcuring completed assembly except vacuum pressure only was used. The assembly was postcured 6 hours at 604K (625°F) and 2 hours at 619K (650°F) with maximum cool down rate of 0.8K (1.5°F) per minute.

"I" BEAMS

--MECHANICALLY FASTENED PANELS (Figure 56)

The procedure for fabricating mechanically fastened "I" beam panels was the same as for the bonded panels through the making of the "I" beams by the bonding of the C webs and cap strips and the curing of the 24 ply flat panel. The 3 bonded "I" beams were then bolted to the 24 ply panel on both flanges with 4.8mm (0.187 inch) hex-head, high strength bolts on 19mm (0.75 inch) centers (Figure 56). The component parts were postcured prior to assembly, using the same postcure cycle used for the secondary bonded "I" stiffened panel.

--COCURED PANELS (Figure 57)

The cocured "I" beam stiffened panel was fabricated from basically the same component parts as the bonded and mechanically fastened assemblies. The "C" shaped web panels were fabricated per D180-20545-5 which consisted of vacuum forming 2 ply kits over six 305mm (12 inch) long tools until 12 plies were completed $(\pm 45^{\circ})_{6T}$. A 12 ply $(0^{\circ},90^{\circ})_{6T}$ panel was layed up and cut into six 51mm X 305mm (2 inch X 12 inch) strips. The 24 ply panel $(0^{\circ},\pm 45^{\circ},90^{\circ})_{6T}$ was layed up in two 12 ply kits, staged 16 hours at 308K (95°F) with Celgard microporous polypropylene film and then mated prior to assembling structure. Assembly of the structure was similar to the assembly of the bonded structure with the exceptions that all components were uncured and no adhesive film was used. The structure was cured on a 12.7mm (0.5 inch) perforated caul with one ply of 120 and 6 plies of 181 glass fabric bleeder against the 24 ply flat panel. Three plies of 120 and 3 plies 181 glass fabric and a 1.27mm (0.050 inch) thick titanium caul were used on top of the assembly. Assemblies were cured per D180-20545-5 Method 1. They were then returned to the tooling and postcured under vacuum pressure for 8 hours at 604K (625°F) and 2 hours at 619K (650°F) with maximum cool down rate of 0.8K (1.5°F) per minute.

--MULTIPLE HAT STIFFENED PANELS

Layup procedure for the multiple hat web and 24 ply flat panel was the same for the three types of multiple hat stiffened stringer panels (i.e., bonded, mechanically fastened, and cocured). The multiple hat web component consisted of 8 plies $(\pm 45^{\circ})_{4T}$ constructed of 2 ply kits which had been tacked with methanol and compacted under vacuum pressure to remove entrapped air (see D180-20545-5). The kits were compacted on to the multiple hat section tool (Figure 58) with vacuum. Aluminum bars machined to fit the tool aided in the forming of the prepreg to the tool (Figure 58). The 24 ply flat panels were fabricated as previously described for the "I" stiffened panel. A 23,200 square mm (36 square inches) 14 ply 0° control panel was fabricated with each component part. See Table XXXIX for properties.

--BONDED PANEL

The 8 ply $(\pm 45^{\circ})_{4T}$ multiple hat web component for bonded panels was cured in a matched die mold (Figure 58) 254mm (10 inches) wide and 356mm (14 inches) long. The basic layup procedure is as described in D180-20545-5 with the following modifications. Three plies of 181 glass bleeder were used on both sides of layup. The part was vacuum bagged and cured per D180-20545-5 with four vacuum lines. The 24 ply flat panel components were cured on a tool with 4 vacuum ports evenly spaced in the center of the panel. The panels were bled from both sides with one ply of 120 and 6 plies of 181 glass bleeder. A 9.5mm (0.375 inch) thick perforated caul was used on top of the panel. Component parts were NDI tested before assembly.

The bonding surfaces were sand blasted and primed with dilute A7F adhesive resin. The multiple hat web panel was placed on one-half of the matched die mold with aluminum bars used to fill the spaces. 0.3mm (0.012 inch) A7F film adhesive was applied to the bonding surfaces and the 24 ply component was placed on top. A 12.7mm (0.5 inch) aluminum plate was used as a pressure plate. The assembly was vacuum bagged and cured for 2 hours at 604K (625°F) with 1378 kPa (200 psi) pressure and vacuum. Bonded assemblies were postcured for 8 hours at 604K (625°F), followed by 2 hours at 619K (650°F) and cooled at 0.8K (1.5°F) per minute (see Figure 59 for a picture of the completed part).

--MECHANICALLY FASTENED PANELS

Multiple hat web and 24 ply flat component parts were fabricated the same way as used for the bonded panels. Instead of bonding the panels were bolted together (Figure 60) with 4.8mm (0.188 inch) hex-head, high strength bolts. Component parts were postcured prior to assembling using the same cure cycle as previously described.

--COCURED PANELS

The 8 ply $(\pm 45^{\circ})_{4T}$ pre-formed multiple hat web layup was placed on one-half of the matched die mold over 3 plies of 120 glass bleeder. Machined aluminum bars were used to fill the spaces. The 24 ply staged flat panel was positioned on top of the layup, covered by a ply of 120 and 6 plies of 181 glass bleeder, and covered with a 12.7mm (0.5 inch) thick perforated aluminum caul. The assembly was cured per D180-20545-5 with four vacuum lines. Assemblies were postcured 8 hours at 604K (625°F) and 2 hours at 619K (650°F) with a cool down rate of 0.8K (1.5°F) per minute (Figure 61).

--LARGE AREA BONDED MULTIPLE HAT STIFFENED PANEL

The large area multiple hat assembly was fabricated from two components: a 330mm X 1270mm (13 inch X 50 inch) 8 ply $(\pm 45^{o})_{4T}$ multiple hat web, and 330mm X 1270mm (13 inch X 50 inch) 8 ply $(0^{o},\pm 45^{o},90^{o})_{2T}$ flat panel. The web panel was layed up per D180-20545-5, which included 2 ply kits, tacked together with methanol, and vacuum formed to the center 330mm (13 inches) of the large match die mold (Figure 62). The layup was cured with 1 ply of 120 and 2 plies of 181 glass bleeder on both sides of layup in the matched die mold. This was the only deviation to D180-20545-5. See Figure 33. The 330mm X 1270mm (13 inch X 50 inch) 8 ply flat panel was fabricated in a similar manner only on a flat steel tool with center vacuum ports (Figure 64). Both components were fabricated from Lot 2W4448 and NDI tested before bonding. A 23,200 square mm (36 square inch) 14 ply 0^{o} process control panel was fabricated with each component.

The bonding surfaces on both components of each assembly were prepared for bonding by roughing the surface of the composite by sand blasting and then cleaning the surface with MEK solvent. The faying surfaces were primed with BR-34 polyimide adhesive thinned to 60% solids, and baked for 30 minutes at 377K (220^{o}F). (The BR-34 FM 34 adhesive system was used in this application because high temperature, high pressure tooling was not available.) The assembly was bonded together on one-half of the mold with FM 34 with a 330mm X 1270mm (13 inch X 50 inch) caul on top. The assembly was cured for 90 minutes at 450K (350^{o}F) under 240 kPa (35 psi) and full vacuum pressure. The stringer panel was removed from tooling and postcured for 8 hours at 604K (625^{o}F) and 2 hours at 619K (650^{o}F) with a cool down rate of 0.8K (1.5^{o}F) per minute (Figure 65).

6.3 CELION 6000/PMR-15/POLYIMIDE GLASS HONEYCOMB SANDWICH PANELS -- TASK F

Six honeycomb panels, each 254mm x 254mm (10 inches X 10 inches) in size, were fabricated and inspected to demonstrate processing methods for large graphite/polyimide sandwich panels. The following materials were used in the fabrication: 12 ply PMR-15 $(\pm 45^{\circ})_{6T}$ skins, BR-34/FM 34 polyimide adhesive, and HRH 327, 56 kg/m^3 (3.5 lb/ft^3), 9.5mm (0.378 inch) cell size by 15.9mm (0.625 inch) thick glass/polyimide core. Two panels were fabricated, one 305mm X 1295mm (12 inches X 51 inches) and one 305mm X 305mm (12 inches X 12 inches). (See Figure 66 for example.) Panel sizes were determined by the size of tooling and by the problem of bonding with a high volatile adhesive system without the use of perforated core. Skins were fabricated in two panels, one 762mm X 1295mm (30 inches X 51 inches) and one 305mm X 610mm (12 inches X 24 inches) and cut to size for assemblies. The skins were prepared for bonding by roughing the surface of the composite by sand blasting and then cleaning the surface with MEK solvent, then primed with BR-34 diluted to 60% solids and baked for 30 minutes at 372K (220°F). The HRH 327 core was vapor degreased in trichlorethylene, roller-coated with BR-34 (81% solids), and baked for 30 minutes at 378K (220°F). Panels were assembled with 660 g/m^2 (0.135 lbs/ft^2) FM 34 film adhesive and cured for 90 minutes at 450K (350°F) with 517 kPa (75 psi) pressure and full vacuum. Assemblies were cut into 254mm X 254mm (10 inch X 10 inch) panels. Flatwise tensile specimens were prepared and tested from excess material (see Table XXXX). Panels were postcured at 604K (625°F) for 8 hours. For more detailed description of the fabrication process, see the secondary bonding method described in D180-20545-5.

6.4 CELION 6000/PMR-15 CHOPPED FIBER MOLDINGS

Six chopped grahite/polyimide fittings (Figure 67) were compression molded to demonstrate the suitability of the molding formulation and molding parameters established during Task B studies. The tool design for these molded parts are shown in Figure 68 along with a picture of the three piece mold in Figure 69.

6.5 SIMULATED SPACE SHUTTLE AFT BODY FLAP -- TASK H

A 762mm (30 inch) wide section of the aft body flap was fabricated as a representative Space Shuttle component (Figure 70). Fabrication of this section utilized all the graphite/polyimide processing technology developed during the program. The approximate size of the flap section 762mm X 2030mm X 559 tapered to 152mm (30 inches X 80 inches X 22 tapered to 6 inches) was sufficiently large to demonstrate applicability of this technology to large graphite polyimide structures. The design of the aft body flap section is shown schematically in Figure 71. The tooling on which the components were fabricated are shown in Figures 72 through 74. The number of components used along with their dimensions and pictures are given in Figures 75 through 83.

1. 2 Skins $(0^{\circ},\pm45^{\circ},90^{\circ})_{2T}$ Balanced 813mm X 2108mm (32 inches X 83 inches) (Figure 75)
2. 2 Honeycomb sandwich panels 2083mm (82 inches) long tapered from 559mm (22 inches) down to 152mm (6 inches) (Figure 76).

   Skins $(0^{\circ},\pm45^{\circ},90^{\circ})_{2T}$
   Core 9.5mm (0.375 inch) Cell, 56 kg/m^3 (3.5 lb/ft^3), HRH 737
   Adhesive BR 34/FM 34

3. 24 each 178mm X 610mm (7 inch X 24 inch) multiple hat section $(\pm 45^{o})_{4T}$ (Figure 77)
4. 1 each "C" 559mm X 762mm (22 inches X 30 inches) $(\pm 45^{o})_{4T}$ (Figure 78)
5. 9 angles 90° 2083mm (82 inches) long $(0^{o},\pm 45^{o},90^{o})_{2T}$ (Figure 79)

The flat laminates were fabricated per D180-20545-5.

MULTIPLE HAT SECTIONS

The multiple hat sections were fabricated using the previously described multiple hat section tool (Figure 62) per D180-20545-5 processing document (Appendix C).

"C" SPAR AND ANGLES

The "C" spar section and angles were fabricated using their respective section tooling (Figures 84 and 85) per D180-20545-5 processing document (Appendix C). "C" spar layup orientation was 8 plies of $\pm 45^{o}$ balanced construction and the angles were $(0^{o},\pm 45^{o},90^{o})_{2T}$ balanced construction. The only deviation to the process document used during the layup consisted of laying up the 2 ply kits into the 8 ply layup and then forming to the respective tools in place of forming the two ply kits on the tools.

H/C SANDWICH PANELS

The honeycomb sandwichs were fabricated per D180-20545-5 when possible. Due to the change in adhesive used (i.e., to BR 34/FM 34), some deviation to the document occurred. Following is a synopsis of the procedure used to fabricate the panels. Each H/C panel was formed from two pieces of H/C spliced together with a 1 inch overlap. The H/C was cleaned by blowing with clear air. The skins were lightly abraded with 180 grit aluminum oxide sandpaper and solvent cleaned with MEK. The BR 34 primer was thinned as described in the data sheet provided by the supplier and was then sprayed on the skins. The BR 34 used for priming the core was used as received and roller coated on both sides of the core, allowing about 30 minutes to dry before turning over. After 30 minutes air dry, the primed parts were baked in an air-circulating oven for 30 minutes at 377K (220°F).

FM 34 adhesive film was cut to fit the skins, applied to the core, and bagged under nylon film, with adequate support around the perimeter.

The assembly was inserted into an autoclave and cured using the following cure schedule.

Full vacuum was applied and raise part temperature to 450K (350°F) over a 60-minute period. The assembly was held at 450K (350°F) for 60 minutes and was then cooled under vacuum to ambient conditions before removing from the autoclave.

DEMONSTRATION PART ASSEMBLY

The most difficult task throughout the manufacturing of the simulated space shuttle component was the assembly of individual components into the finished hardware. This problem was compounded by the lack of production tooling. In order to accomplish the hardware assembly, make-shift tooling was utilized and in some cases resulted in less than optimum processing conditions. The tooling problem in this type of hardware is quite complex. Following is a detailed description of the assembly of the individual components into the demonstration hardware.

The assembly of the components into the demonstration hardware is schematically represented in Figure 86. The first assembly step was to bond the corrugations and angles to the skins. These components were bonded using BR 34/FM 34 (primer/film adhesive) system. The multiple hat sections and angles were prefitted to the skins and located by the use of small pins. The faying surfaces were abraded, solvent cleaned, and then primed with BR 34 primer. The parts were then dried 30 minutes at 380K (225^{o}F). The FM 34 film adhesive was then cut and applied to the angles and hat sections. The individual components were then assembled on the skins and the tooling pins inserted to maintain their location on the skins. The filler blocks and an aluminum bar were placed over their respective areas to be bonded. A pressure plate was then placed over the filler blocks, the assembly was vacuum bagged and cured using the cure schedule described above (see Figure 87 for a picture of the assembled part).

The next assembly step was to bond the ribs (honeycomb sandwich) to the stiffened skin panels (Figure 88). This was accomplished in two operations. The first operation was to bond the two ribs into one stiffened skin panel. After machining the ribs to size, they were installed into the angles for bonding. The faying surfaces of the ribs and the angles were abraded, solvent cleaned, primed with BR 34 primer, and oven dried. The FM 34 adhesive film was placed on the primed faying surface. Insertion of the ribs was aided by gently prying the bonding surfaces apart and gently working the ribs into the cavity. The assembly was placed on a 6.4mm (0.250 in) thick aluminum caul plate. The rib spacing was maintained by inserting aluminum rods cut to the proper size. (For schematic of the assembly, see Figure 89.) As can be seen in Figure 89, the pressure for bonding was applied by mechanical means. Twenty-two threaded rods, as shown in Figure 89, applied the pressure for bonding the angles to the ribs through 25.4mm X 25.4mm (1 inch X 1 inch) steel bars the length of the angles. Spacers (wood) were used in the center to react against the inside angles. Turnbuckles at the front and rear were used to pull a 12.8mm (0.5 inch) thick aluminum plate against the ribs. The turnbuckles were tightened just enough to make the ribs bottom against the skin. The assembly was cured using the autoclave as an oven. The cure was 90 minutes at 450K (350^{o}F) with a 3K (5^{o}F) per minute rate of temperature rise. After the assembly was cooled to ambient conditions, the adhesive flash was removed and the assembly was prepared for the next operation. The bonding surfaces of this assembly and the other stiffener skin were prepared as previously described and FM 34 adhesive tape was applied to the bonding surfaces. The same operation was used in bonding the second stiffener panel to the assembly. The pressure was applied as before (see Figure 89) and the part was cured. During this step, angles used for attaching "C" spar closeout section were also bonded (Figure 90).

The next operation was to bond doublers to the "C" spar (Figure 91), then prefitting the "C" spar to the assembly and machining holes for use in attaching the close out spar to the hardware (Figure 91). The spar section was attached using 8-32 machine screws and nut plates. The assembly was then trimmed to final size and delivered to NASA Langley.

7.0 CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this program to demonstrate the fabrication of structural elements with the graphite/PMR-15 polyimide resin system. Based on the findings of this program, recommendations are given for future actions.

7.1 CONCLUSIONS

1. Manufacturing processes for graphite/PMR-15 composites, structural elements, chopped fiber moldings, and honeycomb sandwich panels have been established and demonstrated. However, reproducible quality in large composite structures is still limited and dependent upon improved control over resin chemical characteristics and prepreg uniformity in processing.
2. The structural integrity of key structural elements has been verified.
3. Fabrication of large size hardware has been demonstrated.
4. Specification and NDI documentation has been prepared and substantiated.
5. No serious problems were identified that would prevent graphite/PMR-15 composites from being considered for space shuttle hardware.

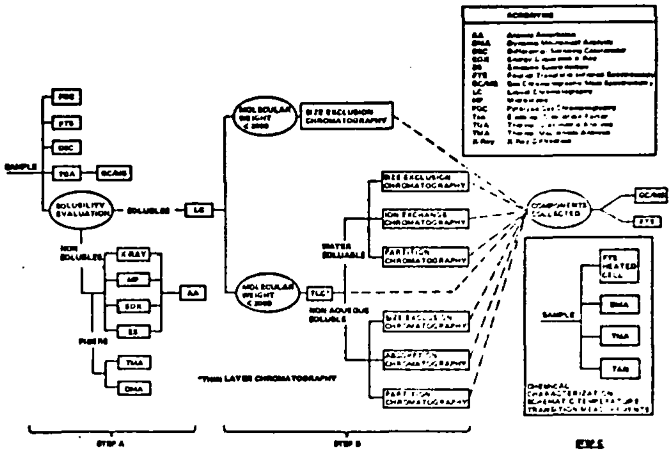
7.2 RECOMMENDATIONS

1. Improve the graphite/PMR-15 reproducibility (program in progress) and optimize processing conditions.
2. Establish design allowables for the graphite/PMR-15 system with respect to its mechanical properties, environmental stability, and as attachments.
3. Design flight hardware and fabricate and test its key elements.
4. Build and qualify full scale flight hardware.
5. Develop and optimize a high temperature adhesive system to be used in conjunction with the graphite/PMR-15 system (program in progress).

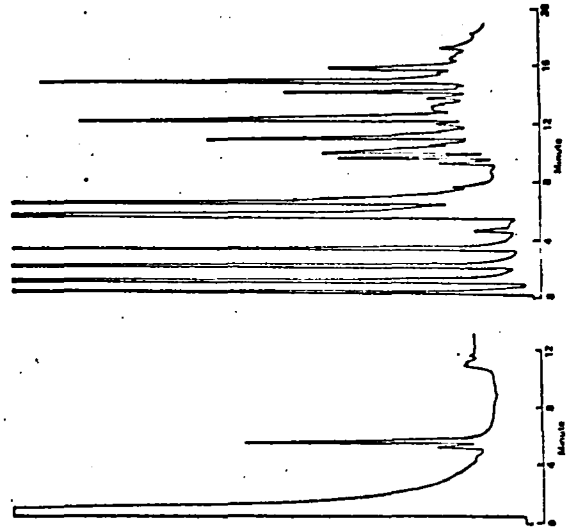
8.0 REFERENCES

(1) S. Check, W. G., "Develop and Demonstrate Manufacturing Processes for Fabricating Graphite Filament Reinforced Polyimide (Gr/PI) Composite Structural Elements," CASD-NAS-77-019-8, NASA Contract NAS 1-14784, 1st Quarterly Report

(2) Spier, Edward, Fredrick Kolouman, "Post Buckling Behavior of Graphite/Epoxy Laminated Plates and Channels," Army Symposium of Solid Mechanics, Composite Materials Mechanics of Failure on Design, Cape Cod, Massachusetts, September 1976



CHEMICAL CHARACTERIZATION SCHEMATIC
FIGURE 1



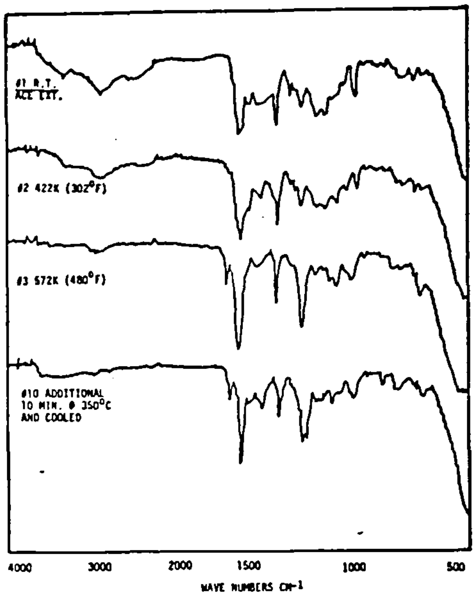
LEFT: CHROMATOGRAM BEFORE PYROLYSIS. SS SE 30 1/8" X 10' S.S. TEMP. PROGRAM FROM 100 TO 300°C AT 20°C/MIN INJECT PORT TEMP. 270°C FID. HELIUM FLOW RATE 30 ML/MIN ATTENUATION X2 RANGE: 10^2

RIGHT: PYROGRAM (PYROLYSIS WITH 12 AMP CURRENT FOR 15 SEC). SS SE 30 1/8" X 10' S.S. TEMP. PROGRAM FROM 100 TO 300°C AT 20°C/MIN INJECT PORT TEMP 270°C FID. HELIUM FLOW RATE 30 ML/MIN ATTENUATION X2 RANGE: 10^2

*A BOEING US PATENT PENDING ANALYTICAL METHOD

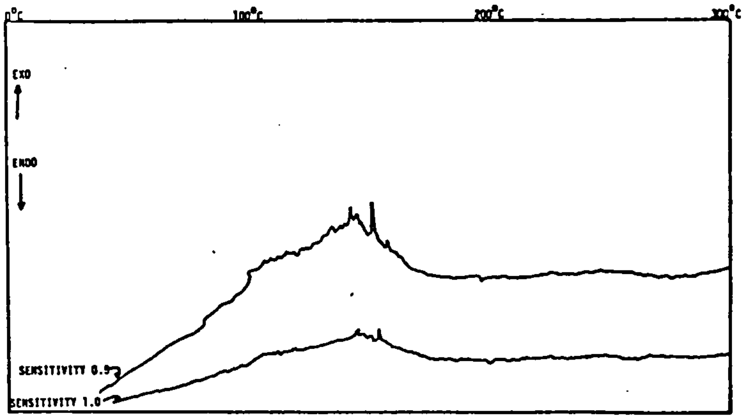
SAMPLE PYROLYSIS GAS CHROMATOGRAPH

FIGURE 2

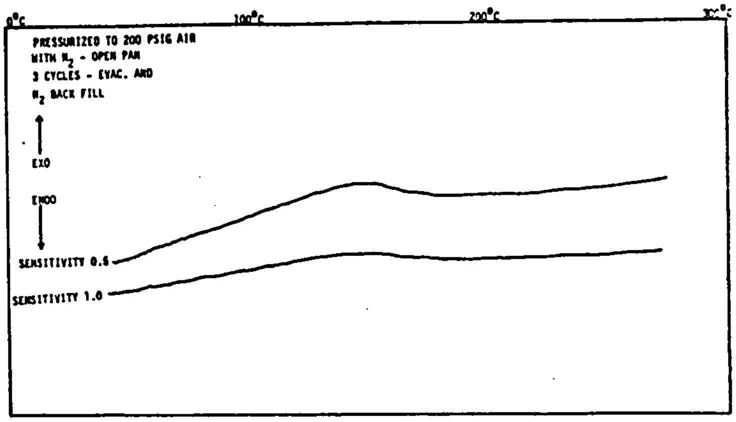


CHROMATOGRAM FROM FOURIER TRANSFORM SPECTROSCOPY

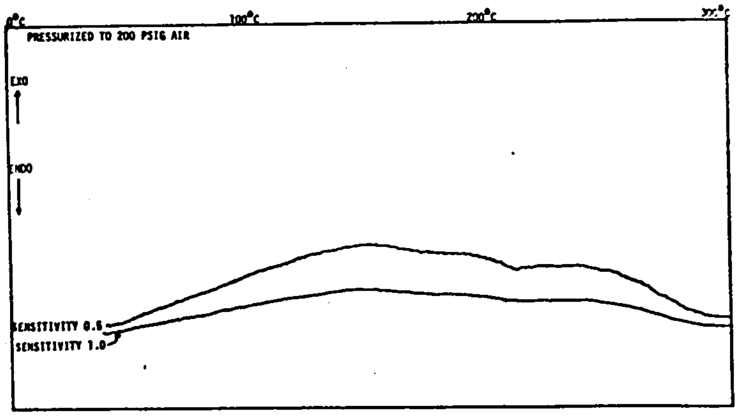
FIGURE 3



SAMPLE OF DSC DATA
FIGURE 4



SAMPLE OF DSC DATA
FIGURE 4



SAMPLE OF DSC DATA
FIGURE 4

PART NO. 950252

DUPONT INSTRUMENTS

SAMPLE:
USP Lot 2W4083
PMR-15 8/11/77

SIZE 26.2 mg.

X-AXIS

TEMP. SCALE 100 °C/inch

SHIFT 0 inch

Y-AXIS

SCALE % mg/inch

(SCALE SETTING X2)

SUPPRESSION 0 mg.

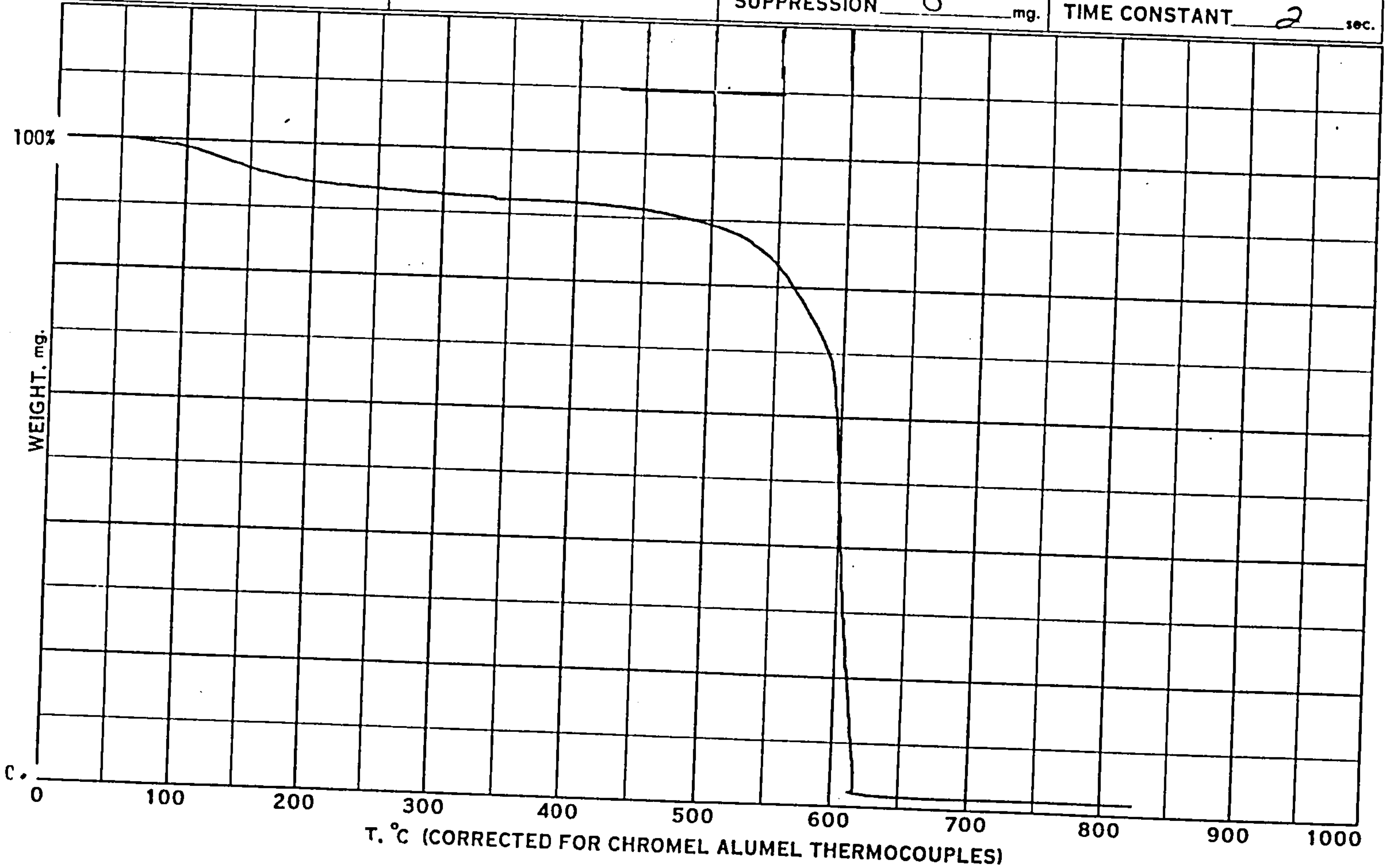
RUN NO. 1 DATE 8-23-77

OPERATOR DL

HEATING RATE 5 °C/min.

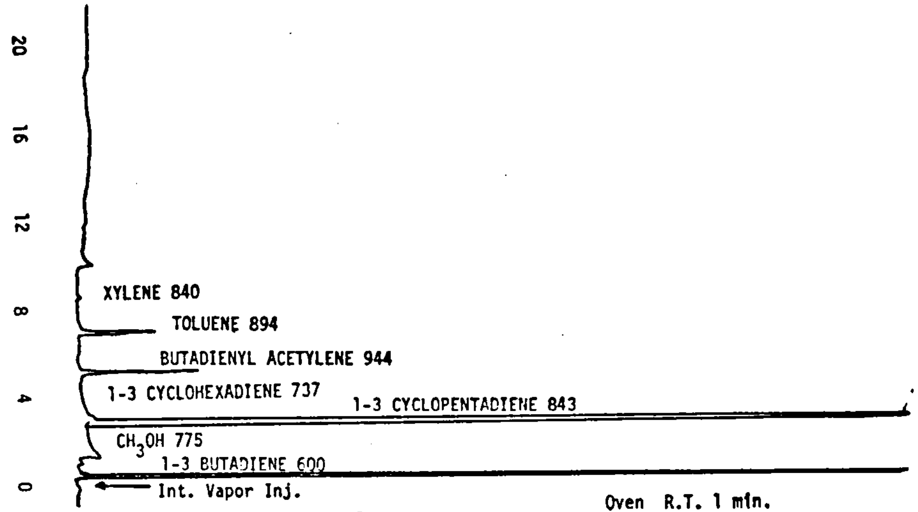
ATM. air .3 l/m

TIME CONSTANT 2 sec.



THERMAL GRAVIMETRIC ANALYSIS

FIGURE 5



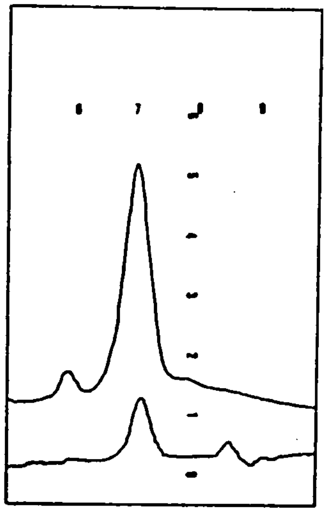
HTS/PMR-15
Pyrolysis Vapor

Oven R.T. 1 min.
Progress to 175°C @ 15°C/min.
Range 10^{-11} x 256
Ch. Sp. .25"/min.

SAMPLE GAS CHROMATOGRAM
FIGURE 6A

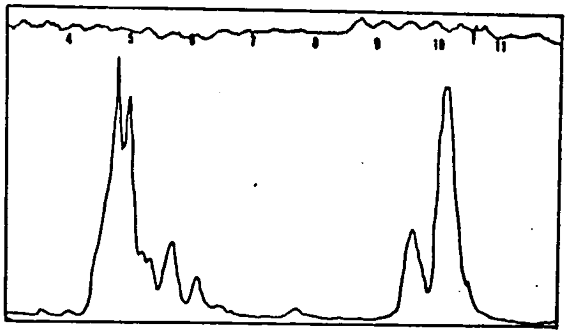
SAMPLE MASS CHROMATOGRAM
FIGURE 6B

Gel Permeation Chromatography Company A
Col 1 @ 500 Å and 4 @ 100 Å Solvent THF
Flow rate 1 ml/min. Chart speed 0.4 ipm
Attenuation UV x 256 RI x 3
Sample weight 0.15239 (1 sq in) in 20 mls



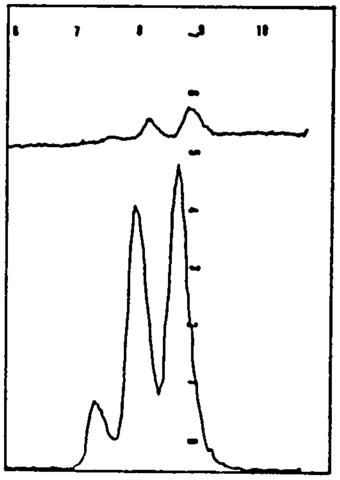
GEL PERMEATION CHROMATOGRAM
FIGURE 7

Liquid Chromatography - Company A
Reverse phase Col. C_{18}
Mobile phase H_2O:THF 45%
Sample size 0.05000 g in 20 ml 1 μl injected
Attenuation RI x 8 UV x 16
Chart speed 1.0 ipm
Flow 0.5 ml/min.

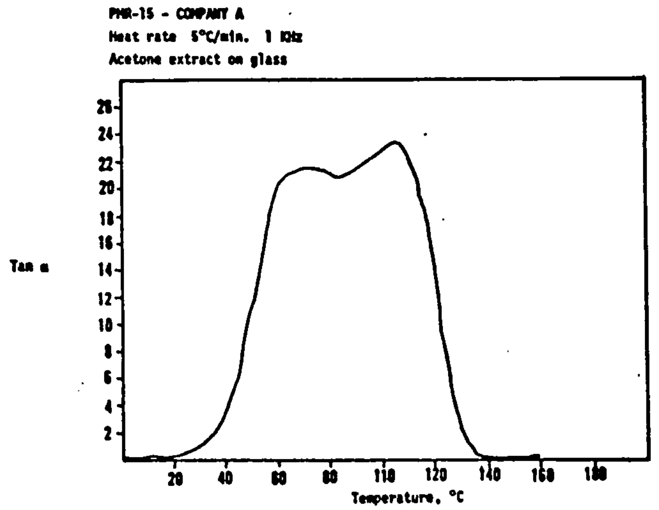


LIQUID CHROMATOGRAM REVERSE PHASE
FIGURE 8

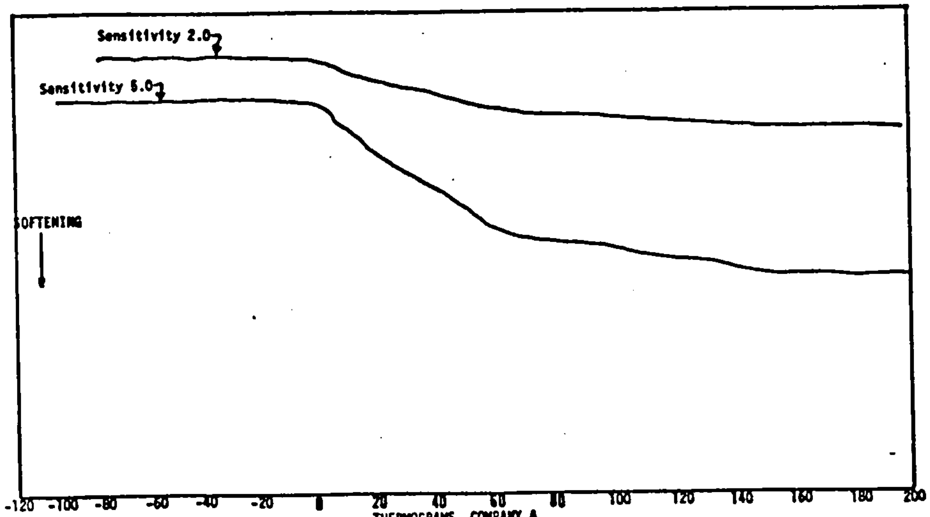
Liquid Chromatography - Company A
Adsorption Col microporasil
Mobile Phase THF
Sample Size 0.138 g/20 mls 10 μl injected
Attenuation RI x 8 UV x 128 Chart Speed 1°/min.
Flow 0.5 ml/min.



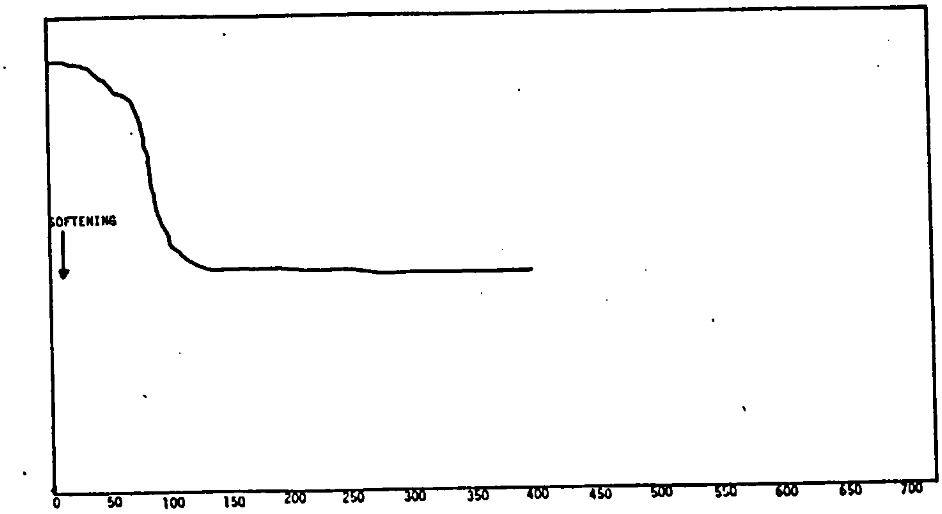
ADSORPTION CHROMATOGRAM
FIGURE 9



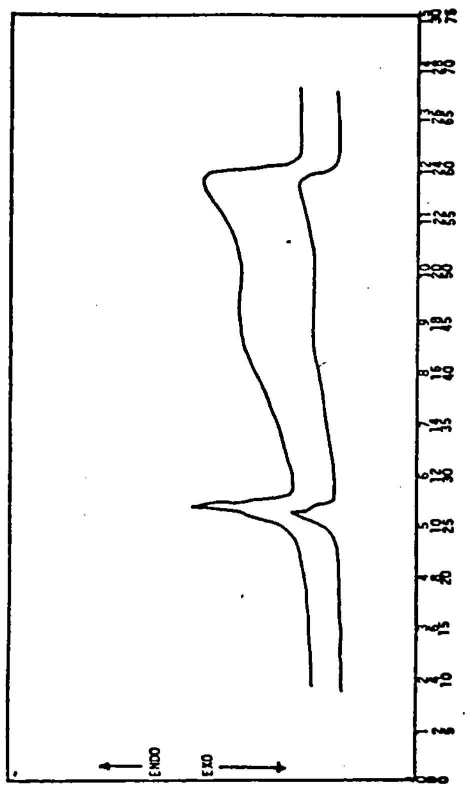
SAMPLE DIELECTROMETRY DATA
FIGURE 10



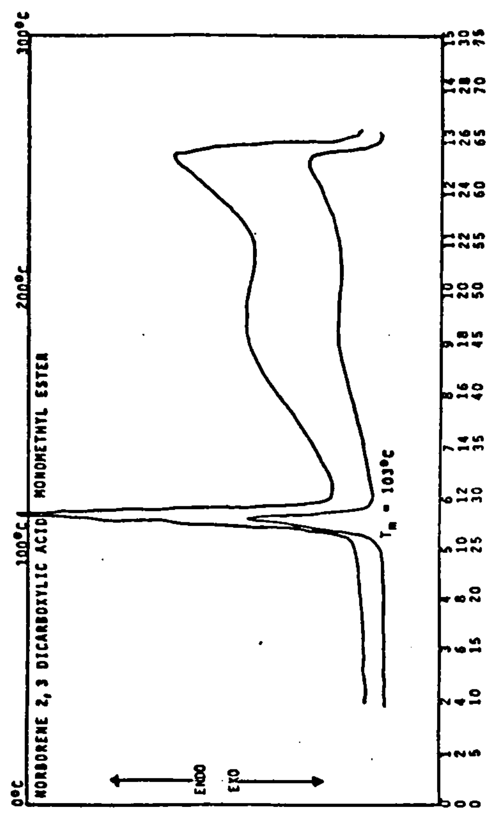
THERMOGRAMS, COMPANY A
FIGURE 11



THEMOGRAMS COMPANY A
FIGURE 11A

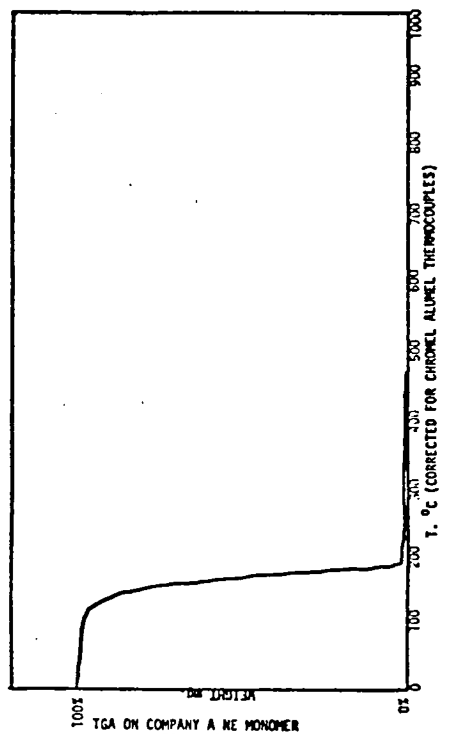


DSC ON COMPANY A NE MONOMER
FIGURE 12

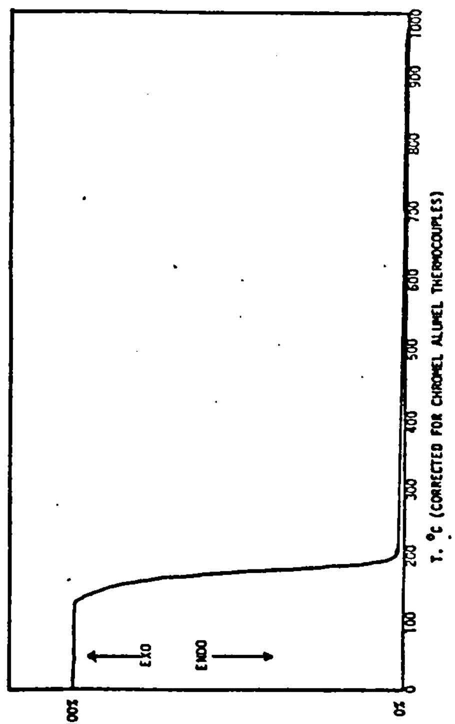


DSC ON COMPANY B NE MONOMER

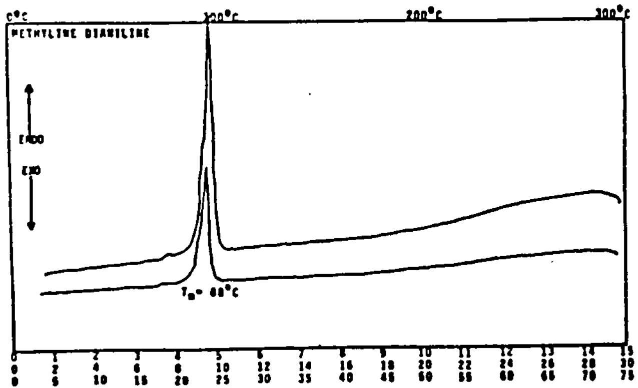
FIGURE 13



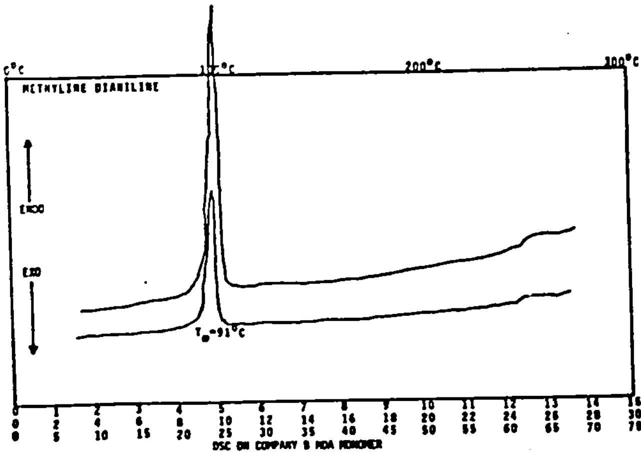
TGA ON COMPANY A NE MONOMER
FIGURE 14



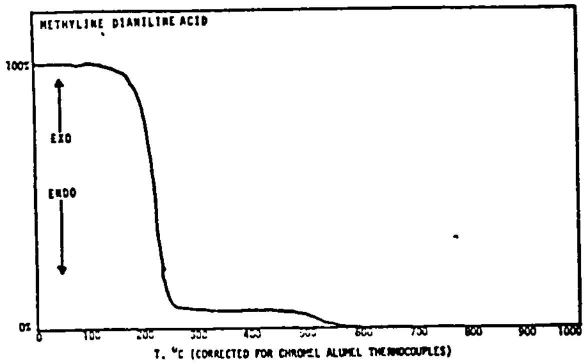
TGA ON COMPANY B NE MONOMER
FIGURE 15



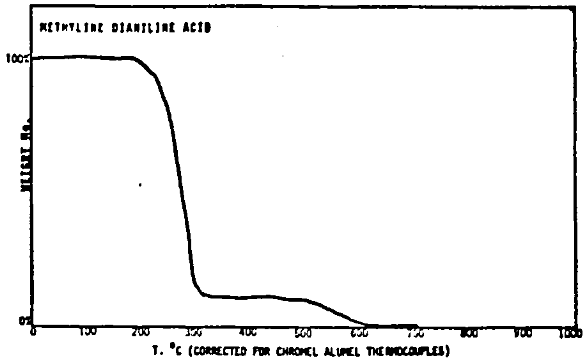
DSC ON COMPANY A MDA MONOMER
FIGURE 16



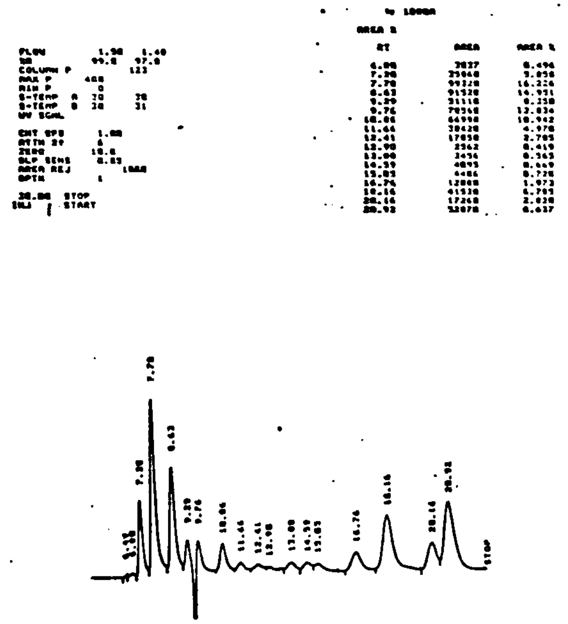
DSC ON COMPANY B MDA MONOMER
FIGURE 17



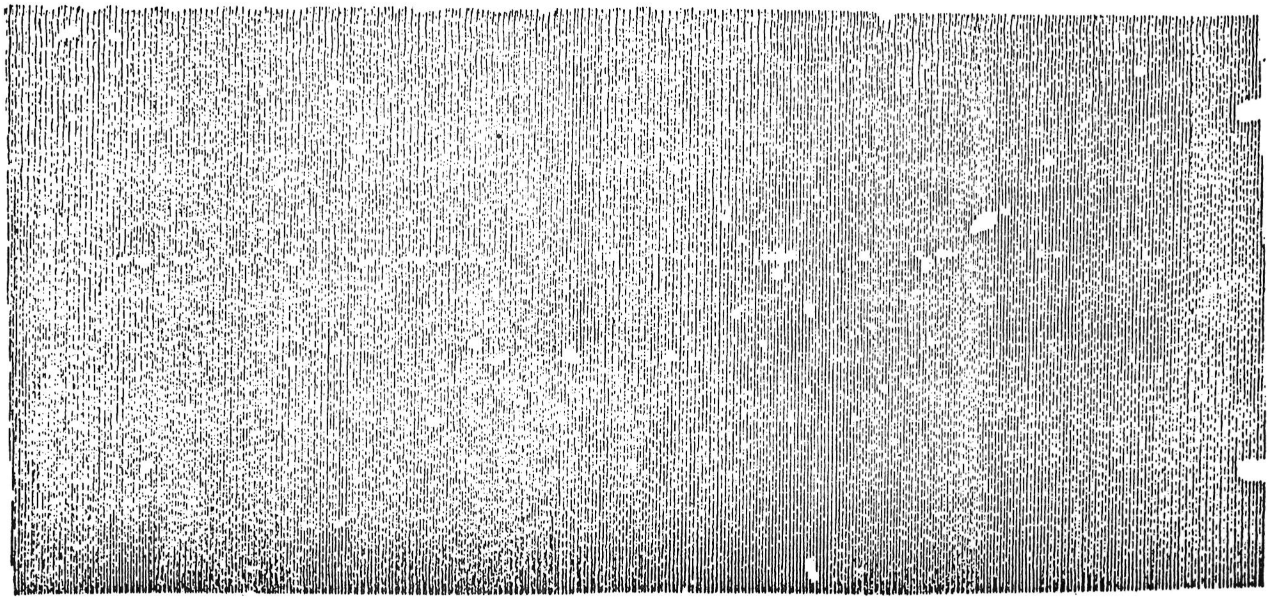
TGA ON COMPANY B MDA MONOMER
FIGURE 18



TGA ON COMPANY A MDA MONOMER

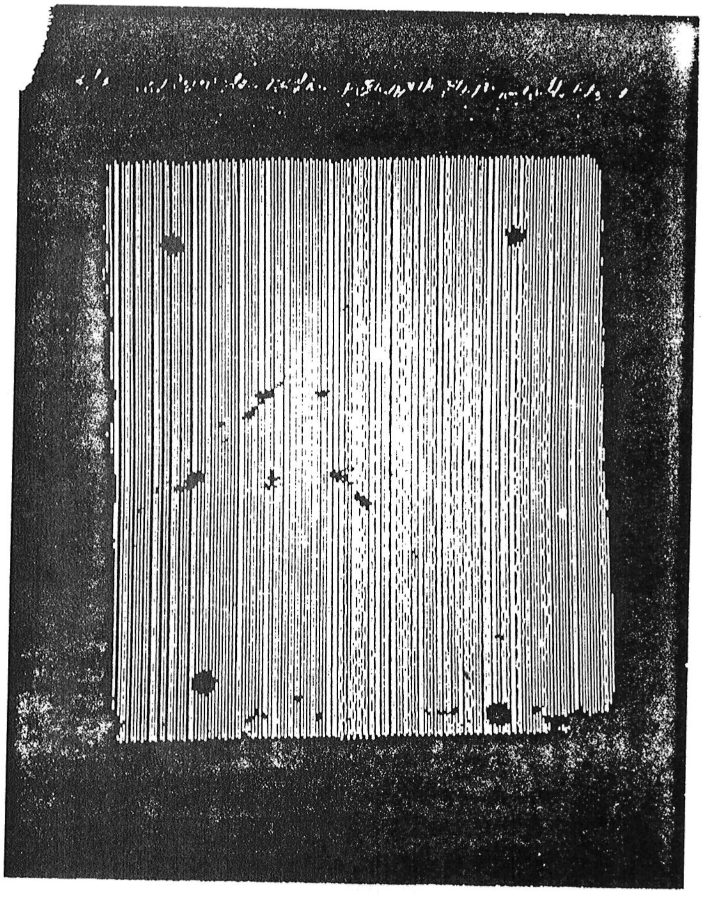


SAMPLE PRINTOUT OF SIZE EXCLUSION/ADSORPTION HPLC PROCEDURE
FIGURE 19



BAC NDI Scan Multidirectional Composite

FIGURE 20

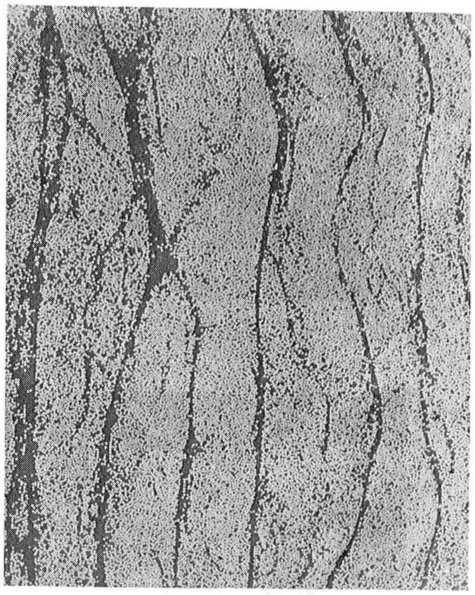


NASA NDI SCAN LOWER HALF
MULTIDIRECTIONAL COMPOSITE
FIGURE 21

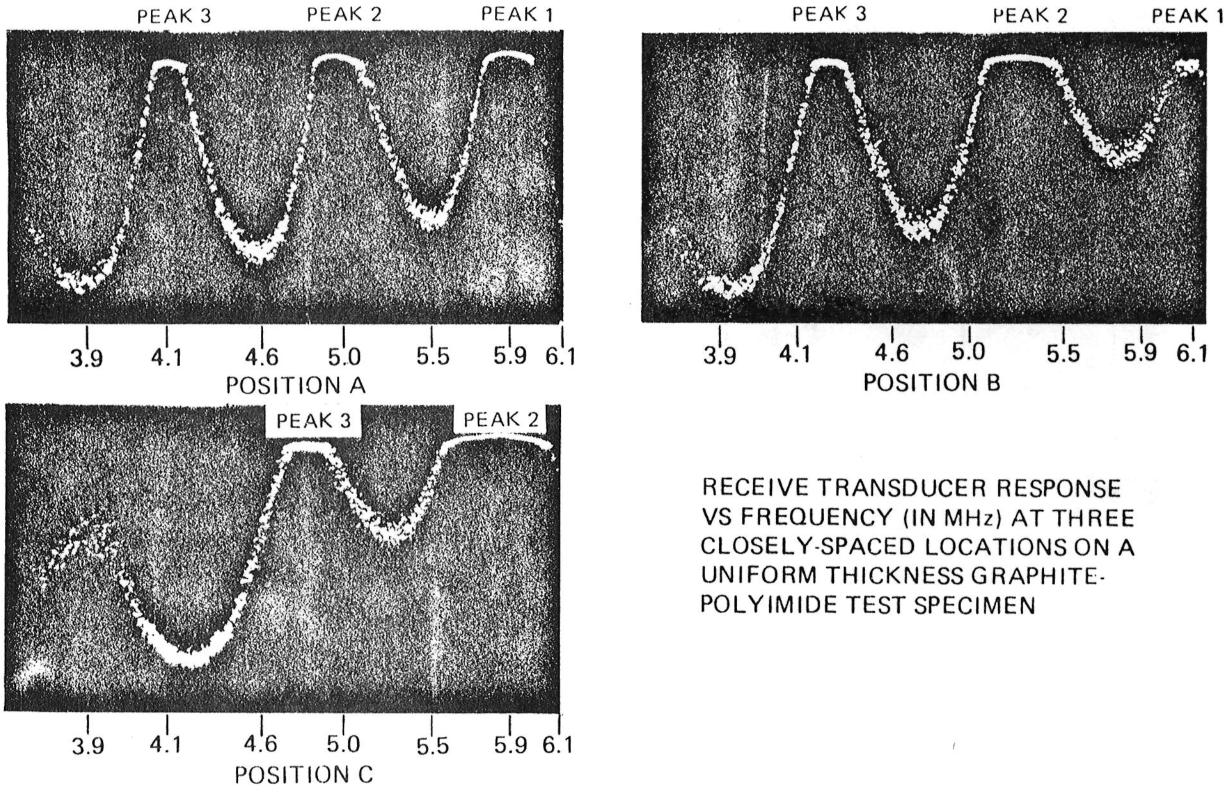
PHOTOMICROGRAPH COMPOSITE
LOT 2W 4083 (HTS FIBER)
FIGURE 22

PHOTOMICROGRAPH COMPOSITE
LOT 2W 4169 (HTS-2 FIBER)
FIGURE 23

PHOTOMICROGRAPH COMPOSITE
LOT 2W 4240 (CELION6000Fiber)
FIGURE 24



PHOTOMICROGRAPH COMPOSITE
LOT2W 4251(CELION 6000 FIBER)
FIGURE 25



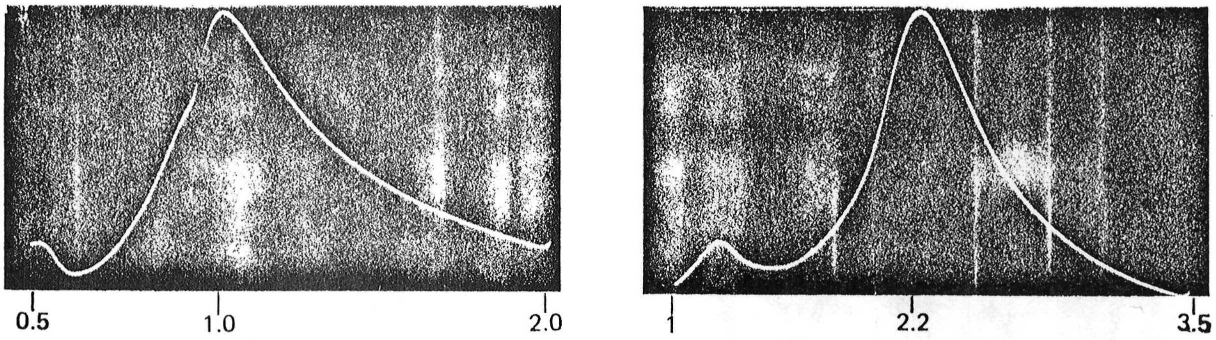
POSITION A

POSITION B

POSITION C

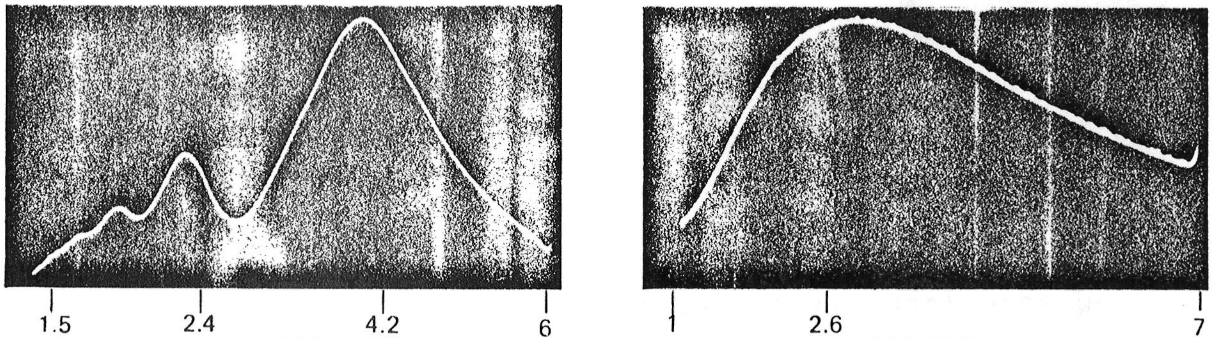
RECEIVE TRANSDUCER RESPONSE
VS FREQUENCY (IN MHz) AT THREE
CLOSELY-SPACED LOCATIONS ON A
UNIFORM THICKNESS GRAPHITE-
POLYIMIDE TEST SPECIMEN

FIGURE 26 *Ultrasonic Resonance Pattern Variation in a Graphite-Polyimide Specimen*



a) 1.0 HMz

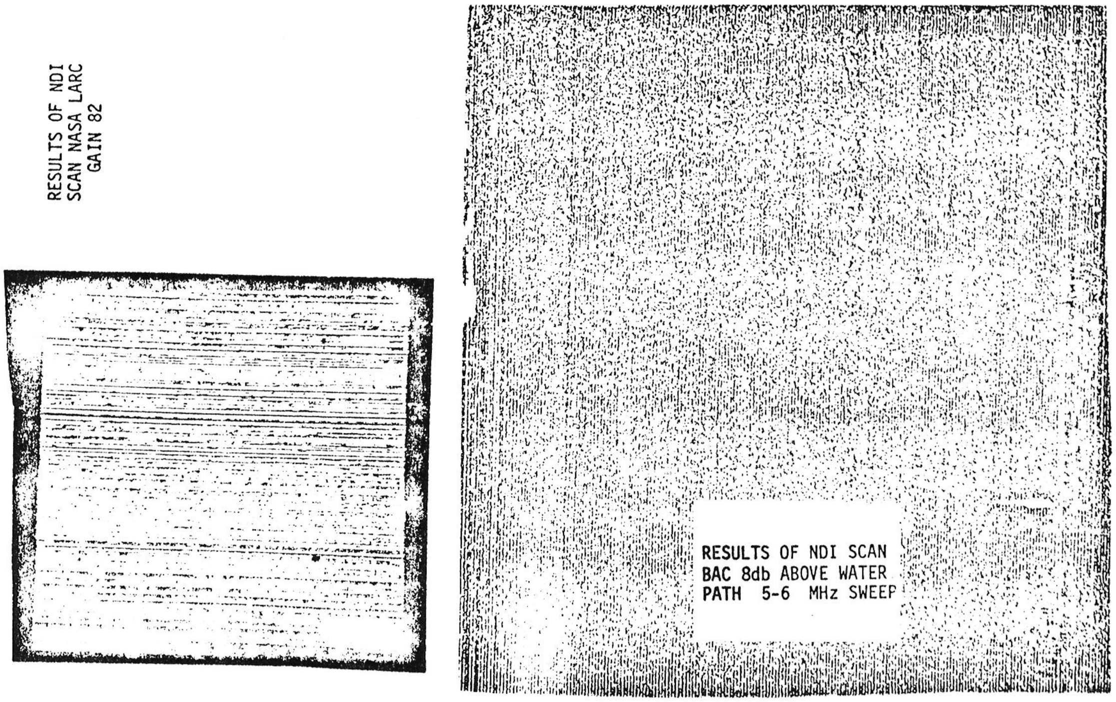
b) 2.25 MHz



a) 1.0 MHz

b) 2.25 MHz

FIGURE 27 *Frequency Response Curves of a Nortec 131 Ultrasonic Test Instrument at Various Frequencies (f) in Mega Hertz (MHz)*

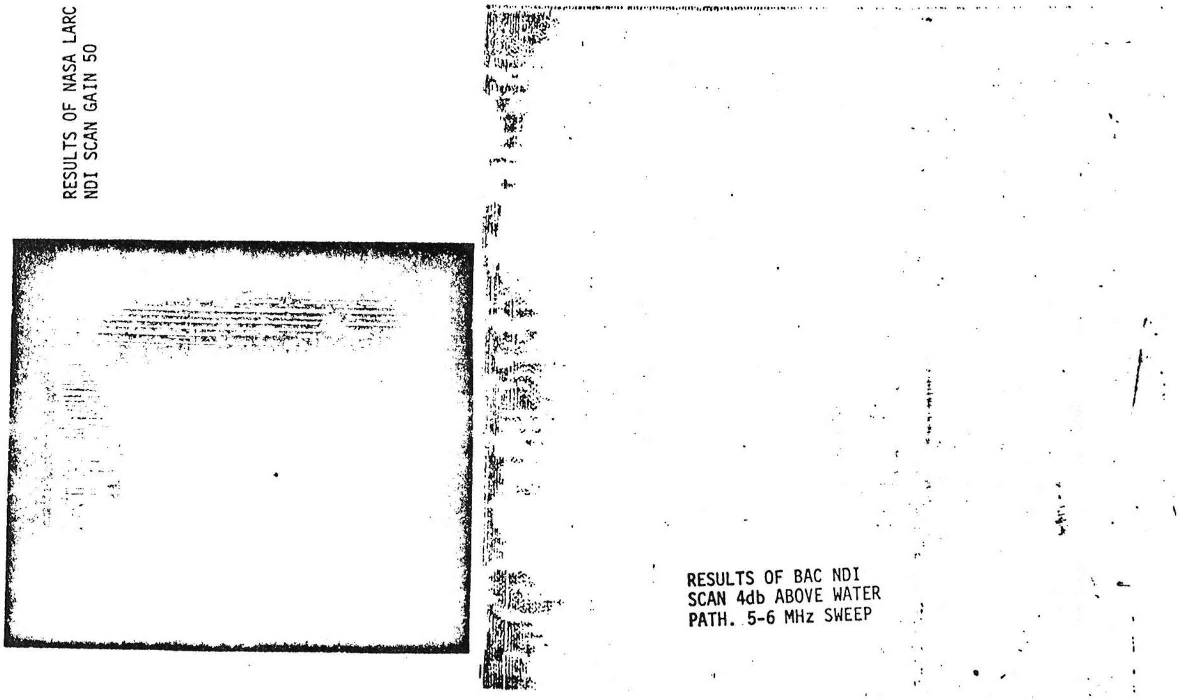


RESULTS OF NDI
SCAN NASA LARC
GAIN 82

RESULTS OF NDI SCAN
BAC 8db ABOVE WATER
PATH 5-6 MHz SWEEP

COMPARISON NDI TESTING BAC AND NASA STANDARD PANEL LOT 2W4240-1

FIGURE 28A

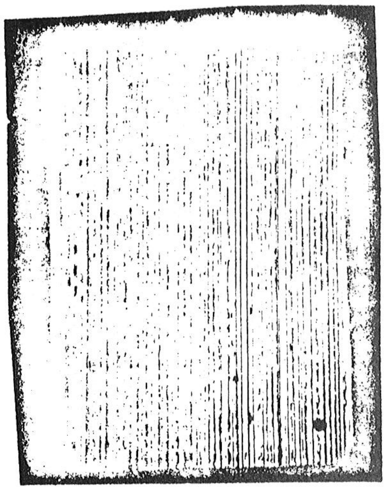


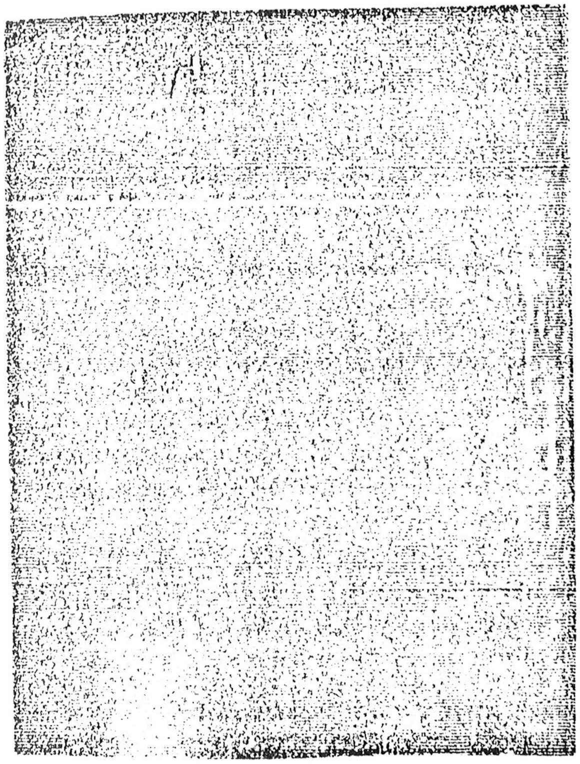
RESULTS OF NASA LARC
NDI SCAN GAIN 50

RESULTS OF BAC NDI
SCAN 4db ABOVE WATER
PATH. 5-6 MHz SWEEP

COMPARISON NDI TESTING BAC AND NASA LARC STANDARD PANEL LOT 2W4240-1
FIGURE 28B

RESULTS OF NASA LARC
NDI SCAN GAIN 50



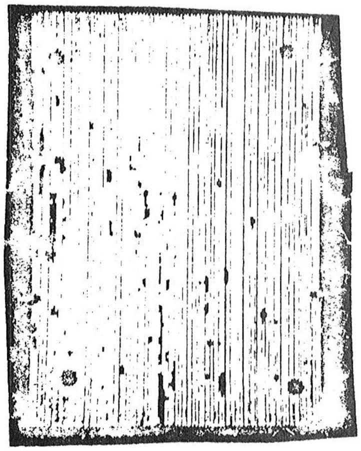


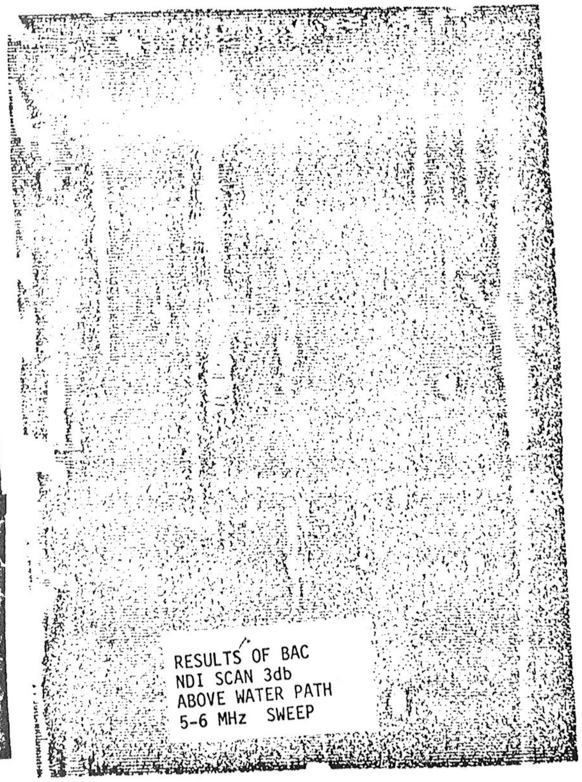
RESULTS BAC SCAN
4db ABOVE WATER
PATH. 5-6 MHz
SWEEP

COMPARISON NDI TESTING BAC AND NASA STANDARD PANEL LOT 2W4251

FIGURE 29A

RESULTS OF NDI SCAN
NASA LARC GAIN 30

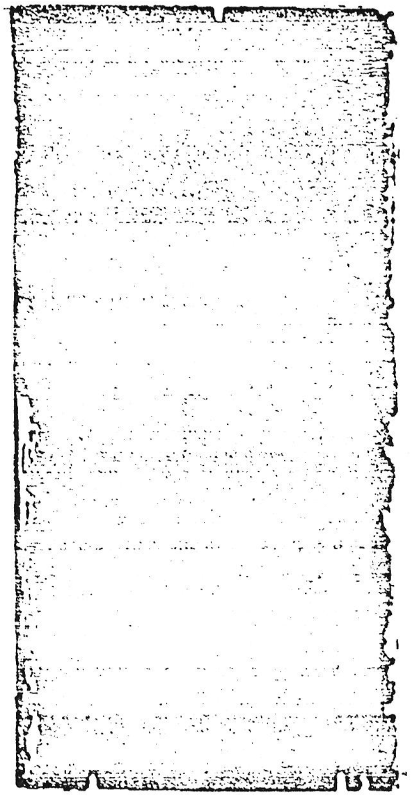




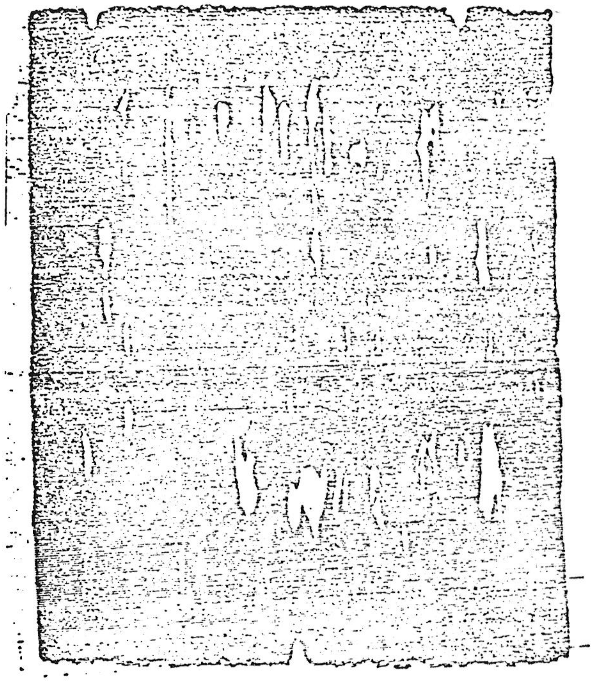
RESULTS OF BAC
NDI SCAN 3db
ABOVE WATER PATH
5-6 MHz SWEEP

COMPARISON NDI TESTING BAC AND NASA STANDARD PANEL LOT 2W4251

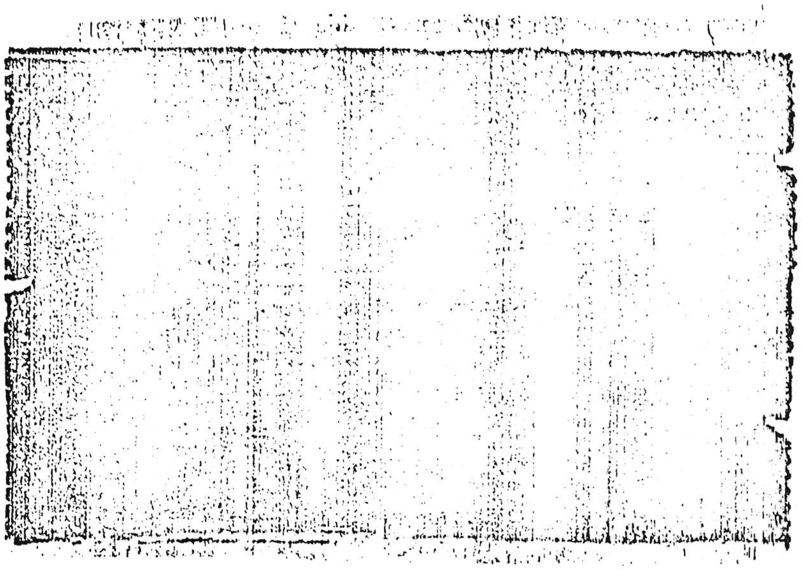
FIGURE 29B



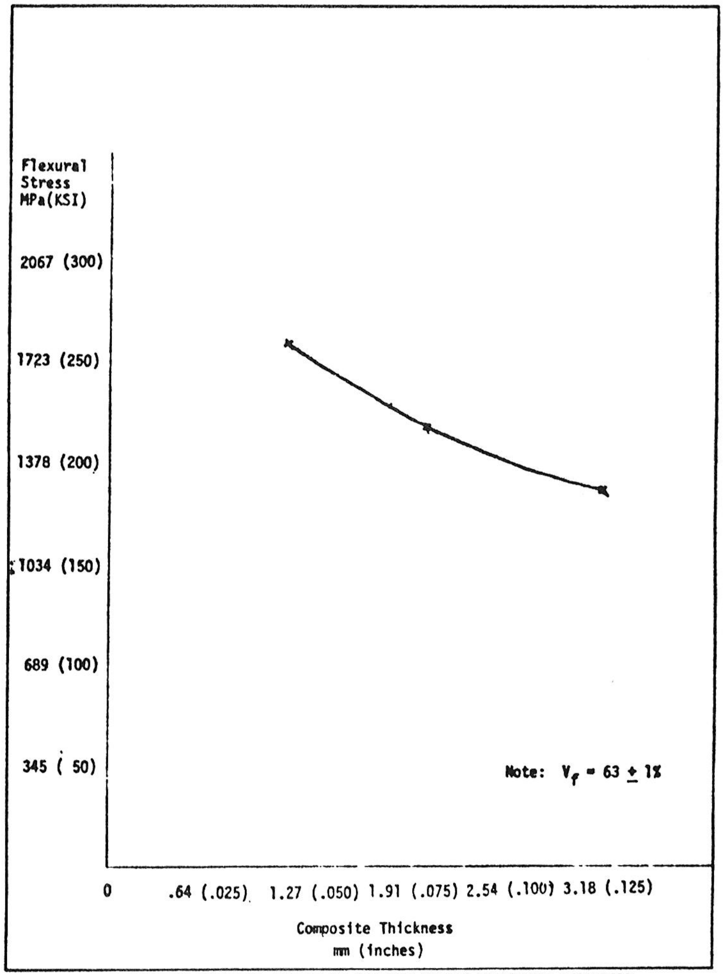
NDI SCAN COMPANY A LOT 2W 4083
FIGURE 30



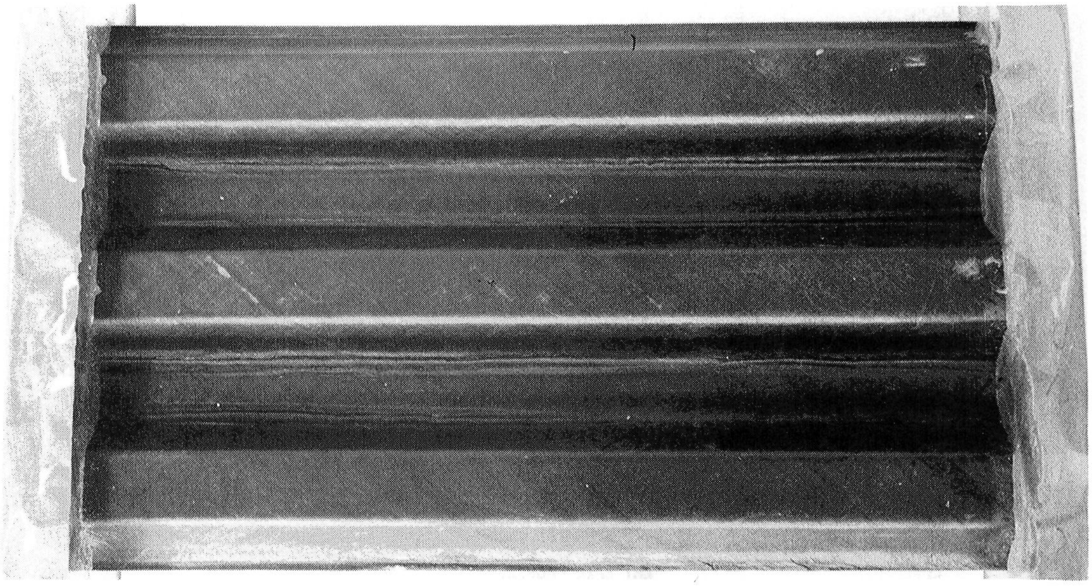
NDI SCAN COMPANY B
FIGURE 31



NDI SCAN COMPANY C
FIGURE 32

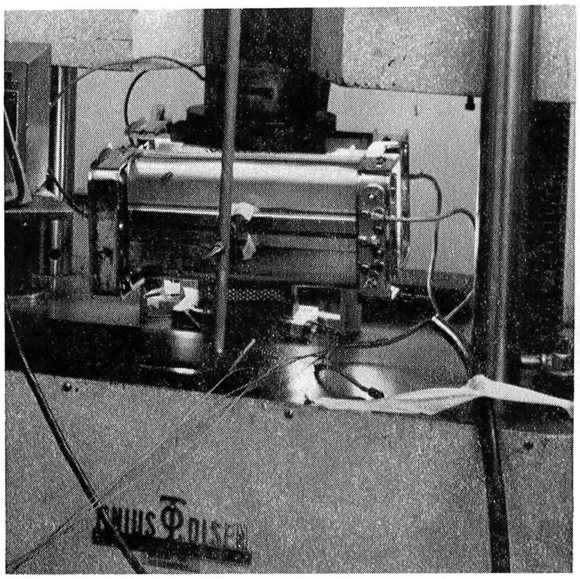


COMPARISON FLEXURAL STRESS AT AMBIENT VERSUS COMPOSITE THICKNESS
FIGURE 33



EXAMPLE OF END POTTING FOR END STABILIZATION

FIGURE 34



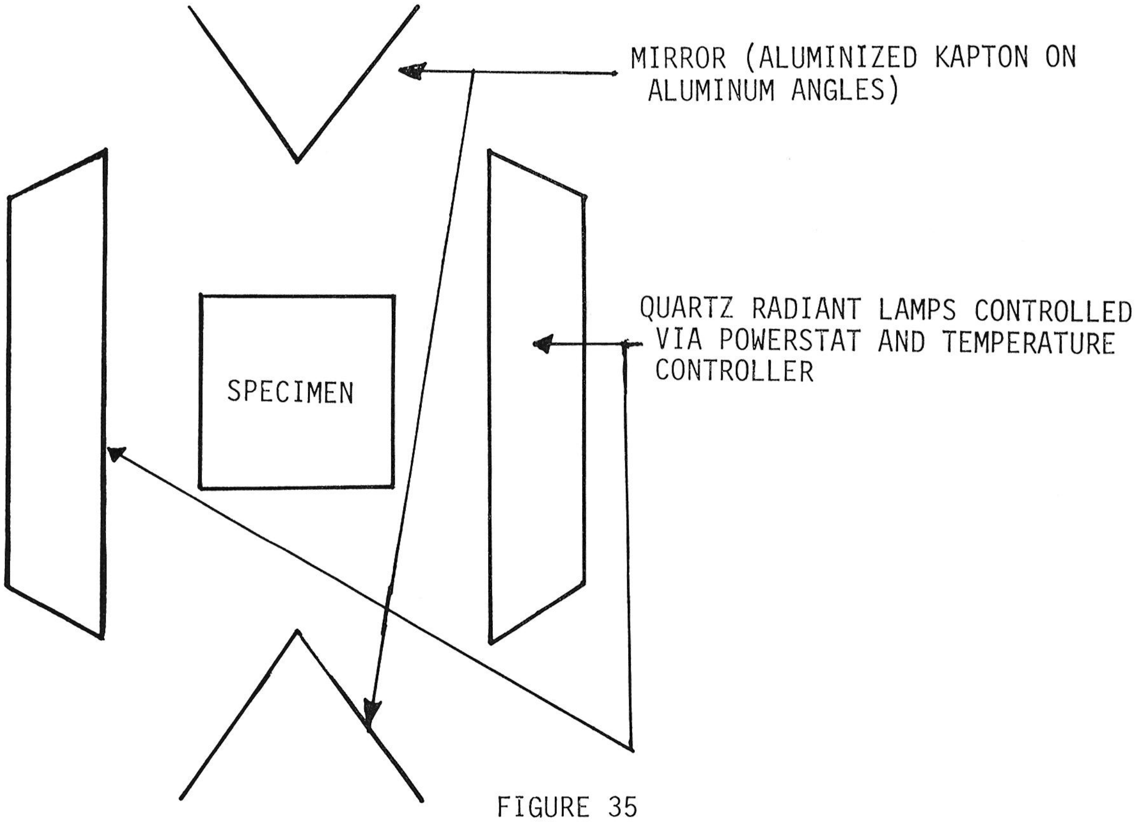
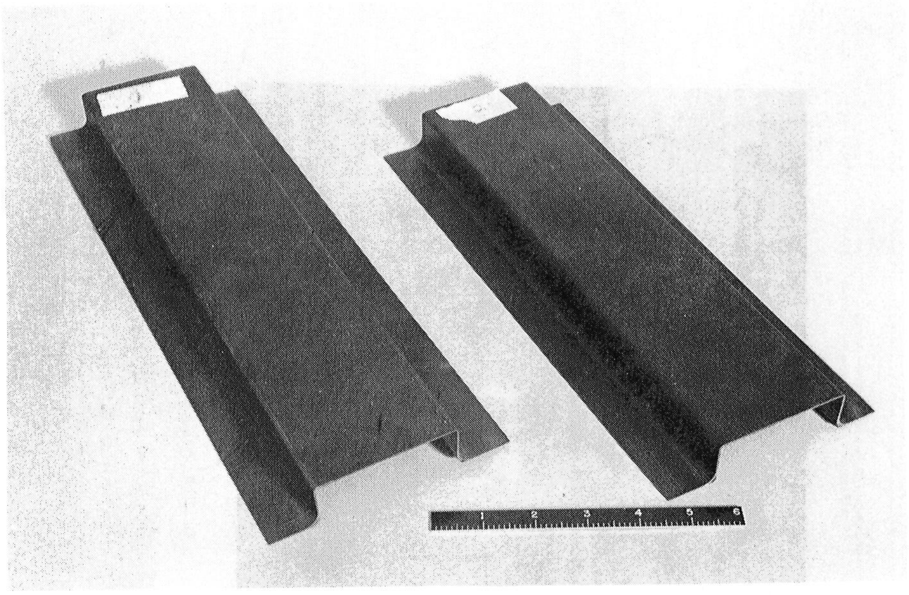
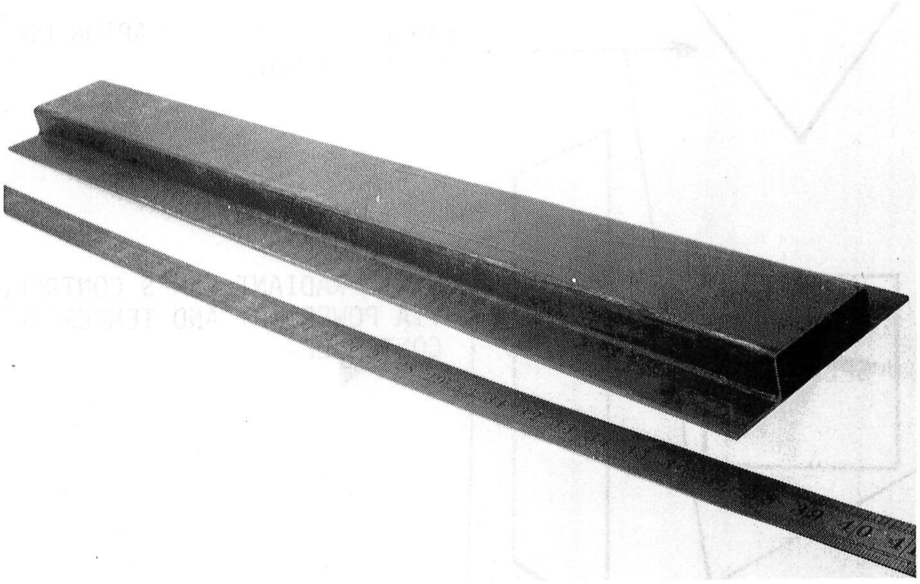


FIGURE 35

TEST ARRANGEMENT FOR 589K(600^{O}F) TESTING STRUCTURAL ELEMENTS

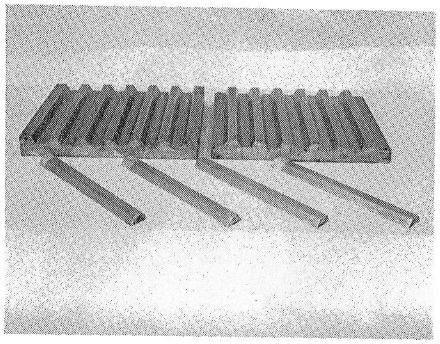


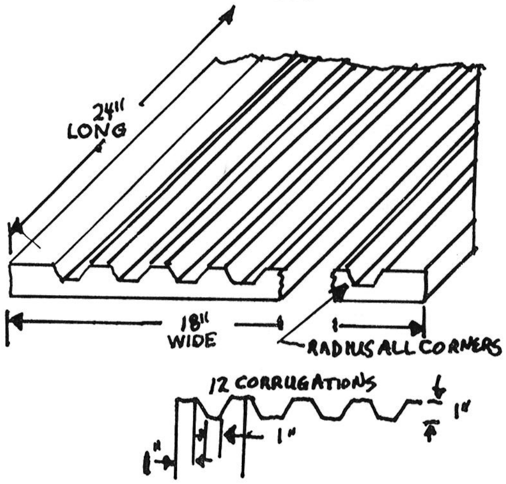
HAT SECTION STRUCTURAL ELEMENTS
FIGURE 36



COCURE HAT STIFFENED PANEL
FIGURE 37

MATERIAL: STEEL (ANY ALLOY)
NUMBER REQUIRED: 1
SIZE: 42" WIDE x 30" LONG
SURFACE FINISH: 125



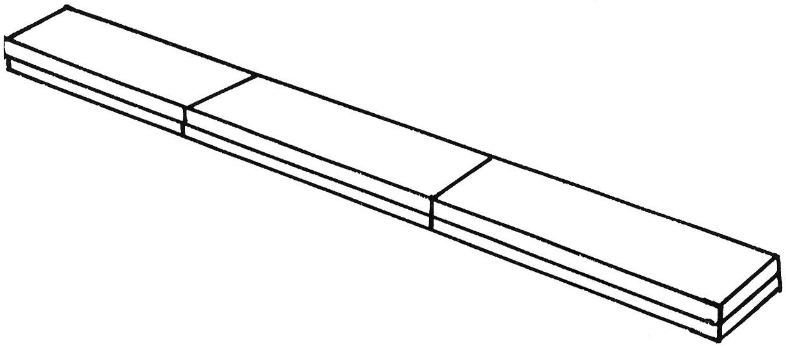


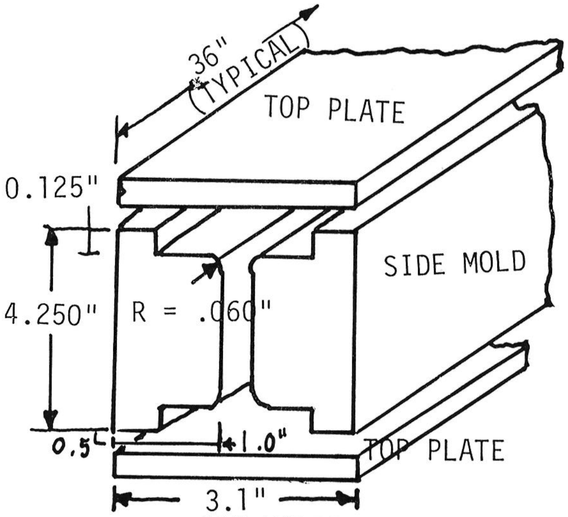
MULTIPLE HAT SECTION - TASK B
CLOSED MOLD CONCEPT

FIGURE 38

TOP PLATES

MATERIAL: ALUMINUM (ANY ALLOY)
NUMBER REQUIRED: 2
SIZE: 3.1" x 1.0" x 36"
SURFACE FINISH: 125



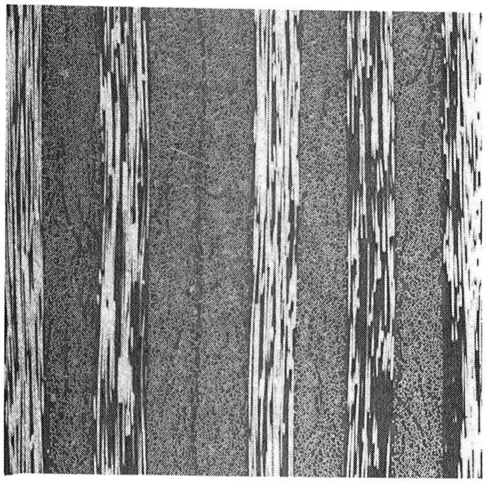


SIDE MOLDS

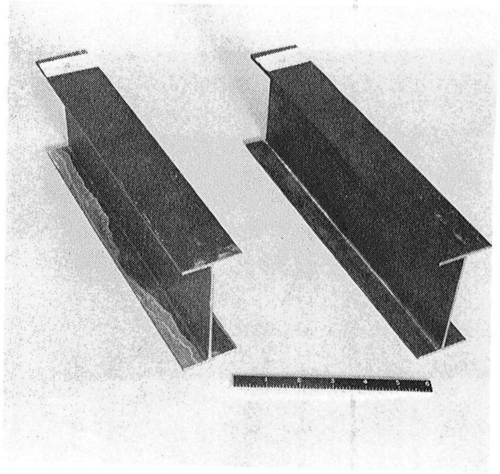
MATERIAL: ALUMINUM (ANY ALLOY)
NUMBER REQUIRED: 2
SIZE: 4.25" x 1.5" x 36"
SURFACE FINISH: 125

"C" SECTION TOOL USED IN "I" BEAM FABRICATION
FIGURE 39

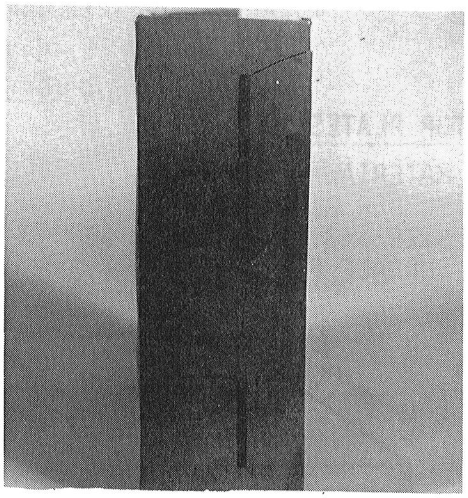
"I" BEAM FABRICATION TOOL



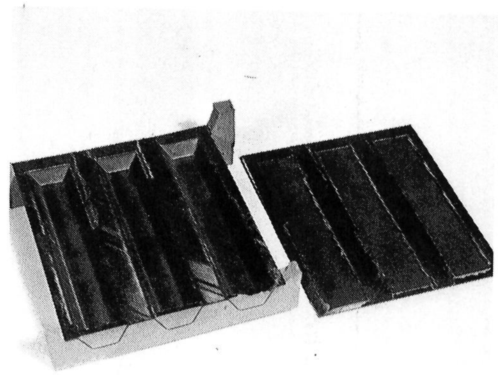
A POLISHED CROSS SECTION OF (0,90)
FIGURE 40



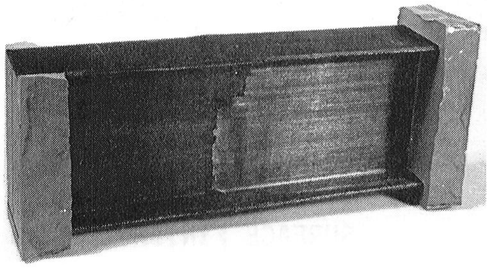
"I" BEAM STRUCTURAL ELEMENTS
FIGURE 41



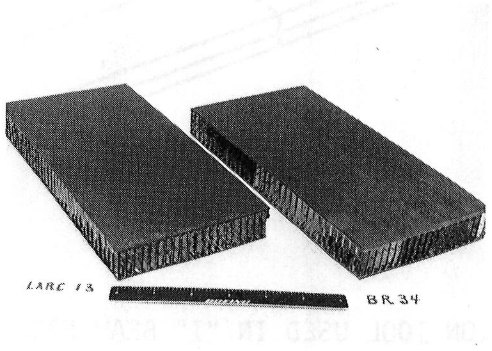
TASK B FAILED HAT SECTION
FIGURE 42



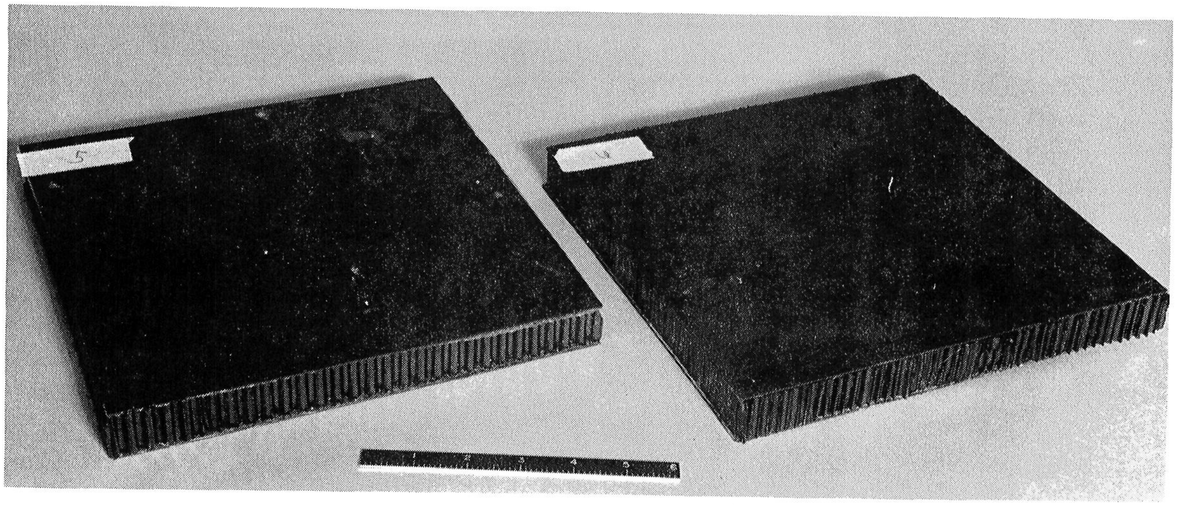
TASK B FAILED MULTIPLE HAT SECTION
FIGURE 43



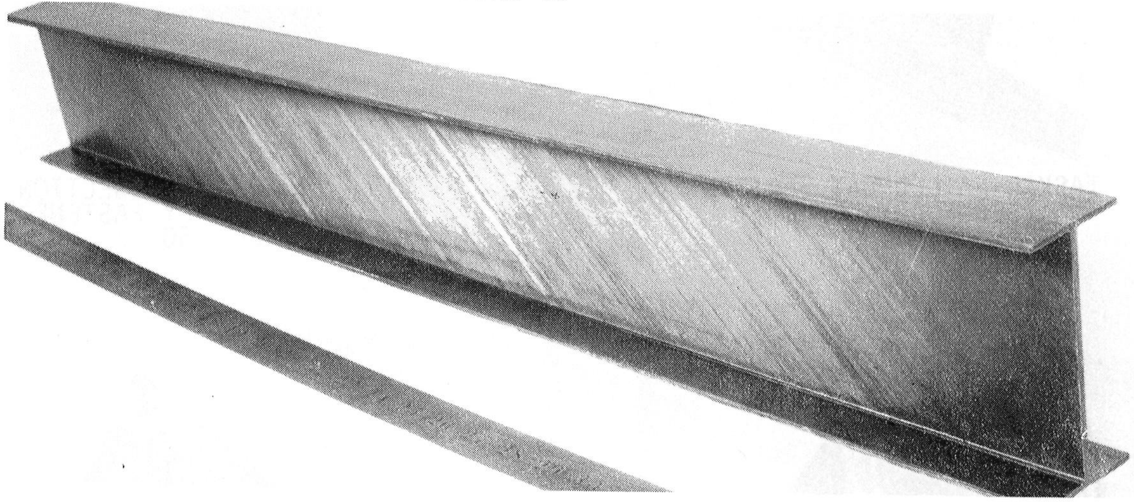
TASK B FAILED SECONDARY BONDED
"I" BEAM
FIGURE 44



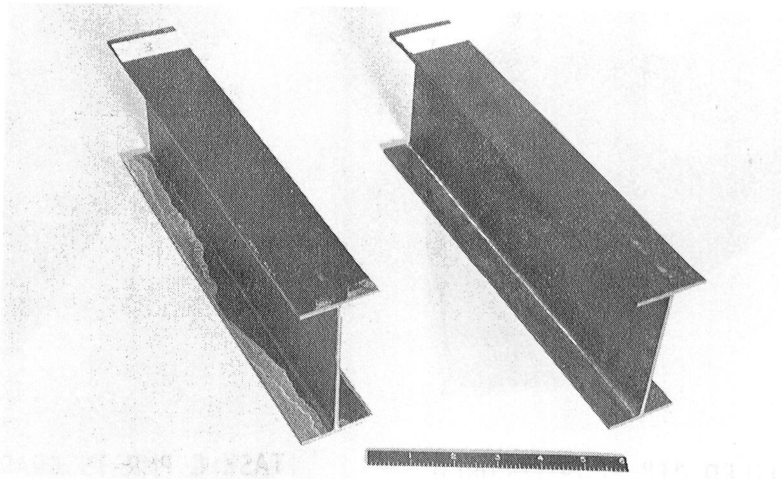
BR 34/FM 34 AND LARC-13
SANDWICH PANELS
FIGURE 45



GRAPHITE HONEYCOMB PANELS
FIGURE 46

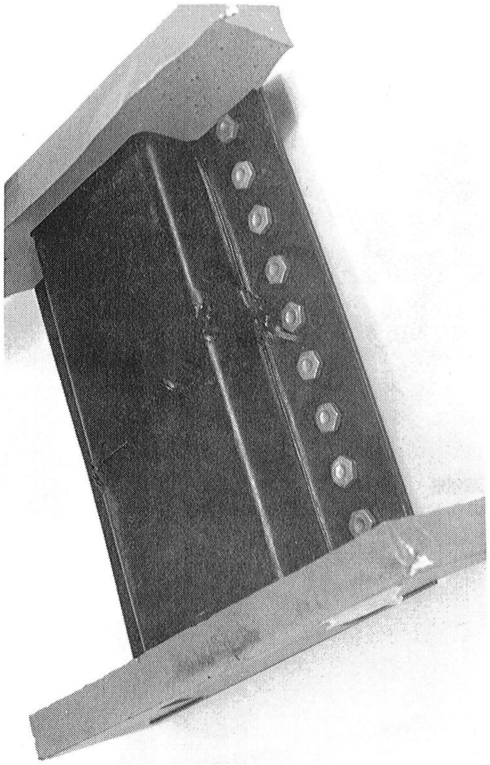


COCURE "I" STIFFENER
FIGURE 47

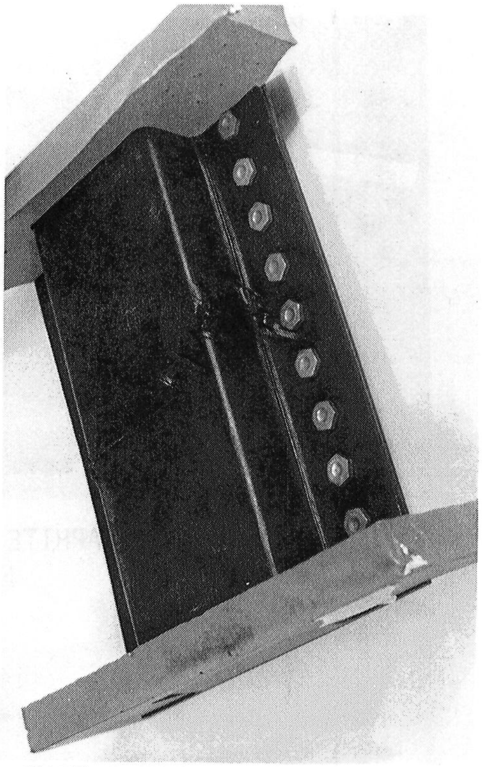


SECONDARY BONDED "I" STIFFENERS BEFORE POTTING

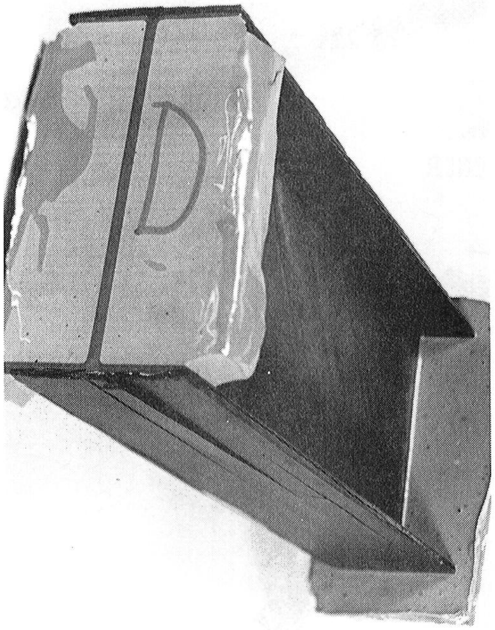
FIGURE 48



TASK C FAILED HAT SECTION
(SECONDARY BONDED)
FIGURE 49

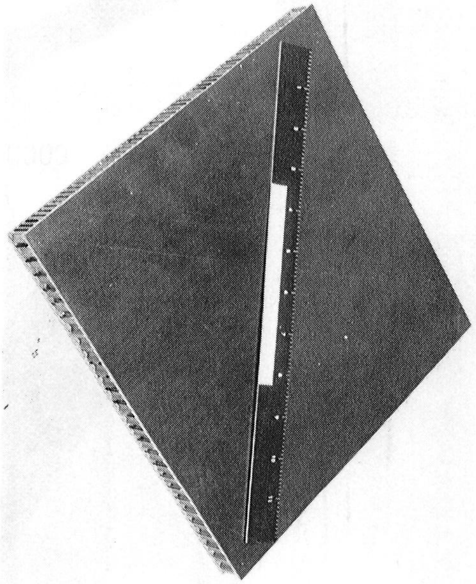


TASK C FAILED HAT SECTION
(MECHANICALLY FASTENED)
FIGURE 50



TASK C FAILED "I" BEAM COCURED

FIGURE 51



TASK C PMR-15 GRAPHITE/POLYIMIDE
FIBERGLASS HONEYCOMB SANDWICH

FIGURE 52

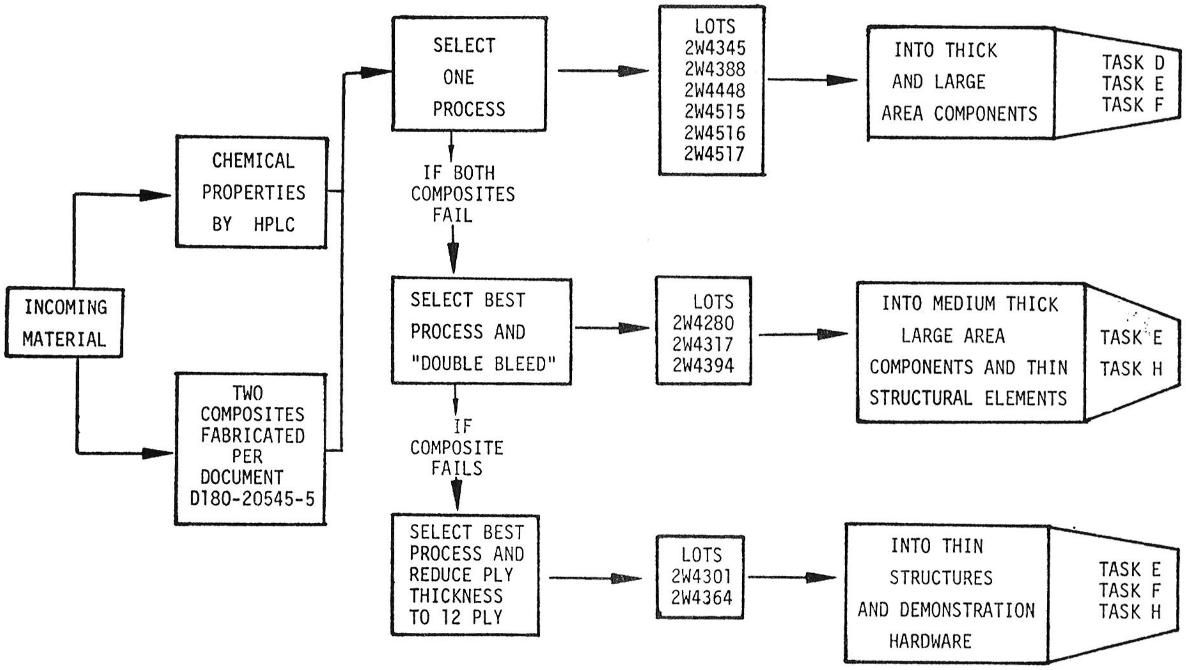
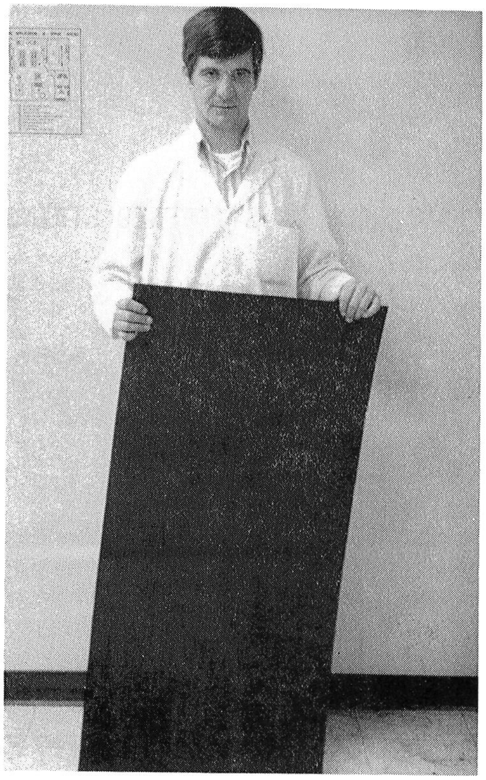


FIGURE 53



SIX-PLY LARGE AREA PANEL

FIGURE 54

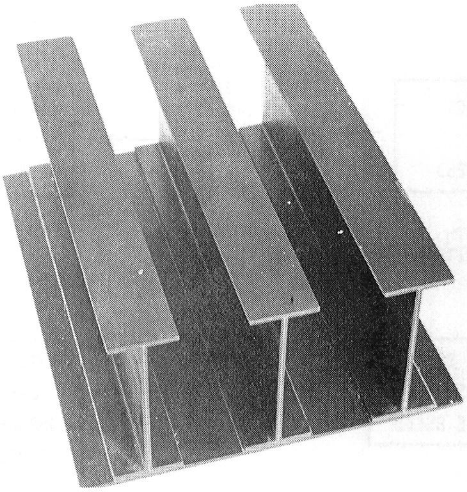


FIGURE 55 TASK E SECONDARY BONDED "I" STIFFENED STRINGER PANEL

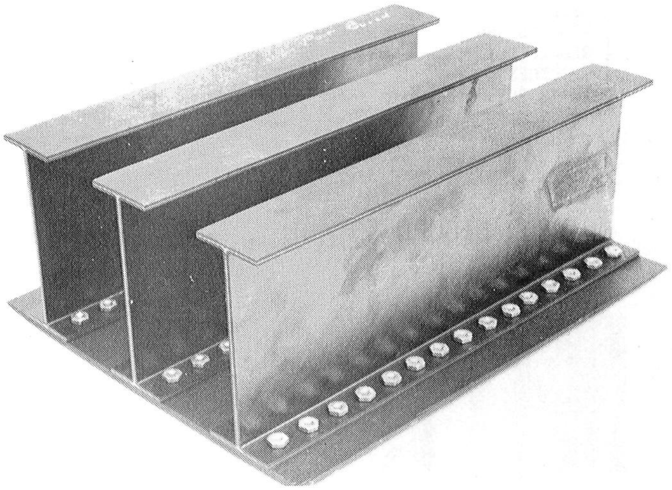


FIGURE 56 MECHANICALLY FASTENED "I" STIFFENED STRINGER PANEL

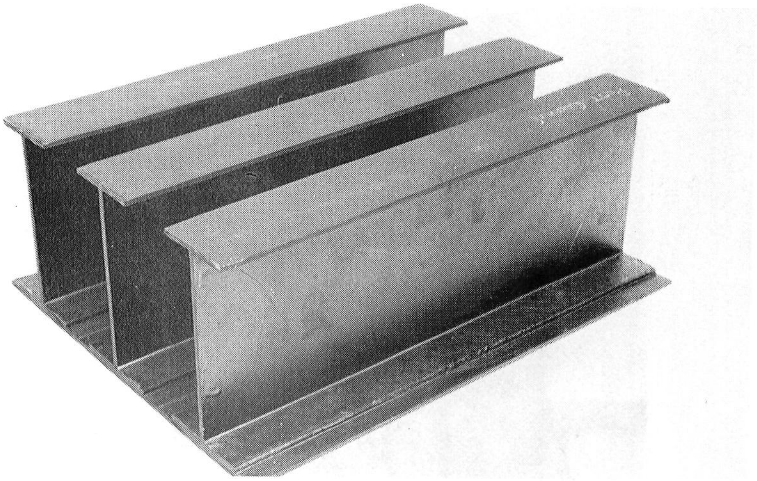
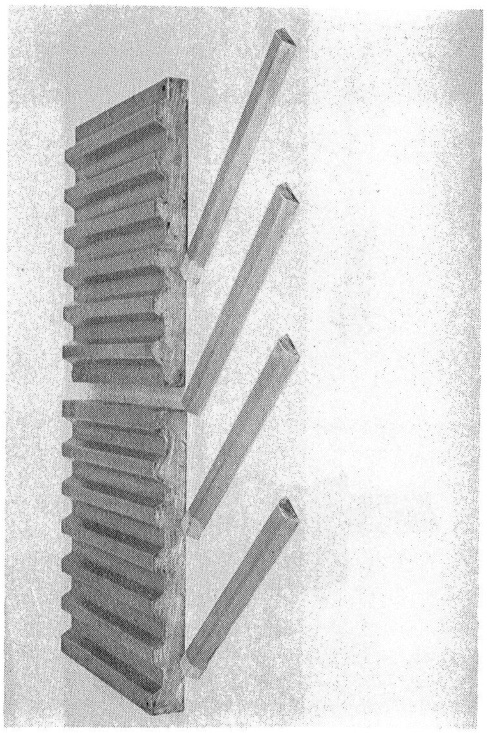
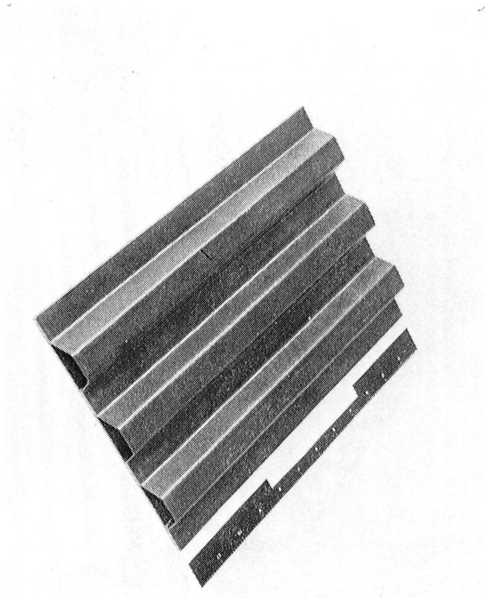


FIGURE 57 COCURED "I" STIFFENED STRINGER PANEL

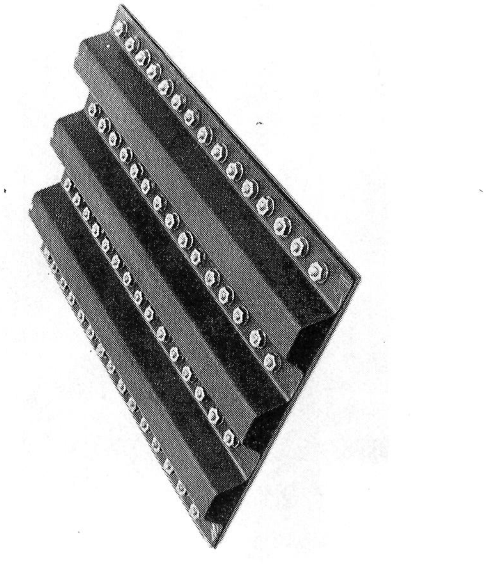


PICTURE OF SMALL MULTIPLE HAT SECTION TOOL AND ALUMINUM BARS
FIGURE 58



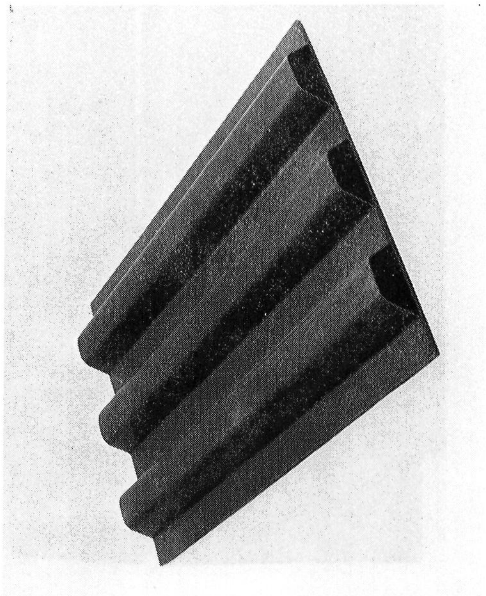
SECONDARY BONDED MULTIPLE HAT SECTION

FIGURE 59



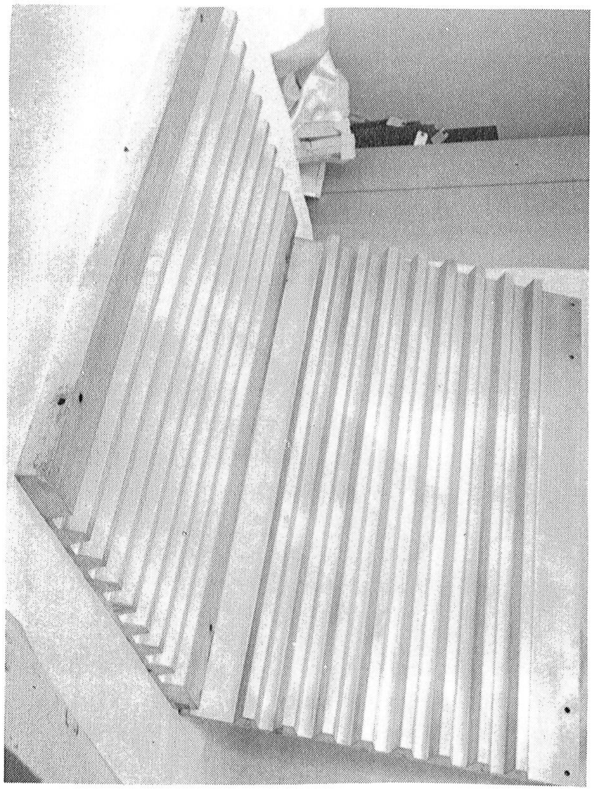
FASTENED MULTIPLE HAT SECTION

FIGURE 60

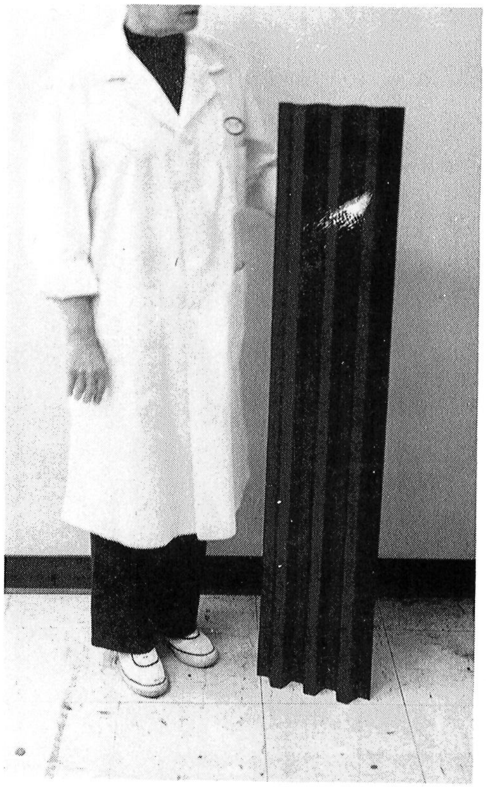


COCURED MULTIPLE HAT SECTION

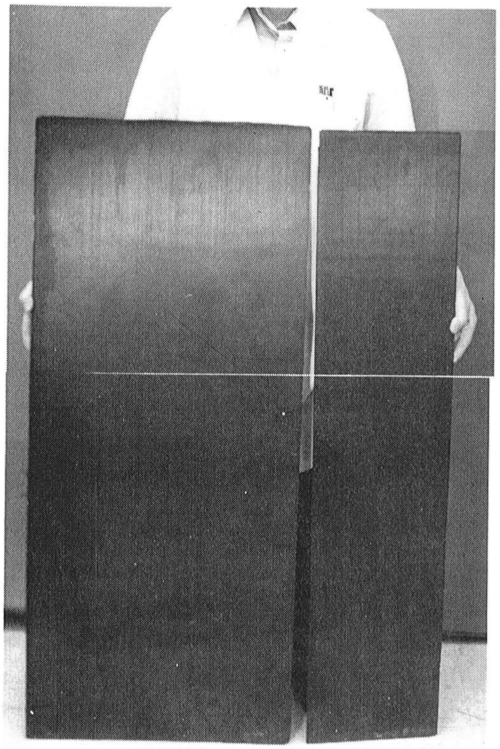
FIGURE 61



TOOLING LARGE MULTIPLE HAT SECTION
FIGURE 62

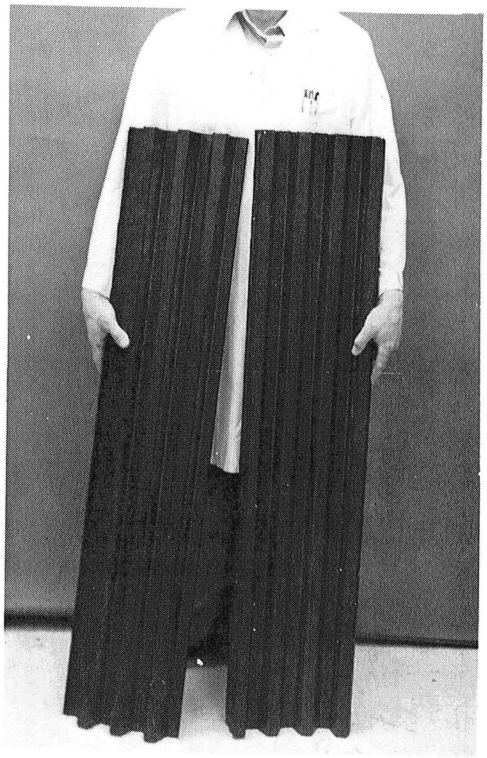


CORRUGATION BEFORE BONDING
FIGURE 63



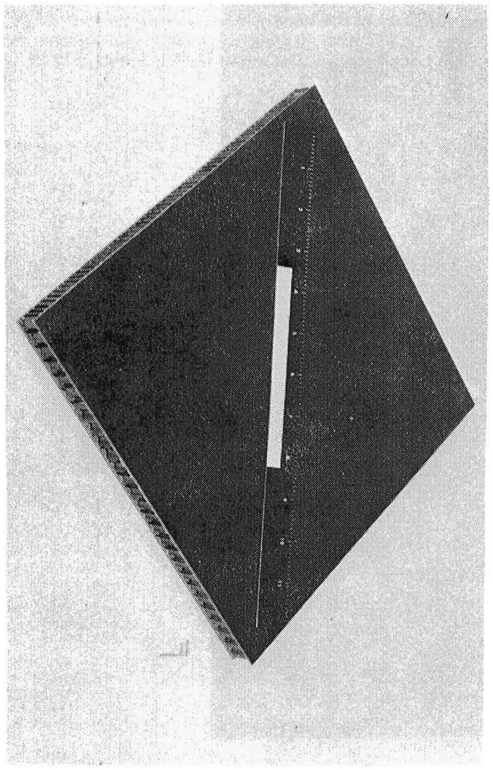
FLAT PANEL BEFORE BONDING

FIGURE 64



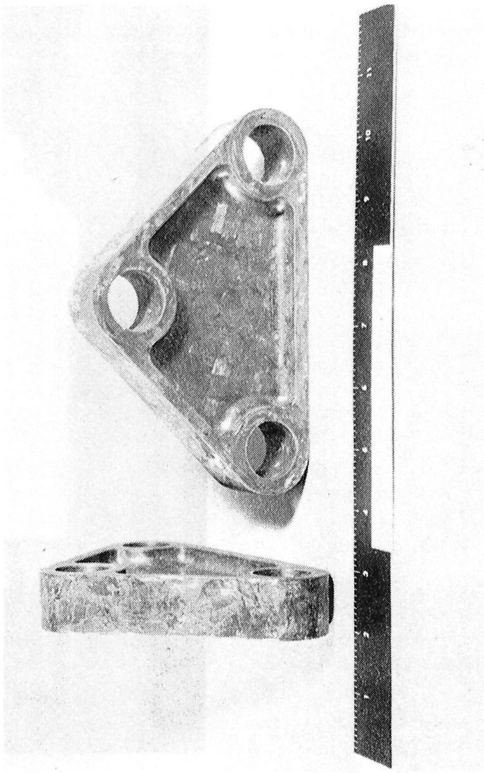
END CORRUGATION

FIGURE 65



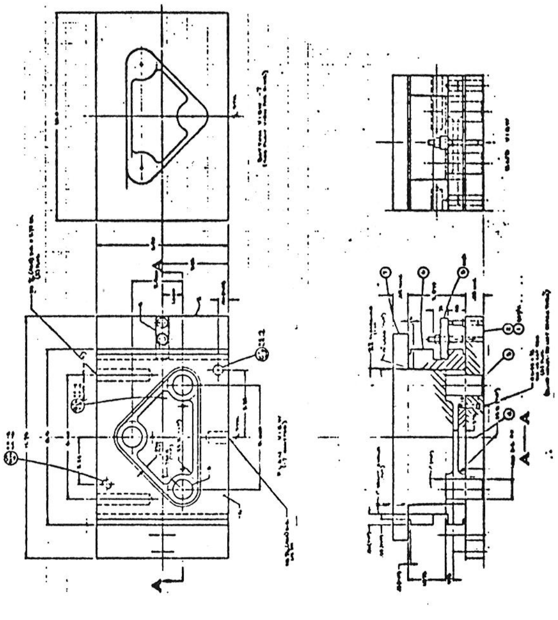
TASK F - PMR-15 GRAPHITE/POLYIMIDE GLASS HONEYCOMB SANDWICH

FIGURE 66



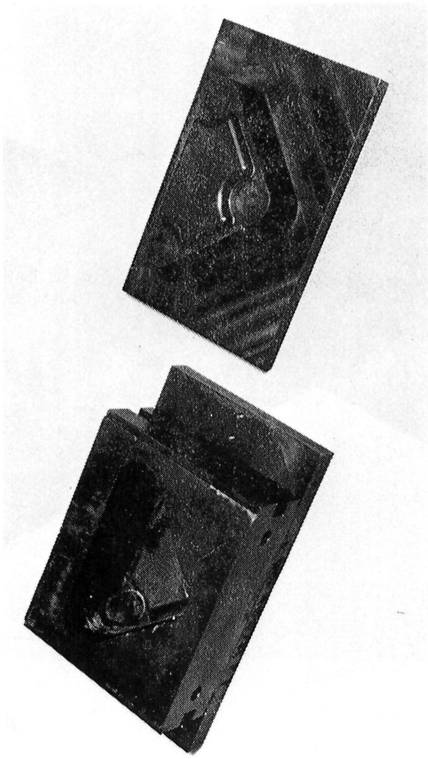
GRAPHITE/PMR-15 CHOPPED FIBER FITTINGS

FIGURE 67



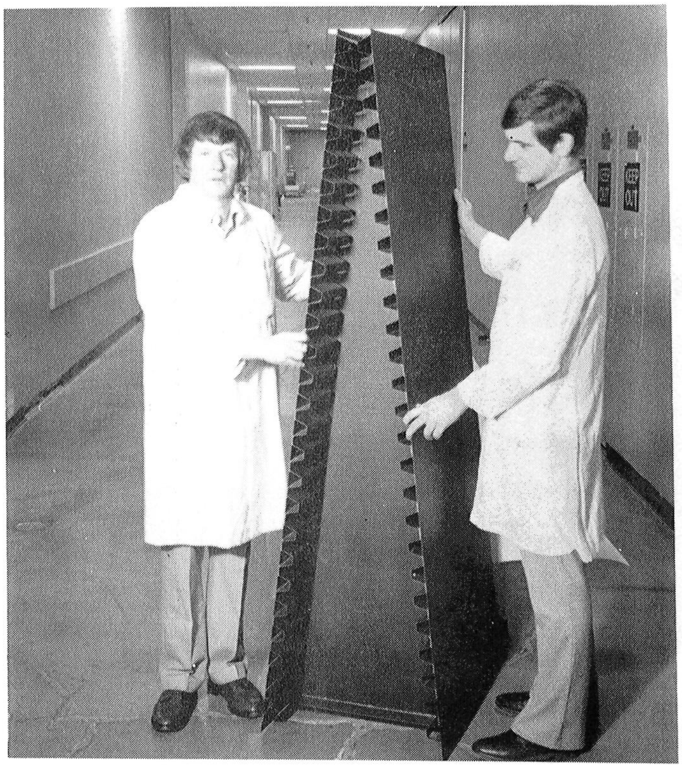
SCHEMATIC TASK G COMPRESSION MOLD

FIGURE 68

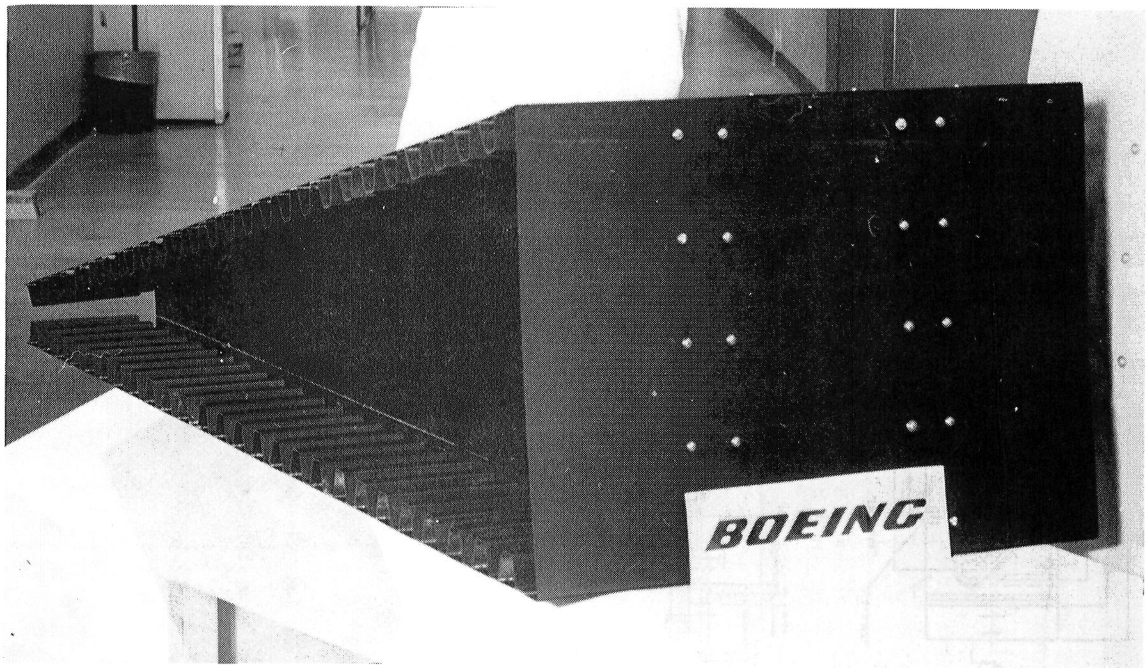


PICTURE OF THREE PIECE TASK G COMPRESSION MOLD

FIGURE 69

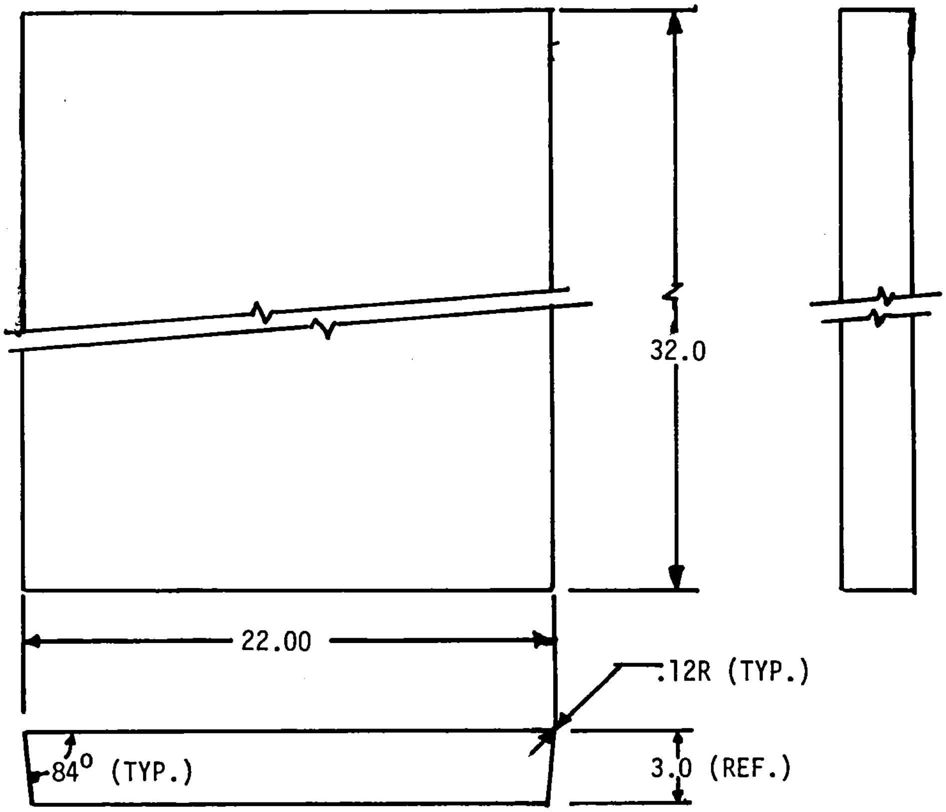


AFT BODY FLAP
FIGURE 70

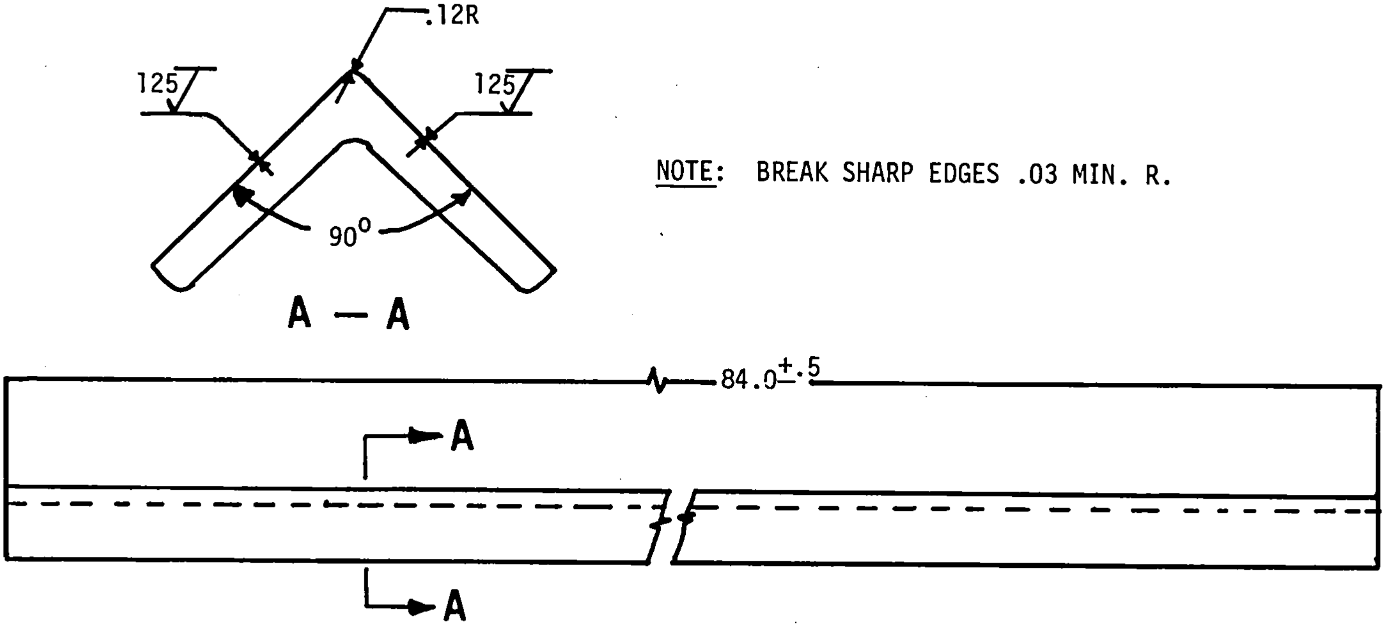


AFT BODY FLAP

FIGURE 71

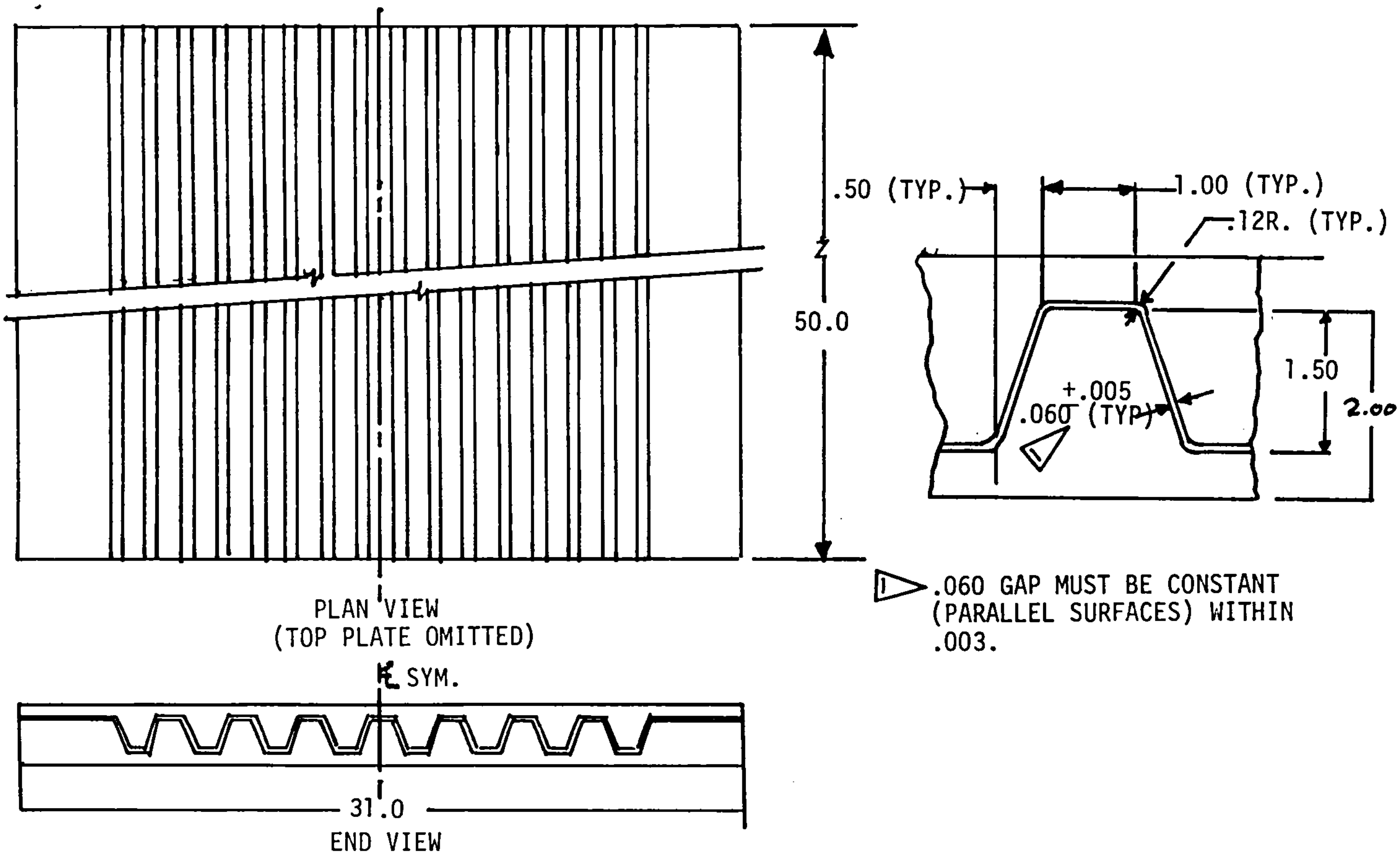


LAYUP MANDREL - END CLOSURE TASK H
FIGURE 72



NOTE: BREAK SHARP EDGES .03 MIN. R.

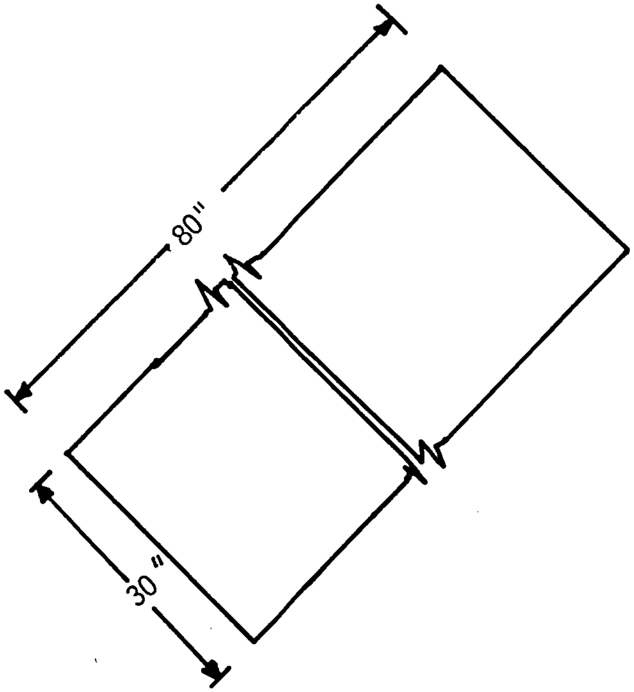
SIDE VIEW
LAYUP MANDREL - 90° ANGLE TASK H
FIGURE 73



1 .060 GAP MUST BE CONSTANT (PARALLEL SURFACES) WITHIN .003.

LAYUP TOOL - CORRUGATION TASK H

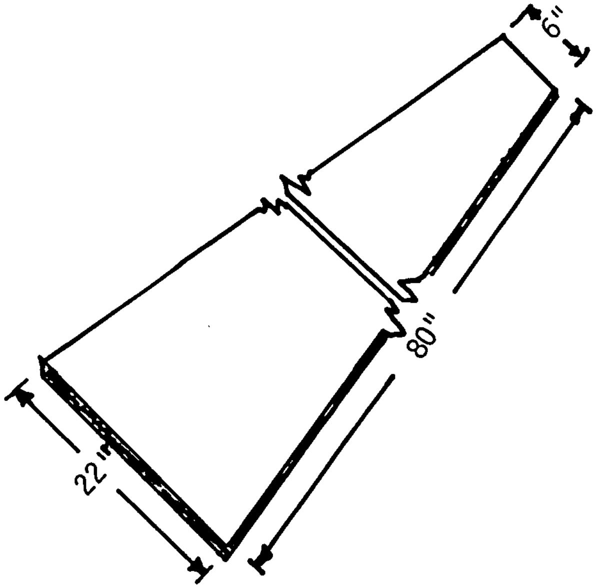
FIGURE 74



REQUIRED: 2 EACH

PLY ORIENTATION $(0, \pm 45, 90)_{2T}$ BALANCED
CELION 6000

SKIN PANELS
FIGURE 75



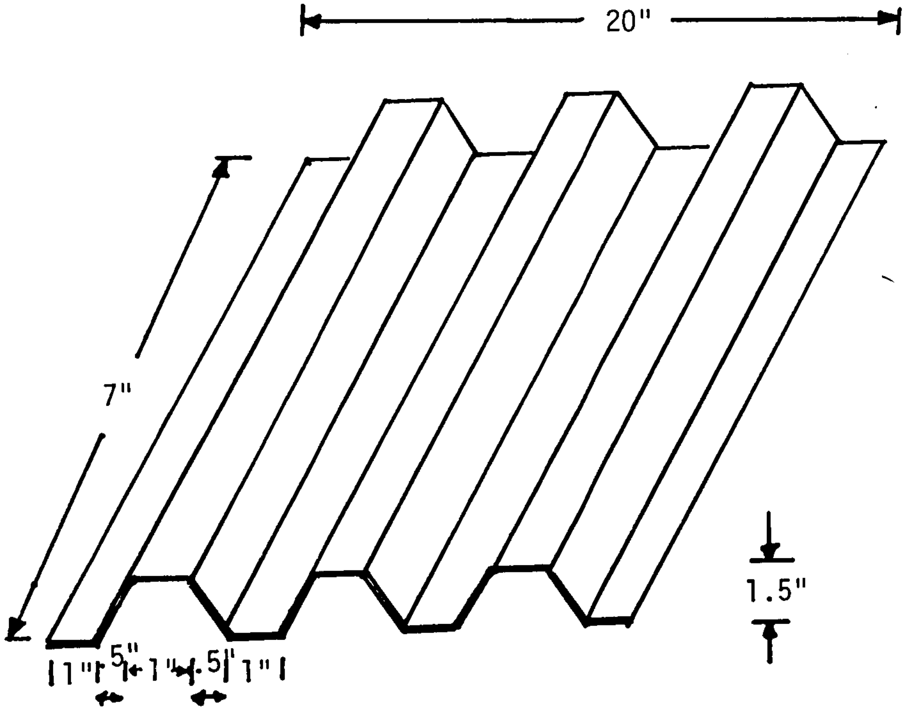
REQUIRED: 2 EACH

PLY ORIENTATION $(0, \pm 45, 90)_{2T}$
CELION 3000

ADHESIVE: A7F

FAB: SECONDARY BOND

SANDWICH
FIGURE 76



REPEAT 6
CORRUGATIONS

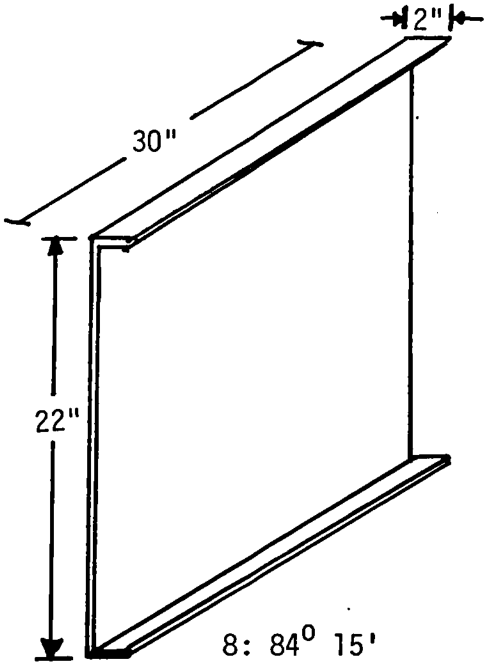
REQUIREMENT: 24

PLY ORIENTATION $(\pm45)_{4T}$

CELION 6000

CORRUGATIONS

FIGURE 77



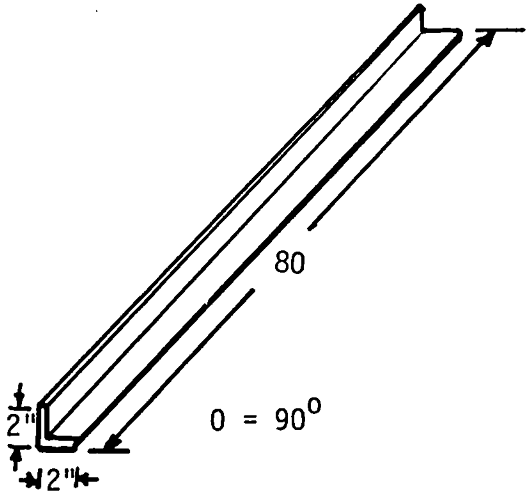
REQUIRED: 1 EACH

PLY ORIENTATION $(\pm 45)_{4T}$

CELION 6000

"C" SPAR

FIGURE 78



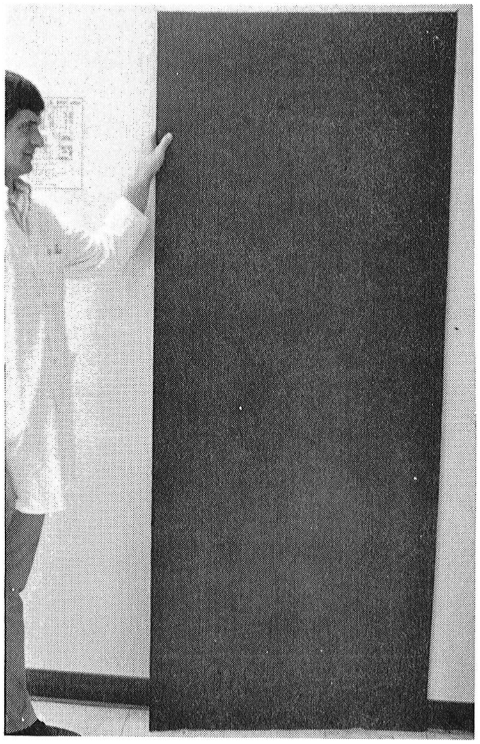
REQUIRED: 8 EACH

PLY ORIENTATION $(0, \pm 45, 90)_{2T}$

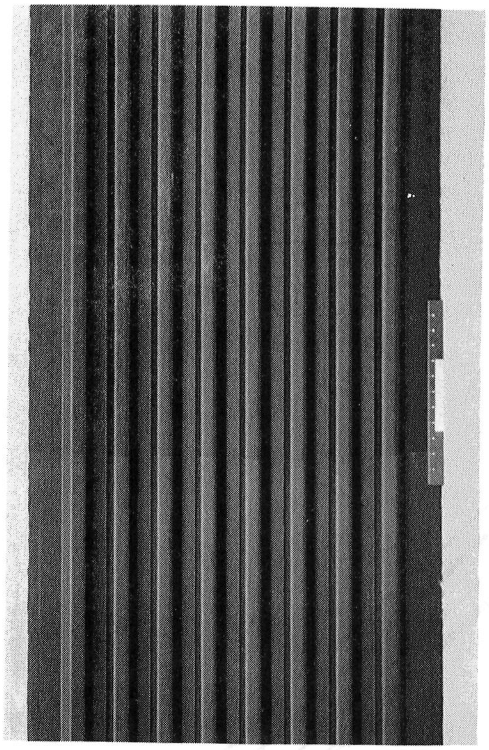
CELION 3000

ANGLE

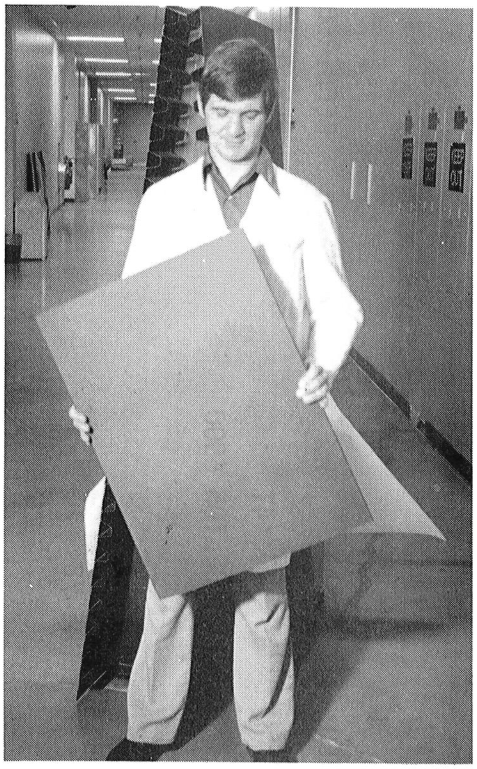
FIGURE 79



COMPONENT SKIN PANEL
FIGURE 80

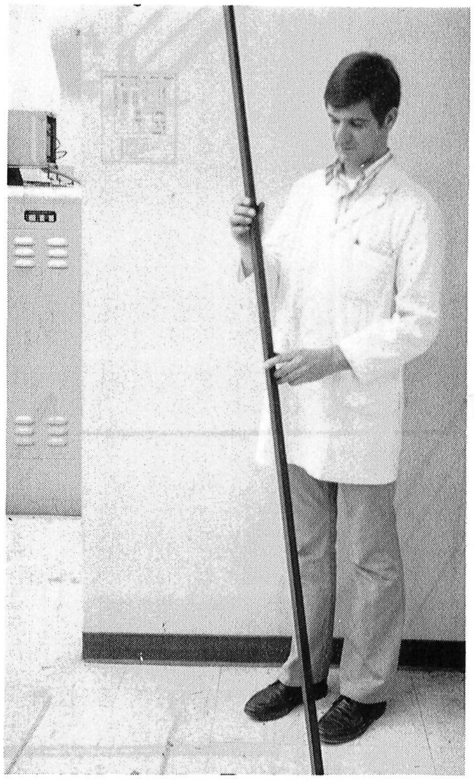


CORRUGATION FOR COMPONENT
FIGURE 81



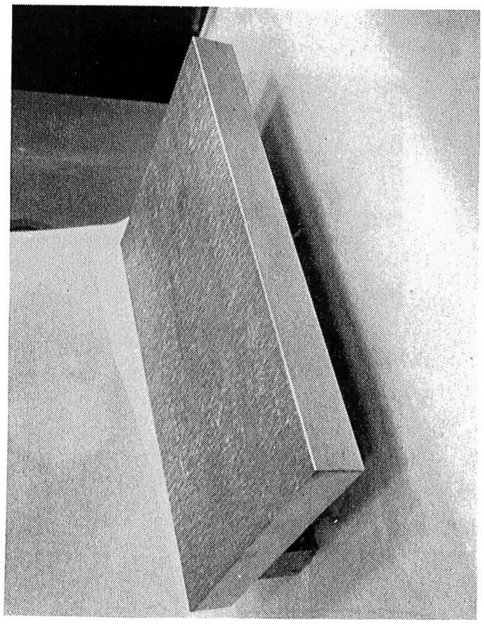
ANGLE FOR COMPONENT

FIGURE 82



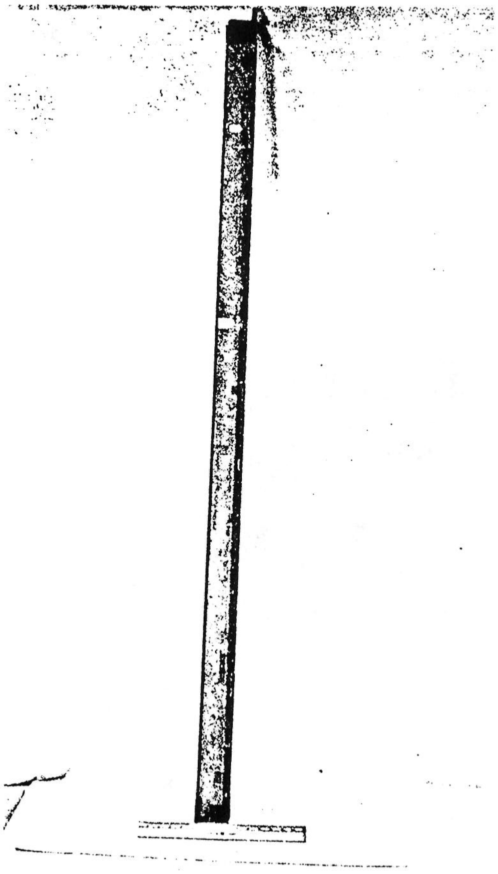
CLOSE OUT C SECTION

FIGURE 83



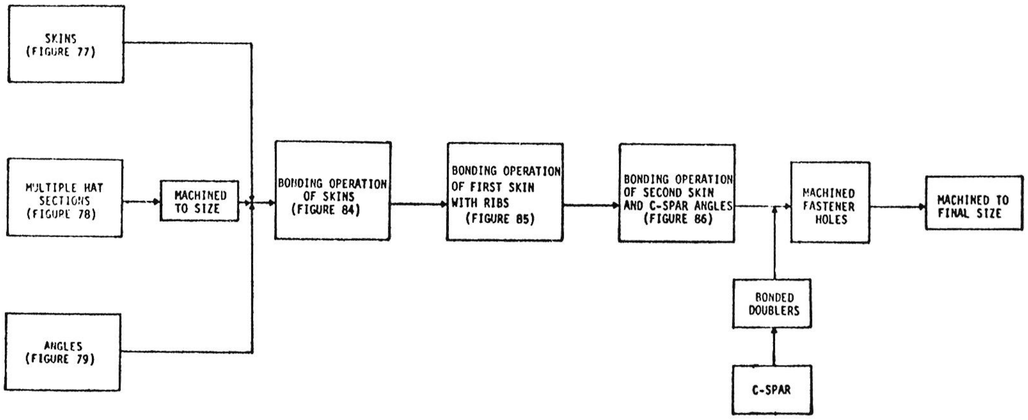
C SPAR TOOLING

FIGURE 84



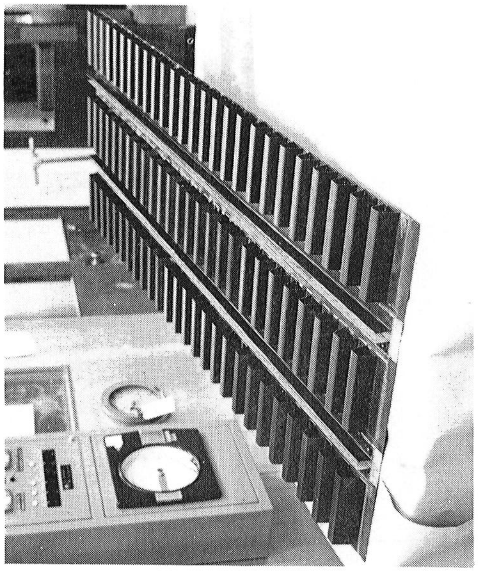
ANGLE TOOLING

FIGURE 85



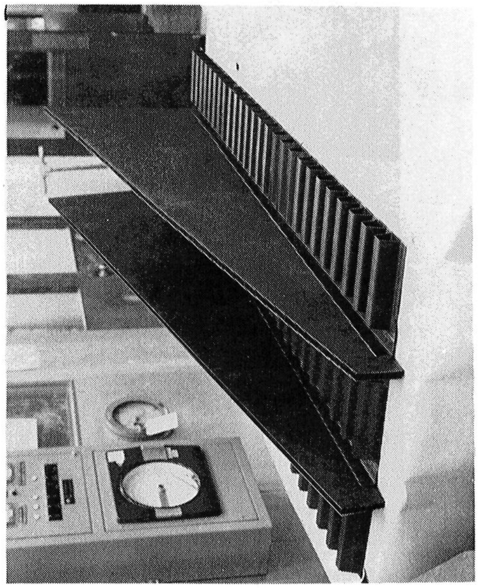
FLOW DIAGRAM OF HARDWARE ASSEMBLY

FIGURE 86



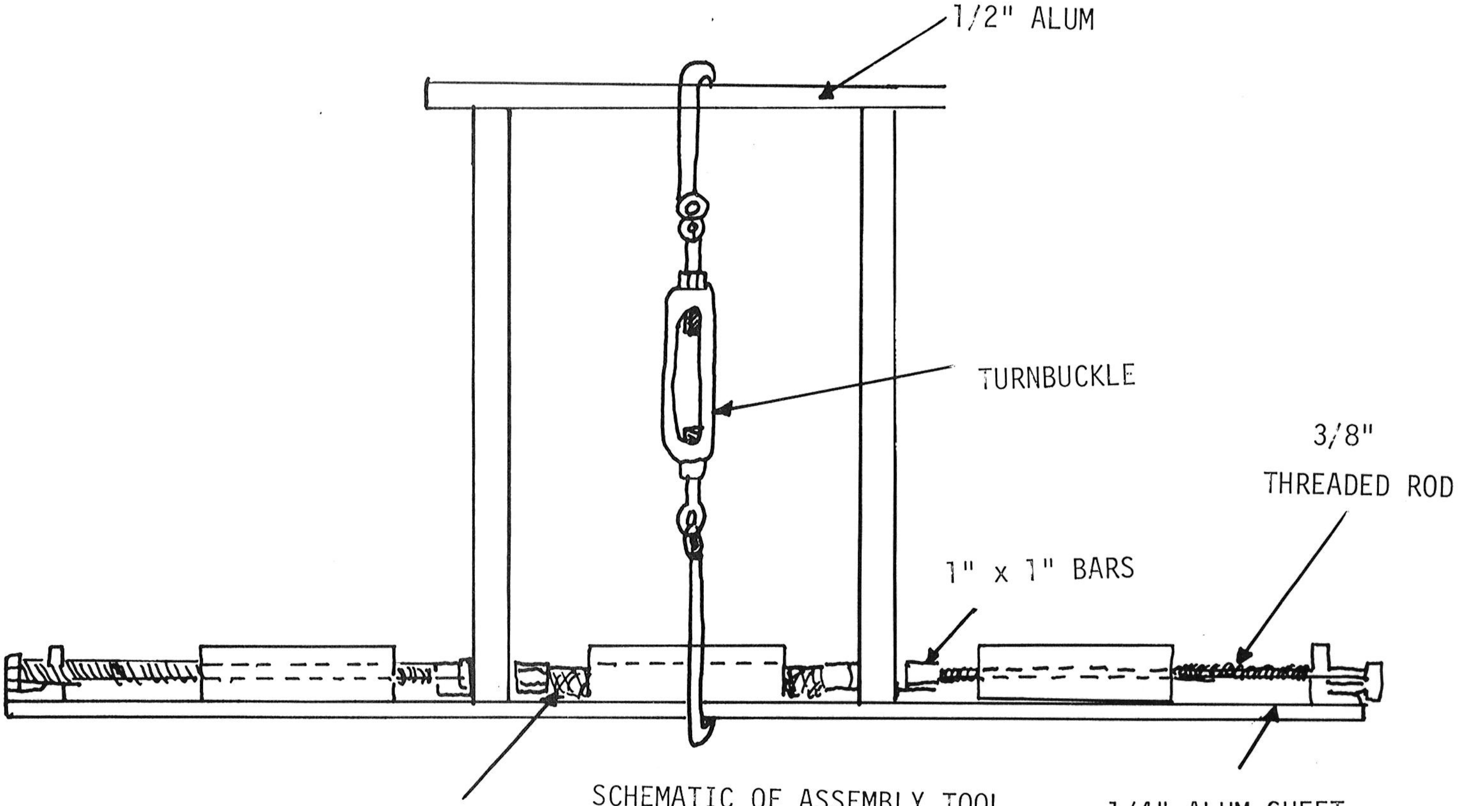
ASSEMBLED SKIN

FIGURE 87



ASSEMBLED SKIN WITH BONDED RIBS

FIGURE 88



SCHEMATIC OF ASSEMBLY TOOL

FIGURE 89

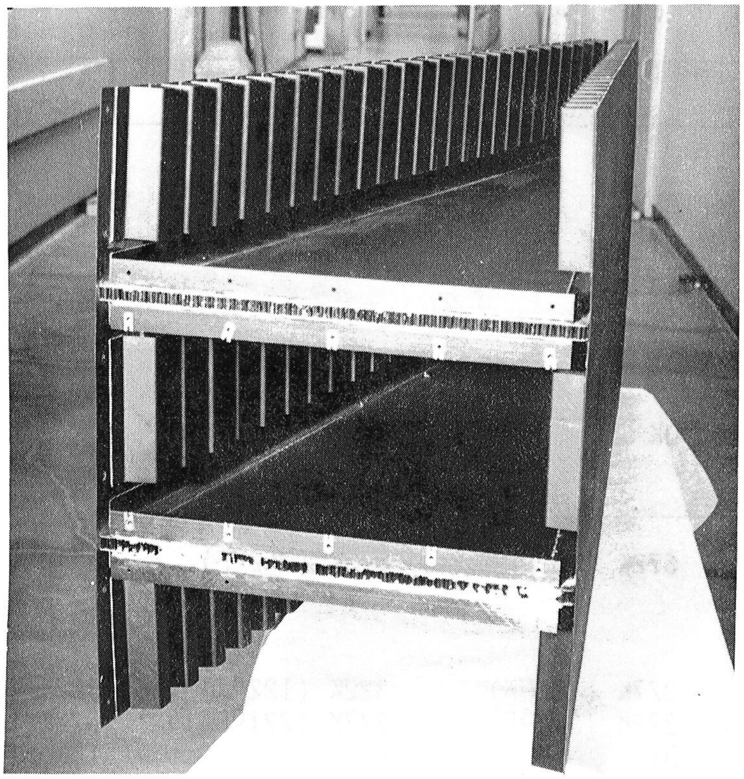


FIGURE 90 BONDED ANGLES FOR CLOSE OUT SPAR

FIGURE 91 STIFFENED CLOSE OUT SPARE

TABLE I
SUMMARY OF CHEMICAL CHARACTERIZATION DATA

Chemical Test	Points of Comparison	Company A	Company B	Company C
GC/MS	Xylene, toluene, butadenyl acetylene 1-3, cyclopentadiene methanol, 1-3 butadiene	OK	Different (Butanol)	OK
IR [1]	No imidization Match standard spectrum	OK	OK	OK
TGA	Thermal degradation	672K (752°F)	672K (752°F)	667K (743°F)
	Outgassing Temp.			
	T_1	327K (131°F)	322K (122°F)	322K (122°F)
	T_2	372K (212°F)	377K (221°F)	372K (212°F)
	Weight Loss	8%	8%	15%
TGA [2]	Weight Retention, Percent			
	362K (194°F)	99	99	98
	472K (392°F)	95	94	88
	672K (752°F)	93	91	85
	922K (1202°F)	2	15	1
Dielectrometry	T_1 - 344K (162°F) T_2 - 37K (221°F) Tan a - 22 ± 2	T_1 - 341K (156°F) T_2 - 377K (221°F) Tan a_1 - 21 Tan a_2 - 23	T_1 - 360K (190°F) T_2 - None Tan a_1 - 12 Tan a_2 - None	T_1 - 345K (163°F) T_2 - 384K (234°F) Tan a_1 - 20.5 Tan a_2 - 21.3
GPC [2]	Elution Volume ± 2% of qualification	V_1 - 14.9 V_2 - 17.9	V_1 - 14.9 V_2 - 17.8	V_1 - 15.3 V_2 - 18.2
	Relative Conc. R - 1.0 ± 0.20	Ratio - .013 3	Ratio - .065	Ratio - .025

[1] Due to the fact no standard scan has been selected, no limits were established. However, the IR scans were compared with no significant differences being noted.

[2] Same as 1 above except some differences were noted among the samples.

[3] Ratio of the peak height of the main component (at 7.1 minutes) and a minor component (at 6 minutes) believed to be the component that determines storage life.

TABLE II

SUMMARY OF CHEMICAL DATA - PMR-15 RESIN

Test	Company A	Company B
Resin		
GC/MS	Normal	Normal
TGA	Normal	Normal
Dielectric Constant	1 - 29 @ 372K (212°F)	1 - absent
	2 - 28 @ 387K (239°F)	2 - 29.9 @ 386K (237°F)
IR	Normal	Normal
GPC (elution time - minutes)	T_1 - 12.15	T_1 - 12.1
	T_2 - 13.0	T_2 - 13.0
	T_3 - 14.0	T_3 - 14.0
Graphite Prepreg		
GC/MS	Normal	THF Solvent
TGA	Normal	Normal
Dielectric Constant	= 5 @ 370K (208°F)	= 15 @ 357K (185°F)
IR	Normal	Normal
GPC (elution time - minutes)	T_1 - 12.05	T_1 - 11.90
	T_2 - 12.83	T_2 - 12.90
	T_3 - 14.15	T_3 - 13.76

TABLE III

COMPARISON OF MOLECULAR WEIGHT OF COMPANY A AND COMPANY B SAMPLE USING GPC

Component	1			2			3		
	V		h	V		h	V		h
Company A	76.9	22.8	60.2	96.8	23.0	143.0	131.0	26.8	97.1
Company B	73.9	26.9	47.5	94.9	26.0	158.5	120.4	33.0	99.0
Company A, Aged	74.0	27.9	61.7	95.2	27.1	149.2	129.7	29.1	88.5
A Company A	686.3			1667.5			1302.4		
A Company B	637.5			2061.8			1633.5		
R_2 Company A	0.41			1.00			0.78		
R_2 Company B	0.31			1.00			0.79		
A Company A, Aged	859.3			2021.7			1289.0		
R_2 Company A, Aged	0.43			1.00			0.68		

V = Elution volume in milliliters

= Base of peak in millimeters of an extrapolated triangle

h = Height of peak in millimeters

A = Area of peak on extrapolated triangle (i.e., 1/2 h)

R = Comparative ratio of components by setting indicated component (as identified by subscript) equal to 1.0.

TABLE IV

COMPARISON OF MOLECULAR WEIGHT OF COMPANY A AND COMPANY B SAMPLES USING GPC (REVERSE PHASE)

Component	1	2	3	4	5	6
V - Company A	123	127.5	146	156.5	245	259
V - Company B	124.5	129.0	145	155.5	243.5	256.5
- Company A	11.5	11.2	11.8	9.2	13.5	14.1
- Company B	14	21	22.1	14.5	15.5	16.5
h - Company A	106.1	91.8	31.0	16.8	37.9	97.5
h - Company B	154.1	131	28	16	56	112.5
A - Company A	610.1	514.1	182.9	77.3	255.8	687.4
A - Company B	1078.7	1375.5	309.4	116.0	434	928.1
R_1 - Company A	1.00	0.84	0.30	0.13	0.42	1.13
R_1 - Company B	1.00	1.28	0.29	0.11	0.40	0.86

Note: In the above table,

V = Elution volume in milliliters

= Base of the peak in millimeters of an extrapolated triangle

h = Height of peak in millimeters

A = Area of peak based on 1/2 h of extrapolated triangle

R = Comparative ratio of components by setting the indicated component (as identified by its subscript) equal to 1.00.

TABLE V

SUMMARY OF TEST DATA PMR-15 RESIN

Chemical Test	Lot 2W4154	Lot 2W4168	Lot 2W4169	Standard (2W-4083)	Points of Comparison
GC/MS	Trace amount of aniline present	ok	Trace amount of acetone present	ok	Xylene, Toluene, Butadenyl Acetylene, 1-3 Cyclopentadiene, Methanol, 1-3 Butadiene
IR	Very slight imidization	No imidization	Very slight imidization	No imidization	No imidization; match standard spectrum
TGA					
Outgassing					
T_1	318K (115°F)	318K (115°F)	313K (106°F)	328K (133°F)	323K (124°F)
T_2	363K (196°F)	363K (196°F)	363K (196°F)	373K (214°F)	373K (214°F)
Weight Loss	7%	10%	9%	8%	14%
Weight Retention					
@ 362K (194°F)	98%	98%	98%	99%	Open
@ 472K (392°F)	94%	91%	93%	95%	
@ 672K (752°F)	92%	88%	90%	93%	
@ 922K (1202°F)	52%	4%	32%	2%	
Dielectric Constant	14.1 @ 357K	19.1 @ 364K (198°F)	1	21 @ 342K (158°F)	22 ± 2 T_1 - 345K (163°F)
		19.1 @ 368K (205°F)		23 @ 378K (223°F)	22 ± 2 T_2 - 378K (223°F)
GPC	2	3	1	---	Elution Volume ± 2% of Qualification Relative Concentration.

---

1 Material varied over three rolls. See Table VI for data.

2 In comparison with standard run this sample has a small amount of a high molecular weight component and two low molecular weight components.

3 In comparison with standard run this sample has small amounts of two low molecular weight components.

TABLE VI
COMPARISON OF GPC AND DIELECTRIC DATA FROM COMPANY A MATERIAL

SAMPLE	PEAK 1			PEAK 2			PEAK 3			DIELECTRIC
(Batch No. and Sample)	v		h	v		h	v		h	(TAN)
2W 4083 (Standard)	338.4	32.5	46.8	363.6	25.6	136.2	401.0	33.6	74.6	21 @ 342K (158^{o}F) 23 @ 378K (223^{o}F)
2W 4169 Roll 1 (-1,-3) 1	337.2	69	60.7	363.6	41.9	136.2	392.7	50.0	155.9	Roll 1 Sample 1 0.7 @ 372K (212^{o}F) Roll 1 Sample 3 5.7 @ 352K (176^{o}F)
2W 4169 Roll 1 (-2)	338.8	54.5	49.5	364.7	36.0	136.2	398.8	41.5	171.3	9.4 @ 342K (158^{o}F)
2W 4168	337.2	75	46.2	356.4	38.5	136.2	397.7	50.5	123.2	1.91 @ 364K (198^{o}F)
2W 4169 Roll 2	337.9	49	58.5	363.6	36.2	136.2	398.8	40.8	176.5	4.6 @ 343K (160^{o}F)
2W 4170 Roll 2,5 1	338.3	30.0	6.14	364.7	26.0	136.2	399.3	29.1	160.9	Roll 5 21.7@384K (234^{o}F) 21.5@373K (214^{o}F) Roll 2 24.0@373K (214^{o}F) 23.4@363K (196^{o}F)

NOTE: All measurements are in millimeters
All peak heights are normalized to peak 2 of standard.

Higher lot number samples have shown an extensive increase quantitatively in peak number 3. The shift in molecular weight distribution represented by this change will have a drastic effect on processing properties.

1 Represents two separate samples yielding the same curves. Samples taken at various positions in roll.

TABLE VII

CHEMICAL CHARACTERISTICS OF NASA MATERIAL LOT 2W-4170
GPC DATA (RETENTION TIMES, MINUTES)

Roll Number							
-1	-1	-2	-3	-4	-5	Avg.	
6.84	6.80	6.86	6.85	6.85	6.76	6.83	0.04
7.24	7.20	7.25	7.23	7.24	7.24	7.23	0.02
7.83	7.78	7.83	7.82	7.83	7.83	7.82	0.02
8.69	8.63	8.68	8.66	8.68	8.68	8.67	0.02
9.35	9.29	9.34	9.33	9.34	9.35	9.33	0.02
9.82	9.786	9.81	9.80	9.82	9.82	9.81	0.02
10.92	10.86	10.91	10.90	10.91	10.92	10.90	0.02
11.71	11.66	11.69	11.69	11.70	11.71	11.69	0.02
12.47	12.41	12.45	12.44	12.45	12.48	12.45	0.02
S	12.90	12.95	12.94	12.96	S	12.94	0.03
13.95	13.88	13.91	13.90	13.91	13.93	13.91	0.02
14.63	14.59	14.62	14.61	14.64	14.60	14.62	0.02
15.09	15.05	15.15	15.11	15.13	15.13	15.11	0.03
N	N	N	N	N	16.30	---	--
16.80	16.76	16.79	16.78	16.79	16.80	16.79	0.02
18.19	18.16	18.19	18.18	18.20	18.20	18.19	0.02
20.19	20.16	20.18	20.19	20.18	20.19	20.18	0.01
20.93	20.92	20.89	20.89	20.89	20.87	20.90	0.02
S	S	S	S	S	22.58	---	--

S - Slight indication of band but below computer threshold.

N - Nothing there

TABLE VIII

CHEMICAL CHARACTERISTICS OF NASA MATERIAL LOT 2W-4170
GPC DATA (AREA UNDER PEAK, AREA PERCENT)

Roll Number								
	-1	-1	-2	-3	-4	-5	Avg.	
6.83	0.50	0.45	0.45	0.43	0.43	1.23*	0.58	0.32
7.23	5.86	5.76	5.49	5.42	5.53	5.75	5.64	0.18
7.82	16.23	16.22	15.26	15.18	15.50	13.76*	15.36	0.91
8.67	14.95	15.02	14.22	14.47	14.46	11.64*	14.13	1.26
9.33	8.35	8.34	8.38	8.86	8.46	9.69*	8.68	0.53
9.81	12.83	13.167	12.65	13.66	12.33	10.65*	12.55	1.03
10.90	10.92	10.90	10.97	11.12	11.08	12.71*	11.29	0.70
11.19	4.97	5.00	4.55	4.71	4.50	3.90*	4.61	0.40
12.45	2.79	3.53	2.56	2.52	2.47	2.62	2.75	0.40
12.94	0.42	-	0.51	0.46	0.51	-	0.48	0.04
13.91	0.57	0.51	0.32	0.29	0.28	0.29	0.38	0.13
14.62	0.67	0.64	0.70	0.67	0.67	0.39*	0.62	0.12
15.11	0.72	0.68	1.16	1.20	1.32	0.96	1.01	0.26
16.30	-	-	-	-	-	0.75	-	-
16.79	1.97	1.87	2.09	1.48	1.53	1.92	1.81	0.25
18.19	1.79	6.59	9.65	9.267	9.94	10.39*	8.77	1.65
20.18	2.82	2.76	1.87	1.15	1.51	2.16	2.11	0.58
20.90	8.64	8.57	9.18	8.78	9.47	10.45*	9.18	0.71
22.58			-	-	-	0.74	-	-

*Value falls outside standard deviation.

TABLE IX

COMPARISON GPC DATA LOT 2W-4169, 2W-4170, 2W-4215
(AREA UNDER PEAK, % AREA)

	LOT		
T (MINUTES)	2W-4169	2W-4170	2W-4215
6.83	**	0.58	0.29*
7.23	5.30	5.64	5.60
7.82	17.77**	15.36	17.44
8.67	20.78**	14.13	11.06*
			11.30*
9.33	3.54**	8.68	3.33
9.81	13.61	12.55	12.80
10.90	8.63**	11.29	12.15
11.69	3.75	4.61	*
12.45	0.42**	2.75	0.23*
12.94	0.28	0.48	*
13.91	1.12**	0.38	0.68
14.62	**	0.62	0.56
15.11	2.78	1.01	1.41
16.30	**	.75	
16.79	0.76	1.81	0.46*
			0.30*
18.19	0.86**	8.77	6.44
	2.82**		0.93*
20.18	**	2.11	0.73*
20.90	13.57**	9.18	14.90
22.58	**	.74	*

* Indicates difference between 2W 4215 and 2W 4170

** Indicates difference between 2W 4169 and 2W 4170

TABLE X

CHEMICAL CHARACTERISTICS OF LOT 2W 4215
GPC DATA (AREA UNDER PEAK, % AREA)

	ROLL						
T(MINUTES)	-1	-2	-3	-4	-5	AVERAGE	
6.83			0.30		0.28	0.29	
7.23	5.33	5.46	5.83	5.52	5.85	5.60	0.23
7.82	17.18	17.43	17.55	17.38	17.64	17.44	0.18
8.67	11.18		11.03	11.04	10.99	11.06	0.08
	11.93	11.29	11.08	11.25	10.96	11.30	0.38
9.33	2.90	3.47	3.35	3.58	3.33	3.33	0.26
9.81	12.95	13.02	12.52	13.29	12.21	12.80	0.43
10.90	11.93	12.31	11.92	12.26	12.32	12.15	0.20
11.69							
12.45	0.23	0.22	0.24	0.21	0.23	0.23	0.01
12.94							
13.91	0.87				0.48	0.68	
14.62	0.48	0.54	0.59	0.54	0.67	0.56	0.07
15.11	1.60	1.49	1.36	1.31	1.28	1.41	0.13
16.30							
16.79	0.51	0.51	0.45	0.47	0.37	0.46	0.06
	0.35	0.33	0.28	0.28	0.24	0.30	0.04
18.19	6.29	6.31	6.49	6.45	6.64	6.44	0.14
	0.94	0.83	0.95	0.81	1.12	0.93	0.12
20.18	0.79	0.77	0.74	0.71	0.66	0.73	0.05
20.90	14.53	14.96	15.34	14.98	14.74	14.90	0.30

TABLE XI

SUMMARY OF HPLC PROPERTIES

Elution Time[1]	Lot (Elution Volume (% Area))											
	2W4169*	2W4170*	2W4215*	2W4240	2W4251	2W4280	2W4282	2W4301	2W4317	2W4364	2W4388[2]	2W4444[2]
6.83	-	0.58	0.29	-	-							
7.23	5.30	5.64	5.60	4.91	7.87	5.59	6.35	10.10	8.60			
7.82	17.77	15.36	17.44	15.67	23.02	24.52	24.40	10.20	8.80			
								22.00	17.80			
8.67	20.78	14.13	11.06	14.41	38.67	43.08	38.10	38.40	32.00			
			11.30									
9.33	3.54	8.68	3.33	12.59								
9.81	13.61	12.55	12.80	16.32								9.67
10.90	8.63	11.29	12.15	9.71	16.78	16.96	17.57	19.21	22.90		9.20	11.36
11.69	3.75	2.75	-		1.01	0.89	1.60			9.30		35.76
12.45	0.42	0.48	0.23		1.57	0.85	1.35			14.38	33.35	
12.94	0.28	0.38	-		0.20					36.07	7.25	31.96
13.91	1.12	0.62	0.68		1.57							
14.62	-	1.01	0.56		-					27.63	22.97	9.29
15.11	2.78	0.75	1.41		0.20							
16.30	-	1.81	0.46		0.43						11.18	
16.79	0.76	-	0.30		0.19					9.43		
18.19	0.86	8.77	6.44	2.81	3.98	3.39	3.92	0.40	0.40			1.96
	2.82		0.93		2.42	1.29	3.90				16.04	
20.18	-	2.11	0.73		-	0.72				1.98		
20.90	13.57	9.18	14.90	5.60	3.87	2.72	2.80	9.60	9.60	1.22		
22.58	-	0.74	-		-							

[1] Normalized for comparative purposes

[2] Materials received on Task J, Material Variability Program

* HTS-2 fibers, remaining fiber Celion 6000 NR15082 sized

TABLE XII

SUMMARY OF MECHANICAL AND PHYSICAL PROPERTIES OF PMR-15 GRAPHITE TAPE SAMPLES

	Manufacturer							
	Company A				Company B		Company C	
Prepreg Physical Properties								
Resin Content, % W/W		38.4[1]	37.7		40.6[1]	42.3	59.8	
Volatile Content, % W/W		15.0	10.6		11.9	11.7	16.7	
Flow Percent		N.D.	8.7		N.D.	6.6	N.D.	
Composite Mechanical Properties								
Flexural								
Ultimate, MPa (ksi)								
R.T.	1311	(190)[2]	1283	(186)	1076	(156)	1201	(174)
589°K (600°F)	725	(105)	80.7	(117)	--		731	(106)
Modulus, GPa (Msi)								
R.T.	114	(16.5)	136	(19.7)	119	(17.2)		
589°K (600°F)	101	(14.6)	120	(17.4)	--			
Short Beam Shear								
Ultimate, MPa (ksi)								
R.T.	81	(11.7)	87	(12.6)	--		77	(11.2)
589°K (600°F)	32	(4.6)	45	(6.5)			40	(5.8)
Composite Physical Properties								
Resin Content, % W/W			41.0		41.2		56.9	
Specific Gravity, g/cm^3			1.53		1.49		1.47	
Void Volume, % V/V			2.6		5.3		2.3	
Fiber Volume, % V/V			51.3		50.0		36.0	

[1] Data furnished by supplier

[2] Specimens aged at 589K (600°F) for 200 hours.
Weight Loss: Flexural specimens, 3.9%; ILS specimens, 6.5%

NOTE: Companies A and B used HTS fiber; Company C used AS fiber.

TABLE XIII

COMPARISON OF COMPANY A PREPREG AFTER STORAGE AT 253K (0°F)

	Control		Aged 50 Days	
Composite Mechanical Properties				
Flexural				
Ultimate, MPa (ksi)				
R.T.	1311	(190)	1481	(215)
589°K (600°F)	725	(105)	737	(107)
Modulus, GPa (Msi)				
R.T.	114	(16.5)	136	(19.8)
589°K (600°F)	101	(14.6)	99	(14.3)
Short Beam Shear				
Ultimate, MPa (ksi)				
R.T.	81	(11.7)	114	(16.6)
600°F	32	(4.6)	41	(5.9)
Composite Physical Properties				
Resin Content, % W/W	41		36.2	
Specific Gravity, g/cm^3	1.53		1.58	
Void Volume, % V/V 1	2.6		1	
Fiber Volume, % V/V 1	51		57	

1 Assume: Specific gravity of fiber 1.76 g/cm^3

Specific gravity of resin 1.30 g/cm^3

TABLE XIV

SUMMARY OF MECHANICAL AND PHYSICAL PROPERTIES OF COMPANY B'S PMR-15 GRAPHITE COMPOSITES [1]

	1	2	3	4	6	IA
Prepreg Physical Properties						
Resin Content, % W/W	32.5	31.8	32.5	32.5	31.8	32.5
Volatile Content, % W/W	12.9	9.4	12.9	12.9	9.4	12.9
Composite Mechanical Properties						
Flexural						
Ultimate, kPa (ksi)						
RT	799 (116)	785 (114)	965 (140)	1633 (237)	606 (88)	--
589K (600°F)	--	--	--	1047 (152)	407 (59)	--
Modulus, GPa (Msi)						
RT	120 (17.4)	132 (19.1)	150 (21.7)	158 (23.0)	130 (18.8)	--
589K (600°F)	--	--	--	164 (23.8)	134 (19.4)	--
Short Beam Shear						
Ultimate, kPa (ksi)						
RT	52 (7.6)	51 (7.4)	59 (8.5)	108 (15.7)	43 (6.3)	--
589K (600°F)	--	--	--	34 (4.9)	30 (4.4)	--
Tensile 0°						
Ultimate, kPa (ksi) RT	80 (11.6) [2]	--	--	--	--	1357 (197)
NDI "C" Scan	Poor	Poor	Poor	Excellent	Poor	Excellent
Composite Physical Properties						
Resin Content, % Weight	30.8	27.5	23.0	28.2	23.7	--
Specific Gravity, g/cm^3	1.50	1.52	1.57	1.54	1.53	--
Void Volume, % [3]	7.1	6.7	4.8	5.2 [3]	7.0	--
Fiber Volume, %	59.0	63.0	69.0	63.0	66.3	--

---

[1] See Appendix C for processing cycles. All panels autoclave except panel 4

[2] Tensile properties at 90° to fiber direction

[3] These values appear to correlate with NDI test results except in panel 4 where NDI indicates an essentially void free composite. Most probable cause is the variability in fiber density.

TABLE XV

SUMMARY OF MECHANICAL AND PHYSICAL PROPERTIES OF COMPANY A PMR-15 GRAPHITE COMPOSITE[1]

	1	3	4	7	1A
Prepreg Physical Properties					
Resin Content, W/W	33.9	34.3	34.3	33.9	33.9
Volatile Content, W/W	10.1	10.1	10.1	10.1	10.1
Composite Mechanical Properties					
Flexural					
Ultimate, MPa (ksi)					
RT	1074 (156)	1323 (192)	1144 (166)	1709 (248)	--
589K (600°F)		923 (134)	834 (121)	951 (138)	--
Modulus, GPa (Msi)					
RT	132 (19.3)	132 (19.2)	126 (18.3)	153 (22.2)	--
589K (600°F)		132 (19.1)	125 (18.2)	138 (20.1)	--
Short Beam Shear					
Ultimate, kPa (ksi) RT	62 (9.0)	74 (10.7)	63 (9.2)	117 (17.0)	--
589K (600°F)		40 (5.8)	43 (6.2)	35 (5.1)	--
Tensile 0°					
Ultimate, MPa (ksi)	--	--	--	--	1185 (172)
NDI	marginal	good	marginal	excellent	excellent
Composite Physical Properties					
Resin Content, % Weight	33.6	28.0	29.6	33.4	--
Specific Gravity, g/cm^3	1.48	1.55	1.52	1.54	--
Void Volume, %	7.6	4.7	6.1	3.9	--
Fiber Volume, %	55.8	63.0	60.8	58.3	--

---

[1] See Appendix C for processing cycles. All panels autoclave except Panel 7

[2] These values appear to be higher than normal based on NDI tests and are probably caused by variability of fiber density.

TABLE XXVI

HONEYCOMB PANEL PROCESS DEVELOPMENT [1]

Core	Bond	Skin Thickness	Testing Flatwise Tension [2] Ambient	589K (600°F)	Edgewise Compression Ambient
HRH-327	Secondary	0.030	3	3	3
	Secondary	0.060	3	3	3
	Secondary	0.125	3	3	3
	Cocure	0.030	3	3	3
	Cocure	0.060	3	3	3
	Cocure	0.125	3	3	3
Cres	Secondary	0.060	3	3	3
Titanium	Secondary	0.060	3	3	3

[1] Celion 6000/PMR-15 Lot 2W 4251

[2] Number of Specimens to be tested

TABLE XVII

COMPARISON DATA OBTAINED FROM PREPREG LOT 2W 4169

PROPERTIES	SAMPLE 1	SAMPLE 2
Prepreg Physicals		
Resin Content %	36.8	37.3
Volatile Content %	10.6	11.5
Gel Time (Seconds)	32	40
Prepreg Characteristics		
Dielectric	1	1
GPC	1	1
Composite Mechanical Properties		
Flexural Stress MPa (ksi)		
295K (RT)	1337 (194)	940 (136) [2]
589K (600°F)	717 (104)	640 (93) [2]
Flexural Modulus GPa (Msi)		
295K (RT)	115 (16.7)	106 (15.4) [2]
589K (600°F)	110 (15.9)	105 (15.3) [2]
Short Beam Shear MPa (ksi)		
295K (RT)	75 (10.9)	72 (10.5)
589K (600°F)	39 (5.7)	31 (4.5)
Resin Content % W/W	34.2	34
Specific Gravity g/cm^3	1.49	1.50
Void Volume % V	1.7	1.1
Fiber Volume % V	59.1	59.6
"C" Scan	Excellent	Excellent

[1] See Table VI

[2] Shear and/or Compression Failure

TABLE XVIII

SUMMARY OF DATA NASA MATERIAL LOT 2W 4170

PROPERTIES	ROLL 1	2	3	4	5
Prepreg Chemical Characteristics					
Dielectric					
GPC	1	1	1	1	1
Composite Mechanical Properties					
Flexural Stress MPa (ksi) 2					
295°K (RT)	875(127)	896(130)	923(134)	985(143)	NT
589°K (600°F)	593(86)	496(72)	572(83)	599(87)	NT
Flexural Mod GPa (Msi)					
295°K (RT)	54(15.6)	53(14.4)	53(15.2)	53(14.2)	NT
589°K (600°F)	102(14.8)	100(14.5)	89(12.9)	103(14.9)	NT
Short Beam Shear MPa (ksi)					
295°K (RT)	53(7.7)	63(9.1)	67(9.7)	65(9.4)	NT
589°K (600°F)	32(4.7)	32(4.7)	32(4.7)	30(4.3)	NT
"C" Scan	Excellent	Excellent	Excellent	Excellent	Very Poor
Resin Content % W/W	35.8	36.4	37.2	37.1	-
Specific Gravity g/cm^3	1.49	1.50	1.48	1.48	-
Void Volume % V	1.3	0.7	1.7	1.7	-
Fiber Volume % V	57.3	57.5	56.0	56.0	-

NT - No Test

1 - See Table VI

2 - RT Flexure failed in Shear and/or Compression
589K (600°F) Flexure failed in Compression

Note: Low strength attributed to HTS-2 fiber which resulted in changing program fiber to Celion 6000.

TABLE XIX

SUMMARY OF DATA ISOTHERMAL AGING GRAPHITE YARN

Time, Hrs.	Percent by Weight Loss HMS	HTS	Modmor II	Celion 3000	Celion 6000
72	0.22	0.74	0.28	1.79	2.10
120	0.26	1.61	0.38	4.38	4.01
166	0.28	2.22	0.46	6.95	6.27
238	0.35	-	0.70	17.70	15.10
334	0.39	5.17	0.79	21.5	18.4
408	0.43	7.26	0.95	29.67	25.5
499	0.48	-	1.14	38.1	33.5
596	0.67	17.2	1.34	47.4	42.4
764	0.63	-	1.68	65.5	58.6
1057	0.77	39.1	2.12	86.2	78.7

	HTS (R)*	Celion 3000 (R*)	Celion 6000 (R)*
97	0.67	3.06	2.92
172	1.32	9.16	8.67
340	2.20	23.5	20.6
628	4.41	40.3	38.1

* Sample repeated because of abnormally high weight loss

TABLE XX

SUMMARY OF ISOTHERMAL AGING DATA OF GRAPHITE YARN

		Weight Loss by Percent					
		Hours					
Manufacturer	Graphite Type	73	233	281	401	473	593
Celanese	Celion 3000 [1] Package 41	1.24	3.03	3.73	5.79	7.58	10.22
Celanese	Celion 3000 [1] Package 208 (U.S.P.)	1.16	2.71	3.25	5.12	6.65	9.13
Hercules	HTS-2	3.78	10.57	12.66	18.22	21.44	25.79
Union Carbide	T-300 (H.P.) [2]	2.42	7.68	10.49	19.50	24.91	32.32
Morganite	Modmor II	0.22	0.36	0.40	0.42	0.49	0.52

[1] Contains a coating of NR150A2 polyimide resin approximately 2% by weight

[2] Contains a high temperature epoxy sizing approximately 1.5% by weight

TABLE XXA

SUMMARY OF THE ISOTHERMAL AGING GRAPHITE YARN

	Time, Hours					
Fiber	72	168	600	672	840	1152
U.S. Polymeric HTS-2, Lot 76-8	0.07 [1]	0.64	0.68	1.39	9.32	54.4
Ferro HTS-2, Lot 76-8	0.07	1.78	1.83	10.7	35.2	65.6

[1] Weight loss in percent

TABLE XXI

SUMMARY DATA TEST METHOD STUDY

	SPECIMEN THICKNESS			
	2.0mm (.080 inch) Bag Side Compression		1.1mm (.045) 2	2.0mm (.080 inches) Bag Side Tension
MECHANICAL PROPERTIES	1	2		
FLEXURAL PROPERTIES				
Ultimate MPa (ksi)				
Ambient	1480(215)	1488(216)	1778(258)	1480(215)
589K (600°F)	590(85)	847(123)	1068(155)	570(83)
Modulus GPa (Msi)				
Ambient	140(20.3)	108(15.7)	147(21.3)	136(19.8)
589K (600°F)	113(16.4)	--	--	106(15.4)
SHORT BEAM SHEAR				
Ultimate MPa (ksi)				
Ambient	92.3(13.4)	104(15.2)	115(16.7)	96.5(14.0)
589K (600°F)	37.9(5.5)	44.8(6.5)	39.3(5.7)	33.1(4.8)
"C" SCAN	GOOD	GOOD	GOOD	GOOD
PHYSICAL PROPERTIES				
Resin Content % W/W	35.4	29.7	28.9	35.4
Specific Gravity g/cm^3	1.57	1.59	1.56	1.57
Void Volume % V	1	1	2.7	1
Fiber Volume % V	57.6	61.7	62.9	57.6

1 Used Lot 2W 4251, 589K (600°F) values low due to unknown causes.

2 Used Lot 2W 4282, problem with 589K (600°F) values corrected by additional postcuring of the composites.

TABLE XXII

SUMMARY OF TENSILE PROPERTIES 0.76mm (.030 in.) COMPOSITES

	Composite Orientation		
Properties	(0^{o})	$(\pm 45^{o})_s$	$(0^{o},90^{o})_s$
Mechanical Properties			
Tensile Ult MPa (ksi)	1213(176)	475 (69)	833(121)
Tensile Modulus GPa (Msi)	108(15.7)	45(6.5)	94(6.8)
Physical Properties			
Resin Content % W/W	37.9	36.4	37.8
Specific Gravity g/cm^3	1.54	1.54	1.54
Void Volume % V	1	1.2	1
Fiber Volume % V	54	56	54

TABLE XXIII

SUMMARY OF 2.03mm (.080 in.) FLAT LAMINATES

Properties	Composite Orientation		
	(0^{o})	$(\pm45^{o})_s$	$(0^{o},90^{o})_s$
Mechanical Properties			
Flexural Ultimate MPa (ksi)			
Ambient	1336(194)	276(40)	620(90)
589K (600°F)	717(104)	--	--
Flexural Modulus GPa (Msi)			
Ambient	96(13.9)	19(2.8)	19(2.7)
589K (600°F)	118(17.1)	--	--
Short Beam Shear MPa (ksi)			
Ambient	96(14.0)	41(6.0)	51(7.4)
589K (600°F)	48(7.0)	--	--
Tensile Ultimate MPa (ksi)			
Ambient	1137(165)	551(80)	723(105)
589K (600°F)	758 (110)	40(58)	517(75)
Tensile Modulus GPa (Msi)			
Ambient	131(19.0)	34(5.0)	38(5.5)
589K (600°F)	96(14.0)	34(5.0)	40(5.8)
Physical Properties			
Resin Content % W/W	37.0	36.0	36.5
Specific Gravity g/cm^3	1.48	1.54	1.53
Void Volume % V	2.0	1.4	1.8
Fiber Volume % V	53	56	55

TABLE XXIV

SUMMARY DATA FROM POSTCURE STUDY LOT 2W 4240

Panel No. Postcure Temp/ Postcure Time (Hrs)	A [2] 589K(600°F)/8	B [2] 589K(600°F/16	C [2] 604K(625°F)/4	D [2] 604K(625°F)/8	E [3] 589K(600°F)/8	F [3] 589K(600°F)/16	G [3] 604K(625°F)/4	H [3] 604K(625°F)/8
Mechanical Properties								
Flexural								
Ultimate MPa (KSI)								
Ambient	1309 (190)	1178 (171)	1178 (171)	1220 (177)	1212 (176)	1199 (174)	1220 (177)	1247 (181)
589K (600°F)	572 (83)	593 (86)	565 (82)	579 (84)	613 (89)	627 (91)	606 (88)	606 (88)
[1] 589K (600°F)	661 (96)	579 (84)	668 (97)	634 (92)	703 (102)	627 (91)	627 (91)	689 (100)
Modulus GPa (MSI)								
Ambient	116 (16.8)	120 (17.4)	123 (17.8)	124 (18.0)	121 (17.5)	125 (18.1)	123 (17.8)	125 (18.2)
589K (600°F)	112 (16.2)	115 (16.7)	107 (15.5)	107 (15.5)	114 (16.5)	120 (17.4)	110 (15.9)	114 (16.6)
[1] 589K (600°F)	113 (16.4)	106 (15.4)	110 (16.1)	110 (15.9)	116 (16.9)	127 (18.4)	119 (17.3)	116 (16.8)
Short Beam Shear								
Ultimate MPa (KSI)								
Ambient	74 (10.8)	75 (10.9)	76 (11.1)	76 (11.1)	79 (11.4)	81 (11.7)	79 (11.5)	78 (11.3)
589K (600°F)	34 (4.9)	37 (5.4)	30 (4.4)	34 (5.0)	34 (5.0)	36 (5.2)	34 (5.0)	37 (5.3)
[1] 589K (600°F)	40 (5.8)	40 (5.8)	41 (5.9)	41 (5.9)	41 (6.0)	42 (6.1)	42 (6.1)	41 (6.0)
Weight loss of flexural specimens/SBS specimens	1.6/2.4	1.3/1.9	1.4/2.0	1.4/1.9	1.3/1.8	1.2/1.7	1.3/1.9	1.1/1.7
Physical Properties								
Resin Content %W	30.4	29.8	30.4	29.2	31.4	29.8	30.4	28.8
Specific Gravity g/cc	1.51	1.51	1.51	1.49	1.50	1.52	1.52	1.52
Void Volume %V	5.0	5.2	5.0	6.6	5.3	4.5	4.4	4.8
Fiber Volume %V	59.7	60.2	59.7	60.0	58.0	60.6	60.1	61.5

[1] Aged 125 hours at 589K (600°F)

[2] Cure Temperature 589K (600°F)

[3] Cure Temperature 604K (625°F)

NOTE: Nominal panel thicknesses - 3.2mm (0.125 inch)

TABLE XXV

SUMMARY DATA TASK B STRUCTURAL ELEMENTS

	HAT SECTIONS			MULTIPLE HAT			I BEAM		
PROPERTY DATA	#1		#2	OPEN MOLD	CLOSED MOLD		BONDED		COCURED
MECHANICAL PROPERTIES									
Crippling Load K_g (LBS) Ambient	54,450(24,250) 1		51,150(23,250) 1	20,688 (45,510)	47,302(21,500) 1		41,250(18,750) 2		38,500(17,500) 1
Compressive Ultimate MPa (ksi) Ambient	174(25,200)		166(24,100)	140(20,300)	(145)(21,100)		131(19,100)		102(14,[illegible]
Compressive Modulus GPa (Msi)	1.9(0.270)		1.7(0.249)	--	11.6(0.231)		2.6(0.371)		1.9(0.280)
Failure Mode	Interlaminar Shear Facing		Interlaminar Shear Facing	Interlaminar Shear Facing	Interlaminar Shear Facing		Middle Buckling		Middle Buckling
"C" Scan	Good Hat		Good Hat		N/A Hat Good Facing		Good Web Good Cap		Poor Web N/A Cap
COUPON PROPERTIES									
Flexural									
Ultimate MPa (ksi)	300(43.6)		--	--	668(97)		174(25.2)		125(18.2)
Modulus GPa (Msi)	21(3.0)		--	--	20(2.9)		12(1.7)		14(2.0)
Short Beam Shear MPa	43(6.3)		--	--	52(7.6)		30(4.4)		19(2.7)
	HAT	FLAT PANEL			FLAT PANEL	HAT	FLANGE	WEB	
Resin Content %W	34.2	34.2	34.0	35.0	34.9	35.8	46.2	45.1	35.6
Specific Gravity g/cm^3	1.51	1.55	1.55	1.54	1.55	1.53	1.53	1.54	1.41
Void Volume %V	3.8	1.1	1.3	1.7	1.1	2.2	3		10.0
Fiber Volume %V	56.5	57.9	58.1	56.9	57.3	55.8	N/A		51.6

1 Specimens failed in interlaminar shear within the flange and/or flat panel portion of the specimen.

2 Specimens failed in buckling in center portion of the specimen.

3 Values not calculated because resin content included adhesive scrim and filler.

NOTE: Hat Sections Web 8 plies $(\pm 45^{0})_S$ Skins 12 plies $(0^{0},90^{0})_S$
I Beams Web 12 plies $(0^{0}90^{0})_S$ Cap 12 plies $(0^{0},90^{0})_S$

TABLE XXVI

HONEYCOMB PANEL PROCESS DEVELOPMENT 1

Core	Bond	Skin Thickness	Testing Flatwise Tension 2 Ambient	Testing Flatwise Tension 2 589K (600°F)	Edgewise Compression Ambient
HRH-327	Secondary	0.030	3	3	3
	Secondary	0.060	3	3	3
	Secondary	0.125	3	3	3
	Cocure	0.030	3	3	3
	Cocure	0.060	3	3	3
	Cocure	0.125	3	3	3
Cres	Secondary	0.060	3	3	3
Titanium	Secondary	0.060	3	3	3

1 Celion 6000/PMR-15 Lot 2W 4251

2 Number of Specimens to be tested

TABLE XXVII

ADHESIVE AGING STUDY

	SYSTEM		
	BM34	LARC-13	A5F
Lap Shear Stress (MPa) (psi)			
RT	(15.2)(2200) 1	(13.8)(2010) 1	(11.9)(1730) 1
589K (600°F)	(7.4) (1080) 1	(13.7)(1985) 1	(12.4)(1805) 1
200 Hour @ 589K (600°F)			
RT	(7.0) (1010) 3	(7.2) (1040) 2	(9.6) (1395) 1
589K (600°F)	(5.9) (860) 3	(7.2) (1040) 2	(8.3) (1205) 1
500 Hour @ 589K (600°9F)			
RT	1	1	1
589K (600°F)			

1 Failure in the HTS/PMR-15 Composite

2 Partial Failure in HTS/PMR-15 Composite

3 Failure in adhesive

TABLE XXVIII

SUMMARY DATA TASK B PMR-15 GRAPHITE/POLYIMIDE GLASS HONEYCOMB SANDWICH PANELS

			Property			
Sandwich Construction			Flatwise Tension		Edgewise Compression	
mm (inches) Skin Thickness	Bond	Core	Ambient MPa (psi) [1]	589K (600°F) MPa (psi)	Ambient MPa (ksi)	Modulus GPa (msi)
(.030)	Secondary	HRH 327	3.31(480)	2.75 (400)	1158(168)	42.7(6.2)
(.060)	Secondary		2.62(380)	2.61 (380)	1288(187) [2]	49.6(7.2)
(.125)	Secondary		3.24(470)	-- --	[5]	--
(.030)	Cocure		3.38(490)	2.31 (335)	758(110)	28.9(4.2)
(.060)	Cocure		3.17(460)	1.89 (275)	1330(193) [1]	33.8(4.9)
(.125)	Cocure [3]		3.65(530)	-- --	951(138) [2]	--
(.060)	Secondary	Cres	2.69(390) [2]	1.92 (279)	903(131) [2]	37.9(5.5)
(.060)	Secondary	Titanium	2.96(430) [2]	1.72 (250)	1350(196) [2]	42.0(6.1)

[1] All failures of HRH 327 sandwiches were in the core.

[2] All failures of sandwiches were between core and facing.

[3] Sandwich made from Lot 2W 4239, all other panels made from Lot 2W 4251.

[4] Failure in facing.

[5] Testing machine not capable of breaking specimens (30,000 pound capability).

TABLE XXIX

SUMMARY PROPERTIES OF HTS-2/PMR-15 CHOPPED FIBER MOLDING COMPOUND

Properties	Lot Wm 3582-1		Lot Wm 3582-2	
Molding Compound				
Resin Content %	32.4	32.4	62.2	62.2
Volatile Content %	6.3	6.3	6.0	6.0
Gel Time (Seconds)	60	60	60	60
Mechanical Properties				
Flexural Stress Ult. @				
Ambient MPa (ksi)	50.3(7.3)	68.9(10.0)	127.5(18.5)	145.4(21.1)
Flexural Modulus @				
Ambient GPa (Msi)	1.3(.19)	2.2(.32)	1.6(0.23)	1.9(0.27)
Tensile Strength @				
Ambient MPa (ksi)	17.9(2.6)	27.6(4.0)	54.4(7.9)	59.3(8.6)
Tensile Modulus @				
Ambient GPa (Msi)	1.4(.21)	--	--	12.1(1.75)
Tensile Strain @				
Ambient mm/mm X 10^{-6} (in/in X 10^{-6})	22,900(900)	--	15,900 (625)	41,300 (1625)
Resin Content %W	30.6	36.6	60.2	60.2
Specific Gravity g/cm^3	1.41	1.44	1.42	1.41
Void Volume %V	7.9	4.5	--	--
Fiber Volume %V	59	55	34	34

TABLE XXX

SUMMARY PROPERTIES OF CELION 6000/PMR-15 CHOPPED FIBER MOLDING COMPOUND

Properties	Lot WM 3994	Lot WM 3995
Molding Compound		
Resin Content %	59.8	42
Volatile Content %	6.3	6.1
Gel Time (Seconds)	70	65
Mechanical Properties		
Flexural Strength Ult.		
Ambient MPa (ksi)	218(31.7)	119(17.2)
Tensile Strength Ult.		
Ambient MPa (psi)	37.9(5500)	16.5(2400)
589K (600°F)	3.9 (570)	3.1 (460)
589K (600°F), aged	6.5 (940)	3.3 (480)
Resin Content %W	58.0	41.0
Specific Gravity g/cm^3	1.41	1.43
Void Volume %V	1.4	4.0
Fiber Volume %V	36	51

NOTE: Lot WM 3994 used 25.4mm (1.0 inch) chopped fibers.

Lot WM 3995 used 12.7mm (0.5 inch) chopped fibers.

TABLE XXXI

SUMMARY LAMINATE DATA "0" ORIENTATION
TASK C[1]

MECHANICAL PROPERTIES	
Flexural Ultimate MPa (ksi)	
Ambient	1579 (229)
393K (250°F)	1288 (187)
449K (350°F)	1247 (181)
476K (400°F)	1082 (157)
533K (500°F)	765 (111)
589K (600°F)	558 (81)
[2] 589K (600°F)	744 (108)
Flexural Modulus GPa (Msi)	
Ambient	119 (17.2)
393K (250°F)	126 (18.3)
449K (350°F)	138 (20.1)
476K (400°F)	121 (17.6)
533K (500°F)	84 (12.2)
589K (600°F)	75 (10.9)
[2] 589K (600°F)	92 (13.3)
Short Beam Shear MPa (ksi)	
Ambient	101 (14.7)
393K (250°F)	80 (11.6)
449K (350°F)	71 (10.3)
476K (400°F)	59 (8.6)
533K (500°F)	40 (5.8)
589K (600°F)	41 (5.9)
[2] 589K (600°F)	44 (6.4)
Resin Content %W	38.6
Specific Gravity g/cm^3	1.54
Void Volume %V	1
Fiber Volume %V	54

[1] Material used in study was Lot 2W 4280.

[2] Specimens aged in 589K (600°F) environments for 125 hours.

TABLE XXXII

SUMMARY LAMINATE DATA
TASK C

Mechanical Properties	Orientation		
	0°	$(\pm 45)_S$	$(0,90)_S$
TENSILE ULTIMATE MPa (ksi)			
Ambient	1171(170)	537(78)	689(100)
589K (600°F)	537(113)	379(55)	510(74)
589K (600°F) aged [1]	889(129)	172(25)	531(77)
TENSILE MODULS GPa (ksi)			
Ambient	133(19.3)	49(7.1)	55(8.0)
589K (600°F)	99(14.4)	36(5.2)	37(5.4)
589K (600°F) aged [1]	103(15.0)	34(5.0)	39(5.7)
COMPRESSION ULTIMATE MPa (ksi)			
Ambient	1027(149)	165(24.0)	689(100)
589K (600°F)	565(82)	116(16.8)	289(42)
589K (600°F) aged [1]	758(110)	68(9.8)	296(43)
COMPRESSION MODULUS GPa (Msi)			
Ambient	133(19.3)	--	71(10.3)
589K (600°F)	103(15.0)	--	68(9.8)
589K (600°F) aged [1]	107(15.5)	--	67(9.7)
BEARING ULTIMATE MPa (ksi)			
Ambient	--	46(67)	48(69)
589K (600°F)	--	21(30)	25(36)
589K (600°F) [1]	--	28(40)	27(39)
"C" SCAN	Excellent	Excellent	Excellent
RESIN CONTENT %W	37.0	38.1	37.4
SPECIFIC GRAVITY g/cm^3	1.54	1.53	1.54
VOID VOLUME %V	1	1	1
FIBER VOLUME %V	55	54	55

[1] Specimens aged 125 hours @ 589K (600°F).

TABLE XXXIII

SUMMARY TASK C GRAPHITE/POLYIMIDE STRUCTURAL ELEMENTS

	HAT SECTION HAT 8 PLIES $(+45°)_S$ FLAT PANEL 8 PLIES $(0°,90°)_S$			"I" STIFFENERS WEB - 12 PLIES $(+45°)_S$ CAP - 12 PLIES $(0°,90°)_S$		
	BONDED	COCURED	FASTENED	BONDED	COCURED	FASTENED
PROPERTY DATA						
Crippling Load Kg (lbs)						
Ambient	31,170(15,585)	18,810(8,550)	25,390(11,540)	50,600(23,000)	50,600(23,000)	43,360(19,800)
589K (600°F)	6,600(3,000)	14,014(6,370)	2	18,150(8,250)	1	4,770(2,170)
589K (600°F) aged	10,010(4,550)	3	2	28,140(12,790)	1	-
Compressive Ultimate MPa (psi)						
Ambient	112(16,200)	101(14,720)	83(12,000)	161(23,400)	135(19,540)	150(21,800)
589K (600°F)	38(5,500)	75(10,870)	2	63(9,190)	1	17(2,400)
589K (600°F) aged	57(8,300)	3	2	98(14,250)	1	-
Failure Mode						
Ambient	Shear (0°,90°)	Shear (±45°)	Buckling (±45°)	Buckling(0°,90°)	Shear(0°,90o,±45°)	Buckling(0°,90°) Shear (0°,±45o)
589K (600°F)	Adh. & Comp. (0°,90°)	Compression (0°,90°)	-	Adh.(0,90,±45) Comp. (0°,90°)	-	Comp. (0°,90°)
589K (600°F) aged	Adh.(0°,90°,±45°)	-	-	Adh.(0°,90°,+45°) Comp. (0°,90°)	-	-
"C" Scan	Good	Good	Good	Good	Poor	Good

1 NDI data on ambient tested "I" beams so poor specimens not fabricated.

2 Tested element data so marginal specimens not fabricated.

3 Elements were not fabricated.

TABLE XXXIV

SUMMARY COUPON DATA STRUCTURAL ELEMENTS

Element/Location	Short Beam Shear Ultimate MPa (ksi)	Physical Properties Resin Content %	Specific Gravity g/cm^3	Void Volume %	Fiber Volume %
Bonded Hat/Flange	61 (8.9)	[1]	[1]	[1]	[1]
Bonded Hat/Web	--	32.6	1.56	1.1	59.7
Cocured Hat/Flat Panel	50 (7.2)	30.0	1.54	2.8	61.5
Cocured Hat/Flange	63 (9.2)	30.6	1.55	2.3	61.2
Fastened Hat/Flange	61 (8.8)	32.1	1.53	2.7	59.3
Fastened Hat/Web	56 (8.2)	31.9	1.57	1.4	60.4
Bonded I/Cap	44 (6.4)	[1]	[1]	[1]	[1]
Bonded I/Web	45 (6.5)				
Bonded I/Cap[4]	24 (3.5)				
Bonded I/Web	28 (4.0)	[1]	[1]	[1]	[1]
Fastened I/Cap	59 (8.6)	32.0 [2] 34.1 [3]	1.59 1.49	[1] 5.1	61.4 55.7
Fastened I/Web	45 (6.5)	32.2 [2] 34.3 [3]	1.59 1.49	[1] 5.1	61.3 57.8
Cocured I/Cap	19 (2.7)	35.6	1.41	10.0	51.6
Cocured I/Web	17 (2.5)	34.7	1.40	8.9	53.5

[1] Aluminum filled adhesive precluded accurate Resin Content and Specific Gravity.

[2] Data from room temperature tested "I" beam.

[3] Data from 589K (600^{o}F) tested "I" beams.

[4] Elements aged 589K (600^{o}F) for 125 hours.

NOTE: Element failure modes precluded obtaining Celanese Compression specimens and/or Flexural test specimens.

TABLE XXXV

SUMMARY OF TASK C HONEYCOMB SANDWICH DATA

Property	A7F	FM 34
Flatwise Tensile, MPa (ksi)		
Ambient	3.02(439)	3.48(505)
589K (600°F)	1.38(200)	2.82(410)
589K (600°F)[1]	1.00(146)	
Edgewise Compression, MPa (ksi)		
Ambient	123.3(17.9)	
589K (600°F)	32.4(4.7)	
589K (600°F)	66.8(9.7)	

[1] Specimens aged 125 hours at 589K (600°F)

TABLE XXXVI

SUMMARY OF TASK C CHOPPED FIBER MOLDING

Properties	Lot Wm 4345
Flexural Stress MPa (ksi)	
Ambient	127.4 (18.5)
589K (600°F)	62.0 (9.0)
589K (600°F) 1	51.7 (7.5)
Flexural Modulus GPa (Msi)	
Ambient	152 (0.220)
589K (600°F)	138 (0.200)
589K (600°F) 1	124 (0.180)
Tensile Strength MPa (ksi)	
Ambient	48.9 (7.1)
589K (600°F)	54.4 (7.9)
589K (600°F) 1	33.1 (4.8)
Bearing Strength MPa (ksi)	
Ambient	115.8 (16.8)
589K (600°F)	206.0 (29.9)
589K (600°F) 1	146.8 (21.3)
Resin Content %W	54.0
Specific Gravity g/cm^3	1.44
Void Volume %V	2.5
Fiber Volume %V	38

1 Specimens aged 125 hours at 589K (600°F)

TABLE XXXVII

QUALITY CONTROL PANEL DATA TASK D

Properties	Panel 6 Ply	 12 Ply	 24 Ply
Flexural Stress MPa (ksi)			
Ambient	1495(217)	1564(227)	1481(215)
589K (600^{o}F)	792(115)	896(130)	799(116)
Flexural Modulus Gpa (Msi)			
Ambient	120(17.4)	127(18.5)	123(17.8)
589K (600^{o}F)	124(18.0)	121(17.6)	120(17.4)
Short Beam Shear MPa (ksi)			
Ambient	100(14.5)	96(13.9)	98(14.2)
Resin Content %W	37.1	35.1	36.0
Specific Gravity g/cm^3	1.54	1.54	1.54
Void Volume %V	1.0	1.6	1.4
Fiber Volume %V	55	57	56

TABLE XXXVIII

QUALITY CONTROL PANEL DATA TASK E

	Stringer Panels				
	I Stiffened		Multiple Hat Stiffened		
			Small Area		Large Area
Properties	Bonded & Fastened	Cocured	Bonded & Fastened	Cocured	Bonded
Flexural Stress Ult MPa (ksi)					
Ambient	1585(230)	1447(210)	1480(215)	1585(230)	1481(215)
589K (600°F)	827(120)	758(110)	792(115)	813(118)	958(110)
Flexural Mod Ult GPa (Msi)					
Ambient	114(16.5)	132(19.2)	130(18.9)	114(16.5)	127(18.5)
589K (600°F)	118(17.1)	109(15.8)	119(17.3)	120(17.4)	118(17.2)
Short Beam Shear MPa (ksi)					
Ambient	99(14.4)	88(12.8)	97(14.1)	95(13.8)	99(14.4)
589K (600°F)	43(6.2)	40(5.8)	44(6.4)	39(5.7)	41(6.0)
Resin Content % W/W	35.0	37.2	36.8	35.0	34.9
Specific Gravity g/cm^3	1.55	1.53	1.53	1.56	1.56
Void Volume % V	1.0	1.0	1.7	1.0	1.0
Fiber Volume % V	57	55	55	58	58

TABLE XXXIX

QC DATA TASK F SANDWICH

Panel Number	Flatwise Tensile MPa (psi)	
	Ambient	589K (600°F)
1	3.01(438)	2.07(300)
2	3.52(509)	2.41(350)
3	3.54(514)	2.23(323)
4	2.99(434)	2.54(368)
5	3.58(520)	2.38(345)
6	2.82(409)	2.14(310)

QC DATA SKINS

Flexural Stress MPa (ksi)	
Ambient	1543(224)
589K (600°F)	737(107)
Short Beam Shear MPa (ksi)	
Ambient	96(13.9)
589K (600°F)	39(5.7)

APPENDIX A1

Receiving Inspection for Control of the PMR-15 Graphite Polyimide Prepreg

Specification: Receiving Inspection Control of PMR-15 Gas Chromatography/
Mass Spectrometry

1.0 Scope

This specification describes the procedures and requirements for receiving inspection control of PMR-15 by gas chromatography/mass spectrometry.

2.0 Classification

None

3.0 References

Except where a specific issue is indicated, the current issue of the following references shall be a part of this standard to the extent indicated herein.

4.0 Facilities

4.1 A gas chromatograph interfaced with a mass spectrometer that has capability of continuously scanning over a preset mass range within preset time intervals. The gas chromatograph must be programmable within the specification limits. A DuPont 21-490 computerized GC/MS or equivalent is acceptable.

4.2 A pyrolyzer with capability of pyrolyzing material in a vacuum under controlled temperature. A Barnes pyrolyzer or equivalent is acceptable.

5.0 Procedure

Pyrolyze a small sample under vacuum by increasing the temperature of the pyrolyzer from room temperature to 1272K (1832°F) within 15 seconds. Continue heating until vacuum is broken. Immediately withdraw one milliliter of pyrolyzate into a syringe and inject into the gc/ms under the following conditions:

a.	Sample size	1 ml
b.	Column	6' x 1/8 W98 @ 10%
c.	Column temperature	Room temperature to 447K (347°F)
d.	Injection port temperature	497K (437°F)
e.	Detector	Flame Ionization Detector
f.	Detector temperature	522K (482°F)
g.	Range	10^{-11}
h.	Attenuation	X256
i.	Chart speed	0.25 in/min.
j.	Source temperature	472K (392°F)
k.	Mass scan	500 to 14
l.	Scan rate	2 secs per decade
m.	Acquisition rate	2
n.	Threshold	1

NOTE: Make sure baseline is stabilized before injecting sample. Also continue the scan until all of the sample has cleared the column and the baseline has once again stabilized.

Identify all components elluted.

6.0 Requirements

Components present should be xylene, toluene, butadienyl acetylene, 1-3 cyclopentadiene, methanol, and 1-3 butadiene. Trace amounts of other materials are allowed as long as there are no other alcohols present.

Specification: Receiving Inspection Control of PMR-15 by Infrared Analysis

1.0 Scope

This specification describes the procedures and requirements for receiving inspection control of PMR-15 by infrared analysis.

2.0 Classification

None

3.0 References

Except where a specific issue is indicated, the current issue of the following references shall be a part of this standard to the extent indicated herein.

3.1 ASTM E275-67, Describing and Measuring Performance of Spectrophotometers

4.0 Facilities

The instrument shall be capable of performing per Reference 3.1. A Digilab Fourier Transform Spectrometer (FTS-15) or instrument capable of producing equivalent spectra is acceptable.

5.0 Procedure

Extract a fresh 1 x 1 inch sample of prepreg with acetone at room temperature. Make sure all of the resin is extracted by manipulating the fibers with a probe. Place a portion of the resin/solvent solution on a salt block. Allow the acetone to evaporate and obtain an infrared scan. The resin film should be of such a thickness to give a transmittance of 10 to 20% at 1730 cm^{-1}.

6.0 Requirements

The spectrum shall match the standard spectrum. In addition, there shall be no evidence of imidization taking place as noted by the presence of the band at 1770 cm^{-1}.

Specification: Receiving Inspection Control of PMR-15 by Thermal Gravimetric Analysis

1.0 Scope

This specification describes the procedures and requirements for receiving inspection control of PMR-15 by thermal gravimetric analysis.

2.0 Classification

None

3.0 References

Except where a specific issue is indicated, the current issue of the following references shall be a part of this standard to the extent indicated herein.

None

4.0 Facilities

The instrument shall be capable of measuring quantitatively the weight loss occurring in a material as a function of time or temperature. A DuPont 951 or equivalent is acceptable.

5.0 Procedure

Place a small fresh sample of prepreg in the thermal gravimetric analyzer chamber. The sample should not be rolled up but should be kept open on all sides as much as possible. Make the analysis using the following parameters:

a.	Sample size	25 ± 5 mg
b.	Heating range	5K/min.

c.	Temperature range	Room temperature to 1072K (1472°F)
d.	Atmosphere	Air
e.	Flow rate	0.3 L/Minute
f.	Y-axis scale	100%
g.	X-axis scale	372K (212°F)

6.0 Requirements

The thermogram shall have the following percent residues remaining at the indicated temperatures.

a.	362K (194°F)	99%
b.	472K (392°F)	94 ± 2%
c.	672K (752°F)	92 ± 2%
d.	922K (1202°F)	1%

Specification: Receiving Inspection Control of PMR-15 by Gel Permeation Chromatography

1.0 Scope

This specification describes the procedures and requirements for receiving inspection control of PMR-15 by gel permeation chromatography.

2.0 Classification

None

3.0 References

Except where a specific issue is indicated, the current issue of the following references shall be a part of this standard to the extent indicated herein.

None

4.0 Facilities

A liquid chromatography instrument, such as the DuPont Model 830 or equivalent.

5.0 Procedures

5.1 Prepare a solution of the resin by dissolving about 0.15 g of prepreg into 20 mls of tetrahydrofuran, uninhibited. Inject 5 of the clear solution into the liquid chromatograph under the following conditions:

a.	Columns	1 @ 500 Å 4 @ 100 Å
b.	Flow rate	1 ml/min

c.	Attenuation	UV x 256 rl x 8
d.	Wavelength	UV 254
e.	Chart speed	0.4 ipm
f.	Carrier solvent	THF uninhibited

5.2 Draw tangents to the sides of each peak in the chromatogram. The intercept marks the elution volume.

5.3 Relative Concentration

Calculate the relative standard concentration as follows:

$$Z = \frac{H_h}{H_m}$$

where -

Z = relative standard concentration

H_h = peak height (in mm) of the corresponding peak on the test chromatogram

H_m = peak height identified on the reference chromatogram, measured in millimeters.

Calculate the relative component concentration as follows:

$$X = \frac{H_x}{H_r}$$

where -

X = relative component concentration

H_x = the peak height of the component to be measured on the test chromatogram

H_r = the corresponding peak height of the component to be measured on the reference chromatogram.

Calculate relative changes in concentration as follows:

$$R = \frac{X}{Z} = \text{relative change in concentration}$$

6.0 Requirements

6.1 Elution Volume

The elution volume must be ± 2% of the qualification value.

6.2 Relative Concentration

$$R = 1.0 \pm 0.20$$

APPENDIX A2

REVISED TESTING PROCEDURE FOR LIQUID CHROMATOGRAPHY

Gel Permeation Chromatography Method for HTS-2 Graphite/PMR-15 Polyimide Resins

1.0 Scope

This method describes a procedure for the analysis of polyimide resins by Gel Permeation Chromatography (GPC) using microstyragel columns.

2.0 Classification

None

3.0 Facilities

A Liquid Chromatograph such as DuPont 830.

4.0 Requirements

4.1 Conditions

Control the following parameters as specified.

a.	Sample size	10 μl
b.	Solvent	Tetrahydrofuran (THF) UF grade Burdick or Waters Associates (No substitutes).
c.	High molecular wt. std.	MW 233,000 Polystyrene Waters Assoc. P/N 41984.
d.	Low molecular wt. std.	Acenapthene 99% m.w. 154.21 Aldrich Chemical Co.
e.	Elution rate	2.0 ml/min.
f.	Chart speed	1.0 cm/min. or 0.4 in./min.

g.	UV attenuation	x8
i.	Columns	One 500 Å, and 4 100 Å microstyragel columns. These columns must meet the specification plate count requirements.
j.	Temperature	295 ± 2K (73 ± 3.6°F)

5.0 Procedure

5.1 Prepare a standard solution of 0.40g Acenapthene and 2.00g of M.W. 233,000 polystyrene per liter of THF. Store in an amber bottle, label, and date.

5.2 Prepare a composite sample by using a sharp 6.4 mm (.25 in) diameter punch to remove a circle of material. Discard any backing. Weigh and place in an 8 ml. vial (VWR P/N 66011-085). Add 5.0 ml of the standard solution and close vial with a polyseal cap. Place on a mechanical shaker for 10 to 15 minutes. Remove solid material. Filter with a millipore or Waters Associates Solvent Clarification Kit into a clean 8 ml vial.

5.3 Inject 10µl of solution into column.

6.0 Reporting

Record material identification, instrument parameters, and date.

Calibration of Microstyragel Columns for PMR-15

1.0 Procedure

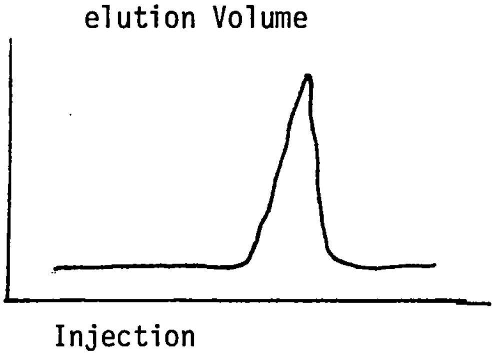
Determine the plate count (N) of each individual column using following conditions:

Flow rate	1.0 ml/minute
Chart speed	1.0 in/minute
Mobile phase	Tetrahydrofuran, uninhibited, distilled in glass, filtered to 0.45 microns (THF)
Standards	SE 2% toluene
Detectors	UV at 254
Injection volume	10 µl
Notes	

2.0 Calculation

a. Extend the baseline to completely enclose the UV peak. Determine the area of the enclosed peak with an integrator.

b. Determine the elution volume by measuring the distance from time of injection to the apex of the peak.



V = elution volume

h = peak height

a = area under curve

c. Calculate the plate count using the following formula:

$$N = 2 \quad \left(h \frac{v}{a}\right)^2$$

where N = plate count

h = peak height ± 0.2 mm

v = elution volume ± 0.2 mm

a = peak area ± 0.5 mm^2

d. Record column identify, plate count, data, and operator initials on log sheet.

3.0 Requirements

The columns must meet the following requirements:

100 Å	5000
500 Å	3000

Size Exclusion Chromatography Method
For Graphite/PMR-15 Polyimide Resins

1.0 Scope

This method describes a procedure for the analysis of polyimide resins by Size Exclusion Chromatography.

2.0 Classification

None

3.0 Facilities

A Liquid Chromatograph such as DuPont 850 or equivalent.

A UV detector such as DuPont 850 or equivalent.

4.0 Requirements

4.1 Conditions

Control the following parameters as specified:

a.	Sample size	3 µl
b.	Solvent	1:1 Water: Tetrahydrofuran plus 0.1% acetic acid (V/V)
c.	Elution rate	1 ml/minute
d.	Chart speed	1.0 cm/min. or 0.4 in/min.
e.	UV wavelength	254 mm
f.	UV attenuation	x8
g.	Columns	2 - SE 60 DuPont size exclusion columns
h.	Temperature	295 ± 2K (73 ± 3.6°F)

5.0 Procedure

5.1 Prepare a composite sample by using a sharp 6.4 mm (.25 in) diameter punch to remove a circle of material. Discard any backing. Weigh and place in an 8 ml vial (VWR pln 66011-085). Add 5.0 mls of tetrahydrofuran and close vial with a polyseal cap. Place on a mechanical shaker for 10 to 15 minutes. Remove solid material. Filter with a millipore or Waters Associates solvent clarification kit into a clean 8 ml vial.

5.2 Inject 3 μl of solution into column.

6.0 Reporting

Record material identification, instrument parameters, and date.

Note: Water must be ultra-pure and tetrahydrofuran is uninhibited, distilled in glass, filtered to 0.45 microns.

DOCUMENT NO. D180-20545-3
APPENDIX B1
TITLE: QUALITY ASSURANCE PLAN

ABSTRACT

Quality Control procedures are specified for control of the PMR-15 polyimide resin, graphite tape, material receiving inspections, in-process controls, and final inspection of fabricated structural elements. The document also specifies the facilities, equipment and tooling which are required during the fabrication of structural elements.

KEY WORDS

PMR-15 polyimide resin
Graphite prepreg
Thermocouples
Potentiometric control equipment
Autoclave
Test equipment

TABLE OF CONTENTS

LIST OF FIGURES

1.0 SCOPE

This document specifies the procedures which are to be followed by Quality Control and provides for resin analysis and control, graphite tape analysis and control, material receiving inspection, in-process controls and final inspection of fabricated composites and/or hardware. It specifies the facilities, equipment, and tooling which are required and the materials which are to be employed.

This document supplements but does not supersede applicable material specifications, process specifications and engineering drawings. In case of conflict, the material specification and/or engineering drawing takes precedence.

2.0 REFERENCES

2.1 BOEING SPECIFICATIONS

Document D180-20545-4	Material Specification for Graphite/ PMR-15 Prepreg
Document D180-20545-5	Process Specification for Graphite/ PMR-15 Prepreg

2.2 OTHER SPECIFICATIONS

ASTM D-790	Flexural Properties of Plastics, Test for
ASTM D-2344	Apparent Horizontal Shear Strength of Reinforced Plastics by Short Beam Method, Test for

3.0 FACILITIES

Adequate facilities shall be provided for the accomplishment of all operations specified herein. Proper control shall be maintained over temperature, cleanliness, and other environmental factors which could adversely affect the operations described in this document. Unless otherwise specified, all operations and processes described herein shall be performed at an ambient temperature (ambient temperature defined as 290 - 304K (65 - 90^{o}F)). Protection must be provided for the graphite tape to prevent either "drying out" or absorption of moisture.

Storage of materials shall be in a freezer capable of maintaining the temperature at 273K to 255K (0 ± 10^{o}F). Temperatures above 278K (40^{o}F) will shorten the useful life of the graphite tape. The materials must be allowed to come to equilibrium conditions at ambient temperature before being removed from its sealed polyethylene bag. Out time shall be held to a minimum and the remaining material be repackaged in the same manner as received from the vendor.

4.0 EQUIPMENT

4.1 INSPECTION OF GRAPHITE PREPREG (FIBERS AND RESIN)

The equipment described below is required for analyzing graphite prepreg.

4.1.1 GAS CHROMATOGRAPHY/MASS SPECTROMETER

A gas chromatograph interfaced with a mass spectrometer that has capability of continuously scanning over a preset mass range within preset time intervals. The gas chromatograph must be programmable within the specification limits. A DuPont 21-490 computerized GC/MS, or equivalent, is acceptable.

A pyrolyzer with capability of pyrolyzing material in vacuum under controlled temperature. A Barnes pyrolyzer, or equivalent, is acceptable.

4.1.2 FOURIER TRANSFORM SPECTROMETER

A Digital Fourier Transform Spectrometer (FTS-15) or other instrument capable of producing equivalent spectra is acceptable.

4.1.3 THERMAL GRAVIMETRIC ANALYSIS

A DuPont 951, or equivalent, is acceptable.

4.1.4 LIQUID CHROMATOGRAPHY

A DuPont Model 850, or equivalent, is acceptable.

4.2 INSPECTION OF GRAPHITE FIBER

4.2.1 WEIGHING DEVICES

All weighing devices shall be calibrated and their accuracy recorded. Balances used for determining properties shall weigh accurately to the nearest milligram with an estimate to the nearest 0.1 milligram.

4.2.2 OVENS

The equipment shall be capable of providing a uniform heating environment from ambient to 644K (700^{o}F) such that the difference between any two thermocouples reading air temperature shall not exceed 5.6K(10^{o}F) for equilibrium or uniform temperature increase rate conditions. During programmed transients and/or temperature correction periods, the difference shall not exceed 8K (15^{o}F).

4.2.3 THERMOCOUPLES

The thermocouple material shall have temperature-EMF characteristics as published in the National Bureau of Standards Circular Number 561.

4.2.3.1 Thermocouples shall have welded junctions and be of a material and gage suitable for the environment in which used.

4.2.3.2 Preferred practice is to use primary thermocouple wire to the point of measuring/recording/controlling. If extension leads are used, they shall be of compensating wire matched to the primary thermocouple wire and used with matching quick disconnect thermocouple material units.

4.2.3.3 The limit of error shall be ± 2.8K (5^{o}F) for thermocouple wires, Types J or K, used to measure temperatures less than 644K (700^{o}F).

4.2.4 POTENTIOMETRIC EQUIPMENT

4.2.4.1 Recorders and controllers for use with thermocouples shall have automatic cold junction compensation.

4.2.4.2 A hand-operated potentiometer shall have a temperature compensating dial or the correction made to the reading at each period of use. A laboratory-type thermometer accurate to 0.3K (0.5^{o}F) shall be used to measure the temperatures at the potentiometer terminals.

4.2.4.3 It is preferred that the maximum temperature of the process being measured should be between 65 and 95% of the range of the controller/recorder being used.

4.2.4.4 The calibration accuracy of the recorders/controllers used shall be ± 0.30 of one percent of range unless otherwise technically justified and approved for the specific application intended.

4.2.4.5 Non-potentiometric control equipment may be used on demonstration of suitability and agreement between the contracting parties.

4.3 IN-PROCESS INSPECTION

4.3.1 AUTOCLAVE

The equipment shall be capable of providing a uniform heating environment from ambient to 644K (700^{o}F) such that the difference between any two thermocouples reading air temperature shall not exceed 5.6K (10^{o}F) for equilibrium or uniform temperature increase rate conditions. During programmed transients and/or temperature correction periods the difference shall not exceed 11K (20^{o}F). The heating rate of the autoclave shall range from a low of 0.5K (1.0^{o}F) per minute to as high as 5.6K (10^{o}F) per minute. The autoclave shall have the capability of 1.7 MPa (250 psi) positive pressure at 644K (700^{o}F).

4.3.2 OVENS

See Section 4.2.2.

4.3.3 PRESSES

The equipment shall possess the following capabilities:

a. Provide a uniform heating environment from ambient to 644K (700°F).

b. Provide for uniform pressure application of 30,000 Kg (50 tons) for the duration of the programmed cycle.

c. Provide for maintaining the press platens ± 5.6K (10°F) of programmed temperature.

d. Provide for the rapid cool-down of platens with either air or water or a combination of the two.

4.3.4 POTENTIOMETRIC EQUIPMENT

See Section 4.2.3.

4.3.5 MECHANICAL PROPERTY TESTING APPARATUS

A properly calibrated testing machine which can be operated at constant rates of crosshead motion over the range indicated, and in which the error in the load-measuring system shall not exceed ± 1 percent. The machine shall be equipped with a deflection measuring device. The stiffness of the test machine shall be such that the total elastic deformation of the system does not exceed 1 percent of the total deflection of the test specimen during test, or appropriate corrections shall be made. The load-indicating mechanism shall be essentially free from inertia lag at the maximum crosshead rate used. The accuracy shall be verified in accordance with ASTM Method E4, Verification of Testing Machines.

5.0 MANUFACTURING CONTROL

The manufacturing sequence for parts fabricated to D180-20545-5 is outlined in the following sections with the overall flow depicted in Figure 1.

5.1 SERIAL NUMBERING

Each production part must be identified with a serial number in addition to the drawing part number and manufacturer's identification.

5.2 PROCESS CONTROL RECORD

a. Record conformance of operating procedures to the requirements of the primary specification, D180-20545-5, and traceability of the materials used on a Process Control Record Form similar to that shown in Figure 2.

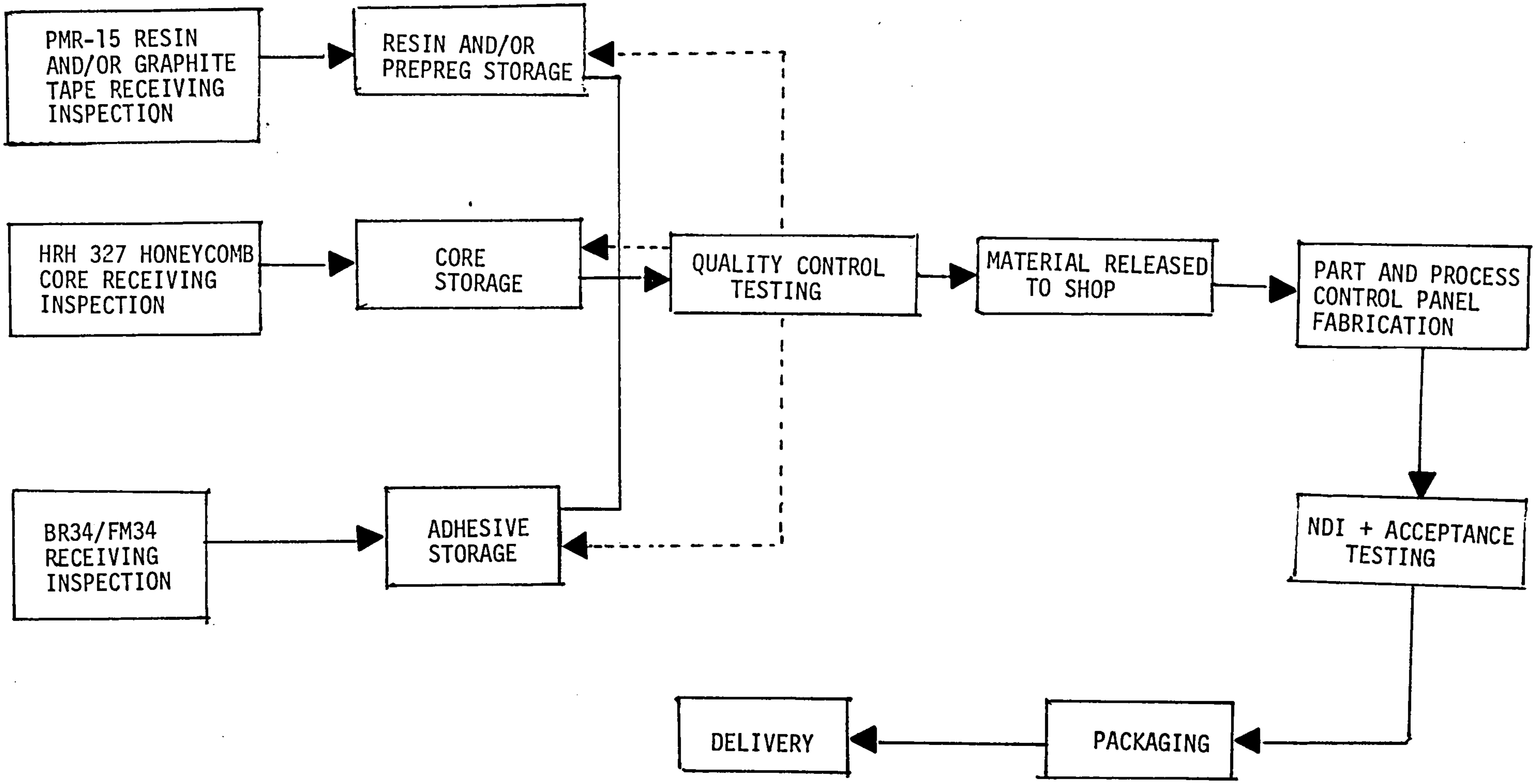


FIGURE 1 - OVERALL MATERIAL FLOW

FIGURE 2 - PROCESS CONTROL RECORD FORM

1. IDENTIFICATION

Serial No.

Drawing No.

Process Control Panel Serial Nos. Date

2. MATERIALS USE AND EXPOSURE

Spec. No.	D180-20545-4 Type I, Class 1	D180-20545-4 Type I, Class 3	BF34/FM34 Adhesive
Batch No.			
Roll or Container Date			
Time Out of Freezer			
Kit/Roll Open			
Step I Process			
Shop Temp. K (°F)			
Shop Rel. Humidity %			

3. PROCESS INFORMATION

Vacuum Leak Rate Before Curing mm (in) Hg in 5 min.

After Curing mm (in) Hg in 5 min.

Vacuum Controller Setting Step I Method 1A

Vacuum Controller Setting Method 1

Cure Time and Temp. for Each Stage

Pressure Application

Post-cure Time and Temperature

4. IN-PROCESS CORRECTION ACCOMPLISHED

5. PHYSICAL TESTS (Process Control Laminate Only)

Resin Content

Specific Gravity

Void Volume

Fiber Volume

MECHANICAL TESTS (Process Control Laminate Only)

Flexure Ultimate, MPa (ksi)

Modulus, GPa (Msi)

ILS Ultimate, MPa (ksi)

b. Process Control Record Forms must be kept on file by the fabricator and available to authorized representatives on request.

5.3 STORAGE AND HANDLING OF MATERIALS.

Quality Control shall enforce the provisions of D180-20545-4 and -5. The prepreg storage and process flow is depicted in Figure 3.

5.4 MATERIALS

Quality Control shall enforce provisions of D180-20545-4 using testing procedures of Section 8 of D180-20545-4 regarding the Graphite/PMR-15 prepreg Types I, II and III, Classes 1, 2, and 3. The materials included in deliverable hardware shall be procured, stored and processed using the applicable materials and/or process document. (See Figure 4 for Material Acceptance Flow.)

5.5 FABRICATION REQUIREMENTS

Quality Control shall enforce the provisions of the processing document, D180-20545-5, and the general process flow is depected in Figure 5. Specific inspection criteria for structural shapes are given below.

5.5.1 FLAT LAMINATES

a. Verify that materials incorporated into the part during fabrication comply with applicable specifications.

b. Verify that materials not incorporated into the part comply with the applicable specification.

c. Verify fabrication area and equipment.

d. Verify fabrication procedures.

5.5.2 HAT SECTIONS, CORRUGATED SECTIONS AND I BEAMS

a. Verify materials used both in the part or used in the part's fabrication.

b. Verify fabrication area, equipment and tooling.

c. Verify fabrication procedures.

d. Verify that process control panel meets specification requirements.

5.5.3 SANDWICH PANELS

a. Verify materials used both in the part or used in the part's fabrication.

b. Verify fabrication area, equipment and tooling.

c. Verify fabrication procedure.

d. Verify that process control panel meets specification requirements.

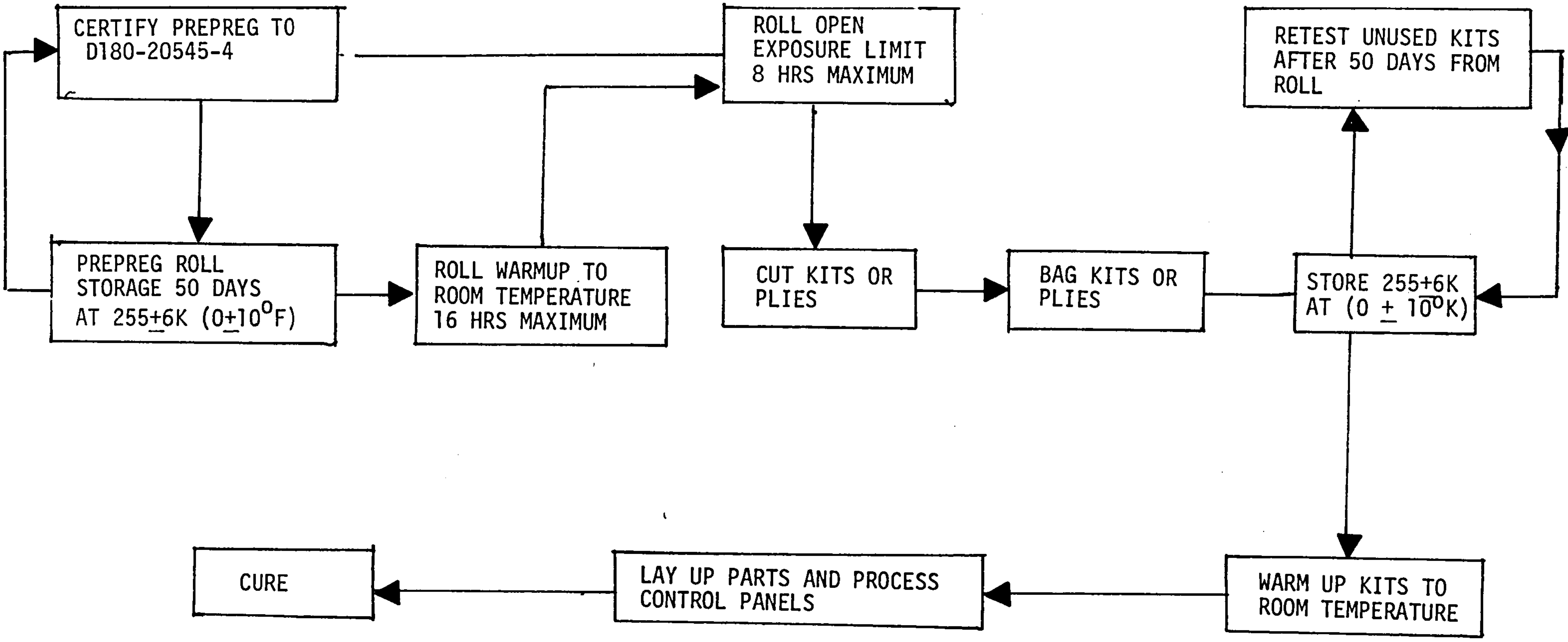


FIGURE 3 - PREPREG STORAGE AND PROCESS FLOW

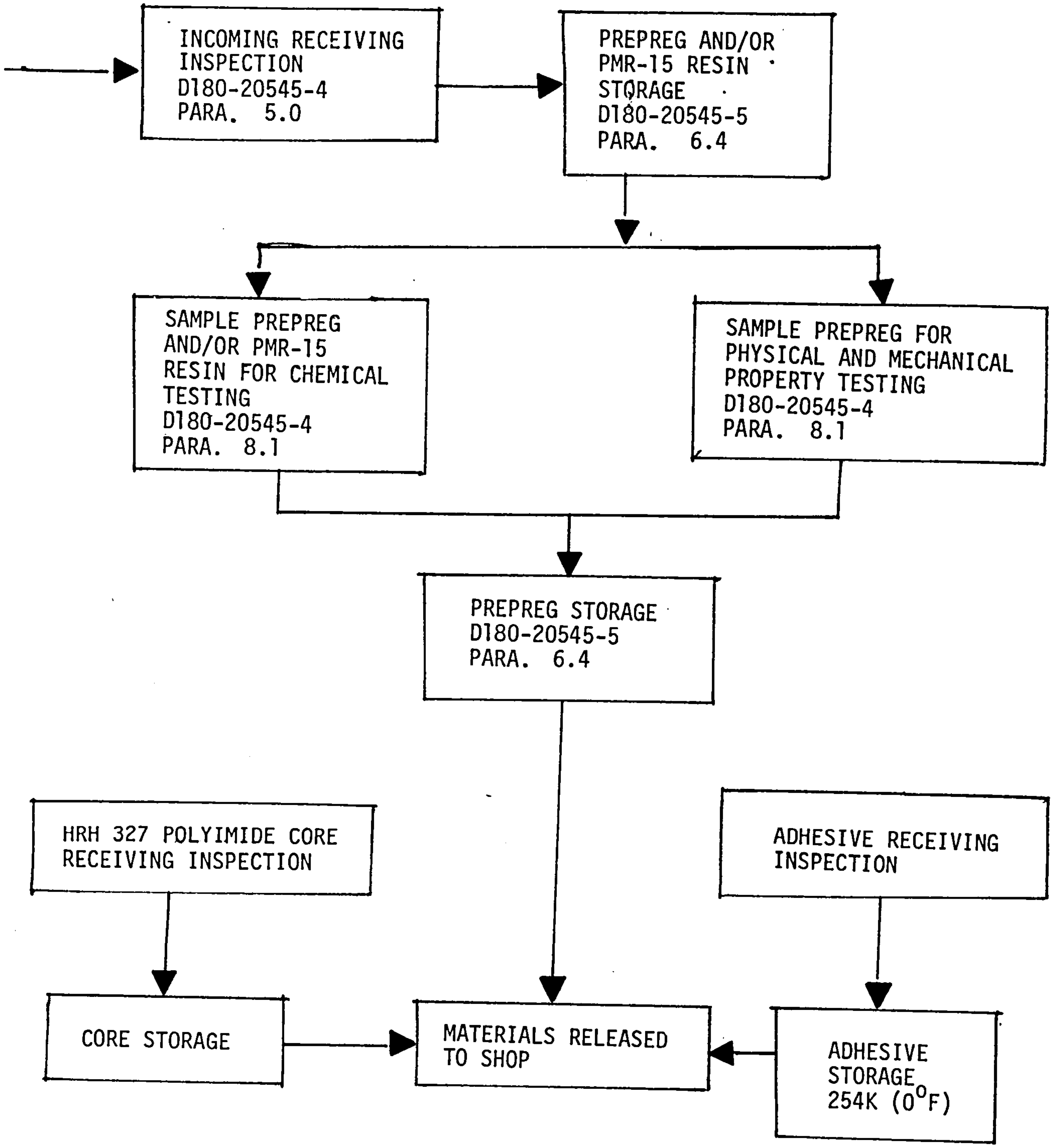
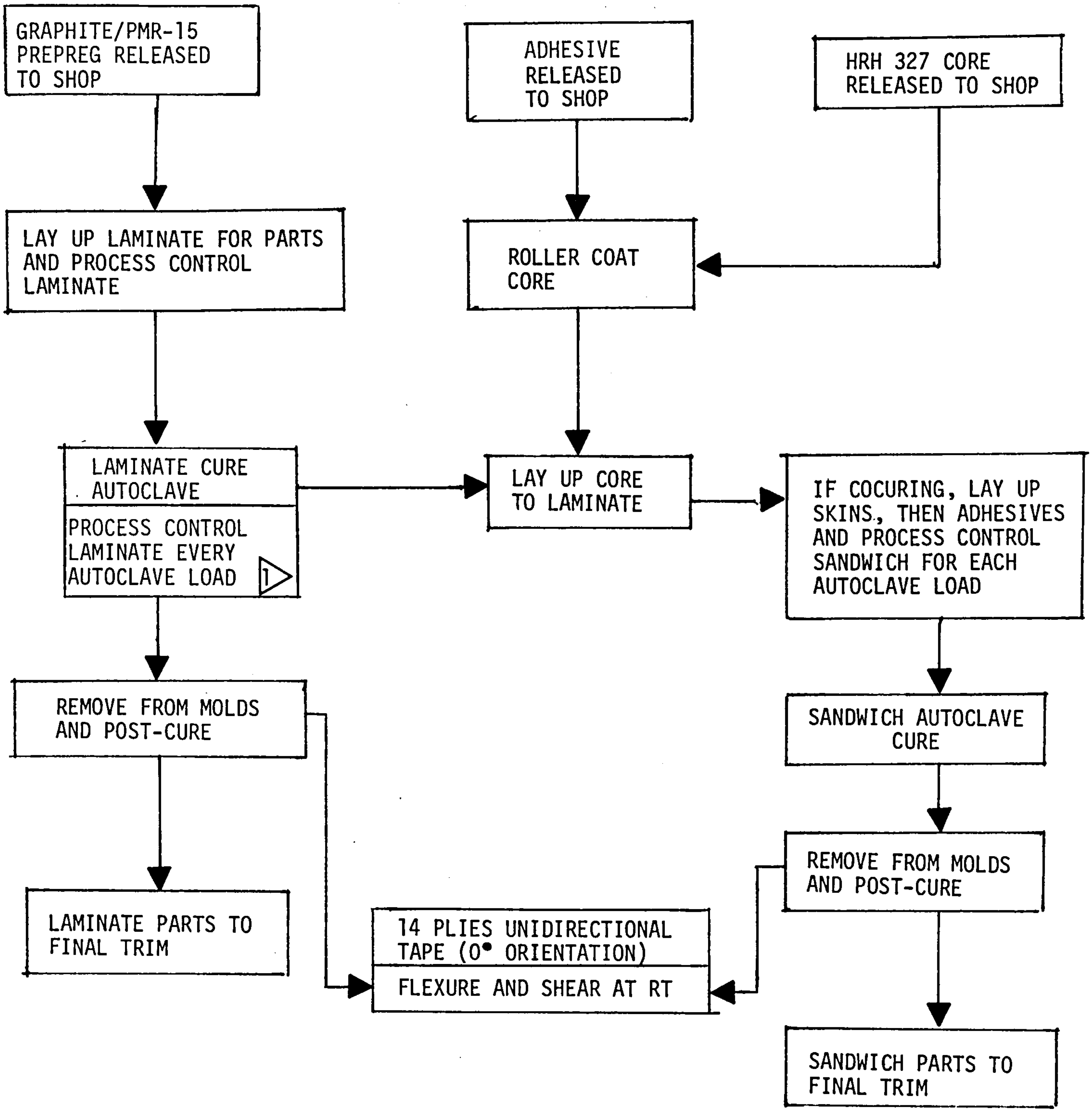


FIGURE 4 - MATERIAL ACCEPTANCE FLOW



1 FIVE SPECIMENS EACH TEST - REPORT AVERAGE AND MINIMUM INDIVIDUAL VALUES

FIGURE 5 - PROCESS FLOW CHART

APPENDIX B2

DOCUMENT NO. D180-20545-4

TITLE: MATERIAL SPECIFICATION FOR.
GRAPHITE/PMR-15 PREPREG

TABLE OF CONTENTS

TABLE OF CONTENTS (CONTINUED)

LIST OF FIGURES

ABSTRACT

Material requirements are specified for Graphite/PMR-15 polyimide prepreg. The requirements include the formulation for making the PMR-15, its chemical characteristics along with its chemical, physical and mechanical properties when it is impregnated using various forms of graphite reinforcement.

KEY WORDS

PMR-15 Resin Varnish
PMR-15 Monomers
Dimethyl ester of 3,3', 4,4' benzophenonetetracarboxylic acid (BTDE)
4,4' Methylenedianiline (MDA)
Monomethyl ester 5-Norborene 2,3 dicarboxylic acid (NE)
Graphite Prepreg
Graphite Fiber
Graphite Composite
Chemical Characteristics
High Pressure Liquid Chromatograph
Wet Resin Content
Dry Resin Content

1.0 SCOPE

This document covers PMR-15 impregnated graphite prepreg for use in the fabrication of high temperature resistant graphite structures.

This document requires qualified products.

2.0 CLASSIFICATION

This document covers unidirectional tape, woven fabric and chopped graphite fiber impregnated with PMR-15 thermosetting polyimide resin. The preimpregnated materials shall be of the following Types, Classes and Grades.

2.1 TYPES

Type shall specify graphite fiber strength and modulus properties.

Type I - Graphite prepreg made from high strength fibers having a minimum strength of 2.76 GPa (400 ksi) and modulus 235 GPa (34 Msi).

Type II - Graphite prepreg made from high modulus fiber having a minimum strength of 2.20 GPa (320 ksi) and modulus of 345 GPa (50 Msi).

Type III - Graphite prepreg made from extremely high modulus fiber having a nominal fiber stiffness of 483 GPa (70 Msi).

2.2 CLASS

The class shall specify the graphite form.

Class 1 - Unidirectional Tape

Class 2 - Woven Fabric

Class 3 - Chopped Fiber

2.3 GRADES

Grades shall specify the tape widths and/or fiber length.

Class 1

Grade 3 - Graphite tape width of 7.6cm (3 inches)

Grade 6 - Graphite tape width of 15.2cm (6 inches)

Grade 12 - Graphite tape width of 30.5cm (12 inches)

Class 3

Grade 3 - Fiber length of 0.8cm (0.3 inch)

Grade 5 - Fiber length of 1.3cm (0.5 inch)

Grade 1 - Fiber length of 2.5cm (1.0 inch)

2.4 FORM

The PMR-15 graphite tape material is to be furnished on spools in required widths with a minimum of 30 meters (32.8 yards) for Types I, II, or III Class I Grade 12 or equivalent in other grades.

Class 3 chopped graphite fiber molding compound will be in quantities not less than 2 kilograms (4.4 lbs).

Rolls of prepreg shall be supported by a core which is not deformed by the material weight. The core diameter shall be 200mm (8 inches) minimum. Core length shall be 0 to 150mm (0 to 6 inches) longer than the carrier width.

3.0 REFERENCES

Except where a specific issue is indicated, the issue of the following references in effect on the data of invitation for bid shall form a part of this document to the extent herein indicated.

a.	ASTM D790	Flexural Properties of Plastics
b.	ASTM D2344	Apparent Horizontal Shear Strength of Reinforced Plastics by Short-Beam Shear Method
c.	ASTM D792	Specific Gravity and Density of Plastics by Displacement
d.	ASTM 638	Tensile Properties of Plastics
e.	MIL-B-117	Bags, Sleeves and Tubing - Interior Packaging

4.0 DEFINITIONS

a. Bleeder - Porous material used to absorb excess resin during cure or to provide a path for reaction products removal.

b. Prepreg Batch - Prepreg containing reinforcement impregnated with one batch of resin in one continuous operation.

c. Chopped Graphite Fiber Batch - A molding compound containing chopped fiber reinforcement impregnated with one batch of resin in one continuous operation.

d. Resin Batch - Resin mixed in one mixer in one operation with traceability to individual monomer lots.

e. Roll - A roll is defined as any section from the batch of prepreg furnished as a continuous roll of a length specified in Section 2.2.

f. Storage Life - That period of time which the material may be kept so that it retains the properties within the limits of this document.

5.0 MATERIAL REQUIREMENTS

5.1 WORKMANSHIP

a. The material shall be uniform in quality and condition, and clean and free from foreign materials, and shall not have characteristics which are detrimental to fabrication, appearance or performance. These defects shall be acceptable only to the limits given in Sections 5.2 and 5.3.

b. Material containing defects shall be allowed if each defect is flagged, and replacement yardage is added to the roll for every defect occurring in that roll. Additionally, no more than one defect may occur in any 5 meters (16.0 ft) of material, or 6 defects per roll.

5.2 VISUAL

a. Class 1

The material shall be essentially free from crimped fibers, gelled resin particles, twists, fiber balling, unwetted fibers and dry or boardy areas. Individual tows shall be parallel to the tape or sheet centerline direction within ±5 degrees.

b. Class 2

Impregnated cloth furnished to this document shall be of quality workmanship. Indications of impurities, dry areas, areas of nonuniformity, incomplete impregnation, gelled resin, hard spots or localized color difference in impregnated cloth shall be marked by tape as nonconforming area.

c. Class 3

The graphite fiber molding compound shall be essentially the same as specified in Section 5.2.a.

5.3 DIMENSIONAL EXAMINATION

a. Open spaces between fibers or tows on the unidirectional tape shall not be more than 0.76mm (0.03 in) wide nor more than 25.4 continuous centimeters (10 in) long for each one square meter (10 sq. ft.) of tape. Gaps in the tape shall not exceed 0.76 millimeter (.03 inch).

b. The alignment of the warp and fill yarns in the graphite fabric shall be perpendicular to each other and shall be parallel to the warp and fill direction of the cloth.

5.4 STORAGE AND WORKING LIFE

a. While not in use, the tape will be stored at 254 ±5 K (0 ± 10^{0}F) in heat-sealed bags meeting the requirements of MIL-B-117. (See Section 10).

b. A rigid cardboard spacer with a metal or plastic plug shall be placed over each end of the core and press fitted tightly into the tube.

c. The material shall be capable of meeting the qualification requirements of this document after 50 days of storage at 254 ± 5 K ($0 \pm 10^{\circ}$F) plus additional exposure of 240 hours at ambient temperature in a sealed bag. Storage life starts at date of shipment.

5.5 PHYSICAL PROPERTIES

The physical properties of tape supplied to this document shall meet the requirements of Table I.

TABLE I

PREPREG PHYSICAL PROPERTY REQUIREMENTS

	Resin Content Percent	Volatile Content Percent	Gel Time Seconds
1 Class 1	34^{+4}_{-2} [1]	10^{+2}_{-1}	50 ± 10 [3]
	41^{+4}_{-2} [2]		150 ± 10 [4]
Class 3	60^{+1}_{-4}	10 ± 2	100 ± 10
	66^{+1}_{-4}		
Test Method	Sec. 8.7	Sec. 8.6	Sec. 8.9

[1] Based on dry resin solids (Method 8.7.1 or 8.7.2)

[2] Based on wet resin solids (Method 8.7.2)

[3] Prepreg that meets condition A requirements (See Table III)

[4] Prepreg that meets condition B requirements (See Table III)

5.6 COMPOSITE MECHANICAL PROPERTIES

When the composite is laminated as described in Section 8.9 and 8.10, material must meet the requirements of Table II.

5.7 PREPREG CHEMICAL PROPERTIES

5.7.1 RESIN VARNISH

The polyimide varnish known as PMR-15 shall be chiefly comprised of monomers and low molecular weight polyamide esters. The monomers used shall be those shown

TABLE II

Composite Mechanical Property Requirements

Material Type	Heat Aging	Test Temp K(^{0}F)	Mechanical Properties			Physical Properties						Composite T_G
			Flexural		Horizontal Shear MPa(KSI)	Resin Content % W	Specific Gravity g/cc(lbs/in^3)	Fiber Volume % V ▷2	Void Volume % V ▷2	Ply Thickness mm(inch)	Composite Thickness mm(inch)	
			Ult Stress MPa(KSI)	Modulus GPa(MSI)								
I Class 1	0	294 (70)	1515(220)	117(17.0)	96(14.0)	30^{+3}_{-1}	1.55+.03 (.056±.001)	60 ± 2	<1	.127(.005)	(1.78-2.0) (.070-.080)	>615K(625°F)
	1/2hr @589K(600°F)	589(600)	757(110)	103(15.0)	41(6.0)							
	125hr@589K(600^{0}F)	589(600)	757(110)	103(15.0)	41(6.0)							
Class 3	0	294(70)	138(20)	1860(.27)	55(8.0) ▷1	58^{+3}_{-1}	1.40±.02 (.051±.001)	32 ± 2	<1	NA	3.18 (.125)	TBD
	½hr@589K(600^{0}F)	589(600)	69(10)	1378(.20)	28(4.0)							
	125hr@589K(600^{0}F)	294(70)	138(20)	1860(.27)	55(8.0)							
	125hr@589K(600^{0}F)	589(600)	69(10)	1378(.20)	28(4.0)							
	TEST METHOD		Section 8.11.1		Section 8.11.2	Section 8.7.1	Section 8.12.1	Sec. 8.12.3	Sec. 8.12.4			Section 8.12.5

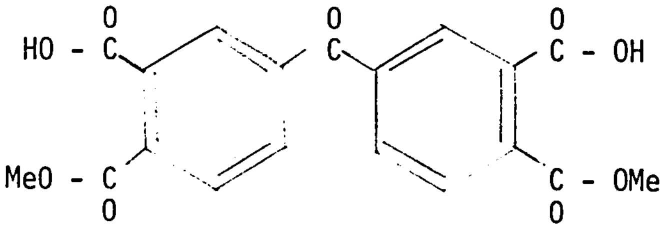
▷1 Tensile properties in place of Horizontal Shear Properties (Section 8.11.3)

▷2 Assume Specific Gravity of PMR-15 Resin to be 1.30 g/cc.
Assume Specific Gravity of Celion 6000 graphite fiber to be 1.76 g/cc.
Assume Specific Gravity of HTS-2 graphite fiber to be 1.66 g/cc.

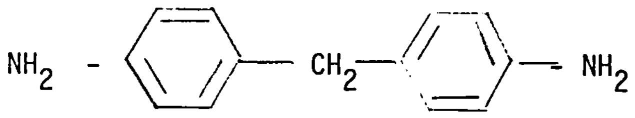
below with the following stoichiometries:

	Moles (Molecular weight)
BTDE	2.084
MDA	3.084
NE	2.000

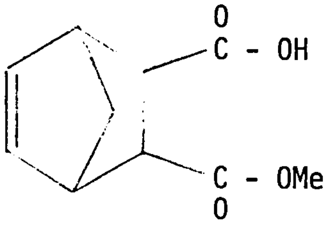
Dimethyl ester of 3,3', 4,4' benzophenonetetracarboxylic acid (BTDE)



4,4' methylenedianiline (MDA)



Monomethyl ester of 5-norbornene 2,3 dicarboxylic acid (NE)



5.7.2 CHEMICAL CHARACTERIZATION OF RESIN

5.7.2.1 Resin Relative Changes in Concentration

Using Method 8.2.1, the composition is acceptable if the material meets the requirements of Table III.

5.7.2.2 Gas Chromatograph Analysis of Resin Varnish

The resin varnish shall meet the following criteria using Method 8.3.

a. The retention time of the peak shall be identical to the time obtained from standard systems.

b. The area under the curves shall be within 10% of standard curves. (See Figures 1 and 2)

c. The only common solvent present that are not associated with decomposition products of PMR-15 resin shall be methanol.

TABLE III

Prepreg Chemical Property Requirements As Measured by Liquid Chromatograph

Elution Time (Minutes)	Elution Volume [2] Condition A		(Percent Area under peak) Condition B
7.23	7.80		6.00
7.82	23.0		16.90
8.67	38.0		12.90
9.33	--		11.50
9.81	--		13.80
10.90	17.0		9.80
11.69	1.0		[1]
12.45	2.0		
12.94	--		
13.91	--		
14.62	--		
15.11	--		
16.30	--		
16.79	--		[1]
18.19	4.0		4.10
20.18	2.0		[1]
20.90	4.0	9.6	5.60

[1] Below Computer threshold for detection

[2] Values shall be within ± 20 percent

5.7.2.3 IR Analysis of Resin Varnish

Using Method 8.4.2, the adsorption bands of the sample shall be superimposable on the IR spectrum shown in Figure 3. (Note: No imidization should be visible.)

5.7.2.4 Thermal Gravimetric Analysis Resin Varnish K (°F)

The TGA properties of the resin varnish supplied to this document shall meet the requirements of Table IV when tested in accordance with Method 8.6.1.

TABLE IV

TGA Properties of Resin Varnish

Types	Thermal Degradiation K (°F)	Weight Loss During Volatilization Percent	Outgassing Temperature K (°F)
Type I Class 1,2,3	625 (660)	14	525 (480)

5.7.3 RESIN SOLVENT

The use of methanol as a solvent to aid in obtaining suitable graphite prepreg is preferred over other solvent systems. No other solvent system may be present in graphite prepreg.

5.7.4 FOREIGN MATERIAL

There shall be no foreign or gelled material present in the PMR-15 varnish.

5.7.5 GRAPHITE YARN

5.7.5.1 Physical and Mechanical Properties of Graphite Yarn

The graphite used as the reinforcement in this document are designated by types (Section 2.1). The fibers used shall exhibit the properties shown in Table V and may contain an approved sizing. The prepreg manufacturer shall submit in writing verifying that the fibers used in tape manufacture meet the values of Table V. (Note: The actual test values on fiber lots can be obtained from the fiber manufacturer).

TABLE V

Minimum Strength and Maximum Weight Loss Properties of Graphite Fibers

Properties	Type I	Type II	Type III
Modulus GPa (MSI)	235 (34)	320 (50)	520 (70)
Specific Modulus 10^6m (10^6in)	13.5 (515)	16.5 (730)	29 (1106)
Tensile Strength MPa (KSI)	2760 (400)	2200 (320)	1860 (270)
Specific Tensile Strength 10^5m (10^6m)	160 (6.0)	0.90 (5.0)	0.9 (5.0)
Density (g/cm^3) (lbs/in^3)	1.75 (010625)	1.90 (9067)	2.07 (0.071)
Weight Loss After 125 Hours 589 (600°F) % W/W	1.0	1.0	1.0
Weight Per Unit Length of Tow (kg/m) (lbs./in)	780 (46)	760 (46)	800 (48)

6.0 QUALIFICATION

A manufacturer may begin to supply material only after qualification samples have been approved for all requirements of this document. In addition, each prepreg manufacturing facility must be qualified individually. The adequacy of the manufacturing facility may be verified, as deemed necessary, by company representatives, by a survey of such facilities. All requests for qualification shall be directed to the company's Materiel Department which will request data and samples when desired for qualification purposes.

a. The qualification samples shall consist of one representative production sample roll [2 meters (6 feet) for Class 1 and 0.5 kg (1.1 lb) for Class 3] of the particular type from each of a minimum of three separate resin mixes. Each type must be qualified individually.

b. The qualification sample submitted for approval shall be accompanied by a certified test report in duplicate which shows that the sample supplied meets the prepreg physical and chemical requirements and composite property requirements of this document. The supplier qualification report must contain:

   (1) Supplier product designation

   (2) Prepreg type in accordance with document

   (3) Test results including individual test values

c. All suppliers shall have test facilities or access to test facilities required to test in accordance with this document. (The chemical characterization requirements are included). The adequacy of test facilities may be verified, as deemed necessary, by company representatives by a survey of such facilities.

d. Qualification testing shall consist of a demonstration of the conformance of the sample supplied in accordance with Section 6.a to all of the requirements of this document.

e. This document requires approved supplier listing in the Qualified Products List Supplement to this document for preimpregnated materials and thereafter the materials and methods of manufacturer must not be changed without prior notification and approval in writing. A supplier's product designation is required for a specific formulation and any change in formulation requires a change in this designation as well as approval. Requalification after any change in formulation may be required, as deemed necessary.

7.0 QUALITY CONTROL

Material purchased to this document will be subjected to inspection to determine conformance to the requirements stated herein.

7.1 SUPPLIER QUALITY CONTROL

Supplier Quality Control shall provide a system of in-process records which assure product integrity. These records shall be made available to authorized company representatives.

a. The following tests shall be performed on each sample of prepreg obtained in accordance with Section 8.1.a.

Percent Volatile Content - Test in accordance with Section 8.6

Percent Resin Content - Test in accordance with Section 8.7

b. The following test shall be performed on the samples obtained from the first roll of each batch of prepreg.

Gel Time - Test in accordance with Section 8.8

IR - Test in accordance with Section 8.4

TGA - Test in accordance with Section 8.5

GPC - Test in accordance with Section 8.2

GC - Test in accordance with Section 8.3

7.2 SUPPLIER CERTIFICATION OR TEST RESULTS

The supplier must state, with each production shipment, that the materials and methods of manufacture have not changed from those used in the qualification sample (Section 6.a). A test report on the production batch shall also be supplied which contains test values demonstrating conformance of the tape to the requirements of this specification. Traceability of individual rolls of prepreg to master batches of graphite yarn shall also be provided. Actual weight and yardage of individual prepreg rolls shall be shown on the test report.

7.3 PURCHASER QUALITY CONTROL

a. Reject any rolls which are improperly packaged, i.e., punctured or poorly sealed bags.

b. Prepreg rolls must be allowed to warm to a temperature at which condensation will no longer form on the sealed bag prior to opening.

c. The areas where prepreg is exposed (for sampling and testing) shall conform to BSS 7001, Class 400,000.

d. Open the packaging bag only long enough to take the material sample required in accordance with Section 8.1.b and then heat seal the bag.

e. Quality Control tests shall consist of those tests listed in Table I through V except when material fails the chemical characterization tests, then the 125 hour, 589K (600°F) flexural ultimate stress and modulus and horizontal shear are final acceptance criteria. In the case of Class 3 material, the tensile ultimate and modulus are required.

f. Additional tests will be performed as deemed necessary to assure production shipments meet the requirements of this document, and that no changes have been made to the system since initial qualification.

g. All test data and records must be kept on file and be readily available for review.

8.0 MATERIAL TEST METHODS

8.1 SAMPLING

a. The supplier shall obtain a 2 meter (6 ft.) swatch at the start of roll No. 1 and from the end of each roll of prepreg.

b. The purchaser shall obtain a sample from a prepreg roll representing each unit of product included in the shipment. Multiple shipments from the same batch shall be treated as separate batches. Identify the sample by prepreg batch number and roll number. Sample size shall be

Type I Class 1 - 2 meters (6 ft.)

Type I Class 3 - 0.5 kg (1.1 lb.)

8.2 LIQUID CHROMATOGRAPH ANALYSIS PMR-15 GRAPHITE PREPREG

Prepare a composite sample by using a sharp 64mm (0.25 inch) punch to remove a circle of material. Discard any backing. Weigh and place in an 8ml. vial (Van Water and Rogers per 66011-085). Add 5.0mls of tetrahydrofuran and close vial with polyseal cap. Place on a mechanical shaker for 10 to 15 minutes. Remove solid material. Filter with a millipore or Waters Associates solvent Clarification kit into a clean 8ml vial. Inject 5μl of solution into column with the Liquid Chromatograph containing the following columns and settings.

Columns - 2 SE 60 duPont size exclusion columns
Sample Size - 5 μl
Solvent - 3:1 Water: tetrahydrofuran (water must be ultra pure and THF is uninhibited distilled in glass, filtered to .45) plus 1% W/V glycine and 0.5% W/V glutamic acid
Elution rate - 1 ml/minute
Chart speed - 10mm/minute or (0.4 in/minute)
UV wavelength - 254 mm
UV attentuation - x8
Temperature - 295 ± 2K (73 ± 3.6°F)

8.3 GAS CHROMATOGRAPH METHOD FOR POLYMER PMR-15 GRAPHITE PREPREG

A Hewlett Packard FM Scientific 5750 gas chromatograph or equivalent using the following parameters.

a. Sample size-1ml
b. Column-61 x 1/8 W98 @ 10%
c. Oven temperature-RT to 447K (347°F)
d. Detector-Flame Ionization Detector
e. Detector port temperature-523K (482°F)
f. Injection port temperature-498K (437°F)
g. Carrier gas
h. Carrier flow rate
i. Range
j. Attenuation
k. Chart speed

Before injecting the sample, stabilize the baseline. When the baseline is stabilized, inject the sample and mark the injection event as time zero. Allow time for all of the sample to clear the column and the baseline to stabilize again. Once the analysis is complete, program the column at 20K/min to upper limits of the column to assure that none of the sample is retained in the column.

8.4 INFRARED ANALYSIS OF PMR-15 GRAPHITE PREPREG

A Fourier transform spectrophotometer or equivalent using the following IR scan parameters:

a. resolution - 8.0 cm^{-1}

b. number of scans in sample beam - 16

c. number of scans in reference beam - 16

d. wave numbers per in. - 200

e. spectral range 500-4 cm^{-1} (standard plot)

Place a portion of the resin/solvent solution on a NaCl salt block after extracting from graphite tape using acetone. The sample shall be of sufficient thickness to produce a spectrum whose strongest bond indicates 15^{+5}_{-10}%T. Allow solvent to evaporate and scan the sample.

8.5 THERMAL GRAVIMETRIC ANALYSIS

8.5.1 THERMAL DEGRADATION

This test shall be performed using a Dupont 951 or equivalent while controlling the following variables:

a. Sample size 25-30 mg

b. Heating rate 5K/min (9^{o}F/minute)

c. Temperature range 273-1273K ($32-1832^{o}$F)

d. Atmosphere and flow rate 0.3L/minute, air

e. Y axis scale percent weight loss 0-100

The temperature of degradation is determined as the point of deviation from an extended baseline.

8.5.2 PERCENT VOLATILES

This test shall be performed using a Dupont 951 or equivalent while controlling the following variables:

a. Sample size 25-30 mg

b. Heating rate 5K/minute

c. Temperature range 273-1273K($32 - 1832^{o}$F)

d. Atmosphere and flow rate 0.3L/minute, air

e. Y-axis scale percent weight loss 0-100

The percent volatiles lost is determined to the temperature of degradation.

8.5.3 OUTGASSING TEMPERATURE

This test shall be performed using a Dupont 951 or equivalent while controlling the variable per paragraph 8.6.

The outgassing is determined as the point of deviation from an extended baseline.

8.6 PREPREG VOLATILE CONTENT

a. Obtain three specimens (2.0 to 4.0g) from each swatch obtained in accordance with Section 8.1 in a pattern that will be representative of the entire swatch.

The specimens taken near the edge must be at least one inch from the edge of tape. The specimens shall be identified by tape batch number, roll number, and specimen number.

b. Remove the release paper backing from each specimen, place in a tared aluminum dish and weigh to the nearest milligram. The aluminum dish with specimen is placed in an air-circulating oven regulated to 589 ± 5K (600 ± 10^oF).

c. Close the oven door and start a clock. After 30 minutes the aluminum dishes shall be removed and placed in a desiccator to cool. The specimens shall then be weighed to the nearest milligram.

$$\text{Percent Volatiles} = \frac{A - B}{A} \times 100$$

A = Weight of specimen before test

B = Weight of specimen after volatile removal

d. Report the average of three specimens

8.7 PREPREG RESIN CONTENT

Use either of the following methods for determining tape resin content.

8.7.1 RESIN CONTENT ACID DIGESTION

a. Transfer portions of the specimens accurately weighed (0.4 to 0.7g) after the determination of volatile content in accoradnce with Section 8.7 to a 80 ml glass beaker.

b. Carefully measure 50 mls of concentrated sulfuric acid into the beaker containing the devolatilized sample. Cover the beaker with a watch glass, place on hot plate and heat until white fumes are visible above the acid solution.

c. Maintain this condition for a minimum of 20 minutes or until the solution turns black. At this point, carefully add dropwise a 30 percent solution of hydrogen peroxide until the solution turns clear. Continue heating beaker for a minimum of one hour. During this period, add dropwise the hydrogen peroxide solution to clear the acid whenever the acid turns black. Cool the acid solution to room temperature, add 2 mls of hydrogen peroxide and heat until the white fumes appear. Continue heating for 10 minutes, then cool to room temperature. If acid turns black repeat the procedure until acid remains clear. (Note: This process shall be accomplished in a fume hood with air exchange)

d. Filter the acid solution using a fritted glass crucible (coarse), wash a minimum of three times with either distilled or deionized water and then with acetone. The glass crucibles are then dried at 338K (150^oF) in an air-circulating oven a minimum of 30 minutes, cooled to room temperature in a desiccator and weighed. The graphite yarn is then removed and the crucible weight obtained.

$$W_r = \frac{W_1 - W_2}{(W_1)} \times 100$$

W_r = Weight content of resin solids, % W/W

W_1 = Weight of devolatilized sample

W_2 = Weight of graphite yarn after acid digestion of the resin matrix

e. Report the average of three specimens.

8.7.2 RESIN CONTENT BY SOXHLET EXTRACTION

a. Take three specimens (2.0 - 4.0g) from the swatch obtained with Section 8.1 in a pattern that will be representative of the entire swatch. The specimens taken near the edge must be at least one inch from the tape's edge if the material is Type I, II, or III Grades 6 and 12. If the tape is Type I Grade 3 the sample must be the full width of the tape. If the sample is Class 3 of any type a random sample of molding compound shall be tested. The specimens shall be identified by tape or molding compound batch number, roll number and specimen number.

b. Remove the release paper from each specimen, and weigh specimen in a tared soxhlet extraction thimble to the nearest milligram.

c. Place the soxhlet extraction thimble into a soxhlet extraction apparatus. Fill the soxhlet flask three-fourths full of acetone and heat until acetone is gently refluxing. Continue heating until the acetone surrounding the extraction thimble is clear but no less than 60 minutes.

d. Remove the extraction thimble from the apparatus and dry in an air-circulating oven for 30 minutes then after cooling in a desiccator reweigh to the nearest milligram. (Note: Since the dried extraction thimble gains weight, take reading 20 secs. after removing from desiccator.)

$$\text{Wet Resin Content } W_{WR} = \frac{W_2}{W_1} \times 100$$

$$\text{Dry Resin Content } W_{DR} = \frac{W_2 - W_1V}{W_1 - W_1V}$$

W_{WR} = Weight content of wet resin solids %

W_1 = Weight content of original sample

W_2 = Weight content of extract

W_{DR} = Weight content of dry resin solids %

V = Volatile matter content of graphite tape (Section 8.2)

8.8 GEL TIME

a. Preset the temperature on a Fisher-Johns melting point apparatus to 477K (400°F).

b. Insert a 6.35m x 6.35mm, (0.25 x 0.25in) sample of prepreg between two cover glasses and place on the heated platform of the Fisher-Johns apparatus.

c. Start a stopwatch or timer and begin to probe on the top of the coverglass with a wooden pick.

d. Record the time when the resin gels. The gel point is reached when no resin movement is observed through the coverglass when moderate pressure is applied.

e. Report the gel time as the average of three or more determinations.

8.9 COMPOSITE FABRICATION FOR TEST (TYPES I, II, OR III CLASS 1)

a. The number of plies in the test composite shall be such that its cured thickness will be 1.90 ± .127mm (.075 ± .005 in).

b. Each composite shall be of sufficient size to permit testing to the requirements of the document.

c. For prepreg material of Condition A, cut the prepreg plies and stack them on a non-porous Teflon release fabric which has been previously placed on a metal caul plate.

d. Place on the top of the layup a layer of porous Teflon (Taconic # 7015 or equiv.) followed by 3 plies of Style 120 glass fabric, 3 plies of Style 181 glass fabric, a pressure plate and two additional plies of 181 glass fabric as a vent layer on top of the layup. Place metal bars parallel to fiber on the edge of the stacked prepreg to prevent fiber washing.

g. Seal the above assembly in a vacuum bag (Figure 3) in such a manner that no leaks occur and the vacuum source is in contact with the bleeder. Reduce vacuum level to 130mm (5 inches) Hg.

h. Cure in an autoclave in accordance with the temperature, pressure and vacuum profile shown in Process Specification D180-20545-5.

i. For prepreg material of Condition B - Cut the prepreg plies and stack them on a porous Teflon release fabric which has been previously placed on an aluminum caul plate containing 2 plies 181 style glass fabric.

j. Place an aluminum bar, touching the edge of the layup, to prevent fiber washing. Place on the top of the layup one layer of Celgard 4410 followed by 2 plies of 181 style glass fabric. Vacuum bag and heat stage as follows using partial vacuum 104-157mm (4-6 inches of Hg). Over a period of 30 minutes raise temperature to 410K (275°F) and hold for 2 hours. Cool under same vacuum pressure to ambient conditions and remove layup from vacuum bag.

k. Place the devolatized layup on a non-porous Teflon release fabric which has been previously placed on an aluminum caul plate.

l. Place on the top of the layup a layer of porous Teflon followed by 2 plies of Style 120 glass fabric 3 plies of 181, a pressure plate and two additional plies of 181 glass fabric as a vent layer on top of layup. Place aluminum bars parallel to fiber on the edge of the stacked tape to prevent fiber washing.

m. Seal the above assembly in a vacuum bag (See Figure 4) in such a manner that no leaks occur and the vacuum source is in contact with the bleeder. A minimum of 660mm (26 in) Hg shall be maintained on layup during cure.

n. Cure in an autoclave in accordance with the temperature, pressure and vacuum profile shown in Figure 5.

o. Remove vacuum bagging and bleeder materials from cured part, and postcure in an air-circulating over 4 hours, 602K (625^{o}F). Restraint of the laminate is required during postcure.

8.10 COMPOSITE FABRICATION FOR TEST (TYPES I, II OR III CLASS 3)

a. The quantity of chopped fiber molding compound in the test panel shall be such that its cured thickness will be 3.18 ± .25mm (.125 ± .010 inches).

b. Each panel shall be of sufficient size to permit testing to the requirements of the document.

c. The chopped fiber molding compound shall be introduced into a compression mold whose dimensions are 152 x 305mm (6 x 12 inches). The material shall be spread evenly over the mold and 0.7 mm (0.275) stops installed around the mold cavity. The mold is then introduced into a heated press at 373K (212^{o}F) and the mold closed to stops. Slowly raise the temperature to 477K (400^{o}F), remove stops after 60 minutes and apply sufficient pressure to close the mold. Heat the mold to 602K (625^{o}F) and hold for two hours. Cool press to below 336K (145^{o}F) and remove pressure.

d. Post cure the panel in an air circulating oven 4 hours at 602K (625^{o}F). Note: Part shall be restrained during post curing cycle.

8.11 COMPOSITE MECHANICAL PROPERTIES

Test the composites prepared in accordance with Section 8.11 as follows to demonstrate conformity to the requirements of Table II. Test a minimum of five specimens for each mechanical property.

8.11.1 FLEXURAL PROPERTIES

Determine ultimate flexural strength and modulus of elasticity in accordance with ASTM D790 as modified below. The flexural test specimen consists of a straight-sided rectangular cross section having the specified thickness. Span thickness ratio is maintained constant at 32 to 1. Nominal specimen length is 102mm (4 inches) but varies with thickness. The specimen width remains constant at 12.7 mm (0.5 in). The flexural specimens are loaded at quarter span points. Ultimate flexural strength is calculated with the following equation:

$$F_b = \frac{3PS}{4bt^2}$$

F_b = Stress in the outer fiber at failure,
P = Maximum load carried by specimen Newtons (lbs)
S = Major span meters (inches)
b = Width of specimen meters (inches)
t = Thickness of specimen meters (inches)

The modulus of elasticity is calculated as follows:

$$E_b = \frac{11}{64} \frac{S^3}{bt^3} m$$

E_b = Modulus of elasticity in flexure
S = Span (meters) inches
b = Width of specimen (meters) (inches)
t = Thickness of specimen meters (inches)

m = Slope of the initial straight line portion of the loading deflection curve. N/m (lb/in)

8.11.2 INTERLAMINAR SHEAR PROPERTIES

Determine ultimate interlaminar strength in accordance with ASTM D2344 as modified below. The interlaminar shear test specimens are short, rectangular cross-section bars that are loaded in a three-point flexure. Nominal specimen dimensions are the width at 6.4 mm(.25 in.) and the length being 25.4 mm(1 in).

The testing is accomplished on a flexure testing fixture using three-point loading with the span being equal to 4 times the specimen thickness. Interlaminar shear stress at failure is computed from the following equation:

$$T_i = \frac{3P}{4A}$$

T_i = Interlaminar shear stress kPa (ksi)
P = Total load at failure Newton (lbs)
A = Cross-sectional area m^2 (in^2)

8.11.3 TENSILE PROPERTIES

Determine ultimate tensile strength in accordance with ASTM D638. The tensile properties are computed using the following equation:

$$F_T = \frac{P}{A}$$

F_T = Ultimate tensile stress MPa (KSI)
P = Total load at failure Newton (lbs)
A = Cross section area, m^2 (in^2)

8.11.4 ISOTHERMAL AGING PROPERTIES

Isothermal aging tests shall consist of aging flexural specimens (Section 8.11.1) and interlaminar shear specimens (Section 8.11.2) at 589K ($600^{o}F$) for periods up to 125 hours in an air-circulating oven .

8.12 COMPOSITES PHYSICAL PROPERTIES

Test the composites prepared in accordance with Section 8.11 as follows to demonstrate conformity to the requirements of Table II. Test a minimum of five specimens for each physical property.

8.12.1 COMPOSITE SPECIFIC GRAVITY

Determine the specific gravity of the composite in accordance with ASTM D792.

8.12.2 COMPOSITE RESIN CONTENT

Determine the resin content of the composite as described by Section 8.7.1.

8.12.3 COMPOSITE FIBER VOLUME

Fiber content is determined from the results of Composite Specific Gravity (Section 8.12.1) and Composite Resin Content (Section 8.12.2) using the following equation:

$$F_v = (1 - R_c) \left(\frac{D_c}{D_F}\right) 100$$

F_v = Fiber volume on a percent basic

R_c = Weight percent resin in composite (Section 8.12.2)

D_c = Specific Gravity of composite (Section 8.12.1) g/cm^2 (lbs/in^3)

D_F = Density of Fiber Celion 6000-1.76 g/cm^2 (.064 lbs/in^3)

8.12.4 COMPOSITE VOID VOLUME

The composite void volume is determined from the results of Composite Specific Gravity (Section 8.12.1) and Composite Resin Content (Section 8.12.2) using the following equation:

$$V_v = 100 - D_c \left[\frac{R_c}{D_R} + \frac{100 - R_c}{D_F}\right]$$

D_c = Specific Gravity of Composite in grams/cubic centimeters

R_c = Weight percent resin in composite

D_R = Density of PMR-15 resin 1.30 g/cm^2 (.050 lbs/in^3)

D_F = Density of Graphite Fiber Celion 6000-1.76 g/cm^3 (.064 lbs/in^3)

8.12.5 PROCEDURE FOR T_G DETERMINATION OF MULTI-LAYER LAMINATES

8.12.5.1 EQUIPMENT

A. DuPont Model 990 Thermal Analyzer

B. DuPont Model 943 Thermomechanical Analyzer (TMA)

8.12.5.2 EQUIPMENT PARAMETERS

A. X-Axis

1. Scale (°C/inch): 50
2. Programmed Heating Rate (°C/minute): 5
3. Shift (inches): 0

B. Y-Axis

1. Scale (mils/inch) 1.0 (Attenuate as Needed)
2. Probe Load (grams) 5 (Attenuate as Needed)

C. Expansion Probe - Quartz with .100 inch diameter Flat End

8.12.5.3 SAMPLE PARAMETERS

A. Nominal Face Size: 4.76mm (.1875 in) x 4.76mm (.1875 in)

B. Number of Layers: 4 or more

C. Top and Bottom Faces should be parallel with no burred edges

8.12.5.4 DATA

A. On a typical Thermogram of a Laminate sample, the T_G is taken as the extrapolated value where the sample undergoes an increase in its apparent thermal expansion.

B. All measurements are made in air.

9.0 MATERIAL IDENTIFICATION

Each roll of tape shall be permanently and legibly marked with a tag placed on the roll core. The tag shall contain all of the items listed in Section 10.c, except the date of shipment.

10.0 PACKAGING AND MARKING

a. Individual rolls of material shall be packaged in sealed bags meeting the requirements of MIL-B-117.

b. Additional packaging (shipping containers) shall be sufficient to assure safe delivery of the material. Material shall be maintained at 254K maximum (0°F) during shipment.

c. Each roll of graphite tape shall be permanently and legibly marked on the container to give the following information:

1) PMR-15 Resin preimpregnated graphite tape

2) Boeing Document D180-20545-4 and Type Number, Class Number and Grade

3) Batch Number

4) Roll Number

5) Graphite Fiber Master Lot Number(s)

6) Graphite Tape Width

7) Boeing Purchase Order Number

8) Manufacturer

9) Manufacturer's Product Designation

10) Date of Impregnation

11) Date of Shipment (on container tag only)

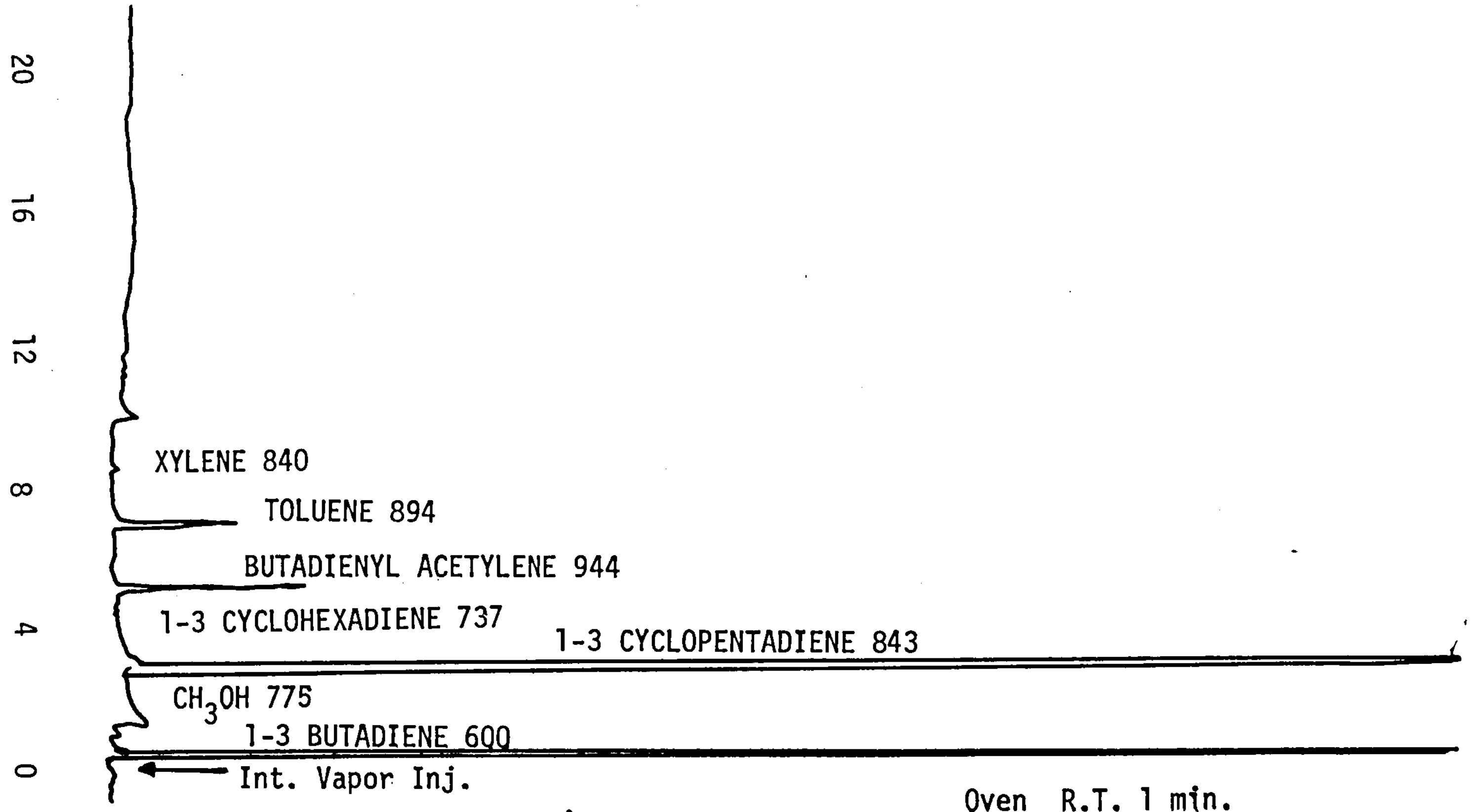
12) Volatile Content

13) Gel Time (first and last rolls only)

14) Resin Content

In addition, each package roll must bear in red letters, at least 1.9 cm (0.75 in) high, the following statement:

"TEMPERATURE MUST BE MAINTAINED AT 254 ± 5 K (0 ± 10°F)



HTS/PMR-15

Pyrolysis Vapor

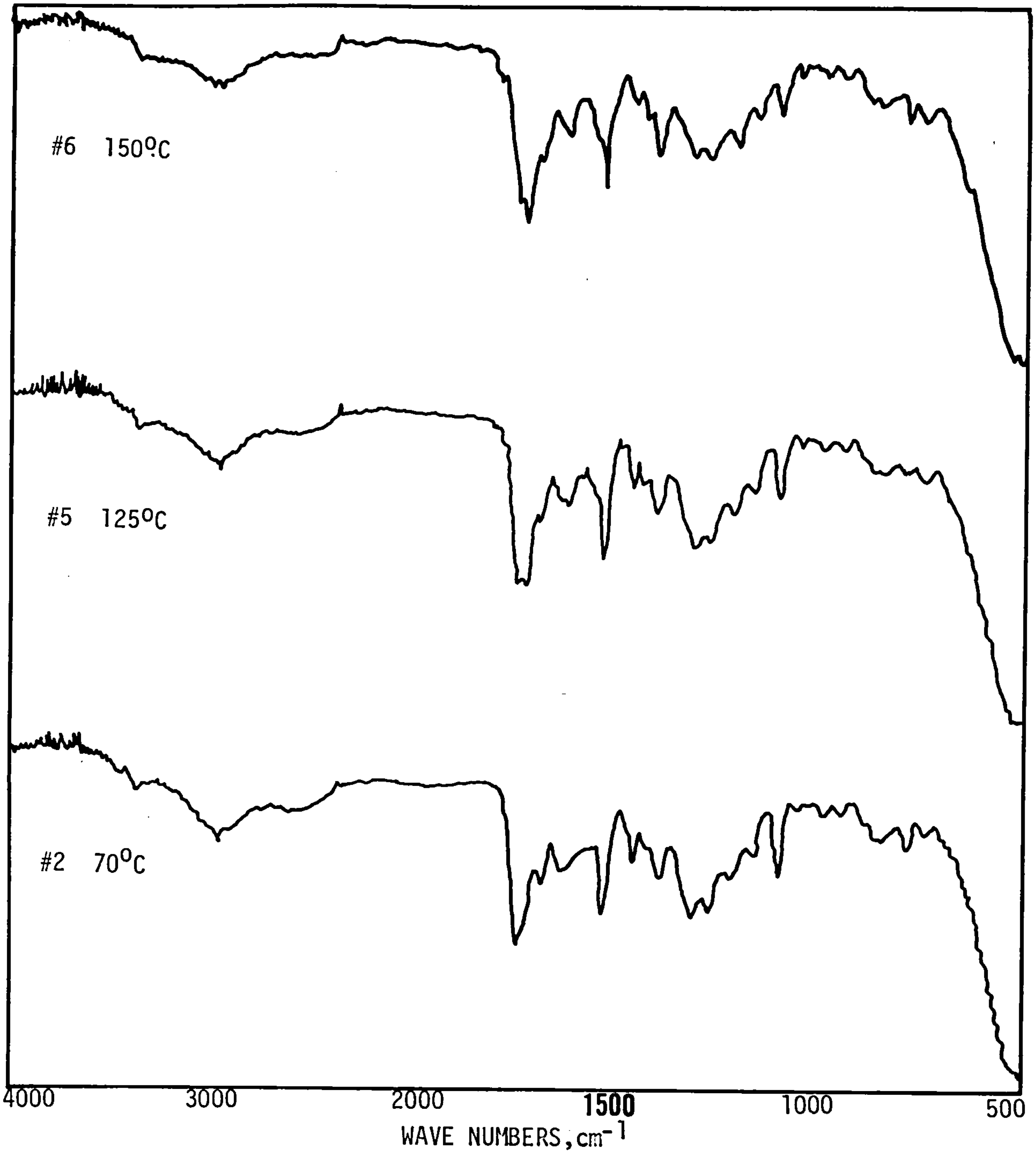
Oven R.T. 1 min.
Progress to 175°C @ 15°C/min.
Range 10^{-11} x 256
Ch. Sp. .25"/min.

STANDARD GAS CHROMATOGRAM GRAPHITE/ PMR-15 PREPREG

FIGURE 1

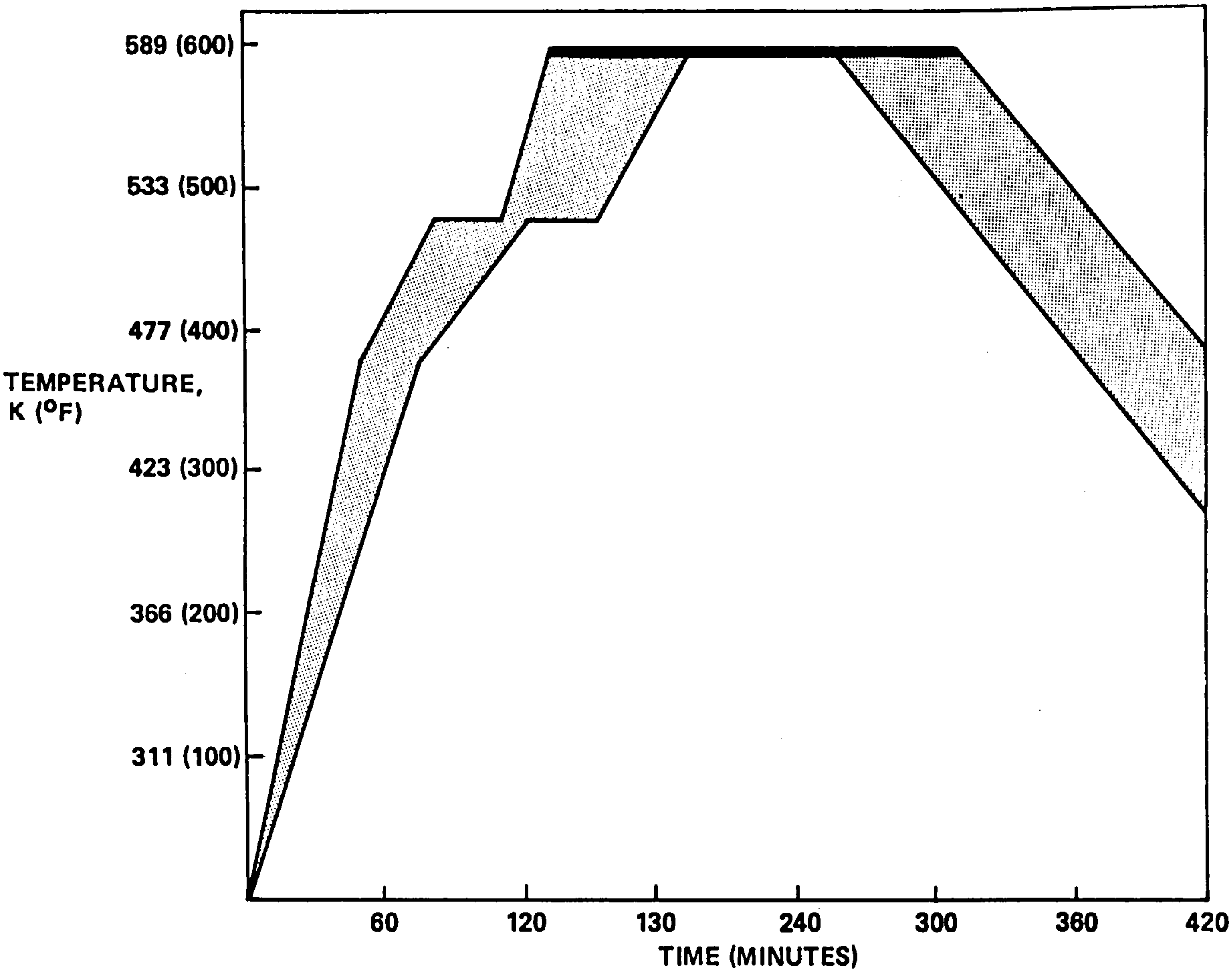
STANDARD MASS CHROMATOGRAM GRAPHITE/ PMR-15 PREPREG

FIGURE 2



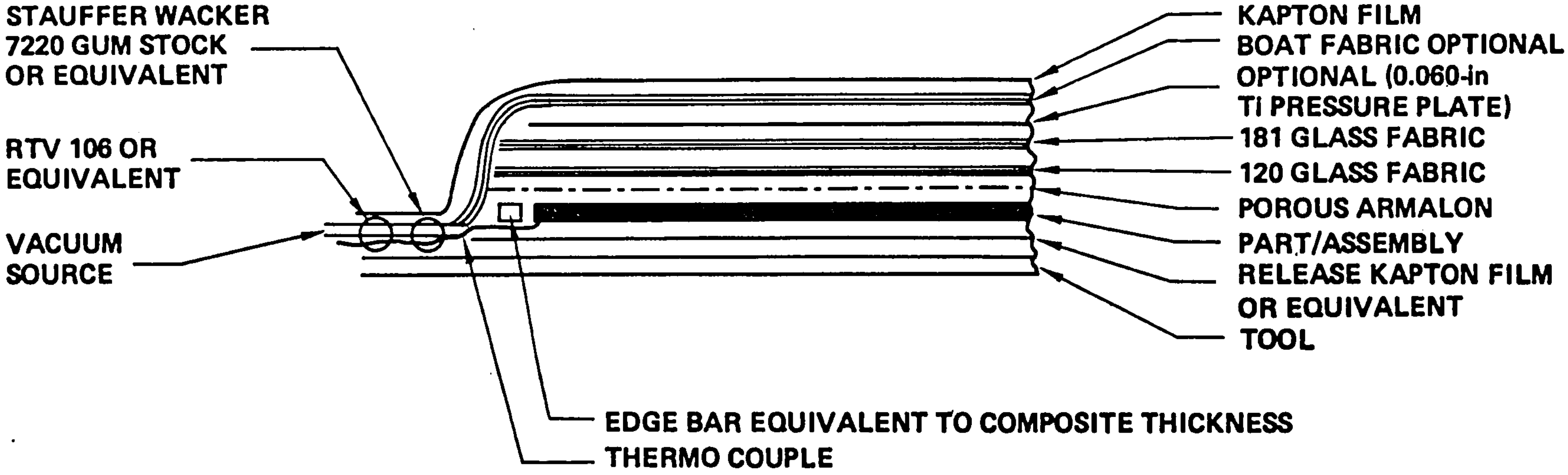
STANDARD FTS IR CURVES GRAPHITE/PMR-15 PREPREG

FIGURE 3



GRAPHITE/PMR-15 COMPOSITE CURE CYCLE

Figure 4



VACUUM BAG SCHEMATIC

Figure 5

APPENDIX B3

DOCUMENT NO. D180-20545-5

TITLE: PROCESS SPECIFICATION FOR PMR-15/GRAPHITE PREPREG

ABSTRACT

Process requirements are specified for Graphite/PMR-15 polyimide prepreg. The requirements include the materials, facilities and equipment required for the fabrication of structural elements. The structural elements includes flat laminates contoured parts such as Hat sections, Corrugations, "I" Beam Sections, and sandwich panels from unidirectional prepreg or graphite woven fabric prepreg. Also included is a method for fabrication of Graphite/PMR-15 chopped fiber molded parts. Quality control requirements are also included in the document.

KEY WORDS

PMR-15 Polyimide
Graphite Tape
Graphite Fabric
Chopped Fiber Molding Compound
Structural Elements
Flat Laminates
Polyimide Fiberglass Honeycomb Core

TABLE OF CONTENTS

Page

TABLE OF CONTENTS (CONT.)

TABLES

FIGURES

1.0 SCOPE

This document establishes the requirements for fabrication of unidirectional tape and woven fabric graphite/PMR-15 polyimide autoclave cured structural parts.

In case of conflict between this document and engineering drawings, the engineering drawings shall have precedence.

2.0 CLASSIFICATION

This process document for structural composite parts shall consist of the following methods:

Method I Graphite Prepreg (D180-20545-4 Condition A), Type I, II, or III Class 1 or 2	Unidirectional graphite prepreg or woven graphite fabric preimpregnated with PMR-15 polyimide resin requiring surface bleed for laminate structure and a polyimide adhesive for honeycomb sandwich bonding. (Note: The type of prepreg designates the reinforcement modulus whereas the Class designates unidirectional or woven fabric prepreg). Use D180-20545-4 Condition A Material
Method IA Same as Method I	Same as Method I except use D180-20545-4 Condition B Material.
Method II Graphite Prepreg (D180-20545-4), Type I, II or III, Class 1	Chopped graphite fiber preimpregnated with PMR-15 polyimide resin requiring compression molding techniques for fabricating composite parts. (Note: The type of Molding Compound designates the reinforcement modulus whereas the Class designates the chopped fiber prepreg).

3.0 REFERENCES

Except where a specific issue is indicated, the current issue of the following references shall be considered a part of this document to the extent indicated herein:

a.	ASTM D790	Test for Flexural Properties of Plastic
b.	ASTM D2344	Test for Apparent Horizontal Shear Strength of Reinforced Plastics by Short-Beam Method
c.	D180-20545-4	Material Specification for PMR-15/Graphite Prepreg
d.	D6-44613	Qualification of Sources for Advanced Composite Parts
e.	MIL-STD-401	Military Standard Sandwich Construction and Core Materials: General Test Methods

4.0 DEFINITIONS

a. Batch of Prepreg - Prepreg containing reinforcement impregnated with one batch of resin in one continuous operation.

b. Bleeder - A porous material used to absorb excess resin during cure or to provide a path for reaction products removal.

c. Bridging - A condition where one or more plies of prepreg tape or fabric span a radius, step, or chamfered edge of core without full contact.

d. Buckle Line - A line of collapsed cells, two to three cells wide, with undistorted cells on either side. (Buckle lines generally appear on the inner radius of the formed core).

e. Core Crush - A collapse, distortion, or compression of the core.

f. Core Depression - A localized indentation or gouge in the core.

g. Core Separation - A partial or complete breaking of the core node bond.

h. Core Splicing - The joining of segments of core by overlapping each segment two to four cells and then drawing them together.

i. Delamination - A separation of graphite plies from each other and/or facing plies from core which can occur during cure or finishing operations.

j. Doubler Ply - Partial plies which extend to areas over honeycomb in sandwich structures.

k. Inclusions - Foreign material particles, chips, films, etc. of varying sizes which are not desired and/or are detrimental to part integrity.

l. Inner Facing - That side of the panel which is cured against the vacuum bag.

m. In-Process Control Form - An outline of the fabrication steps and materials used to prepare a part.

n. Layup Area - The fabrication area where prepreg is cut, plies, assembled or kitted.

o. Prepreg Lot - Material from one batch, submitted for acceptance at one time.

p. Outer Facing - That side of the panel which is cured against the tool (mold, mandrel, etc.).

q. Pin Holes - Small cavities that penetrate the surface of a cured part.

r. Ply Wrinkle - A condition where one or more of the plies are permanently formed into a ridge, depression, or fold.

s. Process Control Record - A record of the materials, process, and process control panel test results.

t. Resin Richness - An area of excess resin, usually occurring at radii, steps, and the chamfered edge of core.

u. Resin Ridge - A sharp buildup of resin on the surface of a part.

v. Resin Starved - An area deficient in resin, usually characterized by excess voids and/or loose fibers.

w. Telegraphing - The dimpling of the composite plies into the core cells.

x. Void - An empty, unoccupied space in an assembly. Voids are associated with bridging, resin starved areas, and processing conditions.

5.0 MATERIALS CONTROL

5.1 DELIVERABLE MATERIALS

The materials listed below are incorporated into the part during fabrication, and must be procured from approved sources.

	Material	Source
a.	D180-20545-4, "Material Specification for PMR-15/Graphite Prepreg"	Qualified Vendor
b.	Polyimide Adhesive, A7F, "Polyimide Paste Adhesive"	Qualified Vendor
c.	Honeycomb Core, HRH 327, kg/m^3 (5.0 lb/in^3) Density, "Reinforced Plastics Honeycomb Core for Continuous Elevated Temperature Service 505-589K (450-600°F)"	Hexcel

5.2 CONTROLLED EXPANDABLE MATERIALS

	Material	Source
a.	Parting Film Materials	
	(1) FEP Film, 1 mil thick	E.I. duPont de Nemours
	(2) Teflon Film, Nonperforated	E.I. duPont de Nemours
	(3) Teflon Release Fabric, Porous, Type 7015	Taconic
	(4) Teflon Release Fabric, Nonporous Type 382-3	Port Plastics
	(5) Celgard 4410 Microporous Film	Celanese

6.0 FACILITIES CONTROL

6.1 LAYUP AREA

The layup area shall be controlled, as a minimum, to the following:

a. Operation of internal combustion engines within the area is prohibited.

b. Motors and equipment which distribute, in any way (spray, throw, etc.) visible droplets of oil, grease, or other lubricants onto the hardware or surfaces which contact the hardware, are prohibited.

c. Operations that generate nonvolatile hydrocarbons are prohibited.

d. Seal and/or cover floors with nonflaking, easily cleaned material, such as plastic, paint, tile, etc.

e. The floors shall be cleaned at least once each working day by vacuum in which the exhaust air is vented outside the work area or filtered, or with polyethylene glycol treated or water damp mops.

f. Waxes, compounds containing uncured silicone, or any material detrimental to adhesion are not allowed in the layup area.

g. All materials, tools, parts, or equipment taken into the area shall be free of dirt, grease, oil, or other contaminants detrimental to adhesion.

h. No eating or smoking is allowed in the layup areas.

i. Personnel (handling prepreg and details that have not completed cure or bond fabrication steps) who do not use the protective creams specified in Section 5.2.c shall at all time keep their hands clean and free of materials detrimental to adhesion.

j. Layup areas shall be separated or isolated from operations or conditions that generate excessive particulate matter (machining and sanding operations, open outside doors, etc.).

k. It is recommended that the temperature in layup and holding areas be maintained at 287 to 304 K (60 to 90^{o}F) and 50% maximum relative humidity.

6.2 EQUIPMENT

a. Autoclave - Use a heated air or gas circulating autoclave to provide the temperatures, heat-up rates, vacuum, and pressure required by this document.

b. Oven - Use a circulating air heated oven equipped with vacuum facilities to provide the vacuum and temperatures required by this document.

c. Temperature Recording Device - Use a multipoint temperature recording device to provide for recording the thermal history of a part while undergoing cure and/or postcure as required by this document.

6.3 MOLDS

a. The mold surface must be nonporous, and free of cracks, pits, and any other irregularities that would affect the quality of the part.

b. The mold must be capable of withstanding indefinitely a temperature of 615K (650°F) at 710mm (28 inches) of mercury vacuum pressure without warping and must not hinder the part on the mold from meeting the cure cycle of this document.

6.4 REFRIGERATED STORAGE

A storage area capable of maintaining temperatures at 254 ± 5K (0 ± 10°F) is required for storage of the prepreg and adhesive.

7.0 MANUFACTURING CONTROL

7.1 STORAGE AND HANDLING OF MATERIALS

7.1.1 PREPREG MATERIALS

a. Store rolls or precut kits of prepreg material in sealed polyethylene bags in accordance with D180-20545-4 material specification. An identification label must accompany the material, inside the bag, with the following information: material type, class, grade, supplier name and designation, batch number, roll number, and date of kit preparation.

b. Method I and II materials shall be allowed 240 hours work life at room temperature before being retested to the requirements of the applicable specification. Retest shall be identical to original receiving inspection tests. Requalified material shall be allowed 160 hours work life before another set of requalification tests is required.

c. When removed from cold storage for use, the prepreg shall remain sealed until it reaches near ambient temperatures (i.e., such that no condensation forms on the outside of the film wrapper).

d. Prepreg rolls that have been partially used can be refrozen only if placed in sealed polyethylene bags. Follow Sections 8.1.1.b and 8.1.1.c for future use.

7.1.2 HONEYCOMB CORE

a. The honeycomb core shall be stored in an original shipping or other suitable container prior to its use in the fabrication of details.

b. Once the core has been cut to size for fabrication, and clearly identified as specified by drawing, the core must be stored in a manner that does not cause core damage or contamination from grease, oil, dirt, and other foreign material detrimental to bonding.

7.1.3 ADHESIVE MATERIALS

Adhesive materials shall be stored and handled for production use as required by their respective specifications.

7.2 PRODUCTION PART IDENTIFICATION

a. Identify each production part with the following information:

   (1) Drawing or part number

   (2) Unit serial number

   (3) Date of manufacture

   (4) Manufacturer's identification

b. Maintain traceability of the completed part to specific processing information and material identification used in the fabrication of that part.

c. Record processing information and material identification used in fabrication on the Process Control Record specified in Section 9.2.d.

7.3 PREPARATION OF MATERIALS

7.3.1 ADHESIVES

Prepare the adhesives for assembly as instructed in their applicable process specification.

7.3.2 PREPREG MATERIAL

Note: To prevent dermatitis, clean, white, lint-free gloves or approved protective hand creams should be used.

a. After removal from freezer, keep prepreg material in polyethylene bags until condensation does not form on the exterior when wiped.

b. Prepreg material must remain free of contaminants during handling.

c. Do not remove prepreg backing until the prepreg is used.

7.4 PREPARATION OF MOLD

Mold surfaces shall be prepared by first cleaning with methyl ethyl ketone (MEK). Parting films described in Section 5.2.a or mold releases described in Section 5.2.b are applied to mold surface prior to part fabrication. Mold releases that are applied to a clean mold shall be baked for 30 minutes at 393K (250°F) prior to start of layup. Mold releases may be air dried for 30 minutes minimum at ambient temperature when applied to a tool surface that has had a 393K (250°F) baked mold release applied previously.

Note: Do not MEK wipe a mold surface on which a mold release has been applied and is to be used for immediate part fabrication. MEK will remove the mold release.

		Material	Source
b.		Mold Release Materials	
	(1)	Frekote FR 33	Frekote, Inc.
	(2)	Mold Release, R671	Dow Corning
c.		Protective Hand Cream (Personnel Protection)	
	(1)	Liquid Glove	Physicians Formula, Inc.
	(2)	Kerodex Hand Cream	Ayerst Lab., Inc.
	(3)	SP 128	Pacific Chemical
	(4)	Gloves, Teflon or Nylon, knitted	W.S. Shamban Corp. Newberry Park, CA
d.		Vacuum Bag Material	
	(1)	Kapton Film, 2 mil (200H)	Fralock Lockwood Industries Van Nuys, CA or DuPont
	(2)	Stauffer Wacker 7220 Gum Stock or equivalent	Stauffer Wacker
	(3)	RTV-102	General Electric
	(4)	Extruded Sealing Compound Schnee-Moorhead #5144	Schnee-Moorehead Chemicals, Inc.
e.		Solvents	
	(1)	Acetone, in accordance with military specification 0-A-5	QPL
	(2)	Methyl Ethyl Ketone in accordance with military specification TT-M-261	QPL
	(3)	Dimethylformamide, Reagent Grade	Wilshire Chemical
	(4)	N methyl pyrrolidinone, Reagent Grade	Wilshire Chemical
	(5)	Methanol, Absolute	Open
f.		Bleeder and Breather	
	(1)	Type 120 Glass Fabric (Bleeder Only)	Open
	(2)	Type 181 Glass Fabric (Bleeder Only)	Open
	(3)	Fiberglass Tape	Open

7.5 FABRICATION REQUIREMENTS

7.5.1 GENERAL REQUIREMENTS

a. Cloth splices in laminates and all sandwich facings - Graphite fabric prepreg lap splices shall be $1.27^{+1.27}_{-0}$ cm ($0.50^{+0.50}_{-0}$ inch). Stagger splices of individual plies within a layup at a minimum of 2.54 cm (1.00 inch). Butt splices are not allowed unless specified by drawing.

b. End tape splices - Cut end tape splices in laminates and over minimum gage sandwich facings and doublers shall be overlapped a minimum of 1.27mm (0.05 in.) and separated/staggered in individual plies a minimum of 2.54 cm (1 inch). Butt end tape splices are not allowed unless specified by drawing.

c. Over Lapping Butt Splices - Exterior (tool surface) unidirectional tape used in sandwich face skins shall have an overlap parallel to the fiber direction of 2.54 ± 2.54mm (0.10 ± .010 inch). Such overlaps shall be separated by a minimum of 2.54 cm (1 inch) between individual plies.

d. Gaps in Butt Splices - Graphite prepreg splices shall be made from tape with a squared edge and shall be butt jointed with the aid of methyl alcohol or application of heat. The butt splices shall have a maximum gap of 0.25 mm (0.010 inch).

e. Adhesive splices - Adhesive film shall be butt spliced maximum 1.5 mm (0.060 inch) gap.

f. Ply orientation - All angularity specified shall be based on fabric warp direction or parallel to tape fiber direction. Orient the warp direction fabric or unidirectional tape as specified with respect to the direction indicator on each detail. The tolerance of each fabric warp ply shall be ±5 degrees and ±3 degrees for unidirectional tape plies unless otherwise specified on the drawing. The drawing shall also specify options, such as (0 degrees/90 degrees), (+45 degrees or -45 degrees), etc. Individual ply directional tolerances shall not be enforced around corners, sharp contours, and highly complex compound contoured parts.

g. Autoclave pressure - Autoclave pressure for laminate structure shall be full vacuum augmented by 1378^{+70}_{-0} kPa (200^{+10}_{-0} psi). Autoclave pressure for sandwich structures shall be 689^{+70}_{-0} kPa (100^{+10}_{-0} psi). Pressure for all structures shall be maintained until temperature is reduced to below 338 K (150°F) upon completion of cure.

h. The use of methyl alcohol is permitted to facilitate layup. If methyl alcohol is used, allow layup to stand at ambient conditions for a minimum of 16 hours. The use of a heat gun or heat blanket is also permitted if part temperature does not exceed 316K (110°F).

i. Do not cut previously applied plies during layup of new plies. Trim upon completion of layup.

j. Application of Vacuum Pressure

(1) Apply vacuum pressure to the part. Approved vacuum bag materials and rubber pressure pads shall not come in direct contact with the prepreg layup, but shall be separated by one of the parting films listed in Section 5.2.a.

(2) Apply full vacuum 610mm (24 inches) of Hg minimum and make the bag conform to the shape of the part. Then check for leaks by disconnecting the vacuum line. The vacuum gage reading must not drop more than 127mm (5 inches) of Hg in 5 minutes.

k. Cure - Follow cure cycles for each material as specified in Sections 7.5.1.n and 7.5.1.o.

l. Thermocouple Requirements

(1) A minimum of one thermocouple in the thickest area of the part or tool shall be required for each 1 square meter (10 square feet) or fraction thereof. Each part shall contain a minimum of two thermocouples.

(2) If a thermocouple failure occurs (as indicated by erratic temperature response), that thermocouple shall be discounted.

m. Cure Cycle Requirements (Method I) (Also See Figure 1)

(1) Place layup (Figure 2) in an autoclave and attach a vacuum source capable of maintaining 100-150mm (4-6 inches) Hg vacuum level.

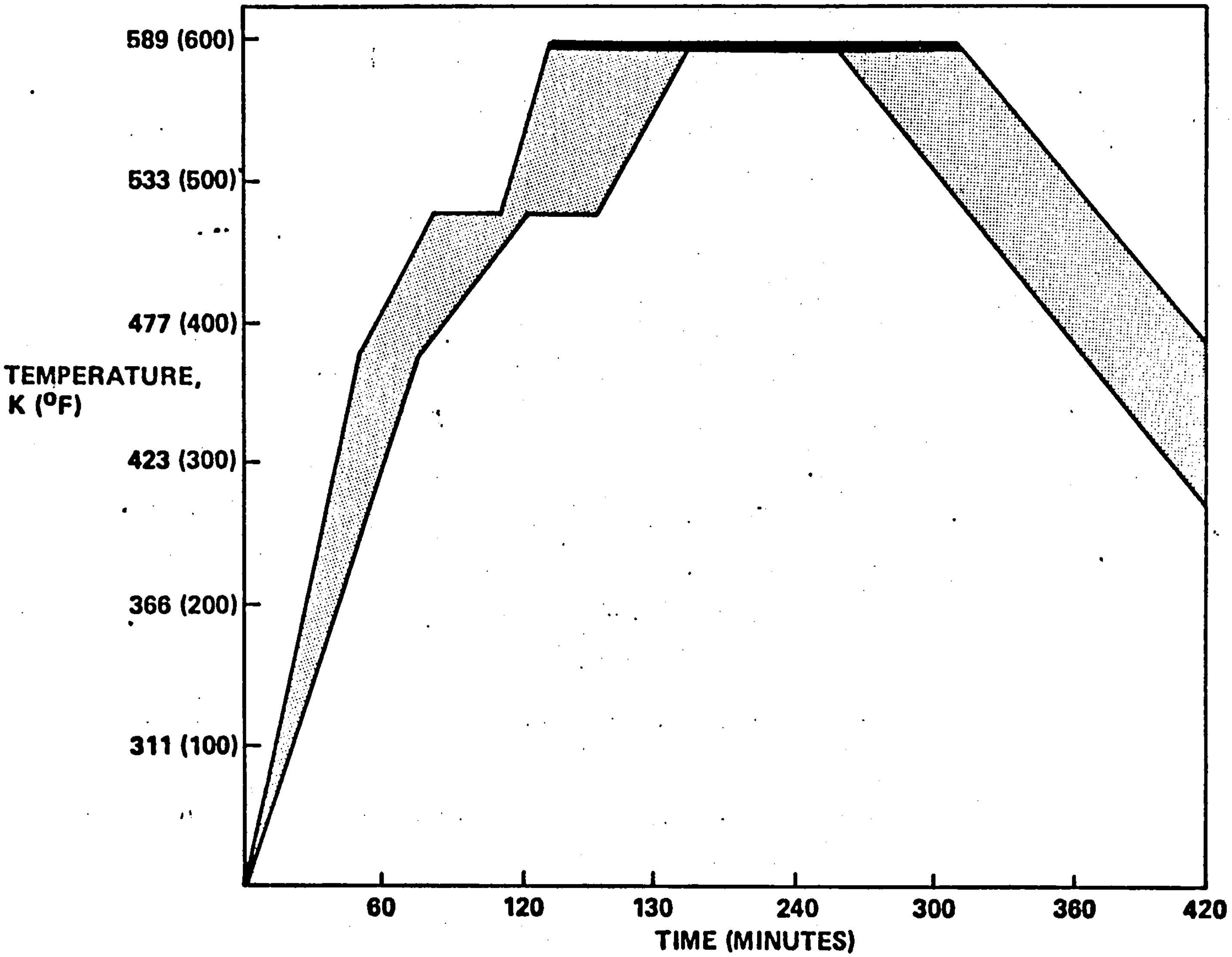
(2) Heat the part/assembly to 463^{+5}_{-0}K (375^{+10}_{-0} $^{\circ}$F) at the rate of 2.0-3.0°K (4 to 6°F) per minute. Change heating rate at 463^{+5}_{-0}K (375^{+10}_{-0} $^{\circ}$F) to 1.1-1.7K (2-3°F) per minute to 522^{+5}_{-0} K (480^{+10}_{-0} $^{\circ}$F).

(3) After the part/assembly has been held for 30 minutes at 522^{+5}_{-0} $^{\circ}$K (480^{+10}_{-0} $^{\circ}$F), apply 610mm (24 inches) Hg vacuum minimum and 1379 kPa (200 psi) positive pressure for the remainder of the cure cycle.

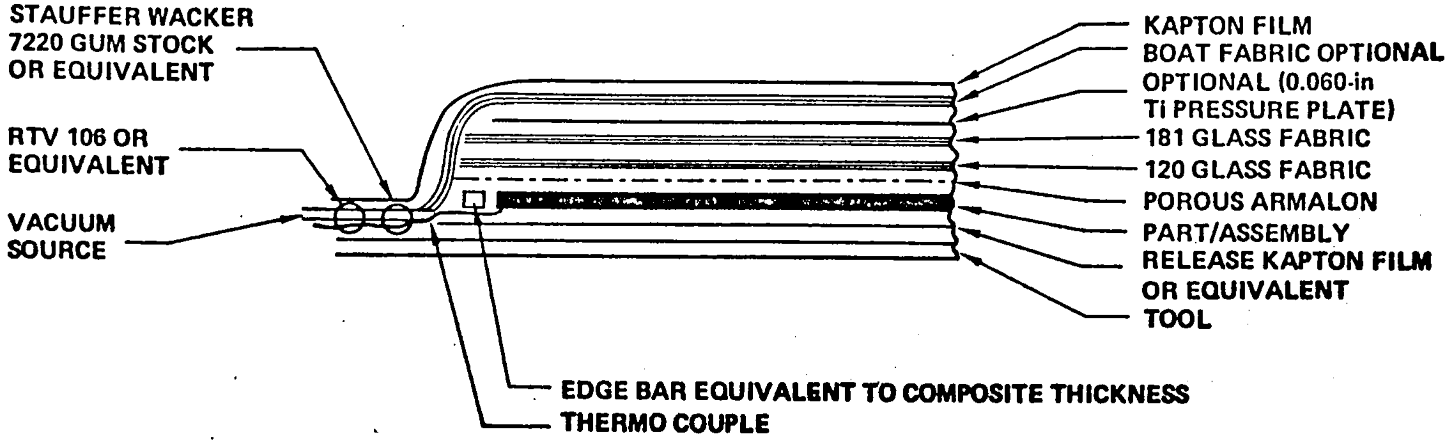
(4) After the 1379 kPa (200 psi) positive pressure has been applied, heat part/assembly at the rate of 1.5-2.5 K (3-5°F) per minute to $589^{+0}_{-5.6}$K (600^{+0}_{-10} $^{\circ}$F). Hold at 589 K (600°F) under pressure for 120^{+10}_{-0} minutes.

(5) Cool the part/assembly under pressure at the maximum of 1.1K (2°F) per minute.

(6) When the part temperature falls below 322K (120°F) pressure can be released and the part removed from the autoclave.

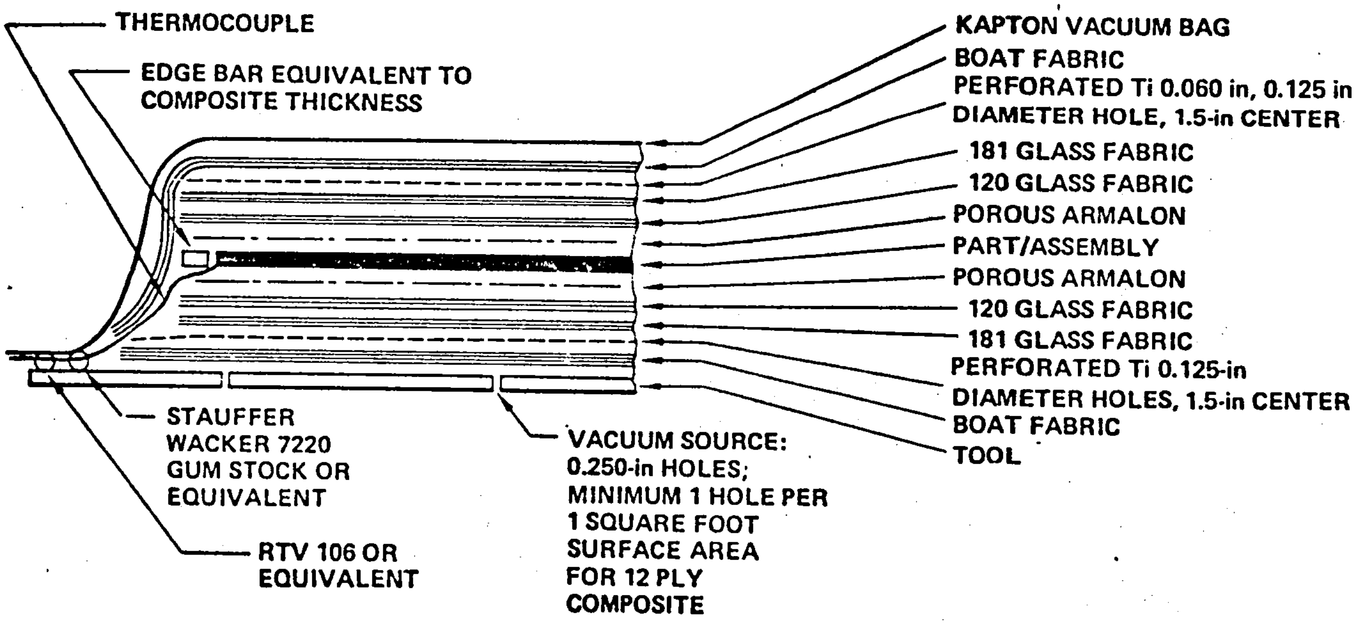


CURE CYCLE GRAPHITE/PMR-15 GRAPHITE POLYIMIDE PREPREG
(D180-20545-4, TYPES I, II, OR III CLASS 1 OR 2) METHOD I
FIGURE 1



TOP BLEED SYSTEM FOR COMPOSITES

FIGURE 2



DOUBLE BLEED SYSTEM * FOR COMPOSITES

FIGURE 2A

***Double bleeder system required on parts exceeding 9 square feet or 8-ply laminate, 6 square feet of 12-ply laminate, and 1 square foot of 24-ply laminate**

(7) After removal of the part/assembly from vacuum bag, postcure in an air circulating oven 6 hours at 602K (625°F). (Note: Part shall be restrained during postcure cycle with Armalon release fabric and minimum of 3 plies 181 glass fabric in contact with part/assembly). Heat up rate to 602K (625°F) shall be 2.0-3.0K (4-6°F) per minute with the cool down rate not to exceed 1.1K (2°F) per minute. Part/assembly temperature shall not exceed 322°K (120°F) before restraining devices are removed.

n. Staging Cycle Requirements (Method IA, Step 1) (Also see Figure 3).

(1) Place layup, as shown in Figure 4, in an autoclave or oven and attach a vacuum source capable of maintaining 100-150mm (4-6 inches) Hg vacuum level requirement for duration of precure.

(2) Heat the part/assembly to 338^{+5}_{-0} K (150^{+10}_{-0} °F) at the rate of 2.0-3.0 K (4 to 6°F) per minute.

(3) After the part/assembly has been held for 60 minutes at 338 K (150°F), raise the autoclave or oven temperature to 407^{+5}_{-0} K (275^{+10}_{-0} °F) at the rate of 1.5-2.5 K (3-5°F) per minute. Hold at 407 K (275°F) under 100-150mm (4-6 in Hg) vacuum for 120 $^{+10}_{-0}$minutes.

(4) Cool the part/assembly to below 332 K (140°F) before releasing vacuum pressure and removing from autoclave or oven.

o. Cure Cycle Requirements (Method IA, Step 2) (Also see Figure 5)

(1) Place layup, Figure 2 in the autoclave under vacuum pressure (no positive pressure) of 610mm (24 inches) of Hg, minimum.

(2) Heat the part/assembly to 476^{+5}_{-0} K (400^{+10}_{-0} °F), at the rate of 2.0-3.0 K (4 to 6°F) per minute.

(3) After 5 minutes at 476 K (400°F), pressurize the autoclave to 1379^{+69}_{-0} kPa (200^{+10}_{-0}psi) over a 5 minute period.

(4) Autoclave pressure is to be held at 1379 kPa (200 psi) throughout the cure for laminates. Autoclave pressure for honeycomb sandwiches is 689 kPa (100 psi). Maintain a vacuum under the diaphragm of 610 (24 inches) of Hg, minimum.

(5) After the part/assembly has been held for 60 minutes at 476 K (400°F), raise the autoclave temperature at the rate of 1.5-2.5°K (3-5°F) per minute to 589 K (600°F). Hold at 589 K (600°F) under pressure for 120^{+10}_{-0} minutes.

(6) Cool the panel under pressure at the maximum of 1.1K (2°F) per minute.

(7) When the part temperature falls below 332 K(120°F) pressure can be released and the part can be removed from the autoclave.

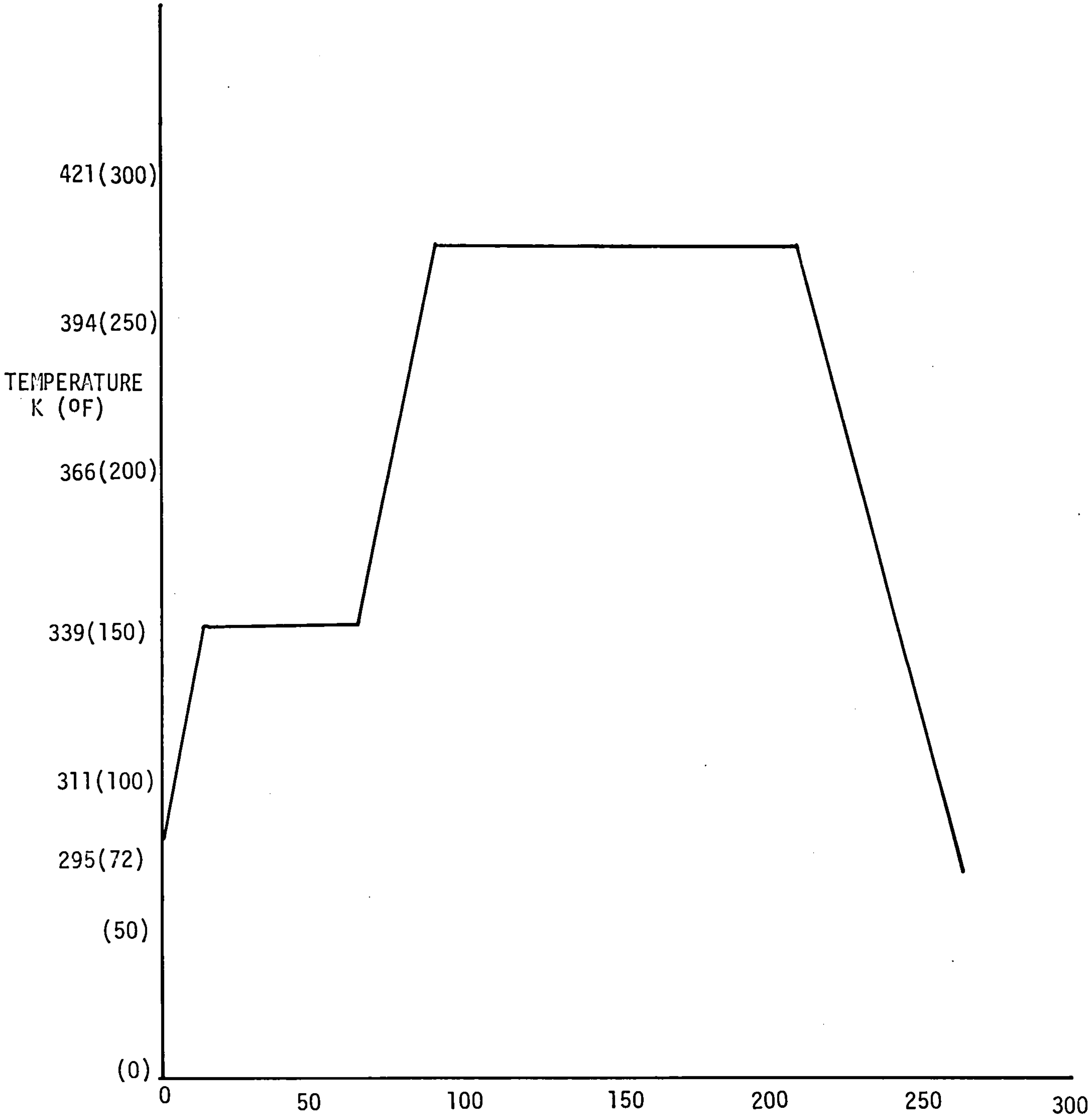
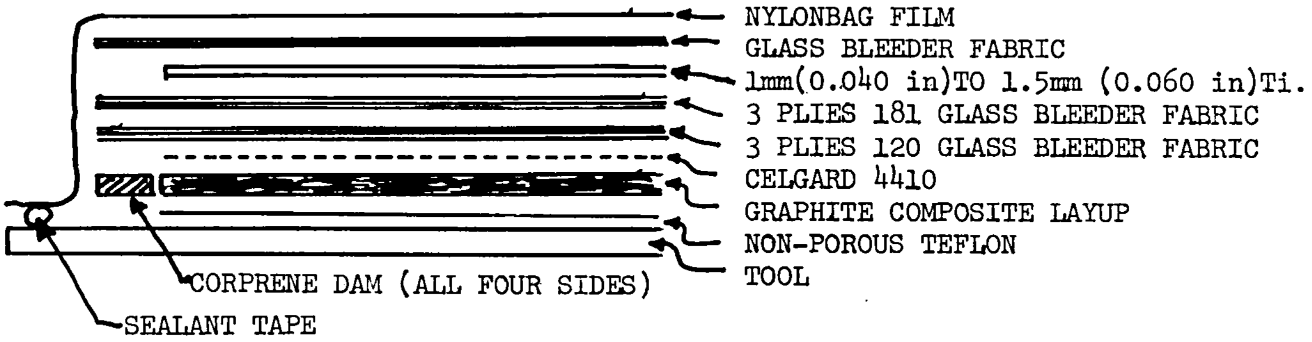


FIGURE 3

STAGING CYCLE GRAPHITE/PMR-15 POLYIMIDE METHOD 1A STEP 1



TYPICAL PMR-15/ GRAPHITE POLYIMIDE LAYUP
(METHOD 1 STEP 1)

FIGURE 4

(8) After removal of the part/assembly from vacuum bag, postcure in an air circulating oven 8 hours at 602K (625°F). Maximum cool down rate shall be 1.1K (2°F) per minute. (Note: Part shall be restrained during postcure cycle with Teflon release fabric and a minimum of 3 plies 181 glass cloth bleeder in contact with part/assembly).

p. Cure Cycle Requirements (Method II)

(1) The chopped fiber molding compound shall be introduced into a compression mold. (There shall be a compression mold for each part type). The material shall be spread evenly over the mold and stops [part thickness plus 6.4mm (0.250 inch)] installed around the mold cavity.

(2) The mold is then introduced into a heated press 373 K (212°F) and closed to stops.

(3) Raise the temperature to 491^{+14}_{-0} K (425^{+25}_{-0} °F) at the rate of 2.0-3.0 K (4-6°F) per minute. Hold part at 491°K (425°F) for 50 minutes then remove stops and apply 2758^{+172}_{-0} kPa (400^{+25}_{-0} psi) positive pressure. Raise temperature to 602^{+0}_{-6} K (625^{+6}_{-10}) and hold for 120 minutes.

(4) Cool part under pressure to below 322 K (120°F).

(5) Postcure the composite/part in an air circulating oven 4 hours at 602K (625°F). (Note: Part shall be restrained during postcure cycle). Heat up rate to 602K (625°F) shall be 2.0-3.0K (4.0-6.0°F) per minute with the cool down rate not to exceed 1.1K (2°F) per minute.

7.5.2 LAMINATE FABRICATION - METHOD I AND IA

7.5.2.1 Flat Laminates

a. Assemble the PMR-15 graphite polyimide laminate structures with proper ply orientation in accordance with the general fabrication requirements specified in Section 7.5.1.a through 1 and process per applicable process as required for applicable D180-20545-4 prepreg condition.

b. Cure laminates in accordance with method described in 7.5.1 either sections m or (n and o) as determined by D180-20545-4 prepreg condition.

7.5.2.2 Hat Sections

Applicable processing cycles shall be determined on Prepreg before proceeding as described below.

a. Assemble the graphite/PMR-15 polyimide laminate with proper ply orientation in accordance with general fabrication requirements specified in 7.5.1.a through 1 on provided tools.

b. During the layup sequence, a vacuum bag is required after the assembly of every three plies for compaction. The tool may be heated with the temperature not to exceed 316K (110°F). Install a vacuum bag as illustrated in Figure 6A. Care shall be exercised to insure the bottom radii of the layup is compacted along with the flat portion of the element.

c. The above assembly is then heated to 316K (110°F) under vacuum of 610mm (24 inches) of Hg minimum and held for 10 minutes maximum.

d. When the proper number of plies have been completed the top bleeder is placed on top of part (see Figure 6B and/or 6C). Use curing cycle as described in para. 7.5.1.n and o, depending on prepreg condition. When using process 7.5.1.m, use only vacuum bag Figure 6C. When using process 7.5.1.n, both vacuum bag assemblies are required on each part/assembly.

e. Cure the assembly in accordance with the methods specified in Section 7.5.1.m or p using 1379^{+69}_{-0} kPa (200^{+10}_{-0} psi) autoclave pressure.

7.5.2.3 Multiple Hat Section

a. Assemble the graphite/PMR-15 polyimide laminate with proper ply orientation in accordance with general fabrication requirements specified in 7.5.1.a through l.

b. During the layup sequence a vacuum bag is required after assembly of every two plies for compaction. Procedures described in para. 7.5.2.2.a through d are applicable with the bleeder and vacuum bag requirements given in Figures 7A and 7B. Note: If D180-20545-4 prepreg is Condition B an additional staging is required and layup will be as Figure 7B. If prepreg is Condition A layup will be as Figure 7B.

c. Cure the assembly in accordance with the methods as specified in Section 7.5.1.m or o 1379^{+69}_{-0} kPa (200^{+10}_{-0} psi) autoclave pressure.

7.5.2.4 "I" Beam Elements

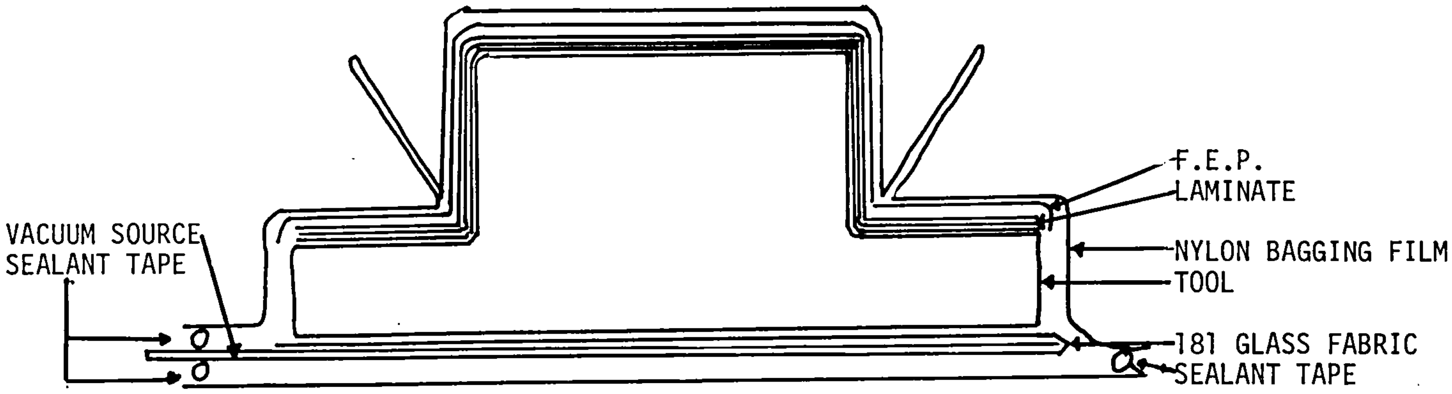
Applicable processing cycles shall be determined on prepreg before proceeding as described below.

a. Assemble with proper ply orientation in accordance with general fabrication requirements specified in 7.5.1.a through l on provided tools.

b. During the layup sequence a vacuum bag is required after the assembly of every two to three plies for compaction. The tool may be heated with temperature not to exceed 316K (110°F). Install vacuum bag over tool like the one illustrated in Figure 6A.

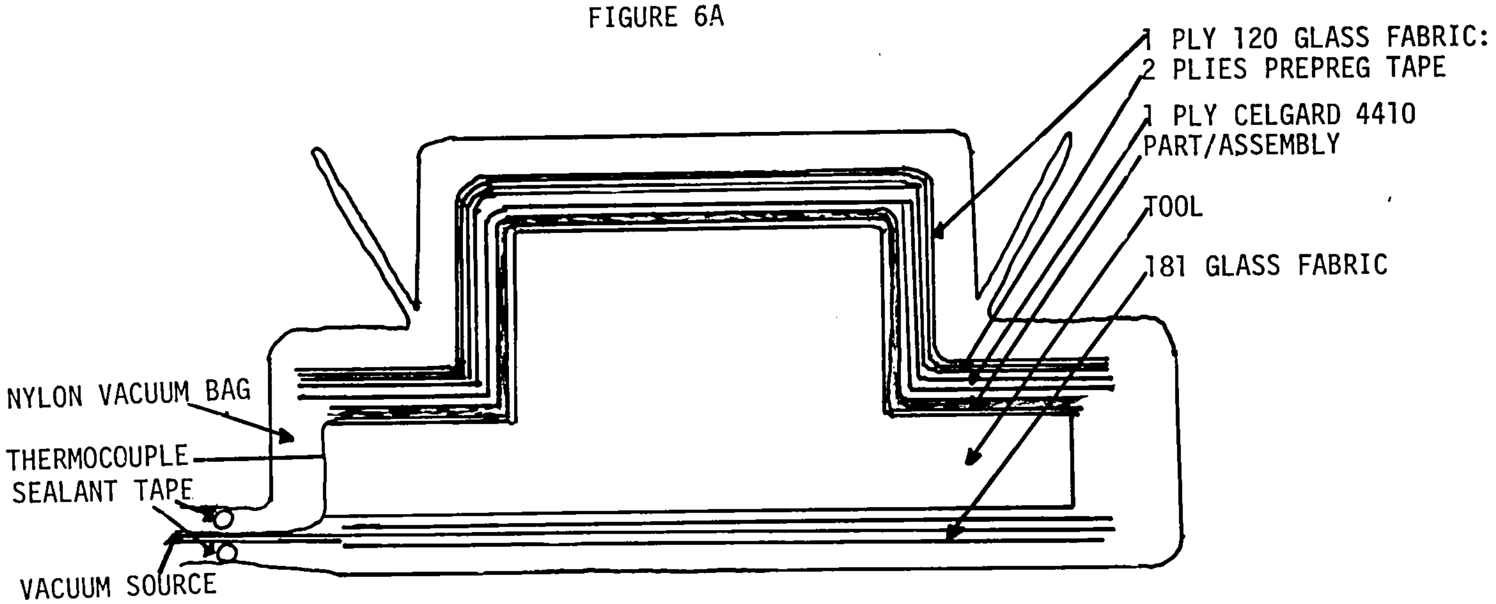
c. The above assembly is then heated to 316K (110°F) under vacuum pressure 610mm (24 inches) of Hg minimum and held for 30 minutes.

d. When the proper number of plies have been completed, the top bleeder is placed on top of part (see Figure 8B). Use curing cycle described in para. 7.5.1.m or o, depending on prepreg condition. If using process 7.5.1.m use only vacuum bag, Figure 8B. If using process 7.5.1.n and o, both types of vacuum bag assemblies are required on each part/assembly.



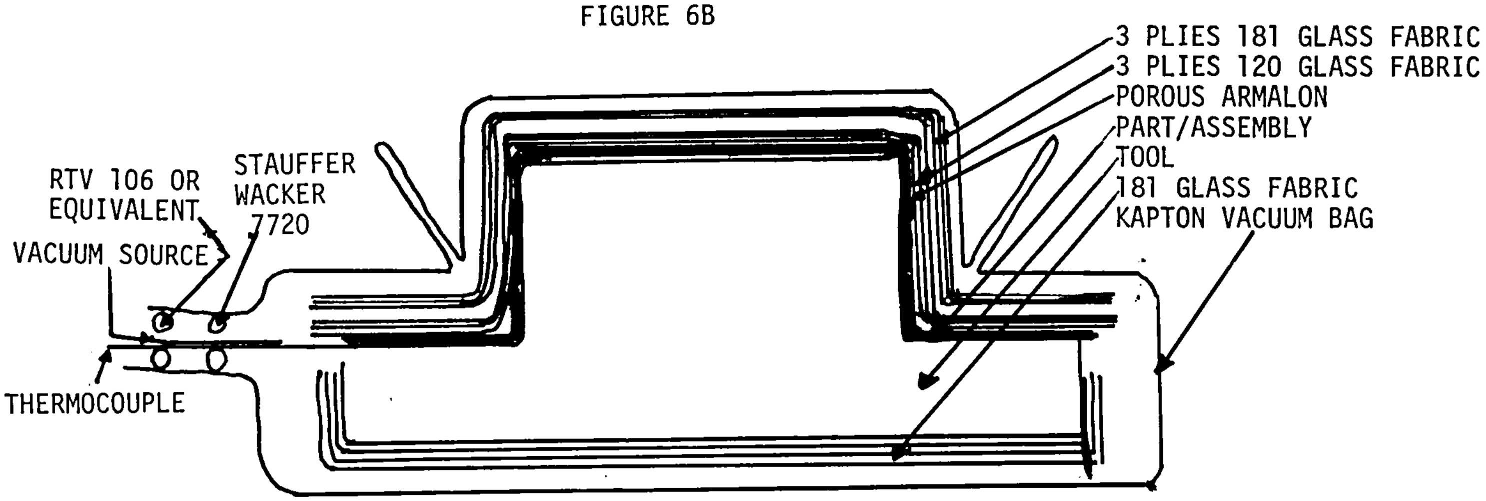
VACUUM BAG SCHEMATIC HAT SECTION LAYUP

FIGURE 6A

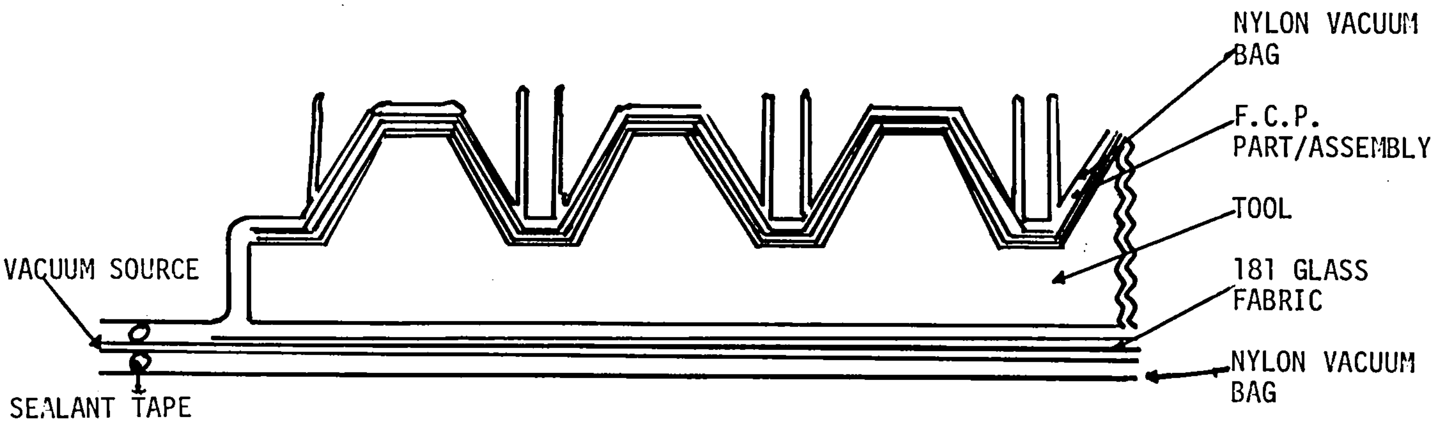


HAT SECTION LAYUP TO "B" STAGE PREPREG
(D180-20545-4 CONDITION B PREPREG)

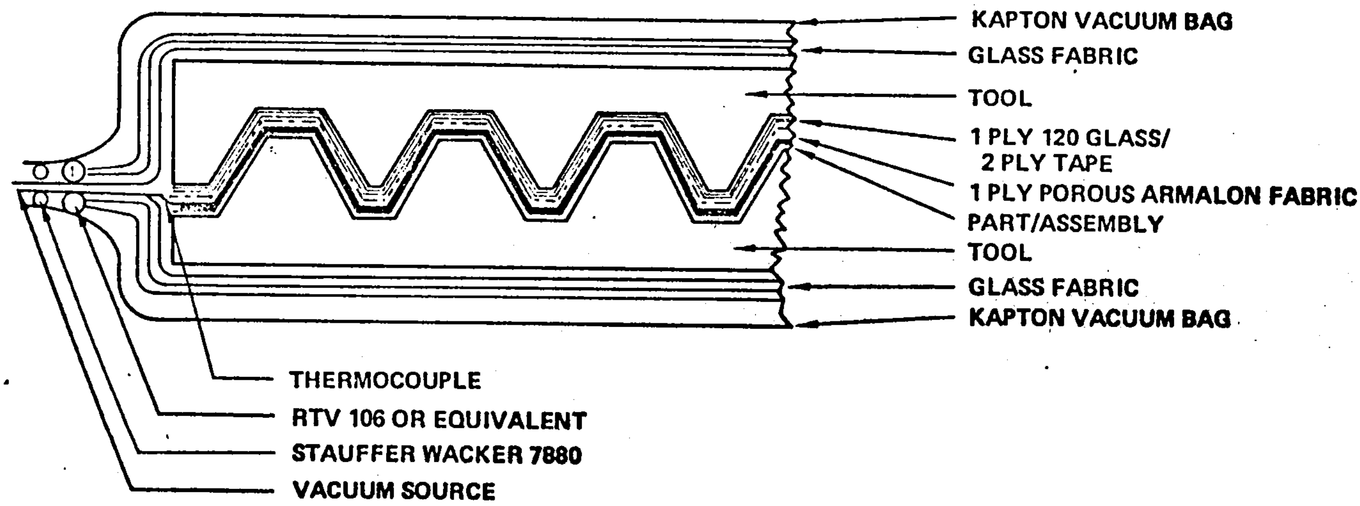
FIGURE 6B



HAT SECTION KAPTON VACUUM BAG SCHEMATIC
FIGURE 6C



VACUUM BAG SCHEMATIC CORRUGATED SECTION LAYUP END VIEW
FIGURE 7A



VACUUM BAG SCHEMATIC CORRUGATED SECTION LAYUP END VIEW
FIGURE 7B

e. Cure the assembly in accordance with the methods specified in Section 7.5.1.m or n and o using 1379^{+69}_{-0} kPa (200^{+10}_{-0} psi) autoclave pressure

f. Process cap strips in accordance with para. 7.5.2.2 with proper ply orientation.

g. After trimming two C sections fabricated in 7.2.2.4.e and two cap strips fabricated in 7.2.2.4.f prepare the faying surfaces for bonding as follows:

   (1) Solvent clean faying surfaces with solvents listed in para. 5.2.e (1) or (2).

   (2) Lightly abrade faying surfaces with "SCOTCHBRITE " pads and/or 400 grit emery paper taking care not to disturb the graphite fibers.

   (3) Solvent clean faying surfaces with solvents listed in para. 5.2.e. Then oven dry at 316K (110°F) a minimum of 10 minutes.

   (4) Prime the faying surfaces with A7F paste adhesive. (Note: A7F paste adhesive may be diluted with Dimethylformamide). Air dry primed surfaces for 30 minutes and then place in 339K (150°F) oven for 15 minutes.

   (5) Assemble the primed C sections and cap strips with A7F film adhesive per Figure 8A. Apply A7F paste adhesvie to fill in depression where C channels meet.

   (6) Envelope bag entire tool with bag per Figure 8B.

h. Cure the assembly in accordance with the methods specified in Section 7.5.5.e using 1379^{+69}_{-0} kPa (200^{+10}_{-0} psi) autoclave pressure.

7.5.3 Laminate Fabrication - Method II

a. Premeasure sufficient quantity of PMR-15/graphite molding compound into mold cavity for desired part thickness.

b. Cure parts in accordance with this method as specified in Section 7.5.1.p.

7.5.4 Cocure Skin Sandwich - Method I

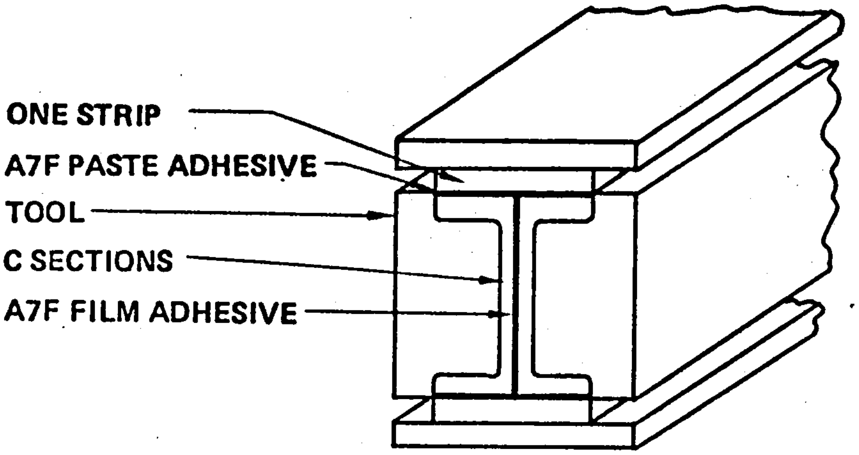
This section is intended for fabrication of PMR-15/graphite honeycomb sandwich with cocured inner and outer skins requiring adhesives.

a. Skin preparation - Assembly laminates as specified in Section 7.5.2 of D180-2-545-4 Condition A prepreg.

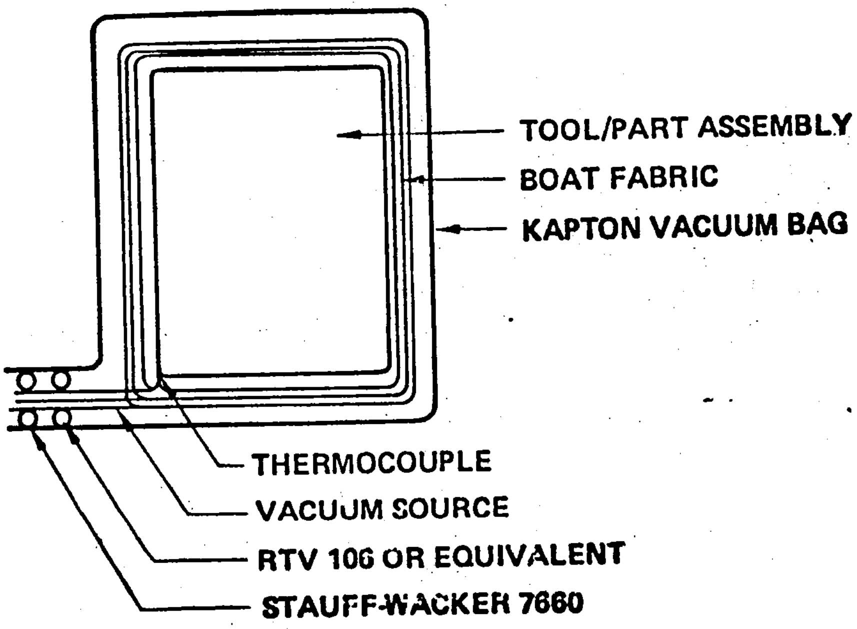
b. Precure laminates as specified in Section 7.5.2 of D180-20545-4 Condition B prepreg.

c. Sandwich assembly - Assemble the sandwich components as illustrated in Figure 9 for square edge configurations.

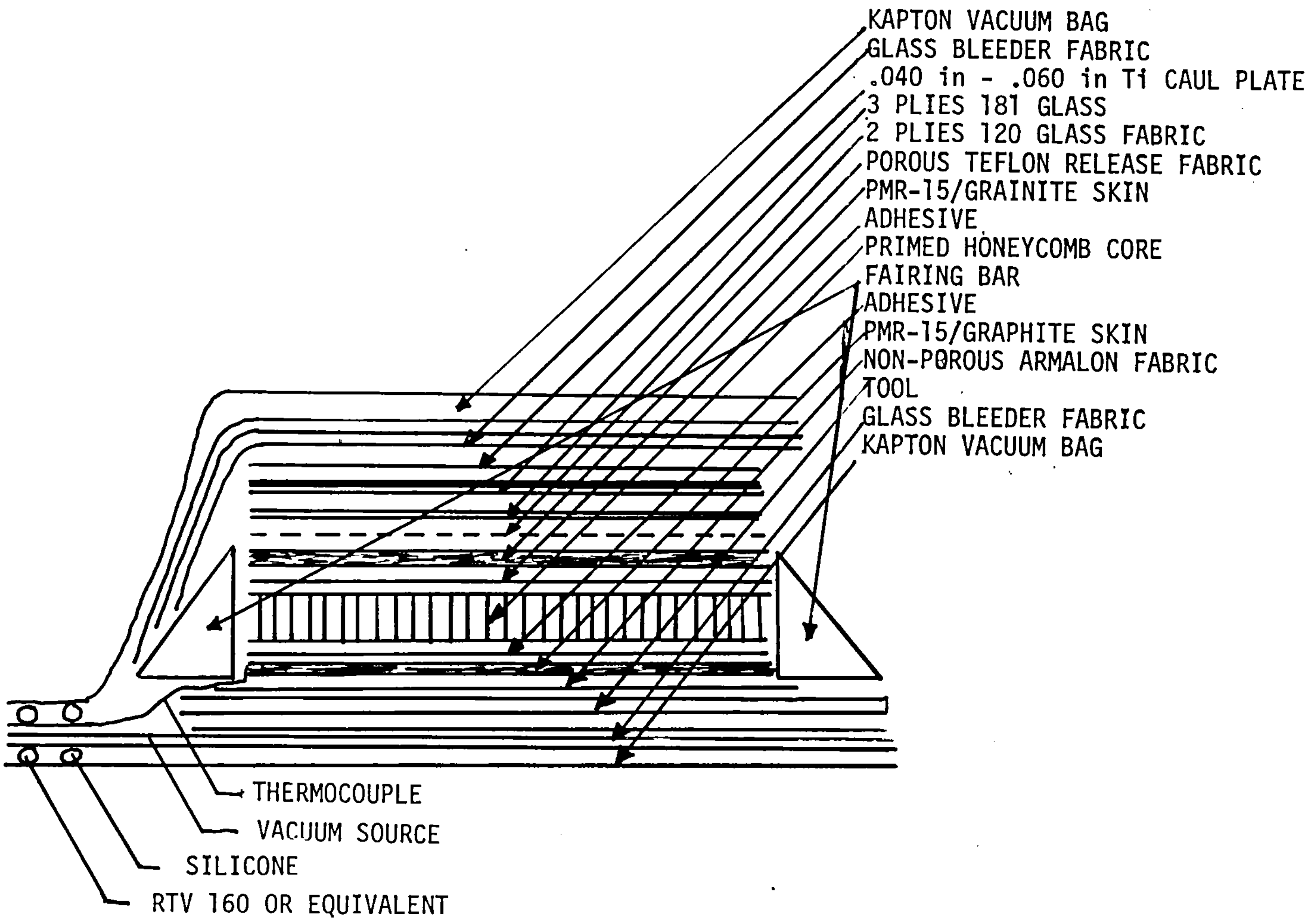
d. Sandwich cure - Honeycomb sandwich assemblies shall be cured in accordance with Section 7.5.2.m or o (Method I or Method 1A Step 2). (Use 1379^{+69}_{-0} kPa (100^{+10}_{-0} psi) pressure.



"I" BEAM LAYUP FOR SECONDARY BONDING
FIGURE 8A

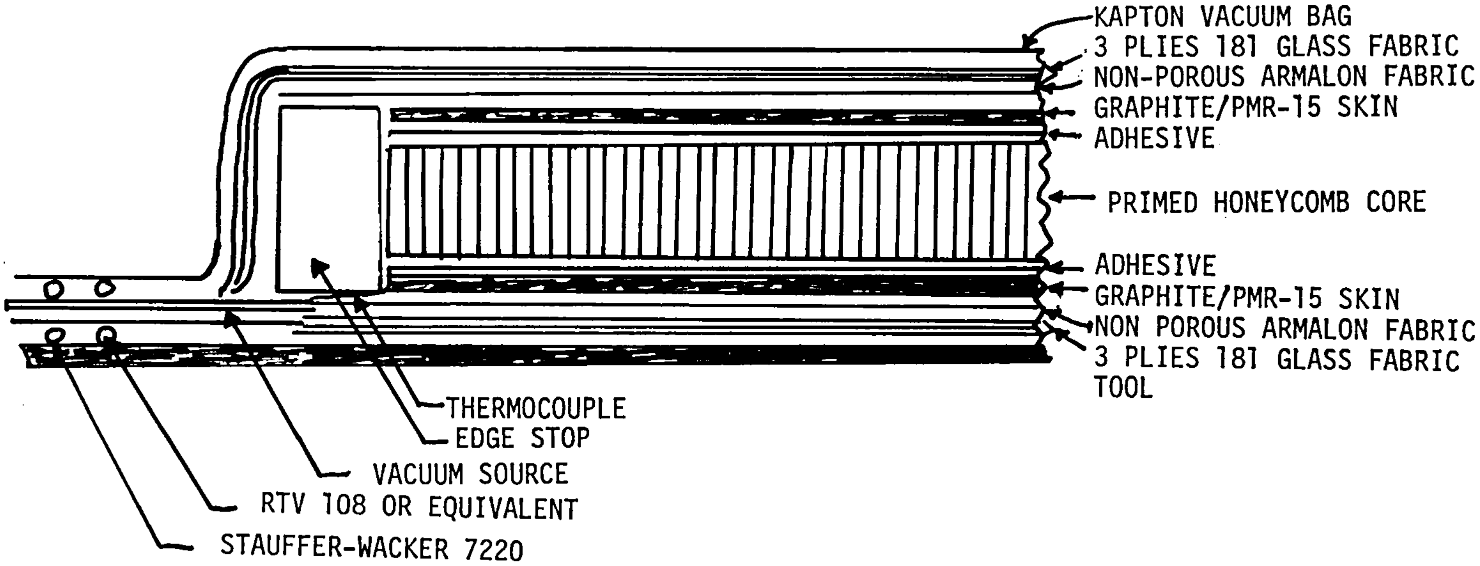


VACUUM BAG FOR "I" BEAM BONDING
FIGURE 8B



SANDWICH ASSEMBLY EDGE VIEW

FIGURE 9



VACUUM BAG SCHEMATIC

GRAPHITE/PMR-15 GRAPHITE-POLYIMIDE HONEYCOMB SANDWICH PANEL

FIGURE 10

7.5.5 SECONDARY BONDED D180-20545-4 GRAPHITE POLYIMIDE HONEYCOMB SANDWICH PANEL

a. Process the PMR-15 graphite polyimide skin laminates with proper ply orientation in accordance with the flat laminate fabrication techniques described in Section 7.5.2.1.

b. Vapor degrease honeycomb core (Note: All honeycomb core except those made from Titanium alloys) and dry 30 minutes at 380°K (225°F). Roller coat the core with A7F adhesive, air dry 30 minutes at ambient conditions, 60 minutes at 338°K (150°F) and 15 minutes at 408°K (275°F).

c. Trim laminates to same size as honeycomb core, lightly abraid with Scotch Brite pads, and prime .05mm (.002 inches) with A7F adhesive.

d. Assemble honeycomb panel using .03mm (.012 inch) A7F adhesive film and vacuum bag as illustrated in Figure 10.

(NOTE: A7F adhesive formulation: 50 Pbw LARC 13 and 50 Pbw Amoco's A1130L resin blend formulated at 40 percent resins solids with 60% Alcoa 101 aluminum powder).

e. Cure the assembly using the following cure cycle, See Figure 11.

(1) Place layup in autoclave with vacuum source capable of maintaining a minimum of 610mm (24 inches) Hg vacuum throughout the curing cycle.

(2) Heat the part/assembly to 477 K (400°F) at the rate of 2.0-3.0 K (4 to 6°F) per minute. Hold at 477K (400°F) for a period of 60 minutes, and apply 689 kPa (100 psi) positive pressure for the remainder of the cure cycle.

(3) After the 689 Pa (100 psi) positive pressure has been applied, heat part/assembly at the rate of 2.0-3.0K (4 to 6°F) per minute to 589K (600°F). Hold at 589K (600°F) under pressure for 120 minutes.

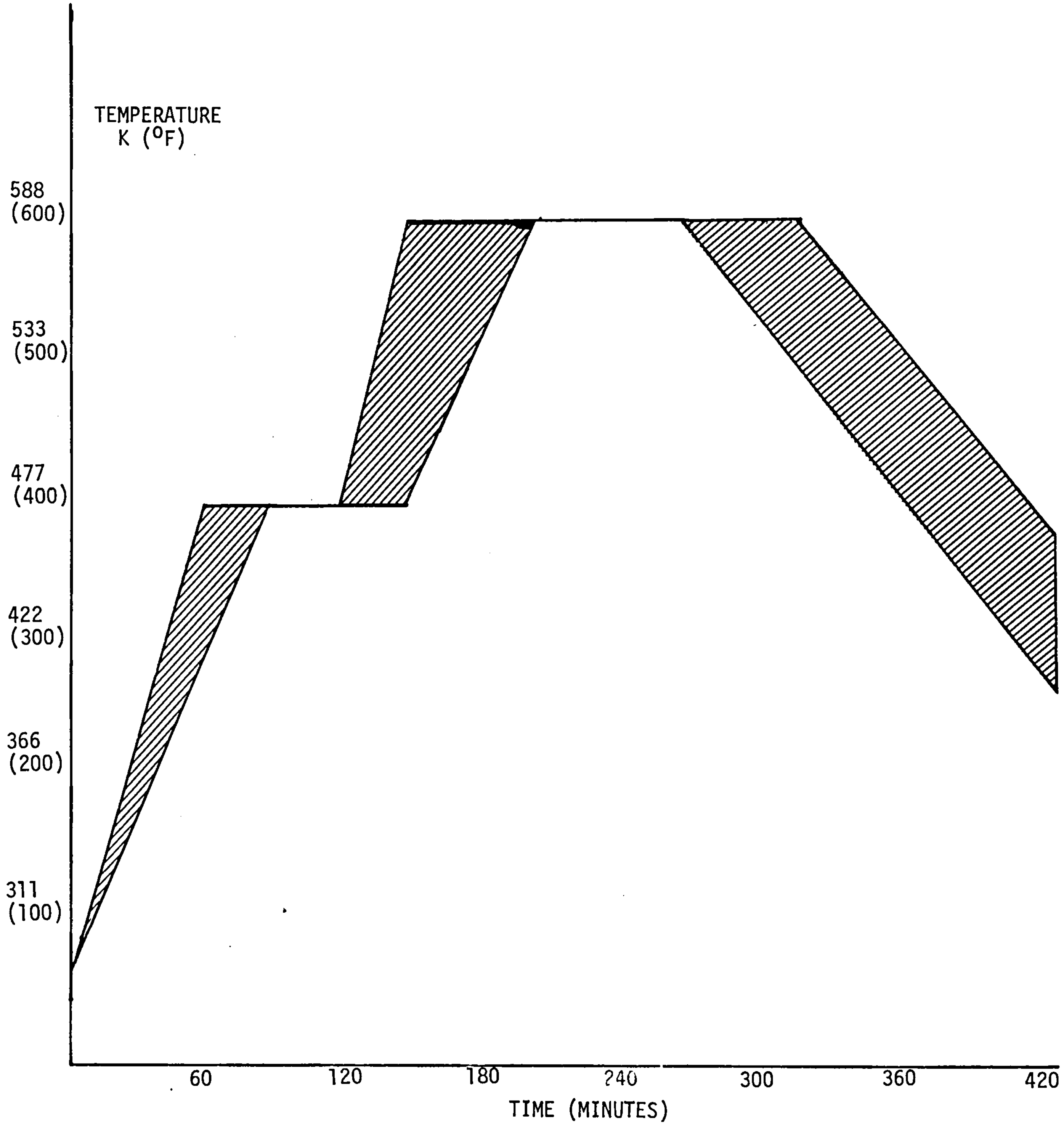
(4) Cool the part/assembly under pressure at the maximum of 1.1K (2°F) per minute.

(5) When the part temperature falls below 322 K (120°F) pressure can be released and the part removed.

(6) After removal of the part/assembly from vacuum bag, postcure in an air circulating oven 8 hours at 602K (625°F). (Note: Part shall be restrained during the postcure cycle with porous Armalon release fabric and 181 glass fabric in contact with part/assembly. Heat up rate to 602K (625°F) shall be 2.0-3.0K (4 to 6°F) per minute with the cool down rate not to exceed 1.1K (2°F) per minute. Part/assembly temperature shall not exceed 322K (120°F) before restraining devices are removed after part has been cooled.

7.6 FINISHING

a. Trimming shall be accomplished in such a manner that delamination and scorching of the part edges do not occur. There shall be no fraying of the surface ply at a trimmed edge where the surface will be subsequently bonded.



CURE CYCLE GRAPHITE/PMR-15 POLYIMIDE HONEYCOMB PANEL
FIGURE 11

b. Drilling shall be accomplished so as to result in the class of hole specified by drawing.

c. Use only filtered (non-oil containing) air, CO_2 or H_2O in drilling operations.

8.0 QUALITY VERIFICATION

Quality Control shall enforce all requirements of this section.

8.1 MATERIALS

a. Verify that materials incorporated into the part during fabrication comply with applicable specifications and sources listed in Section 5.1.

b. Verify that materials not incorporated into the part, but falling under the controlled expendable materials category, comply with the requirements of Section 5.2.

c. Verify storage and handling of composite prepreg materials, honeycomb core, and adhesives as noted in Section 7.1.

8.2 PROCESS

a. Verify that materials preparation and component requirements are as required in Section 7.3.

b. Verify that mold preparation has been done in accordance with Section 7.4.

c. Verify that part fabrication is accomplished in accordance with the applicable sequence in Section 7.5.

d. Review each part process control record (manufacturing plan) to verify that at least the following information is maintained:

   (1) Composite prepreg manufacturer, batch number, roll number, date of manufacture, and total exposure time out.

   (2) Honeycomb core block number.

   (3) The molding pressure, cure temperatures, and times.

   (4) Process control panel test results.

   (5) Part number and serial number.

   (6) Discrepancy corrections accomplished.

8.3 COMPLETED PARTS

a. Verify that results from test panels in the same autoclave load as the part meet the mechanical requirements of the document (Section 8.4.3).

b. Verify that there are no quality defects that exceed acceptable limits as listed in Section 10.

c. Verify that all discrepancy corrections have been accomplished in accordance with Section 10 and that the discrepancies that were corrected fell within the correctable limits.

8.4 PROCESS CONTROL TEST PANELS

8.4.1 TEST PANEL FABRICATION FREQUENCY

Process panels representative of part structure laminate or sandwich shall be cured with each autoclave load.

8.4.2 TEST PANEL CONFIGURATION AND FABRICATION REQUIREMENTS

Additional process control test panel configurations and requirements different from those described in Sections 8.4.2 and 8.4.3 shall be specified by the engineering drawing.

a. Sandwich Panel (Cocured Facing Sandwich)
One flat sandwich test panel must be laid up and cured with each autoclave cure load of production parts containing sandwich details. The test panels shall be fabricated using the same type, batch, and class of acceptable prepreg material as the predominant facing material of the details being cured and shall have been exposed to and fabricated under the same environmental conditions as details being cured. The process control panel must be bagged using the same materials and procedures as those used in preparation of production parts and must be cured in the same autoclave load as the parts which it represents.

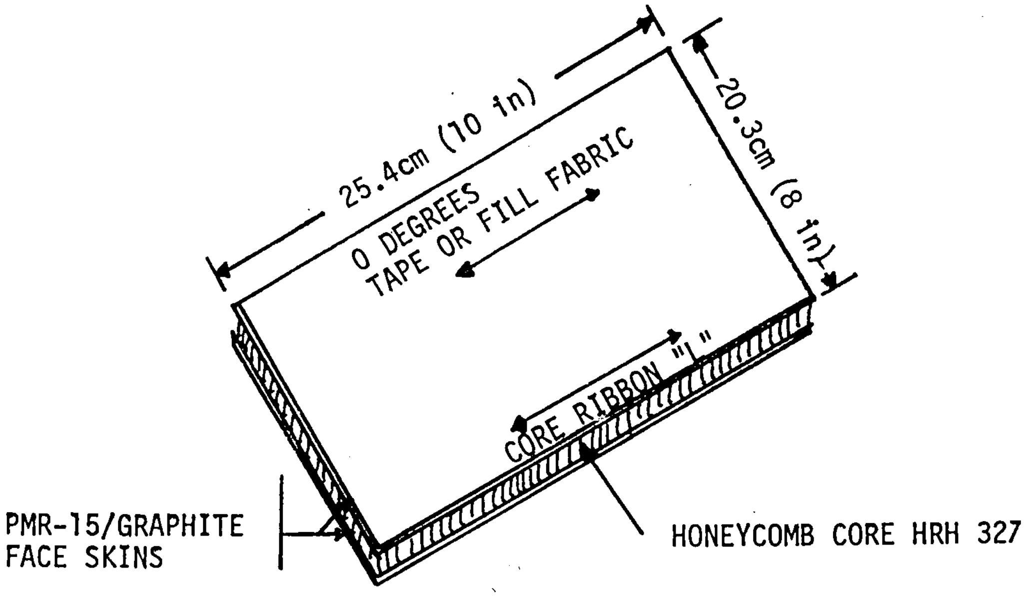
b. Sandwich Panel (Precured Facing Sandwich)
The process control panel must be prepared using the predominant adhesive batch and procedures as used in preparation of the production parts and must be cured in the same autoclave load as the parts which it represents. One flat test panel must be assembled and cured with each autoclave load of production parts. Precured facing shall be fabricated from the same type, class, and grade of facing material used in the production parts.

c. Laminate Panel
One solid laminate test panel must be laid up and cured with each autoclave cure load of laminate production parts. The test panel shall be fabricated using the same type, batch, and class of acceptable prepreg material as the predominant material used in the parts being cured, and shall have been exposed to and fabricated under the same environmental conditions as the details being cured. If the part contains both tape and woven fabric prepregs, then the process control panel shall be constructed from the predominant material.

d. Test Panel Configurations

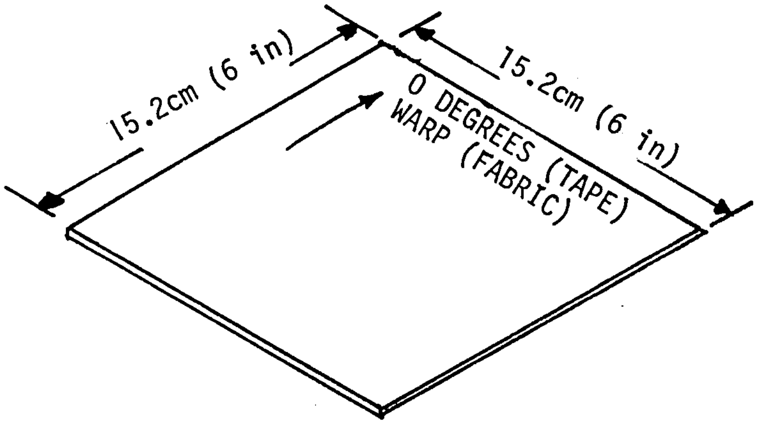
   (1) The honeycomb core and panel shall be as shown in Figure 12.

   (2) Laminate
   The size of the test panel shall be 15.2cm (6 inches) x 15.2cm (6 inches) x 2.54mm (0.1 inch) thick. Tape laminates shall be unidirectional. Fabric laminates shall be oriented (0/90) or warp in the 0 degree direction. See Figure 13.



SANDWICH PROCESS CONTROL PANEL

FIGURE 12



LAMINATE PROCESS CONTROL PANEL

FIGURE 13

e. Test Specimens

(1) Sandwich

(a) Machine edgewise compression test specimens 5.1cm (2 inches) wide x 7.6cm (3 inches long), parallel to the 0 degree direction. Test a minimum of three specimens. The test procedure shall be in accordance with MIL-STD-401. Report ultimate load.

(b) Obtain three flatwise tensile specimens 5.1cm (2 inches) square and bond them to flatwise tensile blocks using a suitable adhesive. Test in accordance with MIL-STD-401. Report the ultimate load in Pascals (pounds per square inch).

(c) Obtain four each specimens 1.3cm (0.5 inch) square, two from bag side and two from tool side. (In case of precured skins, use two from each face sheet). Determine density and resin content using the procedure described in D180-20545-4.

(2) Laminate

The test methods and number of tests required for laminate control panels are as follows:

Test	No. of Specimens
Short Beam Shear (D180-20545-4)	5
Flexural (D180-20545-4)	5
Density (D180-20545-4)	3
Resin Content (D180-20545-4)	3
Void Volume (D180-20545-4)	3
Fiber Volume (D180-20545-4)	3

This method is applicable to the determination of interlaminar shear strength of a cured, resin-impregnated graphite composite.

Determine ultimate interlaminar shear strength in accordance with ASTM D2344 as modified below. The interlaminar shear test specimens are short, rectangular cross-section bars that are loaded in a three-point flexure. Nominal specimen dimensions are width of 0.64cm (0.25 inch) and length of 2.54cm (1 inch).

The testing is accomplished on a flexure testing fixture using three-point loading with the span being equal to 4 times the specimen thickness. Interlaminar shear strength at failure is computed from the following equation:

$$T_i = \frac{3P}{4A}$$

T_i = interlaminar shear stress, MPa (Ksi)

P = total load at failure, Newtons (lbs)

A = cross-sectional area, $mm^2 (in^2)$

This method is applicable for the determination of flexural strength and flexural modulus of a cured, resin-impregnated graphite composite.

Determine ultimate flexural strength and modulus of elasticity in accordance with ASTM D790 as modified below. The flexural test specimen consists of a straight-sided rectangular cross-section having a nominal thickness of 1.8mm (.070 inch). Span thickness ratio is maintained at 32 to 1. Nominal specimen length is 10.2mm (4 inches), but varies with thickness, and the specimen width remains constant at 1.27cm (0.5 inch). The flexural specimens are loaded at quarter-span points. Ultimate flexural strength is calculated with the following equation:

$$F_b = \frac{3PS}{4bt^2}$$

F_b = stress in the outer fiber at failure, MPa

P = maximum load carried by specimen Newtons (lbs)

S = major span meters (inches)

b = width of specimen meters (inches)

t = thickness of specimen meters (inches)

The modulus of elasticity is calculated as follows:

$$E_b = \frac{11\ S^3}{64\ bt^3}$$

E_b = modulus of elasticity in flexure, GPa (Msi)

S = span, meters (inches)

b = width of specimen, meters (inches)

t = thickness of specimen, meters (inches)

m = slope of initial straight line portion of the loading deflection curve, Newtons (lbs/inch)

These methods are applicable for the determination of the physical properties of a cured, resin-impregnated graphite composite:

Composite Specific Gravity

Determine the specific gravity of the composite in accordance with ASTM D792.

Composite Resin Content

Determine the resin content of the composite as described in D180-20545-4.

Composite Fiber Volume

Fiber content is determined from the results of composite specific gravity and composite resin content using the following equation:

$$F_v = (1 - R_c) \left(\frac{D_c}{D_F}\right) 100$$

F_v = fiber volume on a percent basis

R_c = weight percent resin in composite

D_c = specific gravity of composite,

D_F = density of fiber obtained from fiber manufacturer Celion 6000 1.76 g/cm^3 (.064 lbs/in^3)

Composite Void Volume

The composite void volume is determined from the results of composite specific gravity and composite resin content using the following equation:

$$V_v = 100 - D_c \left[\frac{R_c}{D_R} + \frac{100 - R_c}{D_F}\right]$$

D_C = specific gravity of composite in g/cm^3

R_c = weight percent resin in composite

D_R = density of PMR-15 resin 1.30 g/cm^3 (.050 lbs/in^3

D_F = density of graphite fiber Celion 6000 1.76 g/cm^3 (.064 lbs/in^3)

(3) Adhesive

Prior to use, each adhesive system shall be tested for compliance to its applicable process specification.

(4) Honeycomb

Prior to use, the honeycomb shall be qualified to its applicable material document.

8.4.3 PROCESS CONTROL PANEL TEST REQUIREMENTS

The mechanical test requirements for sandwich and laminate process control panels are listed in Table I.

9.0 PROCESSOR QUALIFICATION

Qualification of suppliers to this document shall be accomplished by BAC in accordance with Boeing Document D6-44613.

10.0 DISCREPANCY ACCEPTANCE AND REJECTION

a. A process discrepancy in a part prior to completion may be accepted without correction within the limits described in Section 10.e.

TABLE I

PROCESS CONTROL PANEL REQUIREMENTS

TEST	REQUIREMENT	
	Tape Prepreg (Unidirectional)	Fabric Prepreg
Sandwich Panel		
Edgewise Compression Ultimate strength MPa (ksi)	[1]	[1]
Flatwise Tension MPa (psi)	2.75 (400)	
Density, g/cm^3 [2]	1.54	
Resin Content, % W/W [2]	30 $^{+3}_{-1}$	
Laminate Panel		
Flexural Strength MPa (ksi)	1380 (200)	
Flexural Modulus GPa (Msi)	117 (16.9)	
Short Beam Shear Ultimate, MPa (ksi)	96 (14.0)	
Density, g/cm^3	1.54	
Resin Content, % W/W	30 $^{+3}_{-1}$	
Void Volume, % V/V	1	
Fiber Volume, % V/V	60 ± 2	[1]

[1] Requirements have not been determined

[2] Determined of Facing Only

b. Enter all discrepancies and corrective action accomplished in each part process control record.

c. Nondestructive testing shall be accomplished on each completed part. Defects listed below that are found in completed parts are not allowed.

d. Corrective procedures shall, in general, be applied on an individual basis depending upon the type of structure and type of defect present.

e. The following defects are not allowed:

    (1) Surface scratches

    (2) Surface depressions on tool side of part

    (3) Delaminations

    (4) Voids

    (5) Surface resin ridges

    (6) Material inclusions

    (7) Frayed, burned, scorched, or delaminated areas due to machining or drilling operations

    (8) Resin starved areas

    (9) Resin rich areas

    (10) Ply wrinkles or distortion over flat or simple curved areas

    (11) End splice gaps in tape ply

    (12) Honeycomb core splice gaps

APPENDIX B4

DOCUMENT NO. D180-20545-6

TITLE: NDI Testing Procedures for Graphite/PMR-15 Polyimide Structural Elements

ABSTRACT

This document describes the testing procedure for evaluation of graphite/PMR-15 composites and/or structural elements using Non-Destructive Inspection (NDI) methods.

KEY WORD LIST

"C" Scan
Graphite Composite
Non-Destructive Inspection
Ultrasonic
PMR-15
NDI

1.0 SCOPE

This document describes the Non-Destructive Inspection (NDI) test methods used in the control of Graphite/PMR-15 polyimide structural elements. It is the intent of this document to provide detailed test procedures and necessary equipment to determine quality of finished hardware so that destructive testing is not required. This document is intended to be used on polyimide composites fabricated per D180-20545-5 using material qualified to D180-20545-4 (References 1 and 2).

2.0 CLASSIFICATION

This document for NDI inspection of Graphite/PMR-15 polyimide structural elements shall consist of the following ultrasonic "C" scan test methods.

Method I (flat laminates)	This method is to be utilized only on flat (non-contoured) structural parts made from unidirectional graphite prepreg, woven fabric or chopped fiber molding compound.
Method II (structural elements)	This method is to be utilized only on contoured structural elements such as hat sections, corrugated panels and "I"-beam sections.
Method III (honeycomb core sandwich panels)	This method is to be utilized only on structural elements that contain honeycomb core with various size and/or shape composite facing plies.

3.0 REFERENCES

Except where a specific issue is indicated, the current issue of the following references shall be considered a part of this document to the extent indicated herein.

1.	D180-20545-4	Material Specification for Graphite/PMR-15 Prepreg
2.	D180-20545-5	Process Specification for Graphite/PMR-15 Prepreg

4.0 TESTING PROCEDURES

4.1 SAMPLING

Quality Control shall ensure that all graphite/PMR-15 polyimide composites will be tested in accordance with the applicable test method specified in this document.

4.2 Flat Laminates (Method I)

4.2.1 A HOLOSONIC Model 200 NDI Testing Apparatus, or equivalent, using the test hook-up depicted in Figure 1,Schematic of NDI Test Equipment, shall be used. The equipment shall include at minimum the following items:

a. Model 200 Transmitter

b. Model 200 Gate Detector

c. Model 200 Receiver Amplifier

d. Focus Transmit Transducer (5 MHz)

e. Receiver Transducer

f. Recorder Drive

g. Record Stylus

h. H.P. 3312A Function Generator and H. P. 3556 Attenuator

4.2.2 Prepare the test graphite composite by solvent cleaning the surface with Methyl Ethyl Ketone (MEK) or other suitable ketone solvent. Place the test composite under water (water shall be deaerated by allowing to stand a minimum of 24 hours after addition to the tank) in the tank and carefully remove all surface bubbles using a butyl rubber surfaced tool. Using aluminum (or equivalent) alligator clips, mount test composite in a fixed position for test scanning. Alligator clips shall not overlap the test composite more than 1.27 cm (0.5 inch). The number of alligator clips used shall not exceed four per 929 square centimeters (144 square inches).

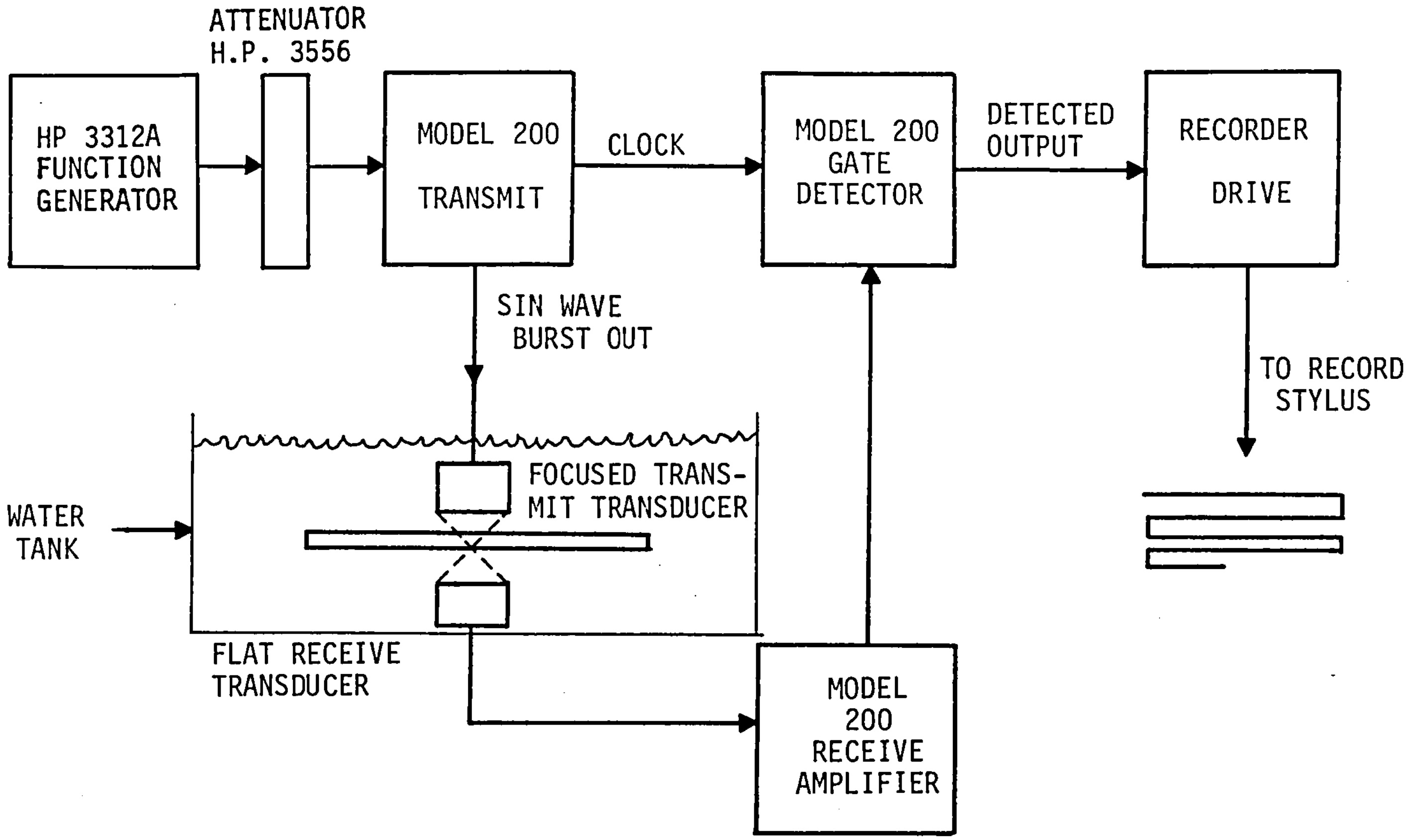
4.2.3 Adjust function generator for 5-6 MHz sweep. Position transducer assembly to a straight water path location and adjust transducers for a maximum receive signal. Install fresh recording paper and turn recorder drive on. Insert 4 db attenuation on attenuator. With low frequency gain full clockwise, adjust transmit power and R.F. gain until recorder current is approximately half on. Turn recorder off and return attenuator to 0 db.

4.2.4 Position transducer assembly to the test composite with the transmitter focus at the composite surface. Make sure the receive transducer has adequate clearance. Adjust transducer to test composite orientation for maximum receive signal. Scan test composite, observing scan conditions of 4.2.5

4.2.5 The scanning conditions$_2$shall be the setting required to insure detection of processing flaws 40m^2 (.0625 square inches) in area.

a. Rate - Maximum of thirty centimeters (one foot) per second

b. Each step not to exceed 0.05 centimeter (0.020 inch) or 50 lines per inch.



5 MHz BROADBAND

MIN @ 3 MHz

FIGURE 1

SCHEMATIC OF NDI TEST EQUIPMENT

4.2.6 If any defects are greater than $40m^2$ (.0625 square inches) and exceed twenty per 465 square centimeters (72 square inches) there is cause for rejection of the part. If a part is rejected by NDI test methods, four interlaminar shear specimens will be obtained randomly from the trim area in the case of 0^o orientation composites greater than 1.80 mm (.070 inch) thick and tested as required in D180-20545-5, Para. 8.4.2.e.2. If the composite is of 0^o orientation with thickness less than 1.8mm (.070 inch) or other than 0^o orientation, the test specimens shall consist of tensile specimens tested as described in ASTM D638. Minimum values for composite acceptance are given in Table I.

4.2.7 All test scans will become part of the composite process control record (Document D180-20545-5, Para. 8.2 d). If either shear or tensile properties are determined they will also become part of the process control record.

4.3 STRUCTURAL ELEMENTS OTHER THAN FLAT LAMINATES (METHOD II)

4.3.1 A Holosonics Model 200 NDI Testing Apparatus or equivalent using test hookup depicted in Figure 1 shall be used. Equipment requirement is the same as Para. 4.2.1.

4.3.2 The same test procedures shall be employed as described in Para. 4.2.1 through Para. 4.2.5. Only the flat surface portion of the structural elements will be scanned.

4.3.3 The acceptance criteria is as described in Para. 4.2.6.

4.3.4 All test scans will become part of the elements' Process Control Record (Document D180-20545-5, Para. 8.2.d). If either shear or tensile properties are determined, they will also become part of the Process Control Record.

4.4 GRAPHITE/PMR-15 HONEYCOMB SANDWICH PANELS (METHOD III)

4.4.1 A Holosonic Model 200 NDI Testing Apparatus or equivalent using the test hook-up as depicted in Figure 1 shall be used. Equipment requirements are the same as described in Paragraph 4.2.1 with the exception of transmit and receive transducers. The frequency used in testing the graphite skin/honeycomb shall be 1 MHz and so appropriate transmitting transducers will be utilized.

4.4.2 The same test procedures shall be employed as described in Paragraphs 4.2.1 through 4.2.5. (Approximate attenuation level is 30 db.) [Note: Panel skins shall have already been NDI tested per paragraph 4.2 before being secondarily bonded to honeycomb core.]

4.4.3 The acceptance criteria shall be the same as Paragraph 4.2.6 except debonded areas shall not exceed $40mm^2$ (.0625 square inches). Use flatwise tensile testing if part is not acceptable in place of shear or tensile tests. (Flatwise tensile value shall be 3.1 MPa (450 psi) minimum).

4.4.4 All test scans will become part of the elements' Process Control Record (Document D180-20545-5, Para. 8.2.d). If flatwise tensile data are determined they will also become part of the process control record.

TABLE I

TEST COMPOSITE ACCEPTANCE REQUIREMENTS

TEST	REQUIREMENT
Short Beam Shear Ultimate, MPa (ksi) Min	96 (14.0)
Tensile Ultimate, MPa (ksi) Min	
(0,90)	758 (110)
(± 45)	482 (70)
(0, ±45)	689 (100)
(0) Less than 1.8mm (.070 inches)	1170 (170)

APPENDIX C1

HTS/PMR-15 PROCESS USED FOR COMPANY A AND COMPANY B POLYMERIC MATERIALS

PANEL			PROCESS
B	A		
1, 1A	1, 1A	1.	Pre-ply laminates in increments of 4 stacks. Air dry 16 hours at RT. Place stack between 3 plies 181 style glass fabric using porous Armalon fabric as the release film. Place in air circulation oven and slowly raise temperature to 405K (270°F) and hold for 2 hours. Use a small caul plate cut the same size as laminate as a weight (approximately 1 kilogram (2.2 pounds)) to prevent preforms from bubbling.
		2.	Lay up laminate to 17 plies using above 4-ply increments and vacuum bag using Kapton film. Bleeder system consists of 3 plies Style 120 glass and 3 plies of Style 181 glass with porous Armalon fabric as the release film. The use of 1.5 mm (0.060 inch) titanium sheet cut to laminate size for a pressure plate is optional. Edge bars are required to prevent fiber movement.
		3.	Cure cycle is the same as D180-20545-5, Para. 7.5.1.0.
B 2		1.	Fabrication per D180-20545-5, except used same bleeder system as Panel 1.

B 3	A 3	1. Fabrication per D180-20545-5, Method 1A, except used 760 mm (29.92 inches) Hg vacuum in Step 1 (Para 7.5.1.n).
B 4	A 7	1. Lay up laminate to desired thickness. 2. Imidize prepreg stack (16 plies with caul plate on top) in air circulating oven. 1 hour at 405K (270°F) and 2 hours at 477K (400°F) 3. Place stack in preheated mold at 505K (450°F). 4. Apply contact pressure and hold 10 minutes. Apply 6.89 MPa (1000 psi) and set controllers to 589K (600°F) and hold 2 hours, then cool to ambient, relieving pressure at 533K (500°F) to 3.86 MPa (560 psi) and at 477K (400°F) to contact pressure. 5. Post-cure 16 hours at 589K (600°F), under restraint.

NASA CYCLE

B A 1. Lay up laminate per D180-20545-5

6 4

2. Cure using the following schedule:
   - (a) Apply 130 mm (5 inches) Hg vacuum.
   - (b) Raise the temperature at 5K (10°F)/minute to 522K (480°F).
   - (c) Hold at 522K (480°F) 25-30 minutes but no longer than 30 minutes, then pressurize to 1.72 MPa (250 psi).
   - (d) Raise temperature at 5K (10°F)/minute to 602K (625°F) and hold 3 hours.
   - (e) Cool under pressure to ambient conditions at 5K (10°F)/minute.
   - (f) Post-cure 16 hours at 589K (600°F).

APPENDIX C2

CURE CYCLES USED IN CURE STUDY LOT 2W4169

Panel 1A

1. Place layup in the autoclave under reduced vacuum pressure 130mm (5 inches) Hg.

2. Heat part to 463K (375°F) at the rate of 2.8K (5.0°F)/minute.

3. Change heating rate to 1.2K (2.3°F) and heat to 522K (480°F).

4. Hold at 522K (480°F) for a period of 30 minutes.

5. Apply 559mm (22 inches) Hg vacuum minimum and 1.38 MPa (200 psi) positive pressure and heat to 602K (625°F) at the rate of 2.8K (5°F/min).

6. Hold at 602K (625°F) for a period of 2 hours then cool to below 338K (150°F) before removing from autoclave.

Panel 1S

Same cure cycle as panel 1A except rate of temperature rise was 2.9K (5.3°F)/minute to 522K (480°K) in place of step 2 and 3. Remaining portion of the cycle with regards to vacuum, temperature, and pressure application was identical to panel 1A.

Panel 2

Same cure cycle as panel 1A with the following exceptions:
(a) 2.2-2.8K (4-5°F/minute) rate of rise to 477K (400°F),
(b) Holding 60 minutes at 477K (400°F) before applying the same vacuum, temperature, and pressure as panel 1A.

Panel 2A	Identical with panel 2 except prestaged composite as described in Method IA, Step I of processing document D180-20545-5 for 1 hour at 338K (150°F).
Panel 3	Same cure cycle as panel 1A with the following exceptions: (a) 2.2-2.8K (4-5°F)/minute rate of rise to 533K (500°F), (b) immediately apply the same vacuum, temperature, and pressure as panel 1A.
Panel 4	Same cure cycle as panel 1A with the following exceptions: (a) 3.9K (7.0°F)/minute rate of rise to 477K (400°F); (b) Hold 90 minutes at 477K (400°F) before applying the same vacuum, temperature, and pressure as panel 1A.
Panel 5	Same cure cycle as panel 1A with the following exception: (a) 1.8K (3°F)/minute rate of rise to 477K (400°F) before applying the same vacuum, temperature, and pressure as panel 1A.
Panel 6	Same cure cycle as panel 1A with the following exceptions: (a) 1.4K (2.5°F)/minute to 522K (480°F)/ (b) Immediately apply the same vacuum, temperature, and pressure as panel 1A.
Panel 7	Same cure cycle as panel 1A with the following exceptions: (a) 1.4K (2.5°F/minute to 522K (480°F) before applying the same vacuum, temperature, and pressure as panel 1A.

APPENDIX C3

HTS-2/PMR-15 CHOPPED FIBER MOLDING COMPOUND PROCESSES

WM 3582-1

Process per D180-20545-4 Process Specification

WM 3582-2

1. Place 225 grams (0.5 lbm) of molding compound in cold mold, making sure fibers are spread uniformly over the mold.

2. Place in press preheated to 372K (212°F) and heat to 477K (400°F) after having inserted 6.3 mm (0.250 inch) stops. Hold at 477K (400°F) for 60 minutes. Remove stops and apply 5.86 MPa (850 psi).

3. Raise part temperature to 589K (600°F) and hold for 120 minutes.

4. Cool to ambient conditions under pressure.

WM 3994, WM 3995, WM 4346

1. Place charge evenly in cold mold.

2. Place in hot press at 372K (212°F), heat to 477K (400°F), hold for 1 hour at contact pressure. Heat to 545K (525°F), apply pressure gradually, watching so that resin and fibers do not squeeze out. When pressure is at 5.86 MPa (850 psi), raise part temperature to 602K (625°F) and hold for 2 hours. Turn heat off and allow to cool very gradually to room temperature under pressure.

APPENDIX D

TEST PROCEDURES FOR CHARACTERIZATION OF GRAPHITE TAPE AND COMPOSITES

Each lot of prepreg used on the program was tested for prepreg properties using the following testing procedures:

D.1 GRAPHITE/PMR-15 PREPREG TEST PROCEDURES

D.1.1 PREPREG VOLATILE CONTENT

a. Obtain three specimens 2.0 to 4.0g (.0044 to .0080 lbm) from each sample obtained in a pattern that was representative of the entire sample.

The specimens taken near the edge must be at least 25.4mm (one inch) from the edge of tape. The specimens shall be identified by tape batch number, roll number, and specimen number.

b. Remove the release paper backing from each specimen, place in a tared aluminum dish, and weigh to the nearest milligram. The aluminum dish with specimen is placed in an air-circulating oven regulated to 589 ± 5K (600 ± 10°F).

c. Close the oven door and start a clock. After 30 minutes the aluminum dishes shall be removed and placed in a desiccator to cool. The specimens shall then be weighed to the nearest milligram.

$$\text{Percent Volatiles} = \frac{A - B}{A} \times 100$$

A = Weight of specimen before test

B = Weight of specimen after volatile removal

d. Report the average of three specimens.

D.1.2 PREPREG RESIN CONTENT

Use either of the following methods for determining tape resin content.

D.1.2.1 RESIN CONTENT ACID DIGESTION

a. Transfer 0.4 to 0.7g (.00088 to .00155 lbm) portions of the specimens accurately weighed after the determination of volatile content in accordance with Section D.1.1 to an 80 ml glass beaker.

b. Carefully add approximately 50 mls of concentrated sulfuric acid into the beaker containing the devolatilized sample. Cover the beaker with a watch glass, place on hot plate, and heat until white fumes are visible above the acid solution.

c. Maintain this condition for a minimum of 20 minutes or until the solution turns black. At this point, carefully add dropwise a 30 percent solution of hydrogen peroxide until the solution turns clear. Continue heating beaker for a minimum of one hour. During this period, add dropwise the hydrogen peroxide solution to clear the acid whenever the acid turns black. Cool the acid solution to room temperature, add 2 mls of hydrogen peroxide, and heat until the white fumes appear. Continue heating for 10 minutes, then cool to room temperature. If acid turns black, repeat the procedure until acid remains clear. (Note: This process shall be accomplished in a fume hood with adequate air exchange to prevent fumes from entering laboratory area.

d. Filter the acid solution using a fritted glass crucible (coarse), wash a minimum of three times with either distilled or deionized water and then with acetone. The glass crucibles are then dried at 338K (150^{o}F) in an air-circulating oven a minimum of 30 minutes, cooled to room temperature in a desiccator, and weighed. The graphite yarn is then removed and the crucible weight obtained.

$$W_r = \frac{W_1 - W_2}{(W_1)} \times 100$$

W_r = Weight content of resin solids, % W/W

W_1 = Weight of devolatilized sample

W_2 = Weight of graphite yarn after acid digestion of the resin matrix

e. Report the average of three specimens.

D.1.2.2 RESIN CONTENT BY SOXHLET EXTRACTION

a. Take three specimens 2.0-4.0g (.0044 to .008 lbm) from the swatch obtained per Section 8.1 of D180-20545-4 in a pattern that will be representative of the entire swatch. The specimens taken near the edge must be at least 25.4mm (one inch) from the tape's edge if the material is Type I, II, or III Grades 6 and 12. If the tape is Type I Grade 3 the sample must be the full width of the tape. If the sample is Class 3 of any type a random sample of molding compound shall be tested. The specimens shall be identified by tape or molding compound batch number, roll number, and specimen number.

b. Remove the release paper from each specimen (if applicable) and weigh the prepreg in a tared soxhlet extraction thimble to the nearest milligram.

c. Place the soxhlet extraction thimble into a soxhlet extraction apparatus. Fill the soxhlet flask three-fourths full of acetone and heat until acetone is gently refluxing. Continue heating until the acetone surrounding the extraction thimble is clear but no less than 60 minutes.

d. Remove the extraction thimble from the apparatus and dry in an air-circulating oven for 30 minutes then after cooling in a desicator, reweigh to the nearest milligram. (Note: Since the dried extraction thimble gains weight, take reading 20 seconds after sample is removed from the dessicator.)

$$\text{Wet Resin Content } W_{WR} = \frac{W_2}{W_1} \times 100$$

$$\text{Dry Resin Content } W_{DR} = \frac{W_2 - W_1 V}{W_1 - W_1 V}$$

W_{WR} = Weight content of wet resin solids %

W_1 = Weight content of original sample

W_2 = Weight content of extract

W_{DR} = Weight content of dry resin solids %

V = Volatile matter content of graphite tape (Section D.1.1)

D.1.3 GEL TIME

a. Preset the temperature on a Fisher-Johns melting point apparatus to 477K (400°F).

b. Insert a 6.35mm x 6.35mm(0.25 x 0.25in) sample of prepreg between two cover glasses and place on the heated platform of the Fisher-Johns apparatus.

c. Start a stopwatch or timer and begin to probe on the top of the coverglass with a wooden pick.

d. Record the time when the resin gels. The gel point is reached when no resin movement is observed through the coverglass when moderate pressure is applied.

e. Report the gel time as the average of three or more determinations.

D.2 GRAPHITE/PMR-15 COMPOSITE MECHANICAL PROPERTIES

Composites prepared during the course of the program were tested as follows. A minimum of three specimens were generally tested for each mechanical property.

D.2.1 FLEXURAL PROPERTIES

Determine ultimate flexural strength and modulus of elasticity in accordance with ASTM D790 as modified below. The flexural test specimen consists of a straight-sided rectangular cross section having the specified thickness. Span to thickness ratio is maintained constant at 32 to 1. Nominal specimen length is 102mm (4 inches) but varies with thickness. The specimen width remains constant at 12.7 mm (0.5 in). The flexural specimens are loaded at quarter span points. Ultimate flexural strength is calculated with the following equation:

$$F_b = \frac{3PS}{4bt^2}$$

F_b = Stress in the outer fiber at failure

P = Maximum load carried by specimen Newton (lbs)

S = Major span meters (inches)

b = Width of specimen meters (inches)

t = Thickness of specimen meters (inches)

The modulus of elasticity is calculated as follows:

$$E_b = \frac{11}{64} \frac{S^3 m}{bt^3}$$

E_b = Modulus of elasticity in flexure

S = Span meters (inches)

b = Width of specimen meter (inches)

t = Thickness of specimen meter (inches)

m = Slope of the initial straight line portion of the loading deflection curve Newton meter (lbs/inch)

D.2.2 INTERLAMINAR SHEAR PROPERTIES

Determine ultimate interlaminar strength in accordance with ASTM D2344 as modified below. The interlaminar shear test specimens are short, rectangular cross-section bars that are loaded in a three-point flexure. Nominal specimen dimensions are the width at 6.4 mm (0.25 in.) and the length being 25.4 mm (1 in).

The testing is accomplished on a flexure testing fixture using three-point loading with the span being equal to 4 times the specimen thickness. Interlaminar shear stress at failure is computed from the following equation:

$$T_i = \frac{3P}{4A}$$

T_i = Interlaminar shear stress kPa (ksi)

P = Total load at failure Newton (lbs)

A = Cross-sectional area m^2 (in^2)

D.2.3 TENSILE PROPERTIES

Determine ultimate tensile strength in accordance with ASTM D638. The tensile properties are computed using the following equation:

$$F_T = \frac{P}{A}$$

F_T = Ultimate tensile stress kPa (ksi)

P = Total load of failure Newton (lbs)

A = Cross section area m^2 (in^2)

D.2.3 COMPRESSIVE PROPERTIES

Determine ultimate tensile strength using the Celanese Test Coupon Method. The compressive properties are computed using the following equation:

$$F_c = \frac{P}{A}$$

F_c = Ultimate compressive stress kPa (ksi)

P = Total load at failure Newton (lbs)

A = Cross section area m^2 (in^2)

D.2.4 ISOTHERMAL AGING PROPERTIES

Isothermal aging tests shall consist of aging flexural specimens (D.2.1) and interlaminar shear specimens (D.2.2) at 589K (600°F) for periods up to 125 hours in an air-circulating oven.

D.3 COMPOSITES PHYSICAL PROPERTIES

Test the composites prepared in accordance with Section 8.11 of D180-20545-4 as follows to demonstrate conformity to the requirements of Table II of D180-20545-4. Test a minimum of five specimens for each physical property.

D.3.1 COMPOSITE SPECIFIC GRAVITY

Determine the specific gravity of the composite in accordance with ASTM D792.

D.3.2 COMPOSITE RESIN CONTENT

Determine the resin content of the composite as described by Section D.1.1.

D.3.3 COMPOSITE FIBER VOLUME

Fiber content is determined from the results of Composite Specific Gravity (Section D.3.1) and Composite Resin Content (Section D.3.2) using the following equation:

$$F_V = (1 - R_C) \left(\frac{D_C}{D_F}\right) 100$$

F_V = Fiber volume on a percent basic

R_C = Weight percent resin in composite (Section D.3.2)

D_C = Specific Gravity of composite (Section D.3.1)

D_F = Density of Fiber obtained from Fiber Manufacturer

D.3.4 COMPOSITE VOID VOLUME

The composite void volume is determine from the results of Composite Specific Gravity (Section D.3.1) and Composite Resin Content (Section D.3.2) using the following equation:

$$V_V = 100 - D_C \left[\frac{R_C}{D_R} + \frac{100 - R_C}{D_F} \right]$$

D_C = Specific Gravity of Composite in g/cm^3

R_C = Weight percent resin in composite

D_R = Density of PMR-15 resin 1.30 g/cc (.050 lbs/in^3)

D_F = Density of Graphite Fiber Celion 6000 1.76 grams/cu cm (.064 lbs/in^3)

D.4 GRAPHITE/PMR-15 HONEYCOMB SANDWICH TEST PROCEDURES

D.4.1 FLATWISE TENSION PROPERTIES

Determine the flatwise tensile strength of sandwich panels in accordance with ASTM DC297. (Note: HT424 scrim adhesive is used in bonding the sandwich specimen to the tension blocks.) The flatwise tension properties are computed using the following equation:

$$F_T = \frac{P}{A}$$

F_T = Ultimate flatwise tensile strength kPa (ksi)

P = Total load at failure Newton (lbs)

A = Surface area m^2 (in^2)

D.4.2 SANDWICH EDGEWISE COMPRESSION STRENGTH

Determine the sandwich edgewise compression strength in accordance with ASTM D 364 with the following exceptions:

a. Use standard specimen; bond 38 mm x 51 mm (1.5 inch x 2 inch) 4 ply polyimide/fiberglass tabs on specimens for load transfer.

b. Machine at least 13 mm (0.5 inch) core from the ends of the specimens and pot using a suitable potting compound (i.e., for ambient conditions use aluminum filled RT curing epoxy and for 589K (600°F) use HT424 aluminum filled epoxy phenolic adhesive).

c. After properly curing potting compound and/or adhesive film, machine ends parallel to ± 0.0254 mm (± 0.001 inch). The edgewise compression properties are computed using the following equation:

$$F_c = \frac{P}{2A}$$

F_c = Edgewise compressive strength kPa (ksi)

P = Ultimate breaking load Newtons (lbs)

A = Cross sectional area of one facing m^2 (in^2)

1. Report No.
NASA CR-159129

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
Manufacturing Processes for Fabricating
Graphite/PMR-15 Polyimide Structural Elements

5. Report Date
February 1979

6. Performing Organization Code
2-3621

7. Author(s)
C. H. Sheppard, J. T. Hoggatt, W. A. Symonds

8. Performing Organization Report No.
D180-20545-2

9. Performing Organization Name and Address
BAC
P.O. Box 3999
Seattle, Washington 98124

10. Work Unit No.

11. Contract or Grant No.
NAS 1 -15009

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, DC 20546

13. Type of Report and Period Covered
Contractor Report,
Aug. '77 - Feb. '79

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Investigations were conducted to obtain commercially available graphite/PMR-15 polyimide prepreg, develop an autoclave manufacturing process, and demonstrate the process by manufacturing structural elements. This program was accomplished in two separate phases; the first concentrated on establishing controls on polymer, prepreg, composite fabrication and quality assurance, while the second phase demonstrated successful material quality control and processes by fabricating major structural elements. The structural elements fabricated during the program included flat laminates, hat sections, "I" beam sections, honeycomb sandwich structures and molded graphite reinforced fittings. Conclusions from successful fabrication of structural elements and simulated section of the Space Shuttle aft body flap are that the graphite/PMR-15 polyimide system and the developed processes are ready for further evaluation in flight test hardware.

17. Key Words (Suggested by Author(s))
PMR-15 Resin
Monomers
Graphite Prepreg
Graphite Composite
High Pressure Liquid Chromatography
Gas Chromatography
Chemical Charaterization

18. Distribution Statement
Unclassified - Unlimited and
Subject Category 24

19. Security Classif. (of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No. of Pages

22. Price*

* For sale by the National Technical Information Service, Springfield, Virginia 22161