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RESIN/GRAPHITE FIBER COMPOSITES

BY

P. J. CAVANO

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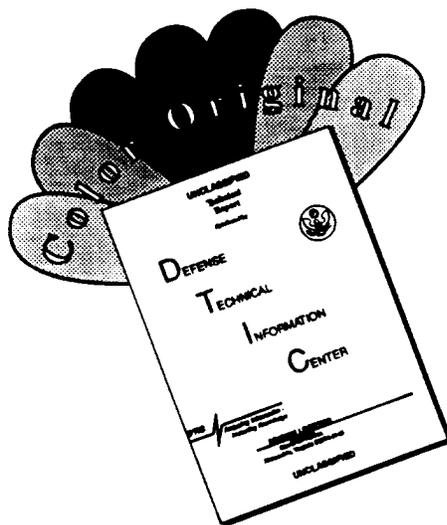
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16. Abstract <p>During the course of the program, techniques were developed that provided thermo-oxidatively stable A-type polyimide/graphite fiber composites using the novel approach of <u>in situ</u> polymerization of monomeric reactants directly on reinforcing fibers, rather than employing separately prepared prepolymer varnish. This was accomplished by simply mixing methylene dianiline and two ester-acids and applying this solution to the fibers for subsequent molding. Five different formulated molecular weight resins were examined, and an optimized die molding procedure established for the 1500 formulated molecular weight system. Extensive ultrasonic inspection of composites was successfully utilized as a technique for monitoring laminate quality. Composite mechanical property studies were conducted with this polyimide resin at room temperature and after various time exposures in a thermo-oxidative environment at 561°K (550°F), 589°K (600°F) and 617°K (650°F). It was determined that such composites have a long term life in the temperature range of 561°K to 589°K. The final phase involved the fabrication and evaluation of a series of demonstration airfoil specimens.</p>			
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FOREWORD

This document represents the final report for the work accomplished between 18 April 1972 and 18 June 1973 by TRW Inc. for the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio under Contract NAS3-15829 on Resin/Graphite Composites. This work was initiated by Dr. Tito T. Serafini of NASA and conducted under the technical direction of Mr. Morgan P. Hanson, NASA Project Manager.

Work on the program was conducted at TRW Materials Technology of TRW Equipment, Cleveland, Ohio. Mr. W. E. Winters was the TRW Program Manager; the TRW Project Engineer was Mr. P. J. Cavano

RESIN/GRAPHITE FIBER COMPOSITES

by

P. J. Cavano

SUMMARY

The principal objective of the program was to develop, define and apply those techniques that would provide thermo-oxidatively stable A-type polyimide/graphite fiber composites using the approach of in situ polymerization of monomeric reactants directly on reinforcing fibers, rather than employing a separately prepared prepolymer varnish. This was accomplished by using the monomethyl ester of 5-norbornene-2, 3-dicarboxylic acid as the end cap component, and 4,4' methylene dianiline and the dimethyl ester of 3,3', 4,4' benzophenonetetracarboxylic acid as the other reactants. These three ingredients were mixed in methyl alcohol and applied directly on the reinforcing fiber for subsequent drying, imidization, and molding. This technique and the polyimide resin thus manufactured have come to be identified as the PMR system from the first letters in the words in the phrase, Polymerization of Monomeric Resultants.

Experimental work included a determination of monomeric reactant solution and prepreg stability. Five formulated molecular weight reactant solutions were examined, and an optimized die molding procedure developed. An extensive composite property evaluation of the 1500 formulated weight material reinforced with HM-S high modulus graphite tow was conducted, and some limited data gathered with the HT-S fiber. Tests were conducted on the composite material at room temperature, 561°K (550°F), 589°K (600°F), and 617°K (650°F) on laminates both unconditioned and after exposure at the given temperatures in an oxidative environment for times up to 1000 hours. Additionally, the material was evaluated after water boil and thermal cycling excursions. Criteria used included the following properties: longitudinal tensile and compression, transverse tensile, cross-ply tensile, short beam shear, longitudinal flexure and thermal expansion. A final phase of the program involved the fabrication and evaluation of six jet engine demonstration blade specimens.

The PMR approach was found to provide excellent processability. Ultrasonic inspection revealed the presence of two unexpected quality related characteristics. These were surface imperfections and voids normally occurring in a characteristic pattern. The void content range (1-3 percent) was considerably lower than normally obtained for polyimide composites.

The composite material was determined to be oxidatively, thermally and hydrolytically stable. Room temperature composite testing indicated that the system produced values comparable with other commercial matrices in utilizing available fiber strengths. Elevated temperature testing indicated that the matrix is suitable for short term use at temperatures as high as 617°K (650°F). Isothermal exposures determined that long time use (ca. 1000 hour) would be possible in the range of 561°K (550°F) to 589°K (600°F). The 561°K temperature is conservative since little or no loss of mechanical properties was observed

at the end of 1000 hours at this temperature, beyond that loss experienced in short term elevated temperature tests.

SUPPLEMENTAL NOTE TO SUMMARY

Investigators at Lewis Research Center had reported previously that the PMR approach provided a means to obtain high-quality void-free composites. In the earlier work performed at the Lewis Research Center, all of the monomers were prepared in their laboratory and were of known composition and purity. The studies performed under this contractual effort utilized commercial sources for the monomeric reactants. The analytical techniques employed for quality control, i.e., infrared spectroscopy and melting point determinations did not indicate the presence of impurities in the commercially obtained monomers.

After the experimental studies required in this contractual program had been completed, the NASA Project Engineer supplied TRW with a monomeric reactant solution which provided a high quality laminate. The details concerning the preparation of the solution are available from the Lewis Research Center Project Engineer. The essential difference between the Lewis Research Center solution and the resin solution utilized throughout this program was that the Lewis Research Center solution was formulated with freshly prepared benzophenone ester instead of material from a commercial source. The C-scan of this laminate did not exhibit the characteristic pattern associated with the presence of defects.

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1.0 INTRODUCTION

This document constitutes the final report on NASA Contract NAS3-15829, initiated 18 April 1972, and describes the work performed between 18 April 1972 and 18 June 1973. The principal objective of the program was to develop, define and apply those techniques that would provide thermo-oxidatively stable A-type polyimide/graphite fiber composites using the approach of in situ polymerization of monomeric reactants directly on reinforcing fibers, rather than employing a separately prepared prepolymer varnish. This was accomplished by using a standard diamine and ester-acids instead of the corresponding anhydrides. The three ingredients were mixed in methyl alcohol and applied directly on the reinforcing fiber for subsequent drying, imidization and molding. This technique and the polyimide resin thus manufactured have come to be identified as the PMR system from the first letters of the words in the phrase, Polymerization of Monomeric Resultants.

This novel approach was originally conceived by NASA-Lewis personnel⁽¹⁾⁽²⁾ and provides a number of potential advantages. Some of these include:

1. Increased safety through the substitution of lower toxicity alcohol for the commonly used polyimide solvent, dimethylformamide.
2. Reduced cost through the use of more economical solvents, in lesser quantities, and the elimination of complicated synthesis procedures.
3. Simplified quality control in production runs because of the ease of mixing liquids and free flowing powders.
4. Elimination of varnish instability as a result of the technique of mixing the required quantity of stable materials at the time required.
5. Reduction of variability in final composite properties through elimination of the synthesis procedure requiring close control and the elimination of the need for storage of varnish solutions with accompanying property changes with time.
6. Improved composite properties through enlarged flexibility in the choice of reactants and the possible improvement of fiber wetting characteristics.
7. Greater flexibility in fabrication through the attainment of higher resin flow characteristics than is normally encountered with many A-type polyimides.
8. Reduction of process sensitivity through the elimination of the dimethylformamide component which boils at a high temperature and is generally felt to enter into the polymerization reaction.
9. Improved materials handling logistics.

Because of these potential advantages, a composite fabrication and characterization development program utilizing the PMR approach was conducted.

The program was divided into four basic tasks; these are given below with a brief comment on the objective of each phase.

TASK I - MATERIALS ACQUISITION

The purpose of this task was to acquire the necessary raw materials and conduct preliminary evaluation of the monomeric reactant solutions and determine the thermo-oxidative stability of the chosen graphite fiber.

TASK II - COMPOSITE FABRICATION AND PRELIMINARY EVALUATION

The purpose of this task was to develop the requisite composite fabrication techniques and to conduct preliminary physical and mechanical property evaluations.

TASK III - ADVANCED COMPOSITE EVALUATION

The purpose of this task was to conduct extensive physical and mechanical property determinations of graphite fiber composites after exposure to various environments.

TASK IV - ADDITIONAL PMR COMPOSITE CHARACTERIZATION

The purpose of this task was to demonstrate component fabrication. This included the fabrication of a number of sub-scale demonstration blade type specimens, an investigation of a suitable wedge adhesive, and further evaluation of improved processing techniques.

The new PMR system was found to be safe, easy to handle, processable with relatively wide process controls, and offered excellent mechanical properties and thermo-oxidative stability. Details of the materials, processing techniques employed, and evaluation methods and results are described in the body of the following text.

2.0 COMPOSITE CONSTITUENT MATERIALS

In the following sections, details of the program fiber choice and quality, as well as the monomeric reactant characteristics and the reactant solution behavior will be given. This discussion will summarize observations on constituent materials noted throughout the course of the program.

2.1 Reinforcing Fiber

Published literature⁽³⁾⁽⁴⁾ has recorded the thermo-oxidative attack sustained at 589°K (600°F) by the "high strength" graphite fibers vs. the "high modulus" type. Since one of the objectives of the program was to evaluate high temperature performance of the PMR resin matrix, it was decided to employ the "high modulus" type reinforcement to avoid any possible masking of high temperature isothermal behavior of the test composites. Specifically, the primary material chosen was Magnamite HM-S tow from Hercules Incorporated, Wilmington, Delaware. Some work was done toward the end of the program with Hercules HT-S tow. Both of these materials are continuous, 10,000 filament tow materials with considerable history in the industry. Both fibers were shear-treated but carried no sizing or finish. Table I provides the vendor limits on strength and modulus as well as the values recorded on certifications for each batch of HT-S and HM-S received and used on the program.

In order to confirm the thermo-oxidative stability of the primary fiber chosen, HM-S, at temperatures planned for subsequent laminate evaluations, six fiber samples (each from a different roll) were subjected to an isothermal gravimetric analysis in air at 589°K (600°F) for a period of 200 hours. A chamber with a volume of $1400 \times 10^{-5} \text{ m}^3$ (855 in³) was constructed and air flow was controlled at 100 ml/minute (6.1 in³/min). Bottled air, with a dew point temperature of 213.7°K (-75°F), was metered into the chamber, itself inside an air circulating oven, through a flow regulator. The copper air feed tube was of adequate length to insure that the temperature of input air was at oven temperature before entering the inner sample chamber.

Original sample weights were approximately 0.7 grams, representing three feet of the fiber tow. All samples were periodically weighed to monitor weight loss during exposure. The table below shows the cumulative weight losses experienced by all six samples. As can be seen, losses were insignificant. The selected fiber clearly displayed adequate thermo-oxidative stability for use in the construction of high temperature resin matrix composites.

Cumulative Bare Fiber Weight Loss in Milligrams
at 589°K (600°F) in Air (100 ml/min)

Hours Exposure	24	92	150	200
Lot/Spool Identification				
2-4/43-3	0	1	1	1
2-4/43	0	0	0	0
2-4/47-4	0	1	1	1
2-4/63A-1	0	0.05	0.05	0.05
2-4/47-6	0	1	1	1
2-4/7C-2	0	1	1	1

2.2 Resin

2.2.1 Monomeric Reactants

The monomer solution solvent used, anhydrous methyl alcohol, was identified as ACS reagent grade, acetone-free, absolute methanol with a water content maximum of 0.05%. The diamine component, 4,4'-methylenedianiline (MDA), was purchased in sealed 500 gram bottles to avoid progressive deterioration possible with repeated openings of larger containers. This material was certified by the vendor to have a melting point range of 364.6-366.1^oK (196.7-199.4^oF).

The required ester-acids were ordered from a specialty organic laboratory with a required melting point range of 1.5^oK. The monomethyl ester of 5-norbornene-2, 3-dicarboxylic acid (NE) and the dimethyl ester of 3,3', 4,4'-benzophenonetetracarboxylic acid (BTDE) were both certified to be free of residual anhydride on the basis of infrared spectrograms. The vendor reported a melting point of 375.1-377.1^oK (215.6-219.2^oF) for the NE. This was rechecked at TRW; a range of 375.6-377.1^oK (216.5-219.2^oF) was determined using a Fisher-Johns hot stage melting point apparatus. The BTDE material was delivered in a high solids solution in methanol; the vendor reported a solids content of 88 w/o. Subsequent determinations in two separate laboratories at TRW yielded a value of 85 w/o. Therefore, this latter value was used in solution makeup calculations in all following work.

These ester lots were used throughout the remainder of the program with no discernible change in appearance or behavior noted. Ten months after receipt, both esters were subjected to infrared spectroscopy and the spectrograms compared with the originals prepared by the vendor. No differences were observed. The TRW spectrograms are shown in figures 1 and 2. Electro-metric Karl Fisher titrations were performed on both NE and the BTDE solution for a check on water content. The BTDE 85% solids solution showed less than 0.03% water, and the NE powder showed 0.10% water. These water contents were not deemed significant.

2.2.2 Reactant Solutions

Because of the ease of mixing the reactant solutions, a fresh batch was ordinarily prepared for use each day. The order of mixing used was as follows:

- Weigh out the required amount of the BTDE solution.
- Add the full complement of methyl alcohol and stir for five minutes by hand, followed by 5-10 minutes with magnetic stirrer.
- Add the NE and stir for 5-10 minutes with the magnetic stirrer.
- Add the MDA and stir for approximately 30 minutes.

All mixing was done at room temperature with the solution capped during stirring with the magnetic unit.

Using the monomeric reactants described above, a series of solutions were made up to check stability over a 96 hour period. Three formulated molecular weight (FMW) solutions at two concentrations (40 w/o and 60 w/o) were prepared using the following stoichiometries:

Mole Ratio of Monomeric Reactants

<u>FMW</u>	<u>NE</u>	<u>MDA</u>	<u>BTDE</u>
1500	2	3.087	2.087
1750	2	3.603	2.603
1900	2	3.913	2.913

The 40 w/o solutions were kept capped throughout, as was one set of 60 w/o solutions. The third set, 60 w/o, was left open. Approximately 400 ml of solution was made up for each FMW-concentration combination. The 40 w/o solutions of all FMW exhibited an initial specific gravity of 0.950; the 60 w/o solutions had a specific gravity of 1.050.

Monitoring techniques included visual observation, infrared spectroscopy, viscosity and acidity determinations. The latter three test methods were employed on the original solutions and 24 and 48 hours later. Visual observation was continued for the full 96 hour period. Test equipment included a Brookfield viscometer, a Perkins-Elmer Infracord 137 (using thin films on salt plates), and a pH meter. For pH determinations, an equal volume of water was added to the solution, which caused the formation of a sludge, and filtrant checked for pH.

It was readily concluded that open storage of the solutions is unsatisfactory and to be avoided. The 1500 FMW lost about 25% of its total weight in a 24 hour period. The higher molecular weight solutions skinned over and consequently lost only 0.1%; however, an immediate increase in viscosity was noted in these systems. The 1750 FMW viscosity increased an order of magnitude in 24 hours from a starting viscosity of $0.080\text{N}\cdot\text{s}/\text{m}^2$ (80 cps) to over $0.900\text{N}\cdot\text{s}/\text{m}^2$ (900 cps). Only a slight decrease in pH was shown and no observable changes in IR spectra could be observed.

Both the 40 w/o and 60 w/o capped solutions showed a slight increase in viscosity, a small decrease in pH, and no change in IR spectra. Viscosity and pH numerical data are shown in table II. As with the uncapped samples, no discernible change in IR spectra was observed. Figures 3 through 5 display the spectra for the 1500 FMS w/o varnish as made up, after 24 hours, and after 48 hours. These are typical of all spectrograms observed. Visual observation of the solutions revealed no significant change in appearance through 96 hours.

As a matter of interest, 21 days after initial makeup on the solutions, the 40 w/o and 60 w/o capped solutions were reexamined. No precipitation of the 40 w/o solutions had occurred. All of the 60 w/o solution samples had precipitated. The precipitate was granular in appearance and was deposited in large quantities. The 1900 FMW showed the least quantity of precipitate and the 1500 FMW exhibited the heaviest deposit.

The conclusions drawn from this series of experiments were that the solutions should be kept covered and no difficulty would be encountered in storing the solutions for at least four days before use. However, it needs to be emphasized that the PMR approach eliminates the need for extended shelf life.

3.0 PROCESSING

The following sections describe the collected experience in preparing prepreg and molding flat laminates by various techniques. The fabrication of blade specimens is described in a separate later section. Additionally, ultrasonic inspection of program laminates, along with variations of standard processing and the effects on void content and ultrasonic patterns, is discussed.

3.1 Prepreg

As was noted earlier, resin solution stability experiments employed both 40 w/o and 60 w/o solutions. It was planned to use the 60 w/o solution in prepregging; however, first trials indicated that, with the prepregging technique employed, a 50 w/o solution gave better wetting and was therefore adopted as a standard for the remainder of the program. The 50 w/o 1500 FMW solution had a specific gravity of 1.000.

Impregnation of the fiber was carried out by dry wrapping the fiber on a 50.8 cm (20 inch) diameter drum and then metering the resin solution onto the fiber surface with a peristaltic pump. Figures 6 through 8 illustrate the technique and equipment used for impregnation. In figure 6, the tow can be seen coming off the spool under a slight tension created by an electrically operated spool brake. The roller and hoop arrangement shown spreads the 10,000 filament tow so that an even fiber placement is achieved. Figure 7 shows the resin solution reservoir and the tubing passing through the peristaltic pump. The pump metering rate is correlated with the traverse speed of the head on the Edwards Wrapping Machine. In this way, the required, calculated amount of resin is deposited on the fiber surface. Figure 8 shows the first drying or devolatilization process carried out before the prepreg is removed from the drum. The six infrared lamps (250 watts each) are on 17.8 cm (seven inch) centers and 15.2 cm (six inches) from the surface of the fiber. Volatiles driven off are removed through an overhead hood mounted over the winding area of the machine.

Tack and drape were controlled by drying procedures. With appropriate procedures, both these characteristics were completely satisfactory. The exposure under the IR lamps for one hour, after a 15 minute exposure at room temperature, brought the total volatile content to 13.0 to 16.0 w/o. The prepreg was still too "wet" at this point and a further devolatilization in an air-circulating oven for 10 minutes at 355°K (180°F) brought the volatile content down to 8 to 11 w/o, which was felt to be the correct level for manufacture of flat laminates.

In the preliminary composite evaluation, a target fiber volume of 50 v/o was used. In the advanced composite evaluation, a goal of 55 to 60 v/o was used. Prepreg was prepared with a 55 v/o with the thought that some resin flow would occur; this fiber volume was equivalent to a resin solids content of 36.5 w/o. Prepreg thickness calculations were based, for the most part, on obtaining a finished molded ply thickness of 0.254 mm (0.010 inch). This was done by using the following formula during the winding operation:

$$N = \frac{T V_f \rho_f}{W}$$

where:

- N = number of tows per inch
- T = thickness per ply
- V_f = fiber fraction
- ρ_f = fiber density
- W = fiber weight per unit length

During the early stages of the program, prepreg material was stored in metal foil lined vapor-proof bags and consumed within three or four days. To determine the real effects of material storage under projected commercial conditions, a series of three experiments were run. Untreated prepreg was stored for 24 days completely exposed in a laboratory environment (nominal 50% RH); untreated prepreg plies were exposed to 95% RH at room temperature for 18 hours; and an imidized preform was exposed to 95% RH at room temperature for 18 hours. Panels from each of the stored materials were then molded, postcured and evaluated by conducting flexure and shear tests at room temperature and 589°K (600°F).

The 95% relative humidity condition was created by holding the test material in a closed desiccator over a saturated solution (with excess solid material present) of dibasic sodium phosphate dodecahydrate ($\text{NaH}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$) at room temperature. The imidized preform picked up 0.4% in weight and the individual plies a total of 2.8%. The individual plies were imidized with the normal technique and both samples were molded using a standard cycle. No unusual behavior was observed in molding except that a slightly higher flow was noted: 9 w/o for the imidized preform and 9.9 w/o for the individual plies specimen. Some few surface defects were observed after molding, and in postcure three or four small blisters were noted at the outer edges of the laminates.

Cross sections of laminates molded from the materials exposed to 95% RH are shown in figures 9 and 10. As can be seen, the presence of voids detected in an ultrasonic inspection were confirmed. The mechanical test data are presented in table III. The material exposed to the 95% RH yielded lower mechanical property values, as might be expected from the void content, than unexposed material. The prepreg exposed to laboratory ambient for 24 days yielded laminates of comparable quality and with properties equivalent to material molded the day after manufacture and in the same family as laminates produced throughout the program.

The conclusions drawn from these trials were that the PMR prepreg was stable under normal conditions and could be, if desired, purchased from commercial prepreggers with no concern about normal shipment times. The material exposed to the 95% revealed that, while affected to some degree under these exceptionally harsh conditions, the system was not completely unusable.

3.2 Imidization

Imidization of A-type polyimides is that portion of the processing in

which the imide linkages are formed and condensation products are released; in the case of the PMR system, these condensation products are water and methyl alcohol. During the course of the program, laminates were produced by imidizing before molding at temperatures from 464°K (375°F) to as high as 517°K (470°F). Two basic techniques were employed; these included imidization in an air circulating oven and in a closed die.

As was noted, condensation volatiles are lost during the process of imidization. A review of the chemistry of the PMR system indicated that theoretically 17.1 w/o of the original solution solids should be lost. This weight loss behavior was confirmed with a short series of laboratory experiments. First, samples of the NE powder, MDA powder and the 85 w/o BTDE solution were each placed separately into a 478°K (400°F) oven. Weight losses on each of the monomeric components after one hour at 478°K were as follows: NE-100 w/o, MDA-36.4 w/o and BTDE-22.2 w/o. Next, samples of 50 w/o 1500 FMW solution were given slightly different oven exposures and weight loss measured. These data are shown below:

<u>Thermal Exposure</u>	<u>Solution Weight Loss, %</u>	<u>Solids Weight Loss, %</u>
15 minutes at 339°K (150°F) plus 1 hour at 478°K (400°F)	57.5	15.0
4 hours at 339°K (150°F) plus 1 hour at 478°K (400°F)	57.4	14.8
15 minutes at 367°K (200°F) plus 1 hour at 478°K (400°F)	57.8	15.6

Two conclusions are of interest. First, while the individual components lose large amounts (100% on the NE material) in separate 478°K exposures, in combination the reactants lose much less. And, secondly, while the weight loss shown on the 50 w/o reactant solutions does not exactly reproduce the 17.1 w/o calculated condensation loss, it closely approaches it, an average of 15.1 w/o. Additionally, it should be noted that, despite varying thermal exposures, essentially the same amount was lost in each case.

In the case of conventional prepolymer varnish, e.g., P13N (a commercially available A-type polyimide), it is possible that some of the condensation material, water, has already been eliminated during polymer synthesis. Additionally, the use of ester reactants in the PMR approach causes both water and methanol to be released during imidization. The methanol has a higher molecular weight than water, so a correspondingly higher weight loss percent is experienced. The lower condensation weight loss experienced with the P13N varnish could be ignored in preparing prepreg without serious discrepancies. This was not the case with the PMR system, so an increase in the amount of resin solution initially applied to the fiber was made to accommodate the 17.1 w/o solids loss experienced during imidizing.

As is noted below, imidizing temperatures of 464°K (375°F) and 478°K (400°F) were initially selected. The 478°K (400°F) value was based on work from NAS3-13203(3) in which a statistically designed experiment was employed to establish an appropriate imidizing time for P13N. The 464°K temperature

was established by running a limited series of weight loss experiments. Staged prepreg was cut into a series of 51 mm x 51 mm (2 inch x 2 inch) four-ply specimens and further drying them at 367°K (200°F) and 464°K (375°F). The data are presented in the two tables shown below.

Cumulative % Weight Loss Data 464°K (375°F)

Specimen	Time (Minutes)					
	10	21	31	60	90	120
1	11.6	11.8	11.9	12.0	12.0	12.0
2	11.7	11.2	11.9	11.9	11.9	11.9
5	11.9	12.1	12.2	12.1	12.1	-
7	10.5	10.7	10.8	11.8	11.9	-
6	11.6	11.7	11.9	11.8	-	-

Cumulative % Weight Loss Data 367°K (200°F)

Specimen	Time (Minutes)					
	15	30	45	75	105	150
3	4.14	5.35	6.16	7.51	7.87	8.47
4	4.00	5.39	6.18	7.48	8.08	8.47

Calculations based on known resin solids of the prepreg and theoretical condensation losses indicate that, of the 12 w/o shown at 464°K, one-third was methanol carrier solvent, and two-thirds was due to condensation products. It was noted in molding 51 mm x 51 mm specimens (2 inch x 2 inch) that only 0.1 or 0.2 w/o additional weight was lost. From these data, it was concluded that the 464°K (375°F) temperature produced essentially complete imidization of the small samples after 10 or 20 minutes. Further, it seems that some imidization occurs as low as 367°K (200°F) since extended exposures at this temperature show weight losses beyond the 4 w/o carrier solvent present in the prepreg. Thus, it was felt that the choice of the 464°K (375°F) temperature for imidizing was a good one since it would produce complete imidization while limiting end cap reaction which would be reflected in reduced resin flow in molding.

Two basic molding cycles were used throughout the program with experimental modifications. These cycles will be described in detail in a subsequent section; however, they may be identified as the 589°K (600°F) insertion temperature cycle and the 505°K (450°F) insertion temperature cycle which subsequently came to be the standard cycle. The 589°K cycle yielded only minimal resin flow with any imidizing cycle. The imidization cycle exerted a limited influence with the 505°K (450°F) cycle. For example, an imidization cycle of 45 minutes at 464°K in an air-circulating oven produced about 9.5% flow with the 505°K mold cycle (1000 psi). Other studies indicated that a one hour imidize at 478°K (400°F) produced about 5.5% flow, and a two hour imidize at this temperature reduced flow to the 2.0 to 3.0% range. For this reason,

the two hour oven imidize at 478°K (400°F) was settled on as standard.

To study the effect of imidization on the PMR resin system, samples of the unreinforced PMR-15 (1500 FMW) resin were dried and then imidized for 45 minutes at 464°K (375°F), ground to a fine powder and examined on the Fisher-Johns hot stage melting point apparatus. These samples showed initial melting at 503°K (446°F) and complete liquification at 513°K (464°F). A sample imidized for two hours at 478°K (400°F) showed a melting point range from 491°K (424°F) to 499°K (438°F). Using the same technique, a sample of P13N A-type polyimide resin showed no melting at all up to 589°K (600°F).

It was observed that the material imidized at 464°K (375°F) appeared quite fluid at the melting point, while the material imidized at 478°K seemed to exhibit a "taffy-like" appearance. It would appear that the melting point was not changed significantly by the higher temperature imidization conditions, but that the viscosity of the molten material was increased. This type of behavior could account for the decreased resin flow observed in molding laminates imidized at the higher temperature.

It was later observed that, with the 505°K (450°F) mold cycle, flow was noted to be relatively constant at the lower level (ca. 3%). For instance, imidization cycles for four hours at 478°K (400°F) and two hours at 488°K (420°F) produced about this same amount of resin flow. These latter imidization cycles were experimental and exhibited no improvement over the selected two-hour oven treatment at 478°K (400°F).

Oven imidizations were conducted in one of two ways, and no observable difference was noted in flow, quality or properties. In both cases, the ply stack was initially preformed at room temperature under 8.6×10^5 Pa (125 psi) for one minute. In the foil wrapped technique, the preform was sandwiched between a single ply of porous, Teflon coated glass cloth and an additional ply of glass bleeder cloth. This sandwich was wrapped in aluminum foil to provide side restraint and a 3 mm thick steel plate placed on top during the oven imidization. In the second technique, the preform was placed between plies of the Teflon coated glass cloth and then held between aluminum honeycomb with a light weight on top. The problem here was to adjust the weight on top to the size of the preform to avoid resin flow and preform deformation during imidization.

One other technique, based on the standard mold cycle (505°K insertion), was evaluated. Unimidized preforms were placed in a cold tool and press and the temperature brought up incrementally. Both residual solvent removal and complete imidization were accomplished in the tool. A typical time-temperature-pressure cycle is detailed in table IV. Both nine ply 10.2 x 20.3 cm laminates and 10.2 cm x 10.2 x 9.5 mm laminates were prepared in this way. Both exhibited smooth surfaces, free of imperfections and adequate flow was easily obtained.

As can be seen from table IV, the weight of the free floating punch was enough to induce resin flow during the die imidization cycle. The punch produced a pressure of 1.4 kPa (0.2 psi); it was later determined that a pressure of half this value was adequate to provide intimate contact during

processing and did not induce flow during this portion of the thermal cycle. It can be concluded that the imidize-in-die technique represents an effective alternate to the oven-imidize approach.

While the two-hour oven imidization at 478°K was selected as standard, it can be seen that alternate temperatures and times were also suitable. Some degree of control of flow was possible by varying the imidization conditions and no difficulty was encountered in imidizing in the tool in a continuous process starting with a cold tool. In summary, this portion of the process was found to be a relatively insensitive part of the fabrication of PMR composites.

3.3 Molding

Basically, two laminate molding cycles were used to prepare program laminates for subsequent evaluation. In the first cycle, an imidized preform was placed in a die preheated to 589°K (600°F) and held at contact pressure for 30 to 60 seconds before the full pressure of 3.4×10^6 Pa (500 psi) was applied. All laminates for the portion of the report designated as "Preliminary Composite Evaluation" were prepared using this technique. In the second cycle, the imidized preform was placed in a die preheated to 505°K (450°F) and held 10 minutes under contact pressure before a pressure of 6.8×10^6 Pa (1000 psi) was applied and the platens set for 589°K (600°F). Laminates used in the "Advanced Composite Evaluation" portion of the program were prepared in this manner.

As was noted above, the first cycle was used for preparing laminates tested in the "Preliminary Composite Evaluation." It was noted that small surface imperfections were present on both sides of laminates prepared in this manner; figures 11 and 12 illustrate typical surface effects at 1.8 times full size. The depressions were only a few thousandths of an inch deep and did not affect the flexure strength or shear strength properties. Cross sections of laminates with these surface imperfections revealed no sub-surface effect (see figure 13). As a consequence, laminates prepared in this manner were used for evaluation in the "Preliminary Composite Evaluation" phase. However, the surface imperfections were undesirable and, since minor molding cycle alterations did not resolve the problem, further work was performed.

To conserve material, a panel 10.2 cm x 10.2 cm (4 inches by 4 inches) with 5 plies was first fabricated. While surface imperfections were faintly discernible, a larger 10.2 cm (4 inch) by 20.3 cm (8 inch) laminate exhibited more imperfections. Since the imperfections must be related to surface area, the larger laminate with 5 plies [final molded thickness of 1.3 mm (0.050 inch)] was used in the remainder of the experiments.

A total of 37 laminates of the 10.2 x 20.3 cm (4 inch x 8 inch) size were prepared, varying the following parameters:

1. Delay between prepregging and imidization (same day to three day hold).
2. Imidization restraint (foil wrap vs. honeycomb sandwich).

3. Imidization time and temperature (two hours to 20 minutes with temperatures ranging from 464°K (375°F) to 517°K (470°F)).
4. Treatment after imidization (ambient cool, desiccator cool, directly from imidization oven into hot tool).
5. Bleeder between part and tool.
6. Final mold temperature [562°K (550°F) to 617°K (650°F)].
7. Dwell time and mold insertion temperature (30 seconds to 15 minutes with temperatures of 617°K (650°F) to 533°K (500°F)).
8. Extended cure (up to four hours).
9. Mold pressure 3.4×10^6 Pa to 6.8×10^6 Pa (500 psi to 1000 psi).
10. Pressure maintenance during cooldown.

The majority of the laminates produced exhibited surface imperfections. Additionally, some of the laminates were found to have a brownish surface color.

An examination of long-time, high-temperature dwell specimens seemed to show a relation of surface imperfections, resin flow and surface discoloration. This latter phenomenon ranged from a surface powder, in one case, to an embedded surface condition producing a grainy appearance. An examination at 30X of the surface showed the presence of tiny blisters and a discontinuous resin layer. Figure 14 shows the surface at 100X of a typical laminate with normal color; figure 15, at the same magnification, shows the appearance of a laminate with discoloration. The lightest areas are blisters and the darkest areas show an absence of a resin layer.

The surface appearance was not found to be deleterious to performance. This statement is based on isothermal gravimetric analysis (ITGA) of three laminates of 1750 FMW at 589°K (600°F) for 600 hours. Composite weight losses at the end of the 600 hour period were as follows:

Laminate No. 16	Standard Color	3.4%
Laminate No. 18	Standard Color	3.5%
Laminate No. 19	Discoloration	3.8%

A conclusion that could be drawn from the result of all cycle variation studies is that the imperfections were created by gas trapped between the die and the still thermoplastic laminate surface. It is hypothesized that gas is liberated during a specific temperature range in molding and that this gas creates local depressions in the still resilient laminate surface. The thermoplastic (without postcure) characteristic of the resin at 589°K (600°F) was later confirmed in short beam shear tests at 589°K (600°F) on laminates postcured for two hours at 589°K (600°F) when these laminates displayed bending rather than fracture during load application.

Two alternate laminate cycles were found to produce acceptable surfaces on molded parts. In each case, the material had been imidized for 60 minutes at 478°K (400°F), and although imidization affected resin flow, it was not found to influence the imperfections. The cycles are as follows:

CYCLE 1

- a) Insert imidized preform into die preheated to 589°K (600°F).
- b) Apply contact pressure and hold 120 seconds.
- c) Apply 6.8×10^6 Pa (1000 psi) and hold for 1/2 hour.

CYCLE 2

- a) Insert imidized preform into die preheated to 505°K (450°F).
- b) Apply contact pressure and hold 10 minutes.
- c) Apply 6.8×10^6 Pa (1000 psi) and set platen controls for 589°K (600°F).
- d) Hold part for 1/2 hour after reaching 589°K (600°F).
- e) Cool under pressure.

Cycle No. 2 produced a laminate with good color, a minimum of tiny imperfections and adequate resin flow. Cycle No. 1 produced a laminate that was free of imperfections, had no perceptible resin flow with the imidizing cycle used, but had some surface discoloration.

The second cycle, utilizing a fully imidized preform into a die preheated to 505°K (450°F), has several advantages. The most important of these include the achievement of high flow characteristics and the use of a low starting temperature suitable for the manufacture of thick parts with a non-critical initial time-temperature relation. The latter cycle was chosen for continued work on the program, i.e., in the "Advanced Composite Evaluation" phase. This cycle is completely described in figure 16.

A modification to Cycle No. 2 was the use of the "imidize-in-the-tool" technique. Table IV describes the temperature-pressure parameters used on a 10.2 cm x 10.2 cm x 9.5 mm (4 inch x 4 inch x 0.374 inch) laminate used for subsequent thermal expansion testing. Figure 17 displays polished cross sections (full size) of this laminate. As can be seen, some voids are apparent. While they give the appearance of being cracks, it is felt that they are elongated voids based on the observation of other laminates on the program. Figure 18 illustrates the cross section at 50X magnification.

This molding technique was also used for 2.3 mm (0.090 inch) thick test laminates and the fabrication of demonstration blade specimens. A complete description of the blade specimen molding process will be discussed in a later section. Mechanical test values of composites prepared by this technique were equivalent to the unmodified Cycle No. 2 in which parts were oven imidized. This can be seen in a comparison of the data shown in Table V in which both the standard cycle and the imidized-in-the-tool method were used.

3.4 Postcure

Initial laminates on the program were postcured for one hour at 366°K (200°F), one hour at 478°K (400°F) and two hours at 589°K (600°F). Room temperature mechanical test specimens showed good property values; however, it was noted that, at the 589°K (600°F) test temperature, short beam shear samples exhibited bending rather than fracture and subsequent samples were then postcured for 16 hours at 589°K (600°F). Further flexure tests indicated that strength after a 600 hour exposure at 589°K was sometimes higher than specimens as postcured and tested at 589°K. At this point, postcures were extended to 16 hours at 617°K (650°F). This change was based on the short beam shear data shown below.

589°K (600°F) Short Beam Shear Strength
As a Function of Postcure Time/Temperature

Postcure Temperature	Postcure Time, hrs	Short Beam Shear Strength	
		psi	MPa
None	None	5600	38.6
		Specimen bottomed in fixture.	
589°K (600°F)	8	5600	38.6
		5900	40.7
589°K (600°F)	16	5800	40.0
		5700	39.3
589°K (600°F)	24	5200	35.8
		6100	42.1
589°K (600°F)	48	5900	40.7
		5700	39.3
617°K (650°F)	2	5600	38.6
		5100	35.2
617°K (650°F)	16	5800	40.0
		6000	41.4
617°K (650°F)	24	5600	38.6
		5900	40.7

Table VI lists data developed on panels prepared with the standard two hour 478°K imidization, molded as shown in figure 16, and postcured for 16 hours at 617°K. Failure modes were appropriate, and, as can be seen, the data reflect good quality laminates.

There was originally some concern that the high postcure temperatures in a normal air environment in an air-circulating oven might lead to a premature failure in subsequent isothermal exposures due to an oxidative catalysis. Table V displays data collected on postcured samples subsequently exposed to flowing air at 589°K for 450 hours. As can be seen, the high temperature postcure did not induce any unexpected degradation in isothermal gravimetric analysis (ITGA).

The cycle used is displayed in Figure 19 and was adopted as the standard postcure cycle for the 2.3 mm (0.090 inch) thick laminates. Cooldown is not shown since the laminates were shown to be insensitive to postcure cool-down rates, and no special care was needed.

3.5 Further Process Investigations

At the conclusion of postcure trials, it was felt that an adequate process cycle had been developed for the molding of the PMR material and the manufacture of laminates for the "Advanced Composite Evaluation" portion of the program was initiated. To evaluate internal quality, an ultrasonic inspection was instituted. A through-transmission method with a C-scan recording was used. The tests were performed at 10 MHz with a 2.38 mm (3/32 inch) diameter sending crystal of the SIL type. The receiving crystal (SIZ) was 12.7 mm (1/2 inch) in diameter. The ultrasonic unit was a Sperry UM-700 with an Automation Industries SR-194 C-Scan recording unit; figure 20 shows this installation. An HFN pulser was used. While the signal screen height was varied originally from 25 to 75%, it was found that the 50% level displayed good contrast between sound and flawed areas and was used as a general standard throughout all subsequent testing. In making repetitive setups, a 3.17 mm (1/8 inch) thick piece of titanium (6Al-4V) was used as a standard to set screen height at 30%.

Figures 21, 22 and 23 display the C-scans of laminates 589-47, 589-51 (part A) and 589-51 (part B), respectively. Parts A and B represent two halves of a 21.6 cm x 21.6 cm (8-1/2 x 8-1/2 inch) laminate which was cut into two pieces for ease of handling. As can be seen, defect indications are present at the end of the laminates. Further, note that the indications in laminate -51 appear to form a circular pattern. Photomicrograph sections were taken from the sound and defect areas of these panels; these appear in figures 24 and 25. It is quite clear that defect density is higher in the areas identified in the C-scans.

Following the identification of defect areas at the ends of laminates, continued examination was made of subsequent laminates. The circular pattern mentioned was repeatedly found in all laminates. Figure 26 is a typical example of the pattern found in all panels fabricated; figure 27 shows two 50X cross sections of the defect area from this panel.

Figure 28 shows the typical incipient circular pattern found even in 10.2 cm x 10.2 cm (4 x 4 inch) laminates. Figures 29 and 30 show cross sections at 50X of sound and sonically identified defect areas found in panels fabricated later in the program.

It needs to be emphasized that the overall void contents of 16 laminates, based on specific gravity of the total laminate, ranged from as low as 0.9 v/o to a maximum of 3.7 v/o. A number of laminates were sectioned and specific gravities determined separately on sound and defect areas. A typical example was laminate 594-80 (see figure 30) in which the sound area yielded a specific gravity of 1.57 and a defect area of 1.55. Using these values and a resin specific gravity of 1.32, a nominal resin solid value of 35 w/o and the fiber density provided by the vendor, the two areas had void contents of

1.0 and 2.0 w/o, respectively. The void content range is considerably lower than normally obtained for PI composites. Furthermore, little or no information has been previously presented using C-scan techniques to characterize laminate quality.

Even though the void contents were not excessive, a further process investigation program was performed. The monomeric reactants were checked by IR. Oven and press temperature controls were re-calibrated, stoichiometry and solution make-up calculations were reviewed, and the press platen and die surfaces were checked for flatness and parallelity. None of these appeared to be the cause of the problem, so a series of process modifications were evaluated. Possible causes for the voids in composites were examined and are listed as follows:

- Entrapped air
- Re-intruded air
- Selective monomer loss
- Condensation products (water/alcohol)
- Degraded monomer
- Cyclopentadiene (created during the pyrolytic polymerization from the norbornene end cap)

Molding experiments based on the above list did not yield void-free laminates.

3.6 Supplemental Processing Note

After the experimental studies required in this contractual program had been completed, the NASA Project Manager supplied TRW with a monomeric solution which provided a high quality laminate. The C-scan of the laminate shown in figure 31 does not indicate the presence of voids or defects. In addition, the surface of the laminate was free of surface imperfections, discoloration and any grain-like structure.

The solution supplied by the NASA Project Manager utilized freshly prepared BTDE instead of BTDE from a commercial source. The monomeric reactant solution provided ease of handling and processability except for reduced resin flow. Details concerning the preparation of the monomeric reactant solution are available from the NASA Project Manager.

4.0 PRELIMINARY COMPOSITE EVALUATION

In this portion of the program, three formulated molecular weight (FMW) levels of the PMR resin were evaluated by isothermal gravimetric analysis and subsequent selected flexure and shear tests. The following sections describe the effort completed.

4.1 Laminate Preparation

A series of 19 unidirectional HM-S laminates of three FMW's (1500, 1750 and 1900) were prepared using the following techniques:

- a) Impregnate fiber with peristaltic pump as described in Section 3.0.
- b) Devolatilize, on the winding drum, under IR lamps for one hour to bring the volatile content (589°K exposure) to 13.0 to 16.0 w/o.
- c) Remove the prepreg from the mandrel and further devolatilize in an air-circulating oven for 10 minutes at 355°K (180°F) to bring the volatile content down to 8 to 11 w/o.
- d) Stack plies and preform at room temperature and 8.6×10^5 Pa (125 psi) for one minute.
- e) Sandwich the preform between a single ply of porous Teflon coated glass cloth and an additional ply of glass bleeder cloth. This sandwich was wrapped in aluminum foil to provide side restraint and a 3 mm thick steel plate placed on top during imidization.
- f) Imidize in an air-circulating oven at either 464°K (375°F) or 478°K (400°F) for the times as shown in Table VII.
- g) Mold at 3.4×10^6 Pa (500 psi) in a die preheated to 589°K (600°F) with either 30 second or 60 second dwell time before full pressure application. Hold 30 minutes.
- h) Postcure one hour at 366°K (200°F), one hour at 478°K (400°F) and two hours at 589°K (600°F).

Table VII lists important criteria for each of the laminates fabricated. As can be seen, limited variation existed among the laminates. Figure 13 displays typical cross sections (taken from the center of the laminate) for the laminates prepared. A target fiber fraction of 0.50 was selected.

4.2 Isothermal Gravimetric Analysis

The laminates prepared as described above were subjected to a 600 hour isothermal gravimetric analysis (ITGA). Figure 32 displays the typical setup in which all isothermal gravimetric analyses were run. The photograph displays the air bottle, flowmeter, specimen stack on a screen and the inner chamber in which air flow was controlled at 100 ml/min. (6.1 in³/min.). Note that at the bottom of the inner chamber a ring is shown. This is a copper tube,

sealed at the end, through which the bottled air was passed; small holes drilled in the copper tube on one inch centers permit an even, regular flow of air up through the chamber. Not shown is a length of copper tubing in the oven designed to preheat the air to oven temperature before discharge into the chamber. The bottled air used had a dew point temperature of 214°K (-75°F). The inner chamber had a volume of $1400 \times 10^{-5} \text{ in}^3$ (855 cubic inches). Temperatures inside the chamber were monitored with calibrated thermocouples.

Portions of 15 laminates, each 3.8 cm (1-1/2 inches) by 19 cm (7-1/2 inches) were subjected to the ITGA. Ten of these pieces were of the 1500 FMW, three of 1750 FMW, and two of the 1900 FMW. Figure 33 is a plot of weight loss vs. time for the three different materials. Note that composite weight losses have been divided by the composite w/o resin to reduce the values to resin loss only to allow for possible variation in resin solids contents among laminates. As can be seen the average values of the 1750 and 1900 FMW systems fall within the range of the 1500 FMW laminates, showing very little difference in thermo-oxidative performance at the end of 600 hours at 589°K (600°F).

4.3 Mechanical Test of ITGA Specimens

Since little difference was shown in the ITGA performance among the three FMW systems evaluated, a review was made of the need to evaluate the higher FMW systems. These had shown less resin flow in molding and an increased incidence of surface imperfections described in Section 3.3. It was decided that these higher molecular weight systems did not display an adequately improved performance to warrant the added processing difficulties encountered and were dropped from further investigations.

The ten laminates of the PMR-15 (1500 FMW) were tested in flexure and short beam shear (test specimens described in Appendix A) at room temperature and 589°K before ITGA and at 589°K after the 600 hour ITGA exposure. These data are shown in table VIII. It can be seen that the data reflect comparable values to those reported in the industry with both epoxy and polyimide resins with the HM-S fiber. Retention of strength at 589°K was quite good after introduction of the 617°K (650°F) postcure, and the loss experienced after the 600 hour ITGA was not excessive. In fact, some values were even higher after the 600 hour exposure, pointing up the importance of 617°K postcure introduced on the latter laminates.

4.4 Confirmation of Reproducibility

To confirm the repeatability of the data collected in both ITGA and mechanical test, three other laminate sections were subjected to the same tests as the laminates described above in Section 4.3.

Laminate 589-51 (21.6 x 21.6 cm) was prepared using the cycle with a two-hour oven imidize and a die insertion temperature of 505°K (450°F) with a final postcure of 589°K. Laminate 589-54 was a 21.6 x 21.6 cm panel prepared by imidizing in the tool but molded with the same cycle as laminate 589-51. The 21.6 x 21.6 cm laminate was divided into two pieces; section A was postcured at 589°K and section B was postcured at 617° (650°F). Figure 34 is a plot showing the ITGA range of 10 previous laminates and the three

sections just described. As can be seen, no difference was shown in the performance of the sections receiving different postcures, and all three laminates fell essentially in the range of previously tested samples. It is felt that the band shown on the plot truly reflects the ITGA characteristics of the system since multiple resin mixes, prepregs, moldings, mold cycles and postcures are represented.

Additionally, the 10.8 x 21.6 cm (4-1/4 inch x 8-1/2 inch) laminate sections exposed in ITGA were machined into flexure and short beam shear specimens. These values at both room temperature and 589°K are shown in table V. As can be seen, the values compare well with others collected during the program and indicate a material very resistant to degradation at 589°K. It should be noted that, with the completion of these tests, laminates were compared that were prepared by three basically different techniques: (1) oven imidize and mold in a die preheated to 589°K, (2) oven imidize and mold at 589°K with an initial die temperature of 505°K and (3) imidize and mold in the tool in a continuous cycle. All ITGA and mechanical data show comparable performance among the laminates.

5.0 ADVANCED COMPOSITE EVALUATION

Having determined in the previous phase that the PMR concept produced laminates with excellent properties, both as fabricated and in thermo-oxidative tests, and having selected a single formulated weight for test, a more extensive characterization of the selected material was undertaken. Table IX shows the planned test matrix followed in this phase of the program and the text below describes the results obtained.

5.1 Laminate Preparation

Using a target fiber volume in the finished laminate of 55-60 v/o, the HM-S fiber was impregnated with the PMR-15 resin, devolatilized using the technique described previously and molded (Cycle No. 2 in Section 3.3). After preforming, the panel was:

- a) Imidized in an air-circulating oven for two hours at 478°K (400°F).
- b) Placed in a die preheated to 505°K (450°F) and contact pressure applied.
- c) Held 10 minutes at this temperature and pressure, after which 6.9 MPa (1000 psi) was applied and the press platens set for 589°K (600°F).
- d) Twenty minutes after the press platens reached 589°K, a one-hour hold was started.
- e) Fan cool to 533°K (500°F) and reduce pressure by one-half.
- f) Continue to fan cool to 478°K (400°F) at which point the pressure was reduced to contact and cooling water introduced into the platens.
- g) Remove part at room temperature.

This molding cycle is shown schematically in figure 16, from which temperature rise and cool times can be noted.

With few exceptions, the unidirectional laminates molded were 21.6 cm x 21.6 cm (8-1/2 x 8-1/2 inches) and nine plies thick. These laminates were cut in half and postcured with a cam controlled 72 hour cycle to 617°K (650°F) as shown in Figure 19. Table X lists important criteria for the panels molded in this way and used subsequent ITGA and mechanical test in this phase of the program.

As can be seen from an examination of table X, resin flash ranged from 0.6 w/o to 4.0 w/o (based on total laminate weight) and mold shrinkage, calculated from a hot tool to a cold part, averaged about 1% when measured perpendicular to the fiber orientation. About 1 w/o additional weight loss was noted in postcure; no thickness change was observed but a continued shrinkage perpendicular to the fiber orientation of 0.6% was measured. Fiber volume determinations indicated an average of 57.3 v/o and a total laminate

void content range of 0.9 to 3.7 v/o; both these calculations were based on a resin specific gravity of 1.32 (see Section 5.4) and the vendor supplied fiber data.

5.2 Isothermal Gravimetric Analysis

The ITGA at three temperatures was performed as described in Section 4.2; panel size (approximately 80 grams) was typically 10.8 cm x 21.6 cm (4-1/4 x 8-1/2 inches). A plot of composite weight loss data is presented in figure 35. The weight loss points plotted in the curves indicate values for every condition tested and, in most cases, represent averages of from two to four specimens. While some spread can be seen in the data, it is felt that this is most probably a reflection of the laminate resin solids values. These ranged from 30.3 w/o to 37.8 w/o with an average of 34.0 w/o.

In examining the curve representing the 561^oK (550^oF) weight loss, it should be noted that the line from 100 hours to 1000 hours is a straight line. It can be seen that, at the end of 1000 hours, only 1.3% of the composite weight was lost; this represents 3.8% resin matrix loss. The specimens exposed at 589^oK lost 4.8%; this represents 14% of the total available resin. The 617^oK (650^oF) figures shows a composite weight loss of 7.6% at 312 hours; this represents a 22% loss of available resin. It would seem that, on the basis of ITGA, the PMR-15 might be assigned a long life temperature of between 561^oK (550^oF) and 589^oK (600^oF). It is clear that the system is not suitable for long times at 617^oK (650^oF).

5.3 Composite Property Determinations

5.3.1 ITGA Mechanical Testing

Composite panels were withdrawn from the ITGA ovens at pre-selected times and machined into mechanical test specimens; a description of specimen geometry is given in Appendix A. All panels were ultrasonically inspected prior to ITGA exposures and C-scan records kept of defect profiles. In machining specimens for subsequent test, the heavier defect areas associated with the circular pattern, discussed in Section 3.5, were avoided where possible. For example, in machining tensile specimens, the heavier defect areas were kept in the section under the tensile grips, while the gage section was chosen to fall in an ultrasonically sound laminate area.

The results of these mechanical tests are summarized in tables XI and XII. As can be seen from an examination of the data in these tables, the 1000 hour aging at 561^oK (550^oF) had little or no effect on the strength of the composites. The 589^oK (600^oF) and 617^oK (650^oF) exposures produced some degradation of properties at the longer time periods investigated. In general, these data confirm the thermo-oxidative behavior illustrated by the ITGA weight loss curves discussed in the previous section. A review of the data would indicate that the PMR-15 system has excellent high temperature properties and long term thermo-oxidative resistance at some temperature between 561^oK and 589^oK. Additional work would have to be performed to identify the exact temperature in this range at which the system begins to seriously degrade.

5.3.2 Hostile Environmental Conditioning

Property retention characteristics were also evaluated in two other environmental conditions; thermal cycling and water boil.

Thermal cycling of the unidirectional composites was accomplished in the test unit shown in figure 36. The upper, electrically resistance heated chamber was held at 589°K while the lower chamber (polystyrene foam) was held at 219°K (-65°F) with dry ice. Residence time in each chamber was 10 minutes and a total of 100 cycles were run (total of 33.3 hours). No visual degradation was observed at the end of the thermal cycling, and the 7.6 cm x 10.2 cm (3 x 4 inch) specimen blanks were machined into standard flexure bars.

Table XIII displays the flexure data gathered after the thermal cycling exposure. The data indicate no loss in properties; in fact, the room temperature strength represents some of the highest values observed on the program. The 589°K flexure test values do not indicate any loss of strength due to the 33.3 hour cycling exposure.

The water boil test was originally planned to be conducted by boiling laminates for two hours and then testing. Due to a delay in mechanical testing, the panels were boiled for two hours, machined into flexure specimens, stored for 38 days at room temperature and then reboiled for an additional two hours and stored in plastic bags until flexure test the next day. These data are given in table XIII. No loss of room temperature or 561°K (550°F) flexure strength was experienced. The 589°K values, however, are significantly lower than that exhibited in unboiled composites. This seems to indicate some loss of hydrolytic stability at this test temperature, but these values should be confirmed with other laminates and tests to make a positive statement.

5.3.3 Strain Gage Testing

Four tensile specimens were tested at room temperature with strain gages attached; two longitudinal specimens and two transverse. Four gages were used with each specimen. An axial and a transverse gage were applied to both sides to cancel bending effects in calculation. The gages were designated EA-13-062TT-120 from Micro-Measurements and were applied with standard techniques. Testing was done on the Instron Tensile Tester using a SR-4 calibration unit and a switching and balancing unit to sequentially provide the multiple gage input to the Instron strip recorder. The following equations were used to calculate Poisson's ratio:

$$\sigma_1 = \frac{E}{1-\mu} (\epsilon_1 + \mu\epsilon_2)$$

$$\sigma_2 = \frac{E}{1-\mu} (\epsilon_2 + \mu\epsilon_1)$$

where:

σ_1, σ_2 = principal stresses
 ϵ_1 = longitudinal strain
 ϵ_2 = transverse strain
 μ = Poisson's ratio

A summary of the data collected from these tests on the HM-S/PMR-15 specimens is given in table XIV. The longitudinal strength of the composites, which reflects primarily the fiber strength, is felt to be slightly lower than similar industry data. It should be noted that both specimens failed at the transition between the fiberglass tab and the gage section of the specimen. The reason for this is unknown since this specimen design has been used successfully in the past and with HT-S/PMR-15 specimens on this program. The other longitudinal data seem to truly reflect characteristics of the material and are comparable with other information on this type of fiber reinforced material. The stress-strain curves for these two specimens are plotted in figure 37.

The transverse properties are felt to be better, for the most part, than data seen in the literature for similar composites. The strain to failure seems reasonably high for a resin of this family of polyimides. The stress-strain curves for these specimens are plotted in figure 38. Note that the curve for specimen number two departs from a straight line indicating a plastic deformation in the higher stress ranges.

5.3.4 Thermal Expansion Testing

Four HM-S/PMR-15 composite specimens were subjected for analysis of linear thermal expansion from 219°K (-65°F) to 589°K (600°F). Samples 50.8 mm x 6.4 mm x 6.4 mm (2 x 1/4 x 1/4 inches) were sent to Dynatech R/D Company, Cambridge, Massachusetts for analysis. Their first step was to measure the initial length of the sample with an accuracy of ± 1 micron. The specimen was then instrumented with a temperature measuring thermocouple in the quartz measuring head of a Netzsch Electronic Automatic Recording Dilatometer. The system was placed at the center zone of an environmental chamber, cooled below -100°F and warmed incrementally to 278°K (40°F). The chamber was then completely sealed, purged with helium and programmed for temperature rise and equilibration to 603°K (625°F). During the entire experiment, the length and temperature of the specimen were recorded continuously, automatically. This procedure was repeated for each sample. The coefficient of linear expansion was derived from the initial sample length and the change in this length over the specified temperature interval.

Average coefficient of linear expansion values for each pair of specimens (two parallel and two perpendicular to fiber orientation) are given in table XV. The data are representative of literature values for materials of these types. In considering the variation shown in the values for expansion parallel to the fiber, it should be remembered that actual movement of the specimen was so small that it was very difficult to measure accurately even with precision equipment. The negative values reflect the characteristic of

the reinforcing fiber; i.e., the fiber has a known negative coefficient of expansion along the length.

5.3.5 HT-S/PMR-15 Mechanical Testing

Since the bulk of the work during the course of the program was with the HM-S fiber, it was felt to be desirable to investigate certain composite properties with the HT-S fiber. Laminates were fabricated and postcured using the standard techniques described earlier. All panels were ultrasonically inspected and wherever possible specimens were machined so that defect areas were not included in specimen gage sections.

The results of these investigations are shown in table XVI. Both flexure and longitudinal tensile values are somewhat lower than seen in the literature for this type of fiber. However, short beam values seem to be about average or slightly higher than other data reviewed. The fiber batch used to fabricate these laminates was certified by the vendor to have a tensile strength of 2.37 GPa (344 ksi); this value is slightly lower than their advertised minimum 2.41 GPa (350 ksi). It is felt that this fiber property is strongly reflected in the composite properties of flexure and longitudinal tensile. The moduli values are comparable to those seen in the industry.

To observe the effect of increasing the fiber deviation angle from unidirectional, 0 degree orientation, a series of balanced and symmetrical shallow angle cross-ply laminates were prepared. As can be seen, as the fiber angle was increased from ± 5 to ± 15 degrees, the tensile strength decreased in what appears to be a logical manner. Little data are available for comparison, but these values seem quite acceptable in light of the value obtained in 0 degree, unidirectional tensile.

5.4 PMR-15 Specific Gravity

In order to obtain a specific gravity value on the cured PMR-15 resin for prepregging and void content calculations, a series of unreinforced moldings were prepared. A number of cycles were used to prepare these "buttons," but the highest value obtained was a specific gravity of 1.28. The "buttons" prepared were sectioned and polished after density determinations; all specimens exhibited voids, limiting the value of the determined density measurements. Another attempt was made to check density by curing resin without pressure and then grinding the powder in a mortar and pestle. This powder was subjected to density measurements on the air pycnometer; values obtained were in the range of 1.38, clearly unrealistically high.

The final value calculated for use on the program was 1.32; this is the same as that reported for P13N polyimide resin. This value was obtained by selecting small portions of the PMR-15 laminates determined to be free of voids by microscopic examination, determining the resin solids contents by replicated sulfuric acid-hydrogen peroxide digestion, and back-calculating from an assumed void content of zero. Multiple determinations yielded the 1.32 value used for all subsequent prepreg and void calculations. The void values reported in table X are based on this value.

5.5 Vacuum Bag Trial

In examining various cycles, in order to minimize defect patterns observed in ultrasonic inspection, a number of trials were run with a vacuum bag surrounding the tool during molding. While the technique did not aid in eliminating voids, one laminate, prepared only with vacuum bag pressure, was of interest. In this case, a 13 ply unidirectional laminate was prepared with HT-S reinforcement and the PMR resin. Two formulated molecular weight pre-pregs were interleaved; 1100 FMW and 1300 FMW. The laminate was imidized in a molding tool, with no vacuum, at 478°K (400°F) for 30 minutes, at which point a full vacuum was applied to the aluminum foil bag which contained the molding tool. The temperature was raised to 589°K (600°F) and held for 30 minutes before the standard cooling cycle was applied.

The finished laminate had a smooth surface and a 3 w/o resin flow was measured. The laminate was macroscopically uncracked and had a thickness/ply value of 10.8 mils; the prepreg had been prepared to yield a 10 mil/ply thickness with more normal processing. No further evaluation was performed except sectioning and polishing. Figure 39 is a 2.5 times size photo of the cross section. A relatively high void content is apparent with some of the elongated type discussed earlier. While the void content detracts from the quality of the laminate, no experimentation was conducted to optimize the vacuum bag cycle. It is felt that, with the straightforward cycle used and the low pressure applied, the quality obtained was surprising.

6.0 BLADE SPECIMEN FABRICATION AND EVALUATION

Six demonstration blade specimens were fabricated. The blade specimen had a simple bi-convex airfoil with a transition from airfoil to splayed root. No twist or taper in the airfoil was included in the specimen design. The tool used was available from a previous TRW program⁽⁵⁾ in which epoxy and polyimide resins were used to fabricate the blade specimens. The following sections describe the choice of adhesive for the aluminum blade wedges, the fabrication of the blade specimens and the subsequent evaluation.

6.1 Selection of Wedge Adhesive

Three basic resin systems were evaluated for integrally bonding the aluminum wedges in the blade specimens. These were the PMR-15 alone, a bis-maleimide (Kerimid 501, Rhodia, Inc.) unsupported adhesive film, and a supported film condensation type polyimide adhesive (FM-34, Bloomingdale Department of American Cyanamid Company). The specimen used to evaluate these materials is shown in figure 40. The aluminum plates were etched and die molded integrally with the previously imidized PMR-15 composite using the standard molding cycle. After molding, a sonic C-scan was obtained to determine the quality of the bond.

In the first trial, the aluminum plates were etched, primed with liquid PMR-15 and imidized one hour and molded integrally with the imidized PMR-15/HT-S preform. The aluminum plates separated upon taking the specimen out of the die. It was apparent that no bond to the aluminum surface was obtained.

In the second evaluation, the plates were etched and an 8 mil film of the maleimide adhesive inserted between the aluminum and the preform. The specimen separated on removal from the die. Again, an adhesive failure to the aluminum was experienced.

The supported polyimide film adhesive was handled in the same way as the previous experiments except the etched aluminum was primed with recommended polyimide primer (BR-34, Bloomingdale Department of American Cyanamid Company). An excellent bond was obtained.

An anticipated problem with the condensation polyimide adhesive was the thickness of the supported film. It was felt this would interfere with ply thickness calculations in the root area. For this reason, an additional experiment was performed using primer with a coat of the PMR-15 liquid resin. This system yielded an excellent bond as indicated by sonic inspection.

The techniques used were as follows:

- a) Vapor blast.
- b) Etch aluminum in standard sodium dichromate-sulfuric acid solution.
- c) Spray primer [0.025-0.051 mm (1-2 mils)].

- d) Dry in successive steps to 410^oF for 45 minutes.
- e) Paint on PMR-15 liquid [0.025-0.051 mm (1-2 mils)].
- f) Imidize one hour at 478^oK (400^oF).
- g) Mate with preform imidized for two hours at 478^oK.
- h) Mold.

As indicated, sonic inspection showed a sound bond. The sonic C-scan is shown in figure 41. To further examine the bond, the 10.2 x 10.2 cm part was subjected to the standard three-day postcure ending in 12 hours at 617^oK (650^oF). The sonic C-scan is shown in figure 42. As can be seen, no significant degradation was observed. On the basis of the behavior described, the polyimide primer/PMR-15 system was chosen as the adhesive for wedge bonding on all six blade specimens fabricated.

6.2 Blade Specimen Molding

Using existing tooling, illustrated in figure 43, six blade specimens were molded from HT-S/PMR-15 prepreg prepared to yield 8 mils/ply in the finished molding. The mold was designed to come down to stops at finished part size. A dimensioned engineering drawing of the blade specimen is shown in figure 44; the overall size is approximately 7.6 cm x 12.7 cm (3 x 5 inches). The root wedges were machined from 6061-T6 aluminum for integral molding with specimen lay-up.

In the previous program in which the tooling, ply shapes and orientation were developed, ply orientation was chosen to be ± 30 degrees for surface plies and ± 15 degrees for the core. This was altered on the subject blade specimen to ± 40 degrees (four plies each side) and 0 degrees for the core (17 plies) to more closely approximate the condition expected on the NAS3-15335 blade. A total of 25 plies was the calculated number required (at 8 mils/ply) to completely fill out the die cavity. Ply shapes used are shown in figure 45.

Preform tooling (base and punch) were not used in laying up the parts; the molding tool was used directly. Half the number of plies were laid up on the base and half on the punch portions of the tool. In the standard layup, an adhesive coated aluminum wedge was put in place after every five prepreg plies. At the conclusion of the lay-up process, the two lay-up halves were mated, the die walls installed; and the punch withdrawn. A conforming piece of porous TFE coated glass cloth was placed on the top of the layup and the assembly transferred to the press where the platens had been preheated to 478^oK (400^oF). The punch was placed on the press platens along side the mold assembly to heat up, and 680 grams of steel shot (preheated to 478^oK) were contained in a ply of glass cloth and placed on top of the layup. In this way, the preform was prevented from distorting during the heatup to 478^oK; the 680 grams were equivalent to 0.7 kPa (0.1 psi), a value previously determined to retain the part, but avoid resin expulsion during imidization. At the conclusion of the imidization cycle, the bag of shot and the TFE cloth were removed from the die.

Table XVII summarizes the time, temperature and pressure parameters used in molding the six specimens. Figure 46 is a plot of the heat rise, taken from the average temperature of two thermocouples installed in punch and die, of two selected parts, S/N 4 and 6. The cool-down cycles are not shown since the same technique was used as was developed for flat laminates. At the conclusion of the molding cycle, heat was turned off and the tool fan cooled to 533°K (500°F) and the pressure reduced by half. The fan cool was continued until 478°K (400°F) and the pressure reduced to contact and cooling water introduced into the platens. Contact pressure was maintained until the tool had reached room temperature; the total cooling process took approximately one hour. Since the parts were not to be evaluated mechanically or thermally, none was postcured.

6.3 Blade Specimen Evaluation

Both destructive and non-destructive methods were used to evaluate the blade specimens. These techniques included: visual examination, dimensional inspection, radiography, ultrasonic testing, and sectioning for photomicrographs. Figure 47 is a photograph taken at an angle to illustrate the geometry of the blade specimen.

As will be noted from table XVII, two basic heating cycles, illustrated in figure 46, were used. For purposes of discussion, these will be termed the "short" cycle, shown for S/N 4, and the "long" cycle, as used for S/N 6. In summary, a review of all available data indicates that the short cycle produced an acceptable root wedge bond, the soundest internal part based on ultrasonic inspection, and a dimpled outer surface. The long cycle yielded a smooth exterior, some lifting of the composite section at the root wedge, and an internal quality inferior to the short cycle.

6.3.1 Visual and Dimensional Inspection

Figures 48 and 49 clearly demonstrate the noted difference in surface appearance quality. In these photographs (approximately 1.6 times size), the smooth exterior of S/N 6 is easily visible. The dimpled surface of S/N 4, fabricated with the short cycle, is just as easily seen. The appearance of each of these specimen faces is duplicated on the reverse side of the corresponding specimen. The dimpled surface is similar to many observed in the early portion of the program and discussed in Section 3.3 on Molding. These dimpled surfaces were unexpected since the development of 505°K (450°F) cycle on flat laminates had been felt to have eliminated these surface imperfections. Table XVIII lists comments on surface appearance of all specimens fabricated.

Table XVIII also notes which cycles produced sound root wedge bonds. As noted in the table, the short cycle produced wedge bonds without the appearance of separation between aluminum and composite. The long cycle produced root wedge bonds with clearly visible intermittent unbond. This condition was most easily noted at the corners of the blade root where the corners of the outer composite lifted from the aluminum. The case of this is unknown. Two hypotheses include: 1) reduced adhesive quality of the PMR or primer, or 2) an altered condition of residual stress in the composite material causing

it to pull away from the underlying aluminum. It is known that process cycle times can have a pronounced effect on either of these characteristics of polymer systems.

Little can be said about the dimensional inspection values shown in table XVIII except in terms of tolerances. These tolerances do not seem excessive in terms of the different prepregs, molding cycles, and ply counts employed in the six specimens. If a single cycle were used, it is felt that further experimental work with ply shapes and number would further minimize the range observed.

6.3.2 Ultrasonic and Radiographic Inspection

Radiographic examination of S/N's 4 and 6 revealed little about the interior quality; the X-rays did, however, indicate axial stress cracks running the length of the blade specimen at an approximate distance of every 6.4 mm (1/4 inch). These were expected and are typical of construction with unidirectional 0 degree core laminates with cross-plyed outer fibers. The presence of these cracks was also observed in an examination of the polished tip cross section. Photomicrographs show these cracks crossing the entire thickness of the core section to each of the cross-plyed surfaces where the cracks were stopped.

The residual stresses, resulting primarily from the the thermal expansion mismatch of fiber and resin, were anticipated from previous theoretical and experimental work. An additional indication of these residual stresses was noted in the "pinging" heard with every specimen molded when it was removed from the constraint of the steel die, even though this was done at room temperature. The "pinging" was observed to continue for as long as 30 minutes after the time the part was removed from the die. Again, this phenomenon is not unusual and is frequently heard even with flat laminates employing the combination of unidirectional and cross-plyed outer fibers.

Difficulty was encountered in developing a suitable ultrasonic through transmission method for the specimens due to their varying thickness and the curved configuration of the airfoil section. This was ultimately achieved by swinging the coupled transducers on an arc equivalent to the radius of the concave side of the specimen. One effect of this technique was to increase the size of the C-scan with respect to the size of the actual specimen since the curved surface of the specimen is essentially developed on the C-scan. Some overrun on either edge of the specimen also contributed to the oversize C-scans.

Figures 50, 51 and 52 display the C-scans of three specimens at two different screen height percentages; as can be seen, in each case the more sensitive 50% setting shows a heavier density of defects. It is clear that the short cycle used on S/N 4 specimen produced the soundest interior quality. S/N 3, with the best surface, reflects a specimen with increased void content. The ultrasonic C-scans of S/N 5 are displayed to point out the fact that the increase of imidization time from one hour to 3-1/2 hours clearly reduced the quality of the resultant part. The soundest specimen observed in the series, S/N 4, was fabricated by a cycle that most closely approaches the cycle

developed for flat laminates and which repetitively yielded the best sonic quality in these laminates.

6.3.3 Photomicrographic Survey

While S/N's 1, 2 and 4 were sectioned and examined, only cross sections of S/N 4 will be discussed since this part had the best interior quality as determined by sonic inspection. While numerous photomicrographs were taken, figures 53 and 54 represent typical characteristics observed. All the sections shown were taken from the middle of the blade; edge examinations revealed a fairly wide distribution of small voids but no large discontinuities as seen in some of the photomicrographs shown.

Figure 53a, taken about 20 mm down from the tip, shows the four outer plies, a stress crack terminating at the cross-ply interface, and one elongated void of the type mentioned in earlier discussion. Figure 53b is an axial section taken near the center of the blade about 4 cm from the tip, and also displays some of the elongated voids seen in previous composites. Figure 54a is a center cross section showing another residual stress crack and a typical void distribution. The final cross section (figure 54b) was taken about 1 cm from the tip of the root wedges. As can be seen here, void content in the fiber bundles themselves is quite low, but interply voids do exist.

This phenomenon of interply voids was observed throughout the program; that is, the presence of voids seemed always to be concentrated between plies of material, while the discreet fiber bundles were relatively free of voids. This effect can clearly be seen in a review of the four photomicrographs described above. No explanation of this characteristic void distribution pattern is available nor has an adequate hypothesis been formulated. It is felt, however, that further study should be devoted to this typical occurrence. This regular distribution, consistently observed and coupled with the circular void pattern observed in flat laminate sonic traces, seems to indicate that some discernible cause could be identified and perhaps corrected by further work.

6.4 Molding Post-treatment

As was noted previously, none of the specimens was postcured. However, one specimen, S/N 5, was subjected to a thermal post-treatment. This was done to determine if the observed surface dimples could be eliminated by a subsequent application of temperature and pressure. The relatively thermoplastic nature of the material before postcure made this seem a practical concept, so S/N 5 was re-installed in the die at room temperature, 13.9 MPa (2000 psi) applied, the temperature brought to 617°K (650°F) and held for one hour. Cooling was achieved in the standard manner.

The experiment was a qualified success in that the objective of eliminating dimples was partially achieved; however, the single experiment did not reveal a usable technique. Surface dimples were reduced, but heavy blistering occurred. Additionally, other gross changes were observed; transverse cracks were induced at the tip, delamination occurred at the transition from root to airfoil, and multiple unbonds in the root wedges were noted after this treatment.

Figure 55 illustrates the reduction of dimples by this treatment. A close examination of the tip area will show the change in dimple density before and after the post-molding treatment. No further work was attempted with this technique due to program time constraints.

6.5 Blade Specimen Summary Comments

It is felt that reasonable progress was made in only six molding attempts. However, while several process cycles were investigated, the best cycle, that used on S/N 4, did not produce a fully satisfactory specimen. Unexpectedly, surface dimples re-appeared with a cycle that produced flat laminates without this characteristic, although one cycle used did yield smooth surfaced parts. Additionally, even the soundest blade specimen did not reveal the same internal quality regularly attained with flat panels. It has to be concluded that further experimental work with complex shaped parts, employing cross-plyed fiber orientation, would be required before superior quality levels could be achieved.

7.0 PROGRAM CONCLUSIONS

Specific conclusions on such things as processing details and material properties are presented in the body of the text. The conclusions below represent those major statements that summarize the overall findings of the program.

1. The polymerization of monomeric reactants approach to the fabrication of thermo-oxidatively stable polyimide laminates was found to be a practical one which fulfilled many of the anticipated advantages. Both resin solution and prepreg were determined to be unchanged within the limits of normal good practice. Prepregging, layup, solvent removal and imidization were found to be safe and straightforward.

2. Molding was achieved by a number of different process cycles with relatively wide control limits and with varied techniques such as imidization-in-the-tool and vacuum bagging of the lower formulated weight systems. Resin flow was found to be ample with most cycles investigated, a characteristic not always found with the A-type polyimides. Fabrication of a jet engine demonstration blade specimen was accomplished without difficulty.

3. The finished composite laminates were found to be thermally, oxidatively, and hydrolytically stable. Room temperature mechanical properties were determined to be comparable to those obtained with other available matrices with the fibers employed and no specific deficiencies were identified. Elevated temperature testing indicated a useful short term operating range of 589°K (600°F) to 617°K (650°F). Long term thermo-oxidative stability was excellent. Isothermal analyses at 561°K (550°F) indicated little or no degradation in mechanical properties after 1000 hours. It is projected that the long life temperature limit would fall in the range of 561°K (550°F) to 589°K (600°F).

4. Unexpected characteristics encountered were that of surface depressions and void contents in the range of 1 to 3 v/o. These imperfections were found to be exaggerated in complex shaped, cross-ply structural components. An extensive evaluation of laminates revealed the voids to occur in characteristic patterns around the periphery and predominantly in interply concentrations.

8.0 RECOMMENDATIONS

It is felt that the multiple advantages of the PMR concept were amply demonstrated in the course of the experimental work described in the body of the text. The single trait found to detract from the merit of the system was that of the presumably related void content and surface imperfections discussed in the body of the text. Because of the outstanding desirability of the system and this sole potentially limiting characteristic, a single recommendation is made. That is that further analytical work be pursued to increase understanding of the polymerization mechanics and reactions of this system so that the cause of these defects may be identified and dealt with.

TABLE I

FIBER PROPERTY SUMMARY FROM VENDOR CERTIFICATIONS

Fiber Type	Lot Number	Ultimate Tensile Strength		Tensile Modulus GPa	Msi	Weight Per Unit Length $\times 10^{-3}$ g/m lb/in $\times 10^{-6}$	Density		
		GPa	Ksi				g/ml	lb/in 3	
HM-S ↓	As Advertised	2.06 min	300 min	365-407	53-59	750-839	42-47	1.86-1.91	0.067-0.069
	2-4	2.24	325	393	57	803	45	1.88	0.068
	3-5	2.25	327	379	55	758	44	1.91	0.069
	5-2	2.23	323	393	57	803	45	1.91	0.069
	8-3	2.22	322	359	52	821	46	1.88	0.068
9-4	2.39	346	372	54	821	46	1.88	0.068	
HT-S ↓	As Advertised	2.41	350 min	248-290	36-42	732-821	41-46	1.72-1.75	0.062-0.063
	5-1	2.37	344	262	38	803	45	1.75	0.063
	9-2	2.87	416	255	37	839	47	1.83	0.066

TABLE II

VISCOSITY AND ACIDITY CHANGES WITH TIME IN CAPPED SOLUTIONS

FMW	40 w/o			60 w/o		
	1500	1750	1900	1500	1750	1900
<u>Initial</u>						
pH	4.40	4.50	4.50	4.50	4.60	4.55
Viscosity, N·s/m ² (cps)	0.020 (20)	0.021 (21)	0.021 (21)	0.069 (69)	0.076 (76)	0.077 (77)
<u>24 Hours</u>						
pH	4.50	4.50	4.50	4.50	4.40	4.35
Viscosity, N·s/m ² (cps)	0.024 (24)	0.023 (23)	0.023 (23)	0.082 (82)	0.093 (93)	0.096 (96)
<u>48 Hours</u>						
pH	4.45	4.45	4.40	4.40	4.40	4.30
Viscosity, N·s/m ² (cps)	0.024 (24)	0.026 (26)	0.024 (24)	0.087 (87)	0.093 (93)	0.096 (96)

TABLE III
MECHANICAL DATA SUMMARY FROM PREPREG EXPOSURE TESTS

	Flexure Strength		Flexure Modulus		Short Beam Shear Strength	
	MPa	KSI	GPa	MSI	MPa	KSI
Laminate 589-78 Imidized Preform Exposed to 95% RH for 18 Hours						
295°K (72°F)	775.4	112.5	165	23.9	58.1	8.4
589°K (600°F)	896.0	130.0	148	21.4	43.2	6.3
Laminate 589-79 Plies Exposed to 95% RH for 18 Hours						
295°K (72°F)	817.7	118.6	160	23.2	61.4	8.9
589°K (600°F)	967.0	140.3	152	22.0	41.4	6.0
Laminate 589-96 Prepreg Exposed 24 Days in a Laboratory Ambient Condition						
295°K (72°F)	929.4	134.8	167	24.2	75.8	11.0
589°K (600°F)	766.7	111.2	141	20.5	40.7	5.9

TABLE IV

MOLDING CYCLE 10.2 cm x 10.2 cm x 9.5 cm LAMINATE

IMIDIZATION IN TOOL TECHNIQUE

Cumulative Time Hrs.: Min.	Platen Set Temperature		Tool Thermocouple		Event
	^o K	^o F	^o K	^o F	
0:0	394	250	RT	RT	Put part in R.T. die in R.T. press.
0:14	-	-	367	200	Resin flow observed. (a)
0:21	-	-	383	230	Resin still bubbling.
0:30	-	-	389	240	Bubbling slowing.
0:32	478	400	390	242	Set change.
0:58	-	-	478	400	
2:47	505	450	478	400	Apply contact pressure.
2:59	-	-	505	450	Start 10 minute hold.
3:09	589	600	505	450	Apply 3.4 MPa (500 psi).
3:19	-	-	550	530	
3:20	-	-	556	540	Increase to 4.1 MPa (600 psi). Resin flow observed.
3:21	-	-	561	550	Increase to 4.8 MPa (700 psi).
3:22	-	-	567	560	Increase to 5.5 MPa (800 psi).
3:23	-	-	572	570	Increase to 6.2 MPa (900 psi).
3:24	-	-	578	580	Increase to 6.9 MPa (1000 psi).
3:27	-	-	589	600	
5:27	off	off	594	610	Start fan cool. End plate bolts removed.
6:27	-	-	478	400	Reduce pressure to 3.4 MPa (500 psi).
6:41	-	-	450	350	Reduce to contact pressure. Water cool platens.
7:04	-	-	300	80	Remove part.

(a) Weight of free-floating punch equal to 1.4 kPa (0.2 psi).

TABLE V
COMPARISON OF HT-S/PMR-15 LAMINATES WITH
ALTERNATE IMIDIZATION AND POSTCURE TECHNIQUES

Laminate Condition Characteristic	Laminate 589-51A Before ITGA	Laminate 589-51B After 450hr 589°K ITGA	Laminate 589-54A After 450hr 589°K ITGA	Laminate 589-54B After 450hr 589°K ITGA
Imidized	Oven	Oven	Tool	Tool
Postcure Temp., °K	589	589	589	617
R.T. Flexural Strength				
MPa	916.3	893.5	--	978.9
Ksi	133.9	129.6	--	142.0
R.T. Flexural Modulus				
GPa	161.0	167.0	--	165.0
Msi	23.3	24.2	--	24.0
589°K Flexural Strength				
MPa	965.8	--	956.9	--
Ksi	140.1	--	138.8	--
589°K Flexural Modulus				
GPa	142.0	--	149.0	--
Msi	20.6	--	21.6	--
R.T. Short Beam Shear Strength				
MPa	77.9	81.3	--	84.1
Ksi	11.3	11.8	--	12.2
589°K Short Beam Shear Strength				
MPa	39.3	--	46.9	--
Ksi	5.7	--	6.8	--

NOTE: Values shown represent average of three specimens.

TABLE VI
MECHANICAL PROPERTIES OF TWO HM-S/PMR-15
LAMINATES POSTCURED AT 617°K (650°F)

		<u>Laminate 589-47</u>	<u>Laminate 589-51A</u>
Fiber Volume, v/o		54.8	51.3
R.T. Flexural Strength			
	MPa	861.2	916.3
	Ksi	124.9	133.9
R.T. Flexural Modulus			
	GPa	156	161
	Msi	22.6	23.3
589°K Flexural Strength			
	MPa	766.0	965.8
	Ksi	111.1	140.1
589°K Flexural Modulus			
	GPa	121	142
	Msi	17.5	20.6
R.T. Short Beam Shear Strength			
	MPa	77.2	77.9
	Ksi	11.2	11.3
589°K Short Beam Shear Strength			
	MPa	39.3	39.3
	Ksi	5.7	5.7

NOTE: Values shown represent average of three specimens.

TABLE VII

SUMMARY OF 10.2 cm x 20.3 cm (4" x 8") MOLDING DATA

LAMINATE CODE	6	7	8	9	10	11	12	13	14
CHARACTERISTICS									
Fiber Batch/Roll	2-4-7c-2	2-4-43	2-4-43	2-4-43	2-4-43	2-4-43	2-4-43-2	2-4-43-3	2-4-43-3
Formulated Molecular Weight	1500	1500	1500	1500	1500	1500	1500	1500	1500
Imidizing Temperature, °K/°F	464/375	478/400	478/400	464/375	478/400	478/400	464/375	464/375	464/375
Imidizing Time, Minutes	75	45	45	75	75	75	60	60	45
Dwell Time, Seconds	30	30	60	60	30	60	30	60	30
Weight Loss in Imidizing, w/o	8.8	10.1	10.0	10.1	8.8	9.1	10.3	10.4	9.6
Weight Loss in Molding, w/o	0.1	0.1	0.6	0.3	0.0	0.6	0.4	1.0	0.8
Resin Flash, w/o	2.2	1.2	1.0	1.8	1.4	0.5	3.7	0.9	2.6
Thickness (Corners), mils	85	95	93	94	90	90	87	90	88
Mold Shrinkage, % (See Note a)	1.2	1.4	1.2	1.2	1.2	1.3	1.3	1.3	1.3
Specific Gravity After Molding	1.59	1.57	1.57	1.57	1.58	1.58	1.59	1.58	1.58

LAMINATE CODE	15	16	17	18	19	20	21	22	23	24
CHARACTERISTICS										
Fiber Batch/Roll	2-4-43-3	2-4-47-6	2-4-47-6	2-4-47-6	2-4-47-6	2-4-47-6	2-4-47-6	2-4-47-6	2-4-47-6	2-4-47-6
Formulated Molecular Weight	1500	1750	1750	1750	1750	1900	1900	1900	1500	1500
Imidizing Temperature, °K/°F	464/375	464/375	464/375	464/375	464/375	478/400	478/400	478/400	464/375	464/375
Imidizing Time, Minutes	45	45	45	60	60	60	60	45	45	30
Dwell Time, Seconds	60	30	60(b)	30	300(b)	30	30	120	60	30
Weight Loss in Imidizing, w/o	9.6	10.0	10.0	10.0	10.3	9.9	9.4	9.1	8.4	8.4
Weight Loss in Molding, w/o	0.4	0.5	0.6	0.6	0.5	0.3	0.1	0.3	0.9	1.6
Resin Flash, w/o	1.4	2.1	1.2	2.0	3.4	0.4	0.5	0.0	1.0	5.0
Thickness (Corners), mils	89	97	97	97	97	95	90	95	90	80
Mold Shrinkage, % (See Note a)	1.3	1.2	1.4	1.2	1.2	1.3	1.2	1.2	1.3	1.2
Specific Gravity after Molding	1.59	1.56	1.55	1.56	1.54	-	-	-	-	-

NOTES: a) Mold shrinkage is the percent change in panel width (hot die to cold part).
 b) Deviated cycle.

TABLE VIII
SUMMARY OF LAMINATE PROPERTIES

Laminate Code	Avg. ^a Flexure Str., MPa		Avg. ^a Flexural Mod., GPa		Avg. ^a S.B. Shear Str., MPa				
	Room Temp.	589°K (600°F) After 600 Hrs.	Room Temp. (600°F) After 600 Hrs.	At 589°K After 600 Hrs.	Room Temp. (600°F) After 600 Hrs.	At 589°K After 600 Hrs.			
6	.507	993.5	--	876.9	159	--	86.1	--	40.7
7	.474	932.1	801.1	721.1	141	135	82.0	40.7	42.7
8	.481	867.3	774.2	736.3	141	130	85.4	42.7	39.3
9	.463	848.0	707.3	734.2	139	123	86.8	41.4	38.6
10	.494	935.6	770.7	761.8	151	127	83.4	40.7	37.9
11	.502	1006.6	692.2	754.9	148	118	85.4	42.1	40.0
12	.491	1004.5	675.6	874.2	163	130	83.4	41.4	42.1
13	.476	863.9	761.8	777.6	152	135	82.7	40.0	43.4
14	--	903.1	883.8d	771.4	150	142d	84.1	41.4d	42.7
15	--	943.8	876.2d	808.0	150	139d	85.5	42.7d	39.3

Laminate Code	Avg. ^a Flexure Str., Ksi		Avg. ^a Flexural Mod., Msi		Avg. ^a S.B. Shear Str., Ksi				
	Room Temp.	589°K (600°F) After 600 Hrs.	Room Temp. (600°F) After 600 Hrs.	At 589°K After 600 Hrs.	Room Temp. (600°F) After 600 Hrs.	At 589°K After 600 Hrs.			
6	.507	144.1	--	127.2	23.1	--	12.5	--	5.9
7	.474	135.2	116.2	104.6	20.5	19.6	11.9	5.9	6.2
8	.481	125.8	112.3	106.8	20.5	18.9	12.4	6.2	5.7
9	.463	123.0	102.6	106.5	20.1	17.9	12.6	6.0	5.6
10	.494	135.7	111.8	110.5	21.9	18.4	12.1	5.9	5.5
11	.502	146.0	100.4	109.5	21.4	17.1	12.4	6.1	5.8
12	.491	145.7	98.0	126.8	23.6	18.8	12.1	6.0	6.1
13	.476	125.3	110.5	112.8	22.0	19.6	12.0	5.8	6.3
14	--	131.0	128.2d	111.9	21.8	20.6d	12.4	6.0d	6.2
15	--	136.9	127.1d	117.2	21.8	20.1d	12.4	6.2d	5.7

- NOTES: a) Values shown are the averages of three specimens for each test.
b) All room temperature test specimens were postcured for two hours at 589°K.
c) All 589°K test specimens were postcured for 16 hours at 589°K except those indicated with a "d".
d) Postcured 16 hours at 617°K (650°F).

TABLE IX

COMPOSITE PROPERTY TESTS REQUIRED IN ADVANCED EVALUATION

Property	Test Temp. °K	Test Temp. °F	Exposure Temp. °F	Exposure Time in Air (hrs)	No. of Specimens
Flexural Strength & Modulus	RT	RT	--	--	5
	561	550	550	0.1	5
Interlaminar Shear Strength				200	5
				500	5
				1000	5
	589	600	600	0.1	5
				200	5
Transverse Tensile Strength				400	5
				600	5
				800	5
	617	650	650	0.1	5
				10	5
				50	5
Compressive Strength	RT	RT	--	--	5
	533	500	550	0.1	5
				200	5
				500	5
	533	500	650	0.1	5
				200	5
			400	5	
Flexural Strength After Thermal Cycling, -65° to 600°F, 100 Cycles, 10 min. Hold at Each Temp.	RT	RT	--	--	5
	589	600	--	--	5
Flexural Strength After 2 Hr Water Boil	RT	RT	--	--	5
	561	550	--	0.1	5
	589	600	--	0.1	5
Poisson's Ratio Longitudinal & Transverse	RT	RT	--	--	2
Thermal Expansion, Parallel & Perpendicular to Fiber	--	-65 to +600	--	--	2

TABLE X
ADVANCED COMPOSITE EVALUATION HM-S/PMR-15 MOLDING SUMMARY

LAMINATE CODE CHARACTERISTIC	589-32	589-34	589-38	589-40	589-44	589-46	589-50	589-52	589-60	589-63	589-95	594-19	594-20	594-7	594-11	594-25	
DATE IMPREGNATED	11-15-72 11-30-72	11-20-72 11-30-72	11-30-72 12-1-72	11-20-72 11-30-72 12-4-72	12-4-72 12-5-72	11-20-72 11-30-72 12-4-72 12-5-72	12-5-72 12-7-72	12-5-72 12-7-72	12-5-72 12-11-72 12-13-72	12-11-72 12-13-72	2-5-73 2-6-73	3-19-73 3-20-73	3-19-73 3-20-73	12-11-72 2-27-73	12-11-72 3-7-73	3-29-73 3-30-73	
DATE MOLDED	11-29-72	11-29-72	12-1-72	12-4-72	12-5-72	12-4-72 12-5-72	12-7-72	12-7-72	12-13-72	12-13-72	2-6-73	3-20-73	3-20-73	2-27-73	3-7-73	3-30-73	
FIBER BATCH/ROLL	5-2/17-2 5-2/17	5-2/17	5-2/20-1	5-2/17 5-2/20-1	5-2/20-1	5-2/20-1	5-2/68-3	5-2/68-3	5-2/68-3 5-2/68-0	5-2/68-3 5-2/68-0	5-2/78-1	8-3/958-6	8-3/958-6	8-3/428-1 5-2/68-3	5-2/68-3 8-3/428-1	8-3/428-1 5-2/68-4	
WT. LOSS IN IMIDIZING, w/o	6.8	6.8	8.3	7.7	8.0	7.5	9.3	8.7	7.6	7.5	8.7	7.7	7.6	6.4	7.0	7.7	
WT. LOSS IN HOLDING, w/o	1.0	1.0	1.7	0.4	0.6	-	0.5	0.7	0.6	0.8	(a)	1.2	1.5	0.6	1.9	2.2	
RESIN FLASH, w/o	3.2	-	1.2	2.2	1.4	-	3.2	2.3	0.6	1.5	-	2.3	4.0	2.6	3.5	3.4	
THICK. (AVG.), MILS	85.5	81.0	91.5	91.2	90.0	89.0	89.0	89.2	91.0	88.5	76.7	84.0	84.0	93.2	93.0	89.5	
MOLD SHRINKAGE, %	-	1.03	-	1.07	1.07	1.05	-	1.07	1.06	1.05	-	-	-	-	-	-	
SF.GR. AFTER HOLDING	1.630	1.640	1.604	1.612	1.619	1.620	-	1.619	1.603	1.625	-	-	-	-	-	-	
WT. LOSS IN POST CURE, w/o(b)	0.87	0.57	0.64	0.59	0.58	1.19	1.44	1.16	0.62	0.92	-	-	-	1.07	0.99	-	
SF.GR. AFTER POST CURE	1.628	-	-	-	-	-	1.636	-	-	-	1.616	1.623	1.611	1.629	1.614	1.625	
RESIN SOLIDS, w/o	33.9	30.3	33.4	35.6	37.4	34.6	33.3	33.6	37.8	30.8	33.2	34.7	33.4	33.8	33.8	33.6	
FIBER VOLUME, v/o	57.8	61.5	58.3	56.3	54.0	57.0	58.5	58.2	53.5	61.2	57.4	56.2	57.0	57.3	55.9	57.4	
VOID CONTENT, v/o	1.80	2.49	3.48	2.00	1.03	3.74	1.56	2.46	1.89	3.15	2.82	0.97	2.12	0.91	2.71	1.21	
DISPOSITION	589°K ITGA 600 HRS. & 800 HRS.	561°K ITGA 200 HRS.	589°K ITGA 400 HRS.	589°K ITGA 200 HRS.	561°K ITGA 500 HRS.	617°K ITGA 50 HRS. & 200 HRS.	561°K ITGA 1000 HRS.	617°K ITGA 400 HRS.	R.T. TEST	617°K TEST	617°K TEST	561°K & 589°K WATER BOIL THERMAL CYCLE	561°K TEST	617°K ITGA 50 HRS.	617°K ITGA WATER BOIL	561°K & 589°K TEST	561°K & 589°K TEST

(a) IMIDIZED IN PRESS (b) NO THICKNESS CHANGE WAS NOTED IN POST CURE

TABLE XI

ITGA MECHANICAL TEST DATA SUMMARY OF HM-S/PMR-15 COMPOSITES

Exposure Time, Hours	Exposure & Test Temperature		Flexure Strength		Flexure Modulus		Short Beam Shear Strength		Transverse Tensile Strength	
	OK	OF	MPa	Ksi	GPa	Msi	MPa	Ksi	MPa	Ksi
-	295	72	871.2	126.4	163	23.6	84.0	12.2	51.0	7.4
0.1	561	550	1005.9	145.9	163	23.6	45.5	6.6	17.2	2.5
200	561	550	941.1	136.5	178	25.8	55.6	8.1	19.3	2.8
500	561	550	959.8	139.2	162	23.5	51.7	7.5	17.9	2.6
1000	561	550	999.6	145.0	164	23.7	55.2	8.0	16.5	2.4
0.1	589	600	959.8	119.7	156	22.6	50.3	7.3	14.5	2.1
200	589	600	923.5	133.9	163	23.6	46.2	6.7	18.6	2.7
400	589	600	853.3	123.8	159	23.1	47.4	6.9	17.2	2.5
600	589	600	896.9	130.1	155	22.5	48.0	7.0	13.1	1.9
800	589	600	767.0	111.2	150	21.7	45.1	6.5	11.7	1.7
0.1	617	650	715.3	103.7	135	19.6	32.7	4.7	16.5	2.4
10	617	650	884.2	128.2	151	22.0	37.9	5.5	11.0	1.6
50	617	650	754.8	109.5	157	22.8	47.6	6.9	4.1	0.6

NOTE: Values represent average of five specimens.

TABLE XII
COMPRESSIVE STRENGTH OF
HM-S/PMR-15 COMPOSITES

Test Temp. °K (°F)	Exposure Temp. °K (°F)	ITGA		Average Strength	
		Exposure Time hours		Ksi	MPa
295 (72)	-- --	--		146.7	1011.5
533 (500)	-- --	--		133.5	920.4
533 (500)	561 (550)	500		130.5	899.8
533 (500)	617 (650)	200		126.9	874.9
533 (500)	617 (650)	400		(a)	(a)

NOTE: (a) Too severely damaged to test.

TABLE XIII

FLEXURE STRENGTH OF HM-S/PMR-15 COMPOSITES AFTER ENVIRONMENTAL CONDITIONING

Laminate No. & Conditioning	295°K (72°F) MPa Ksi	561°K (550°F) MPa Ksi	589°K (600°F) MPa Ksi
<u>Thermal (a) Cycling</u>			
594-19A	1095 158.8	- -	884 128.2
<u>Water Boil (b)</u>			
594-94B	889 ^(c) 129.0	932 135.2	- -
594-11B	870 ^(c) 126.2	- -	592 85.8

NOTES: (a) Thermal Cycling was accomplished by cycling laminates between chambers held at 219°K (-65°F) and 589°K (600°F) with a 10 minute residence time at each temperature. One hundred complete cycles were performed for a total cycle time of 33.3 hours.

(b) Laminates were boiled in water for two hours and stored for 38 days at ambient laboratory conditions. Machined flexure specimens were then reboiled for an additional two hours and tested the next day.

(c) Average of two specimens. All other values in table represent average of five specimens.

TABLE XIV

SUMMARY OF DATA FROM STRAIN GAGED HM-S/PMR-15 TENSILE SPECIMENS

Specimen	Ultimate Tensile Strength		Modulus		Poisson's Ratio	Strain to Failure %
	MPa	ksi	GPa	Msi		
Longitudinal #1	504.7	73.2	157	22.7	0.29	0.32
Longitudinal #2	582.6	84.5	173	25.1	0.28	0.34
Average	543.3	78.8	165	23.9	0.29	0.33
Transverse #1	50.3	7.3	5.10	0.74	0.00	0.65
Transverse #2	46.9	6.8	6.68	0.97	0.00	0.78
Average	48.3	7.0	5.89	0.86	0.00	0.72

NOTE: All tests were conducted at room temperature.

TABLE XV
AVERAGE COEFFICIENT OF LINEAR THERMAL EXPANSION
OF HM-S/PMR-15
 $\alpha \times 10^{-6}$

Temperature °K	Interval °F	Parallel to Fiber		Perpendicular to Fiber	
		Deg K ⁻¹	Deg F ⁻¹	Deg K ⁻¹	Deg F ⁻¹
219 to 283	-65 to 50	-0.4	-0.2	28.1	15.6
283 to 311	50 to 100	-0.7	-0.6	29.5	16.4
311 to 367	100 to 200	-0.5	-0.3	29.9	16.6
367 to 422	200 to 300	-0.5	-0.3	31.3	17.4
422 to 478	300 to 400	-0.7	-0.4	32.0	17.8
478 to 533	400 to 500	-0.5	-0.3	33.0	18.3
533 to 589	500 to 600	-0.5	-0.3	33.1	18.4

NOTE: Average values of two specimens for each fiber orientation.

TABLE XVI
 SUMMARY OF HT-S/PMR-15
 MECHANICAL PROPERTIES AT ROOM TEMPERATURE

<u>Property</u>	<u>Fiber Orientation</u>	<u>HT-S Fiber Lot</u>	<u>No. of Values in Avg.</u>	<u>Avg. Value SI Units</u>	<u>Avg. Value US Units</u>
Flexural Strength	0°	5-1	3	1258 MPa	182.5 ksi
Flexural Modulus	0°	↓	3	125 GPa	18.1 msi
Short Beam Shear Strength	0°		3	100 MPa	14.5 ksi
Longitudinal Tensile Strength	0°		5	962 MPa	139.5 ksi
Tensile Modulus	0°		3	143 GPa	20.8 msi
Strain to Failure ^(a)	0°		3	--	0.55%
Tensile Strength	±5°		2	931 MPa	135.0 ksi
Tensile Strength	±10°		4	611 MPa	88.6 ksi
Tensile Strength	±15°		2	542 MPa	78.6 ksi

NOTE: (a) Determined by extensometer on unidirectional tensile specimens.

TABLE XVII
SUMMARY OF BLADE SPECIMEN FABRICATION EQUIPMENT SETTINGS

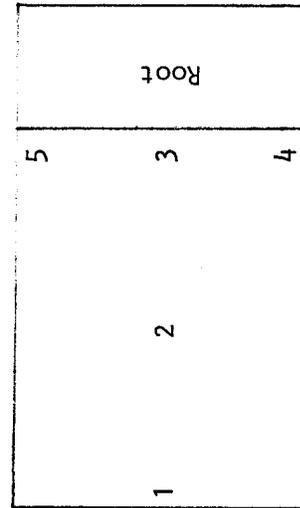
Specimen S/N	No. of Plies	S.I. Units		U.S. Units					
		Imidizing		Imidizing		Molding			
		Temp. OK min	Time min	Temp. OK min	Time min	Pressure Setting psi			
1	25	478	80	478-505	20	400-450	80		
				505		450		80	
				505-589		6.9			450-600
2	30	478	80	589	90	600	1000		
				478-505		20		400-450	0
				505				450	
3	25	478	80	505-589	6.9		450-600	1000	
				589		600	1000		
				478-497		6.9			400-435
497	60	435	60						
525		485		↓					
547		525			↓				
589	600	↓							
4	26		478	80	Same as S/N 1 Above				
5	25	478	210	Same as S/N 2 Above					
6	26	478	80	Same as S/N 3 Above					

TABLE XVIII

BLADE SPECIMEN THICKNESSES AND VISUAL QUALITY

Specimen S/N	Prepreg No. of Plies	Location Thickness, mm					Blade Surface		Wedge Bond Quality
		1	2	3	4	5	Concave	Convex	
RT Die Cavity	-	-	-	-	5.18	4.99			
1	594-51	25	5.16	5.11	5.28	5.38	-	Lightly Dimpled	Acceptable
2	594-51	30	5.84	5.74	5.84	5.84	5.72	Limited Surface Depressions	Acceptable
3	594-60	25	5.08	5.05	5.16	5.16	5.05	Smooth	Corners Lifted
4	594-60	26	5.16	5.08	5.13	5.18	5.13	Dimpled	Acceptable
5	594-83	25	5.11	5.00	5.16	5.26	5.00	Dimpled	Acceptable
6	594-83	26	4.99	4.95	5.11	5.26	5.05	Smooth	Corners Lifted

Inspection Locations



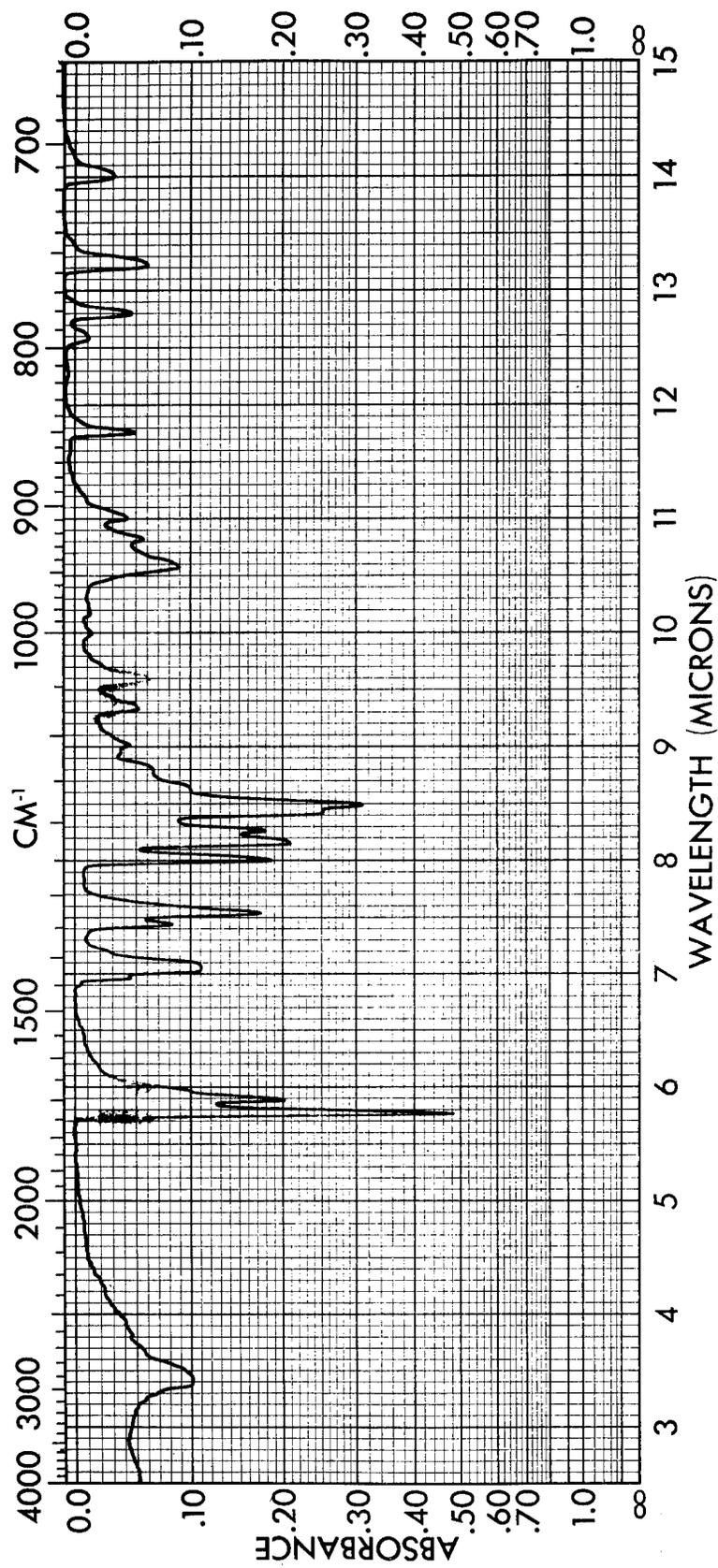


FIGURE 1 INFRARED SPECTRUM OF THE MONOMETHYL ESTER OF 5-NORBORNENE-2, 3-DICARBOXYLIC ACID 10 MONTHS AFTER RECEIPT.

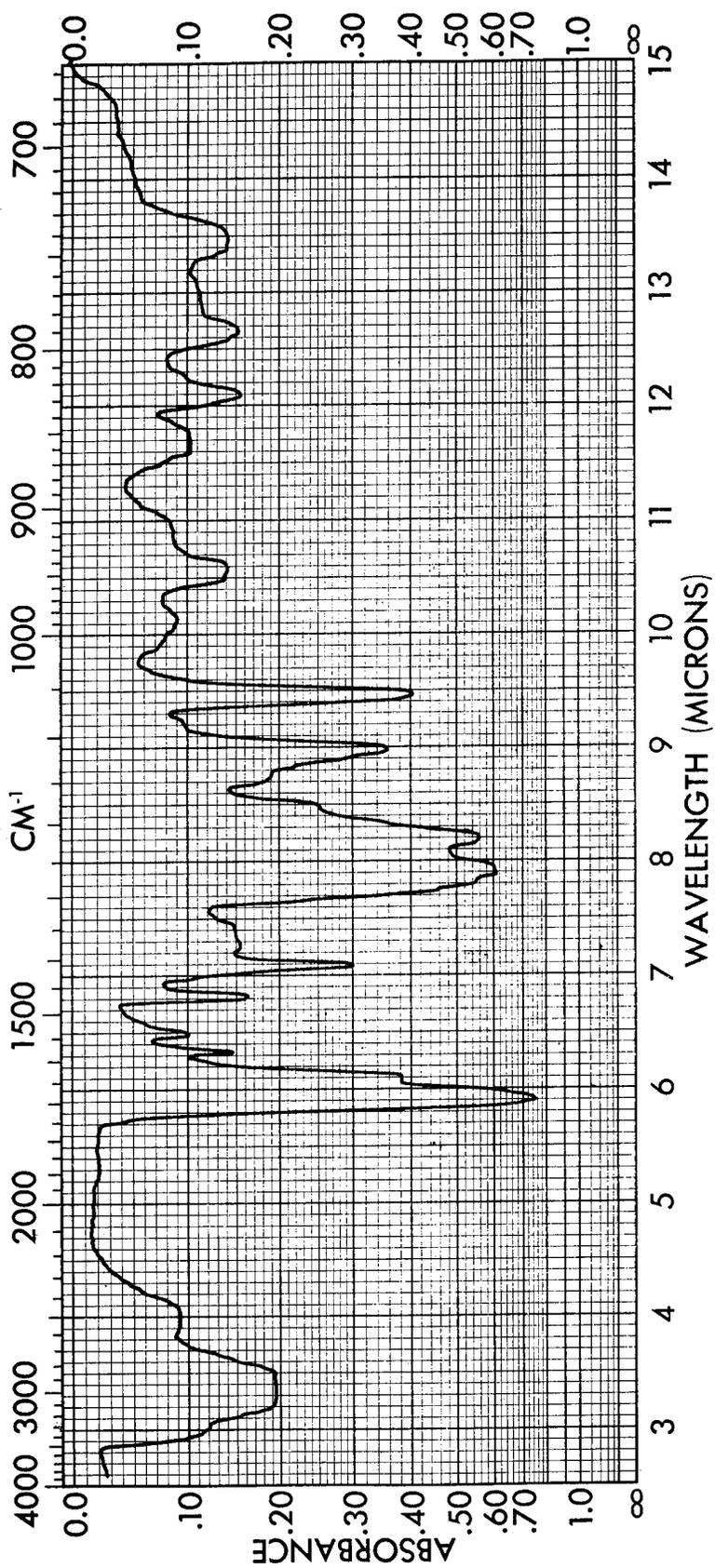


FIGURE 2 INFRARED SPECTRUM OF THE DIMETHYL ESTER OF 3, 3', 4, 4' - BENZOPHENONE-TETRACARBOXYLIC ACID 10 MONTHS AFTER RECEIPT.

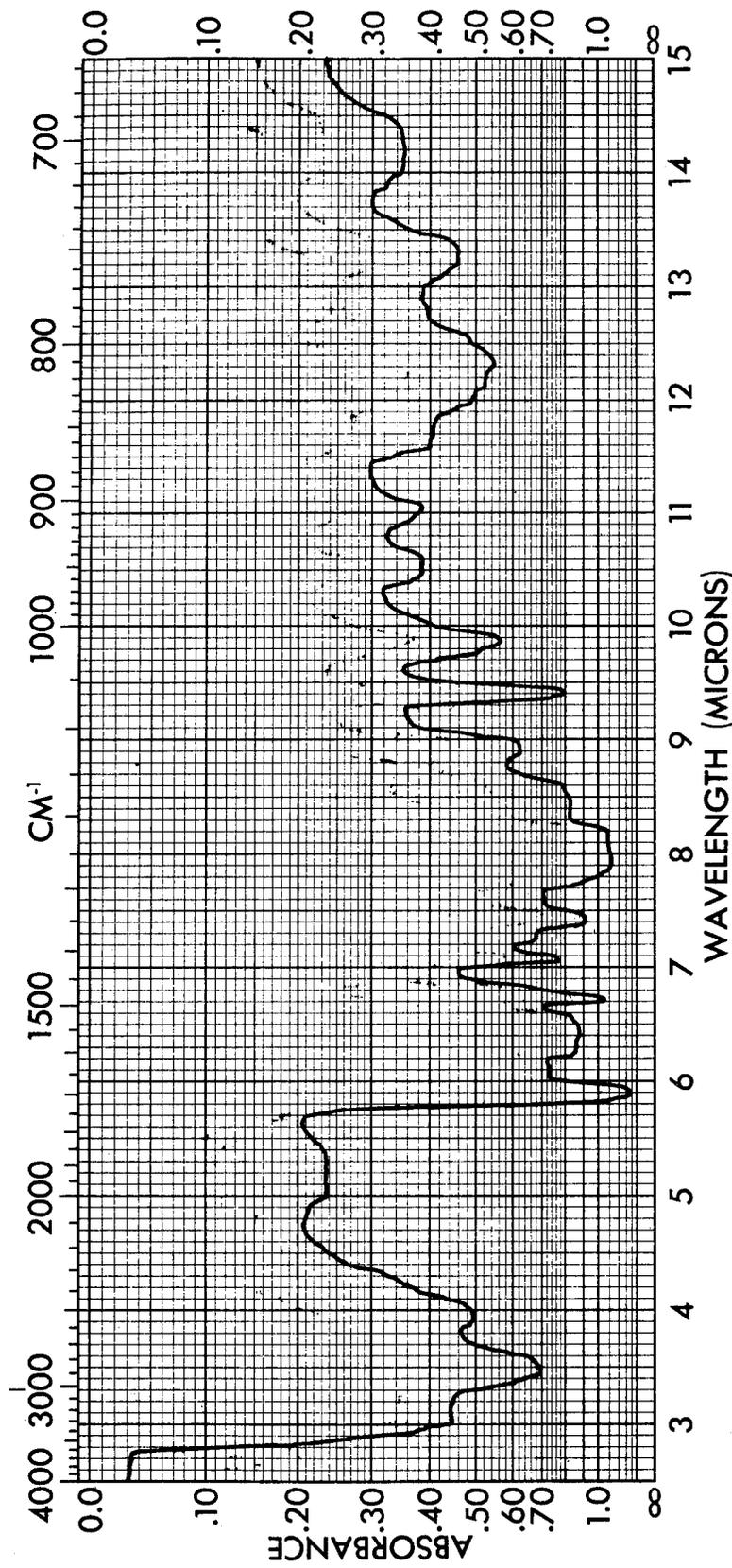


FIGURE 3 INFRARED SPECTRUM OF 1500 FMW (60 w/o SOLUTION) IMMEDIATELY AFTER MAKE-UP.

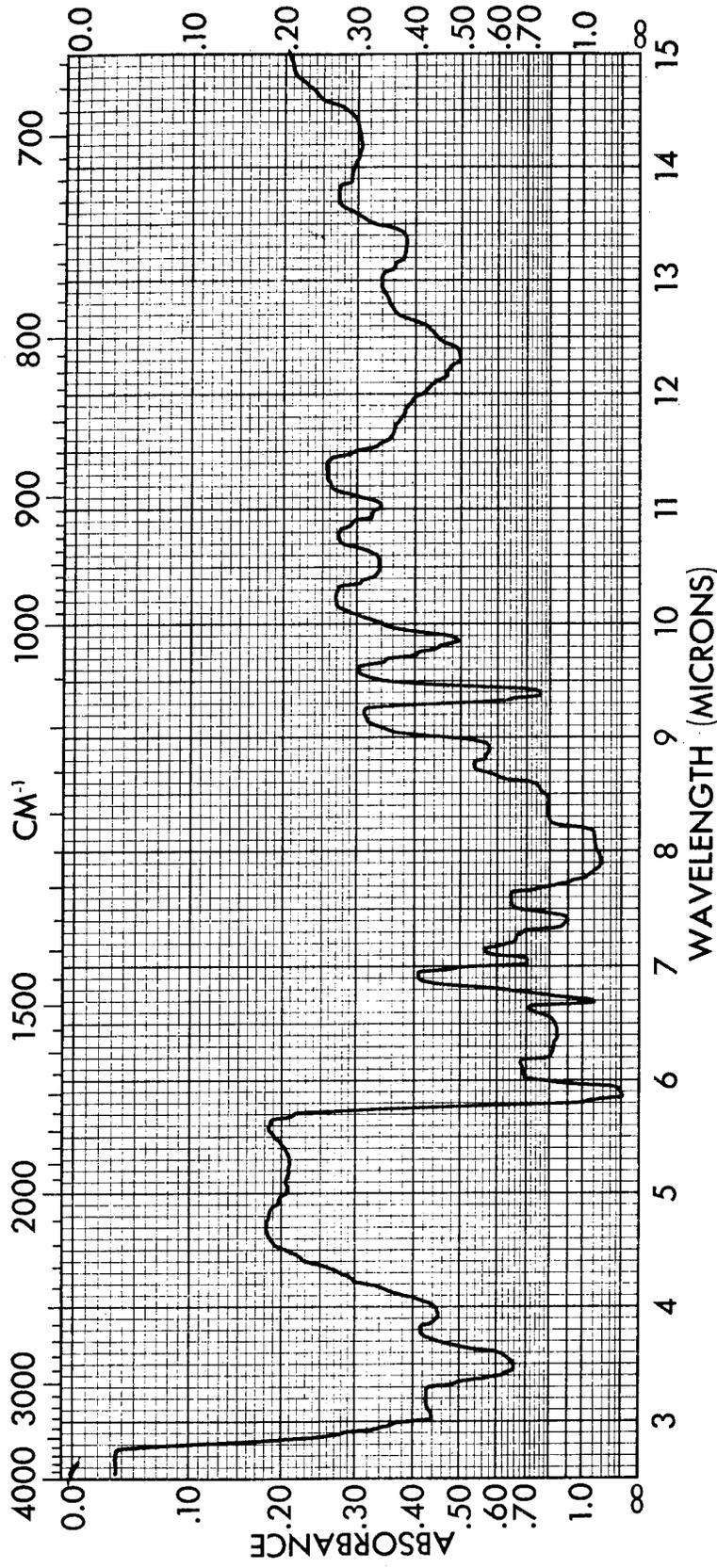


FIGURE 4 INFRARED SPECTRUM OF 1500 FMW (60 w/o SOLUTION) AFTER 24 HOURS IN CAPPED CONTAINER.

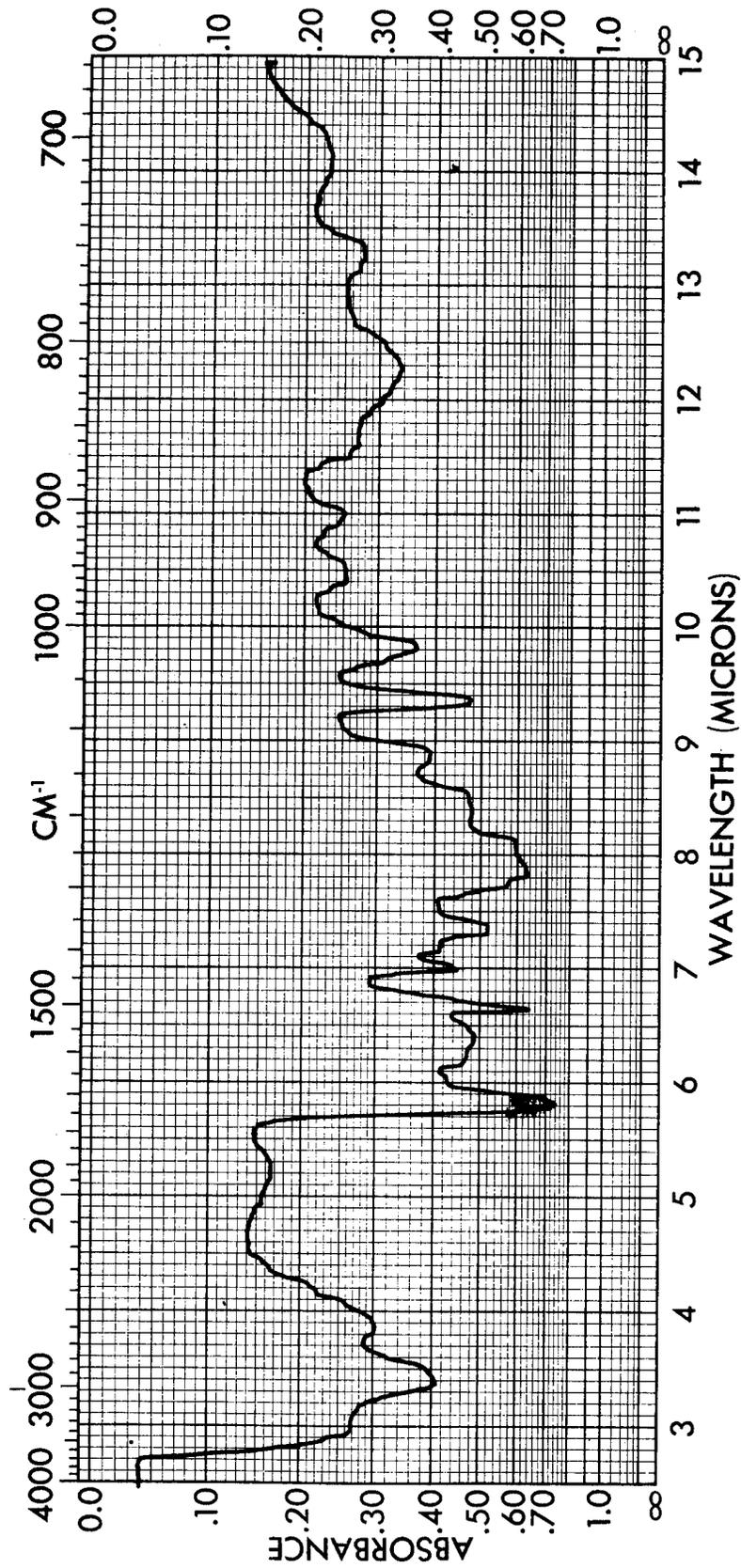


FIGURE 5 INFRARED SPECTRUM OF 1500 FMW (60 w/o SOLUTION) AFTER 48 HOURS IN CAPPED CONTAINER.

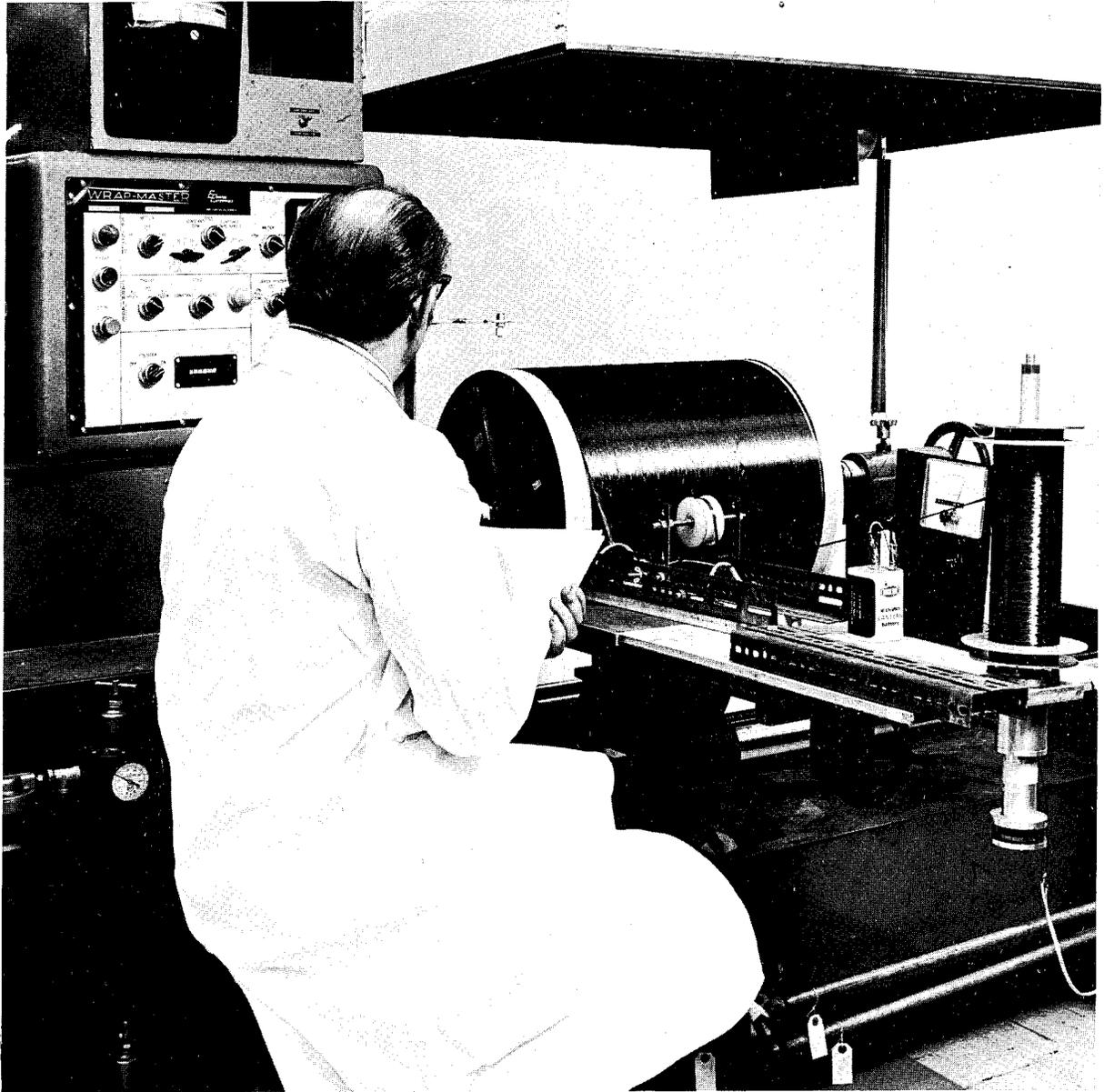


FIGURE 6 DRUM WINDING APPARATUS.

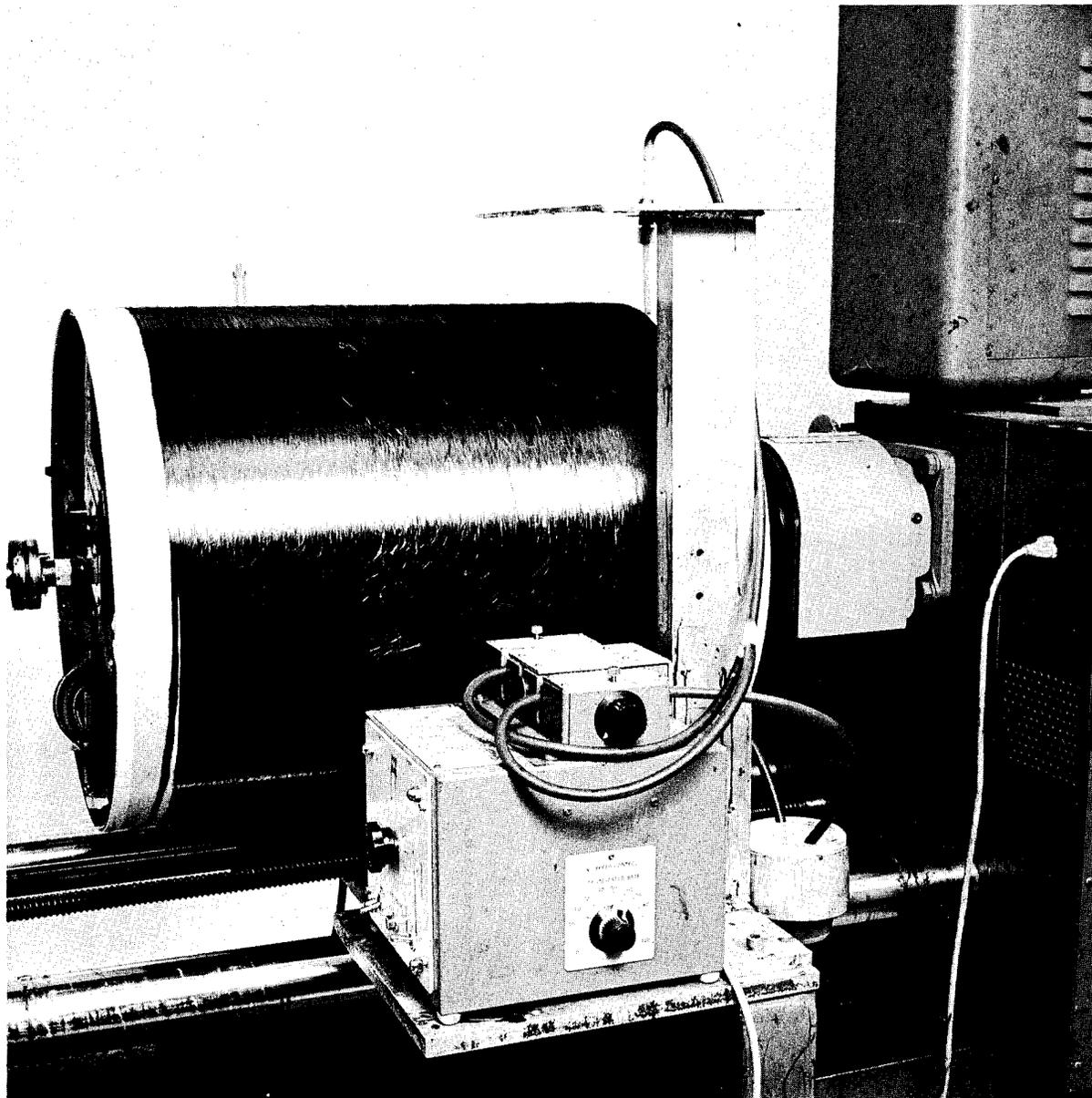


FIGURE 7 PERISTALTIC PUMP FOR METERING RESIN SOLUTION ONTO FIBER

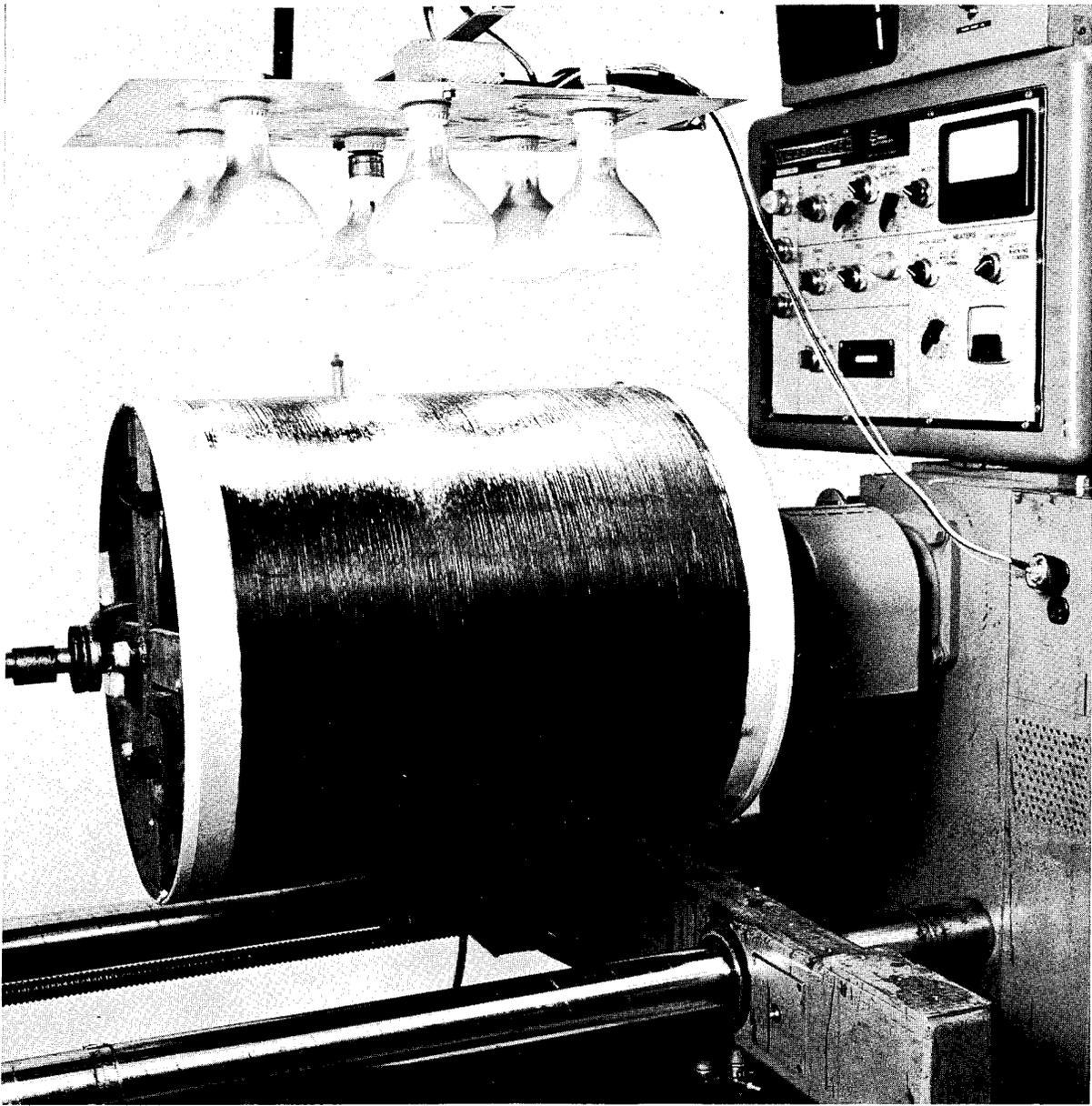
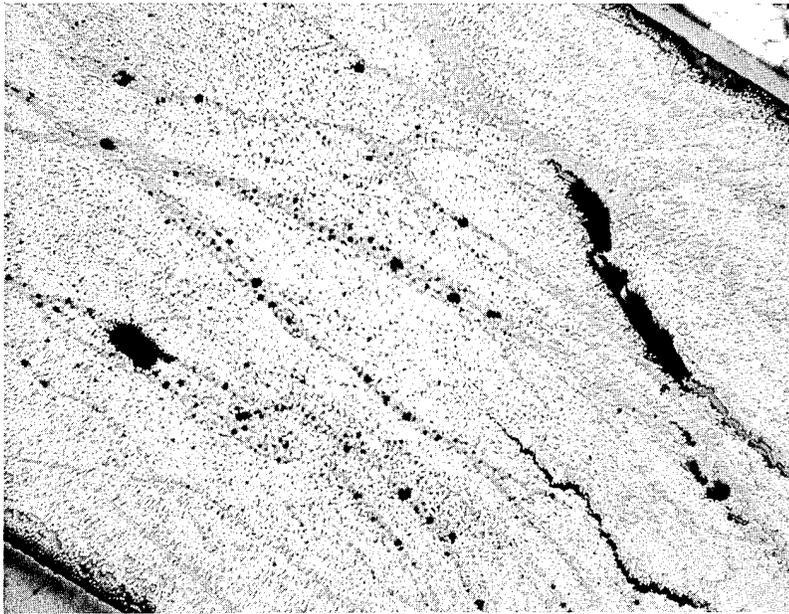
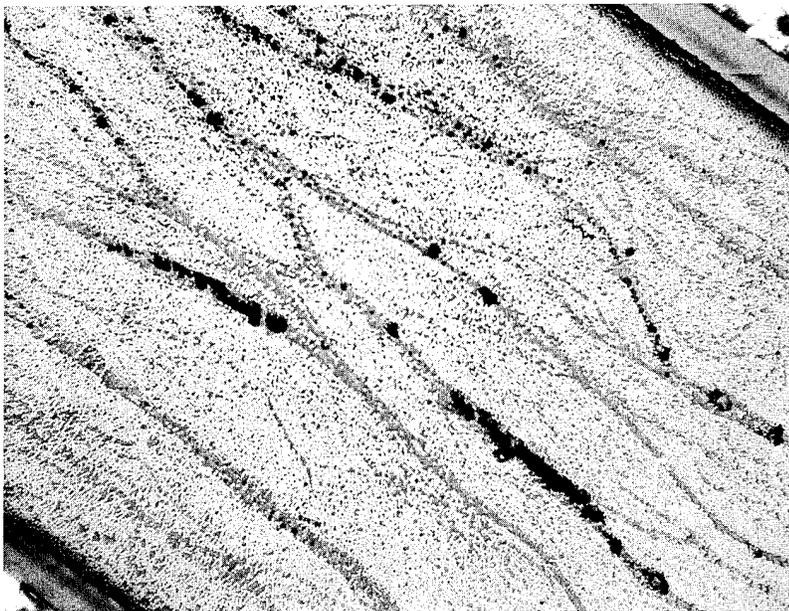


FIGURE 8 INITIAL DEVOLATILIZATION OF PREPREG WITH IR LAMPS



50X

FIGURE 9 CROSS-SECTION OF LAMINATE (AFTER POSTCURE) PREPARED FROM IMIDIZED PREFORM SUBJECTED TO 95% RH BEFORE MOLDING.



50X

FIGURE 10 CROSS-SECTION OF LAMINATE (AFTER POSTCURE) PREPARED FROM PLIES SUBJECTED TO 95% RH BEFORE MOLDING.

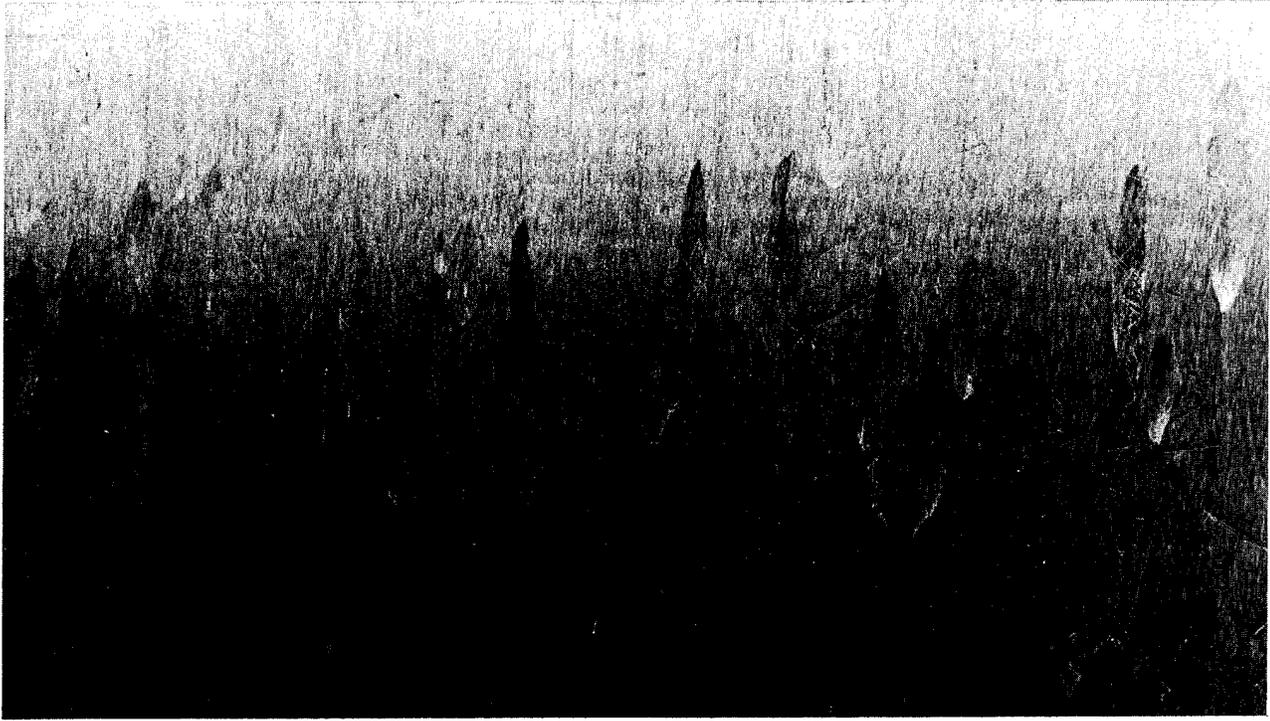
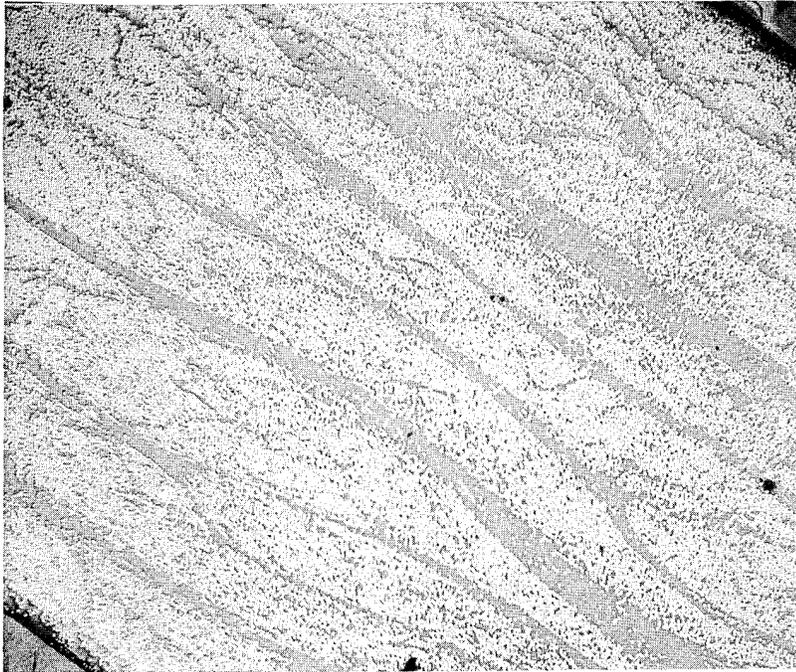


FIGURE 11 SURFACE OF LAMINATE 3 (1500 FMW) SHOWING SURFACE IMPERFECTIONS
(1.8X)



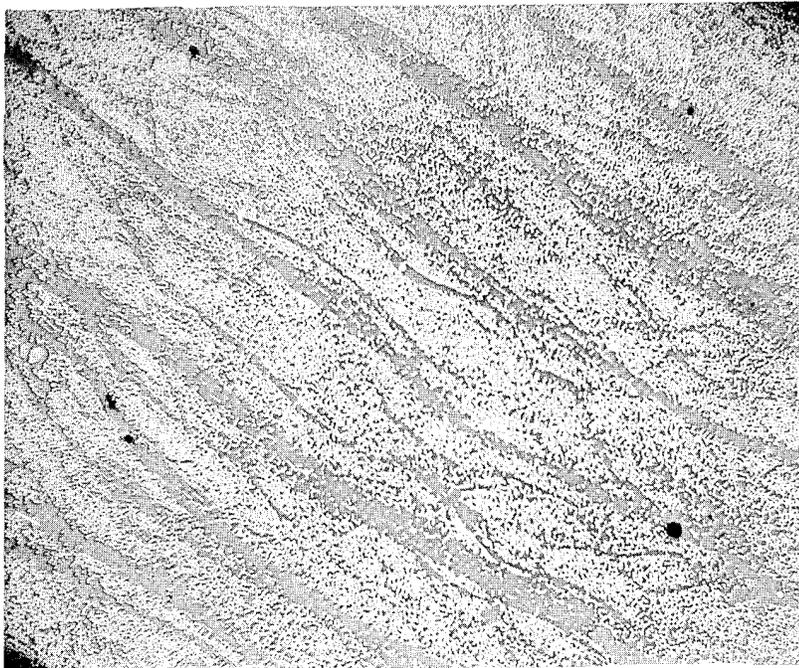
FIGURE 12 SURFACE OF LAMINATE 18 (1750 FMW) SHOWING SURFACE IMPERFECTIONS

(1.8x)



LAMINATE NO. 15 - 1500 FMW

50X



LAMINATE NO. 16 - 1750 FMW

50X



100X

FIGURE 14 SURFACE OF 1500 FMW/HM-S LAMINATE WITH NORMAL COLORATION.



100X

FIGURE 15 SURFACE OF 1500 FMW/HM-S LAMINATE WITH DISCOLORATION

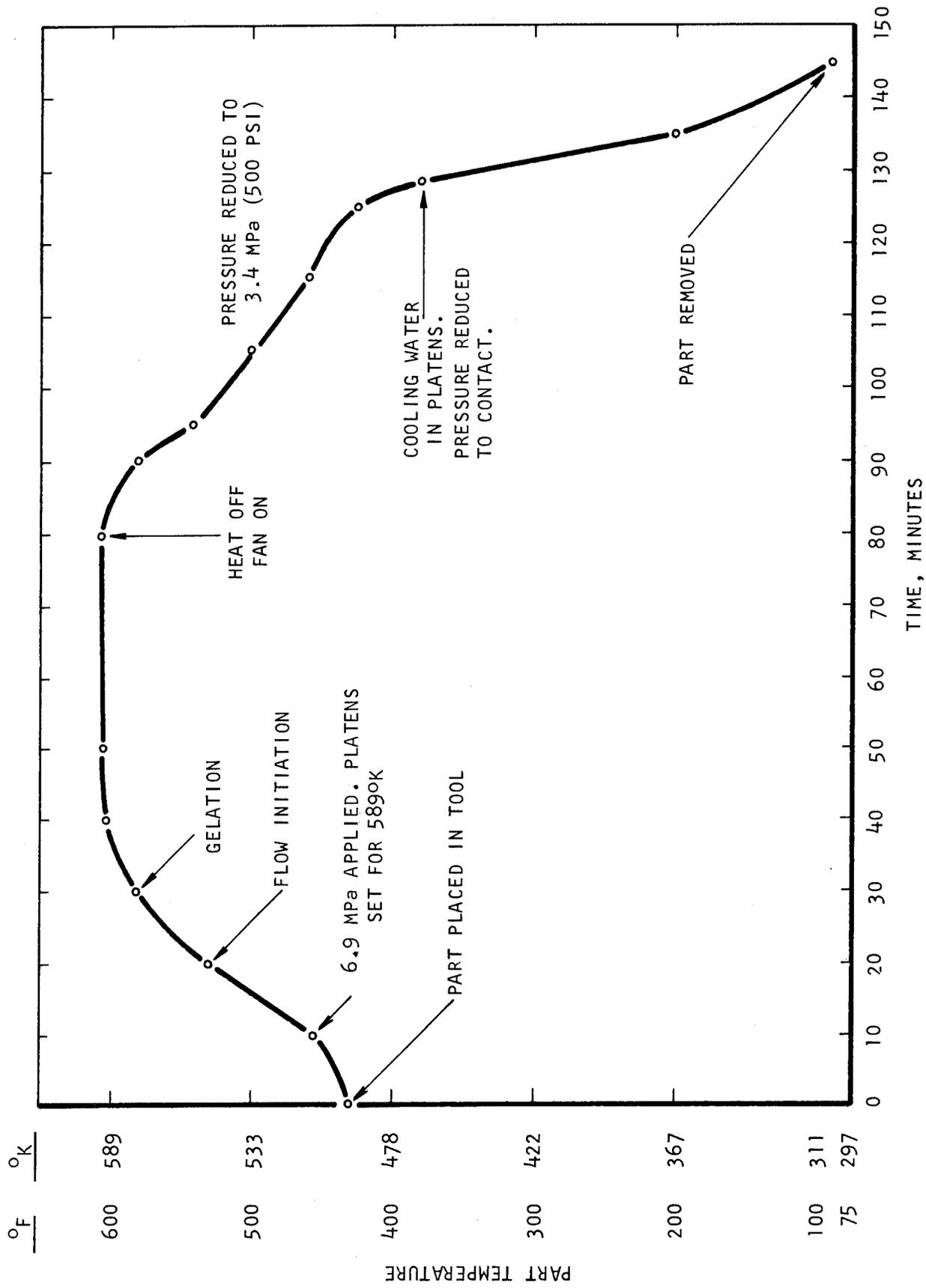
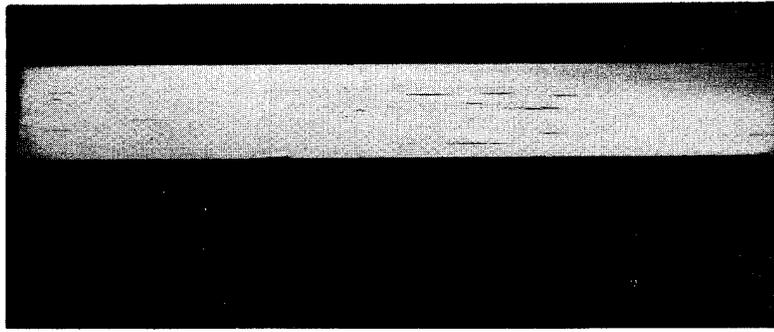
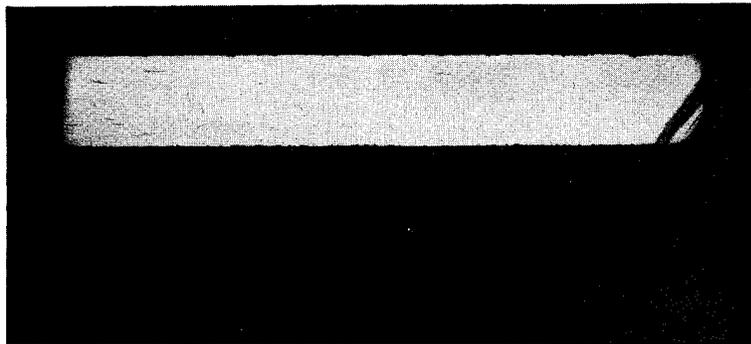


FIGURE 16 STANDARD MOLDING CYCLE FOR 10.2 cm x 20.3 cm x 2.3 mm LAMINATE

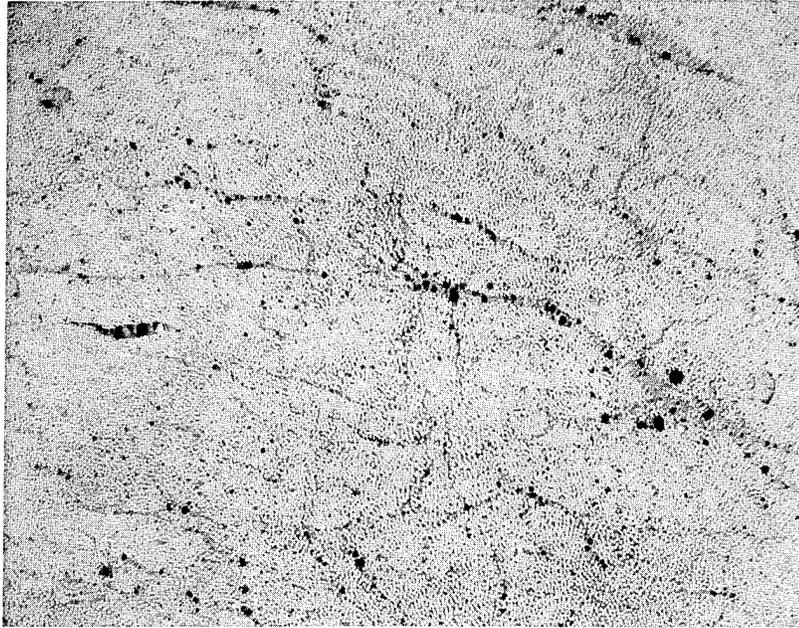


PARALLEL TO FIBER ORIENTATION (NON-POSTCURED).



PERPENDICULAR TO FIBER ORIENTATION (NON-POSTCURED).

FIGURE 17 POLISHED SECTION OF 10.2cm x 10.2cm x 9.5mm
LAMINATE IMIDIZED IN TOOL.



50X

FIGURE 18 CROSS-SECTION OF 10.2 cm x 10.2 cm x 9.5 mm LAMINATE (NON-POSTCURED)
IMIDIZED IN TOOL.

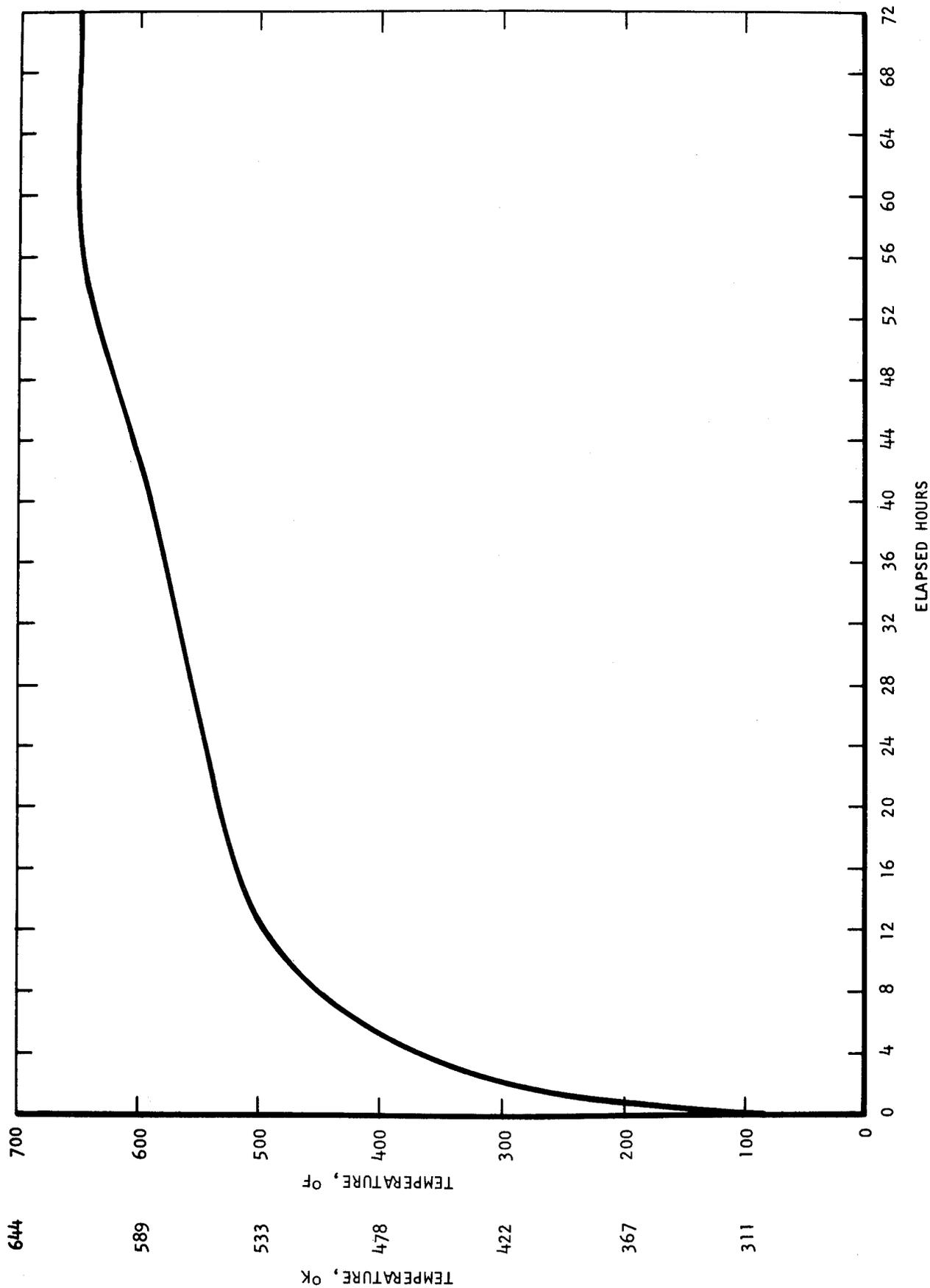


FIGURE 19 POSTCURE TIME/TEMPERATURE PLOT

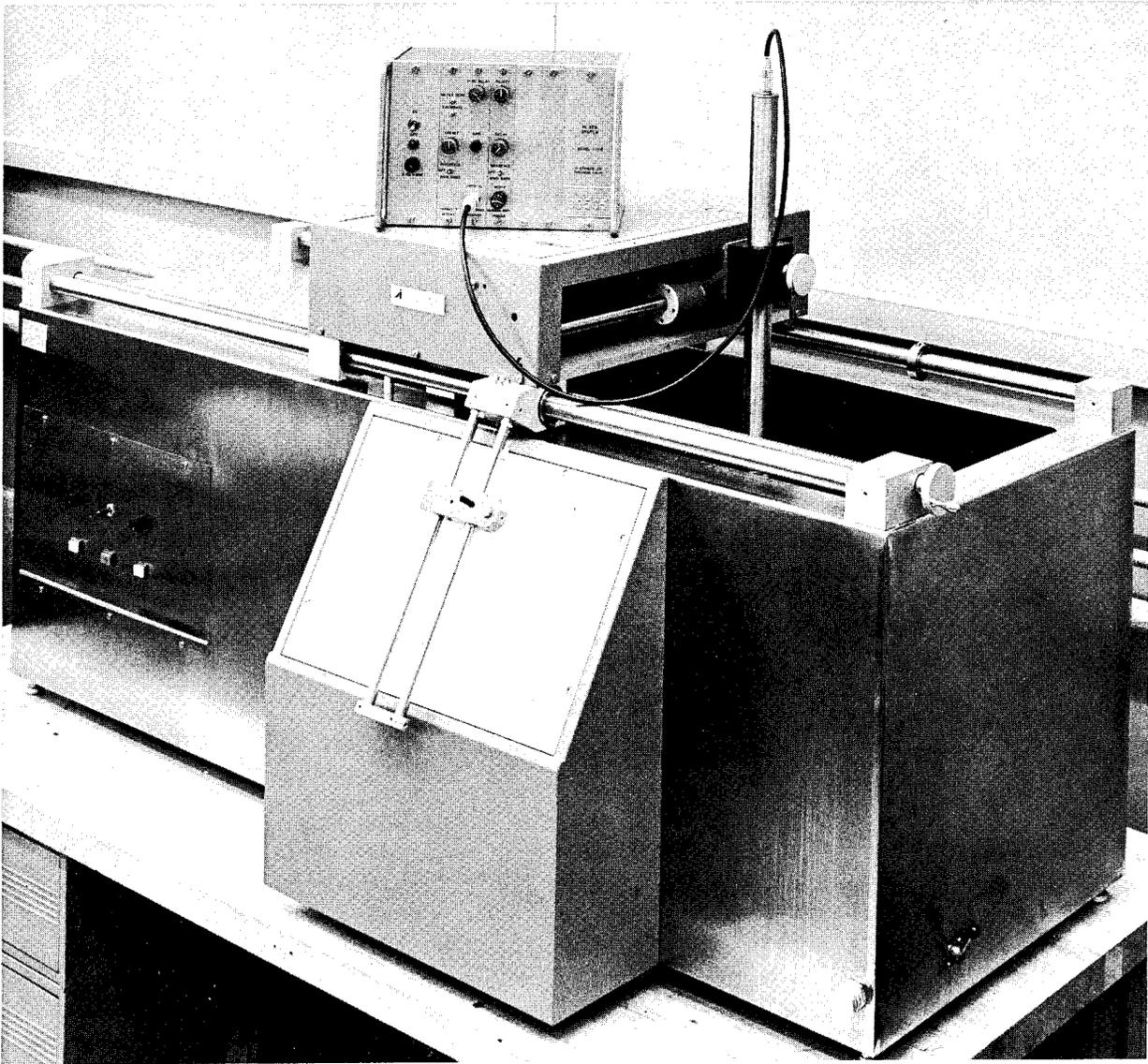


FIGURE 20 C-SCAN RECORDING UNIT.

FIBER ORIENTATION

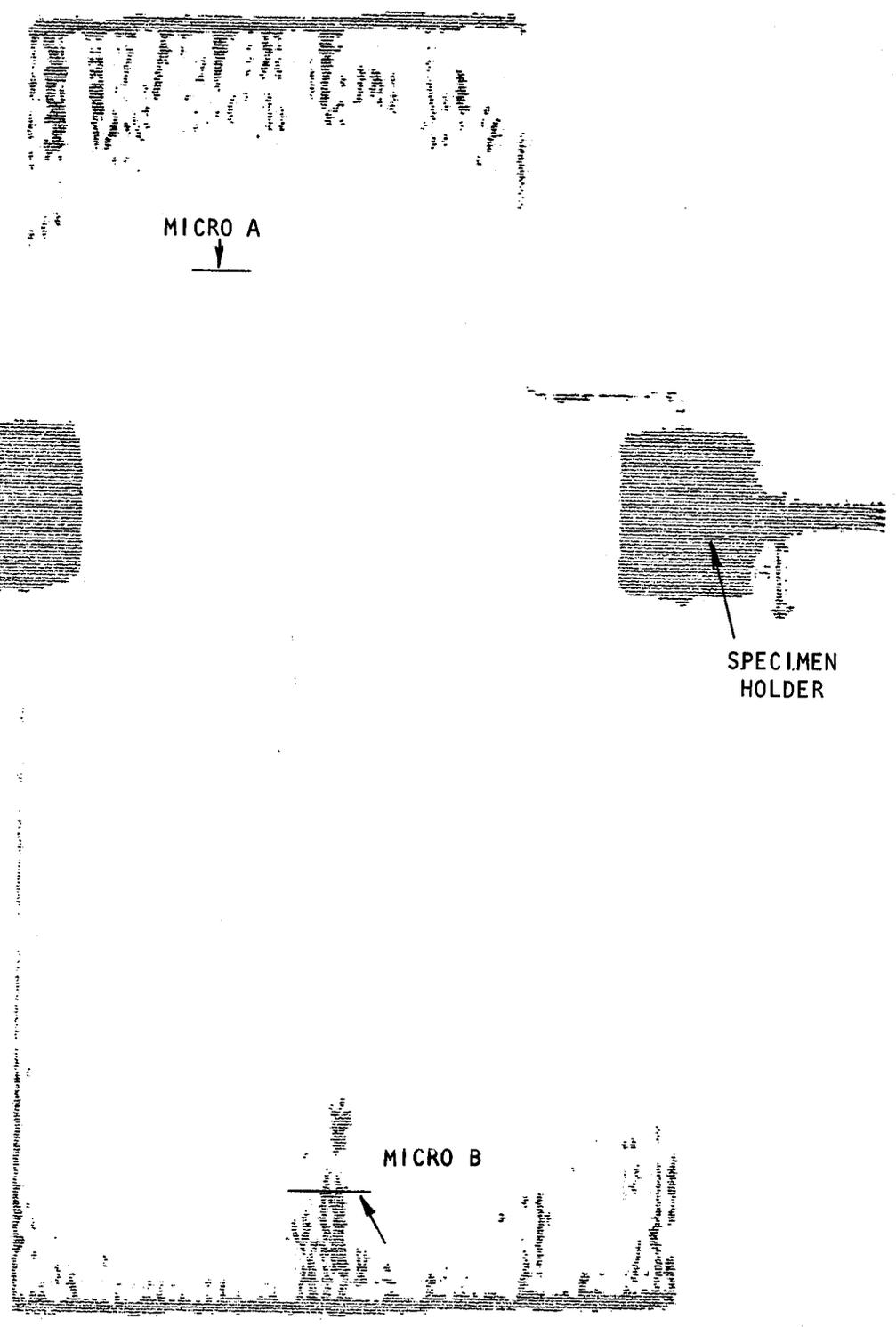


FIGURE 21 C - SCAN OF LAMINATE 589-47

FIBER ORIENTATION
↕

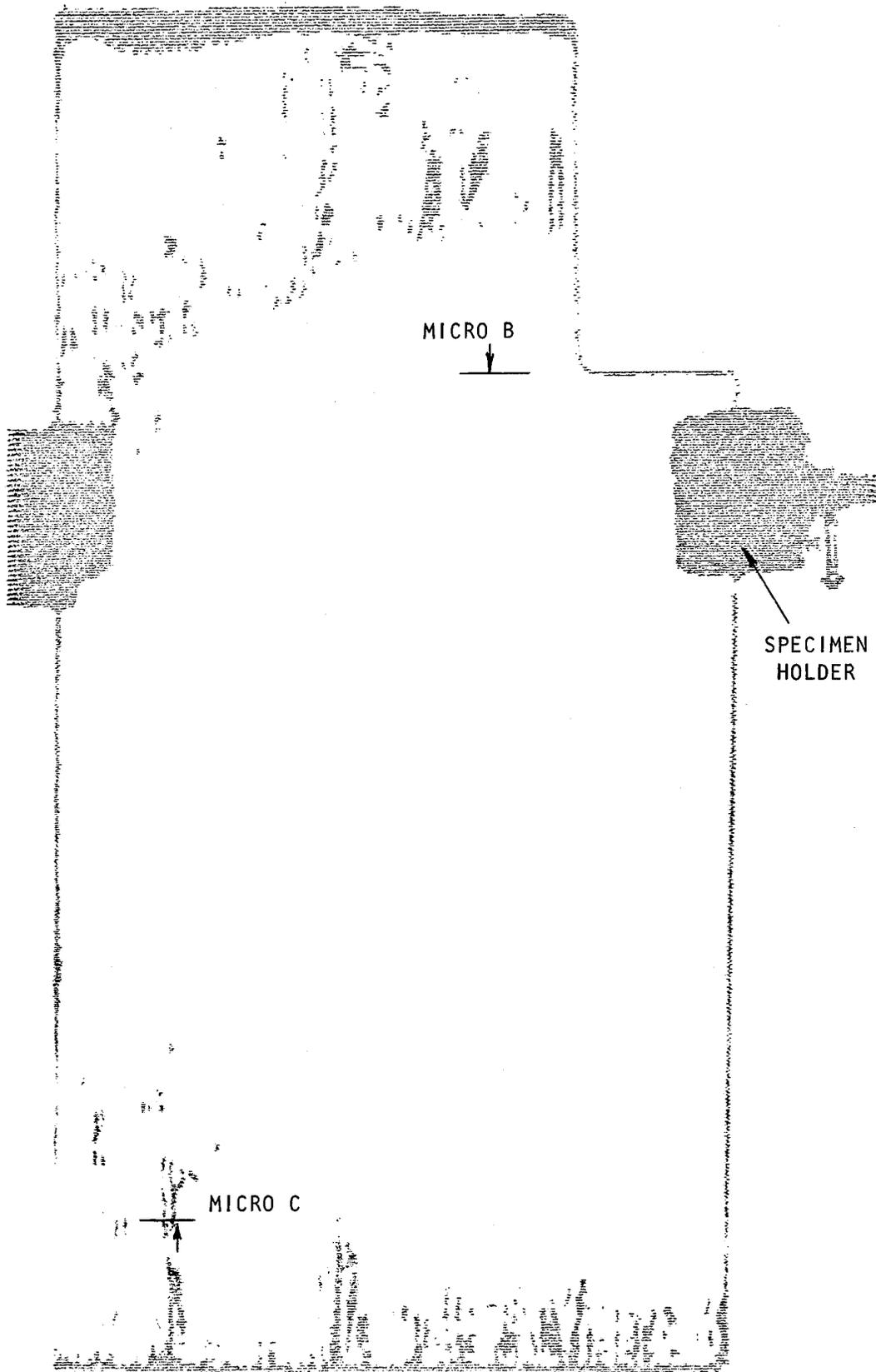


FIGURE 22 C - SCAN OF LAMINATE 589-51 (PART A)

FIBER ORIENTATION

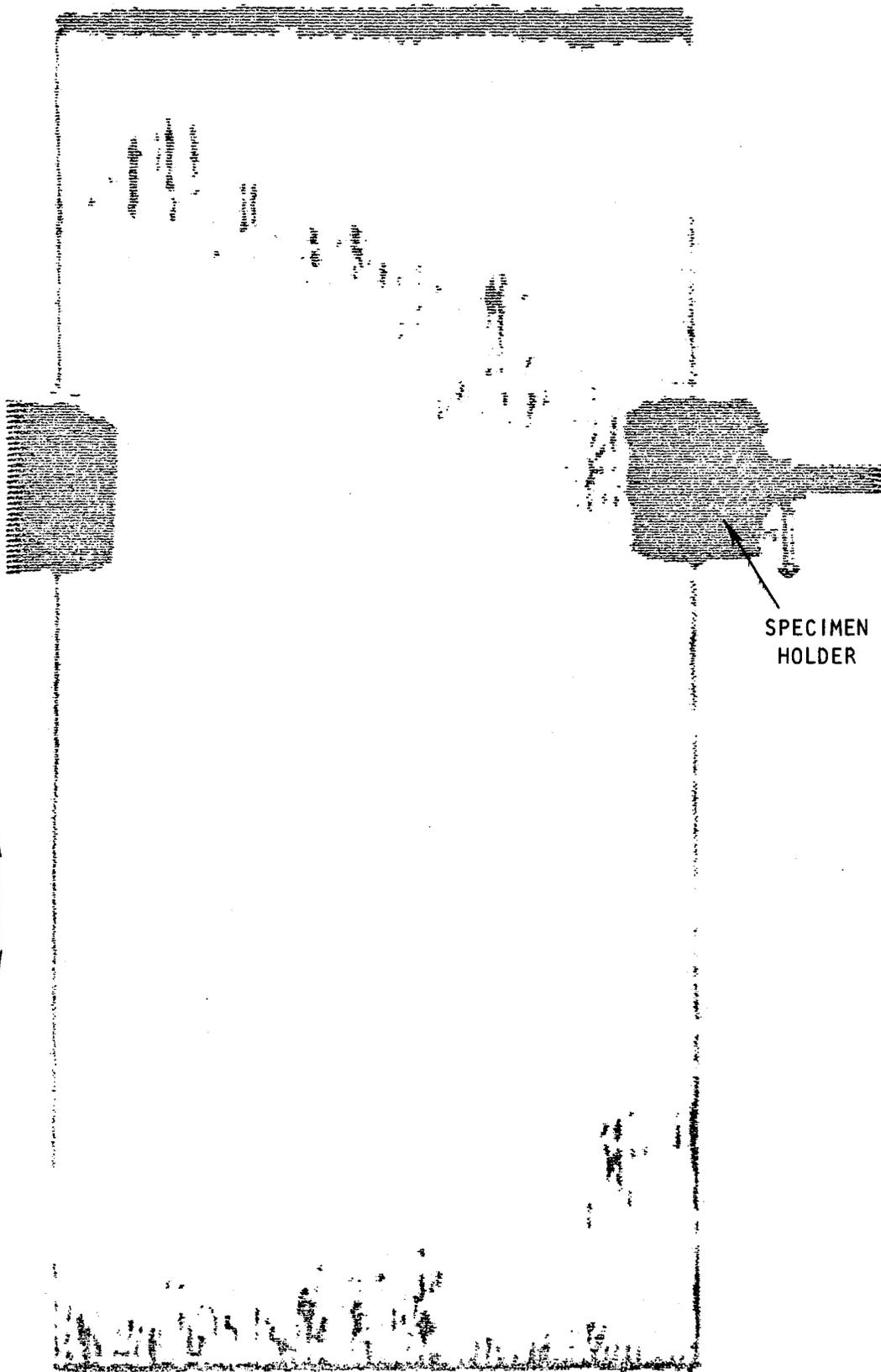
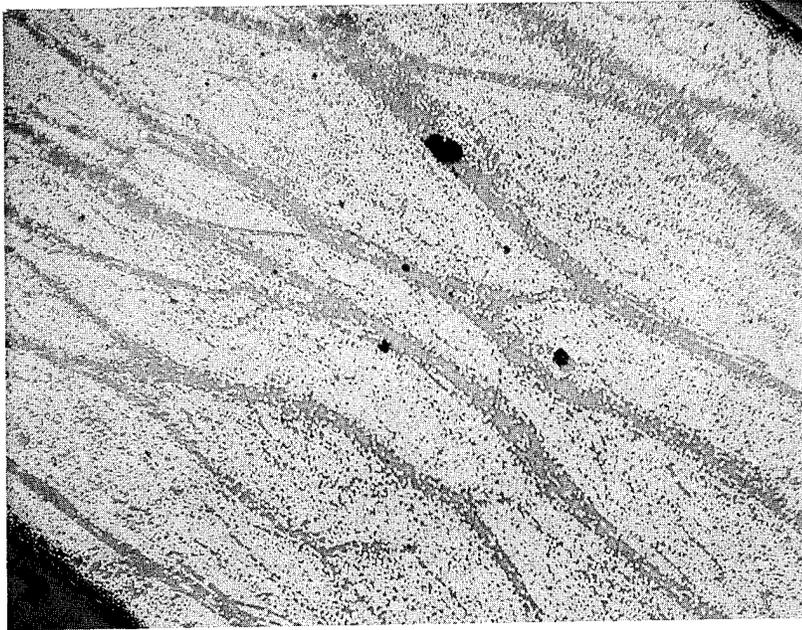
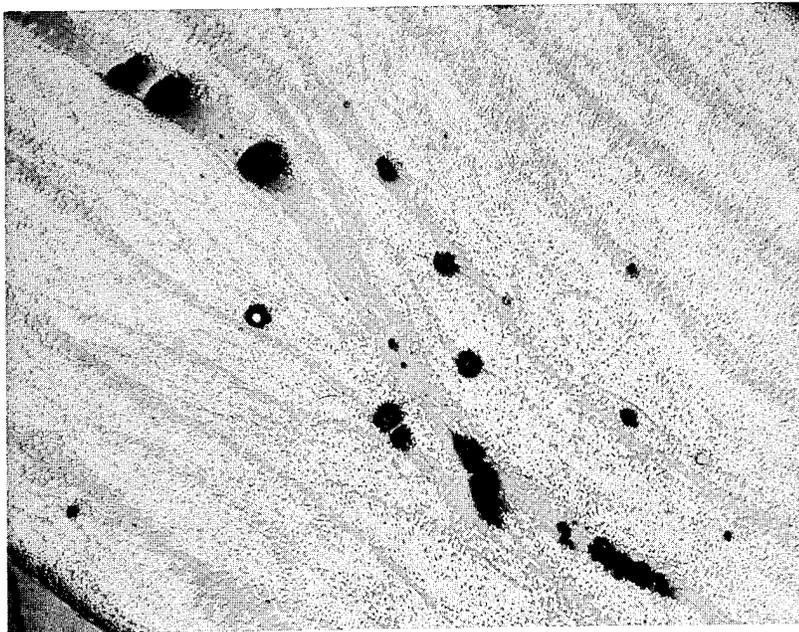


FIGURE 23 C - SCAN OF LAMINATE 589-51 (PART B)



MICRO SECTION A

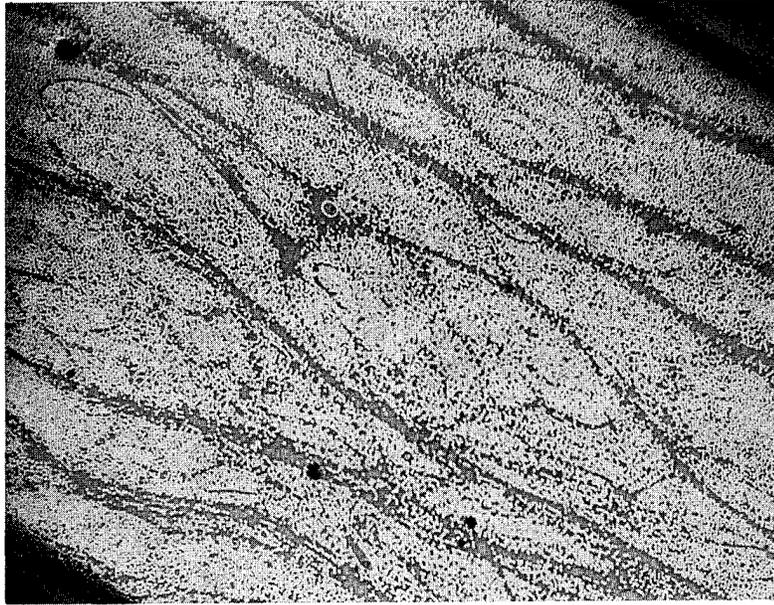
50X



MICRO SECTION B

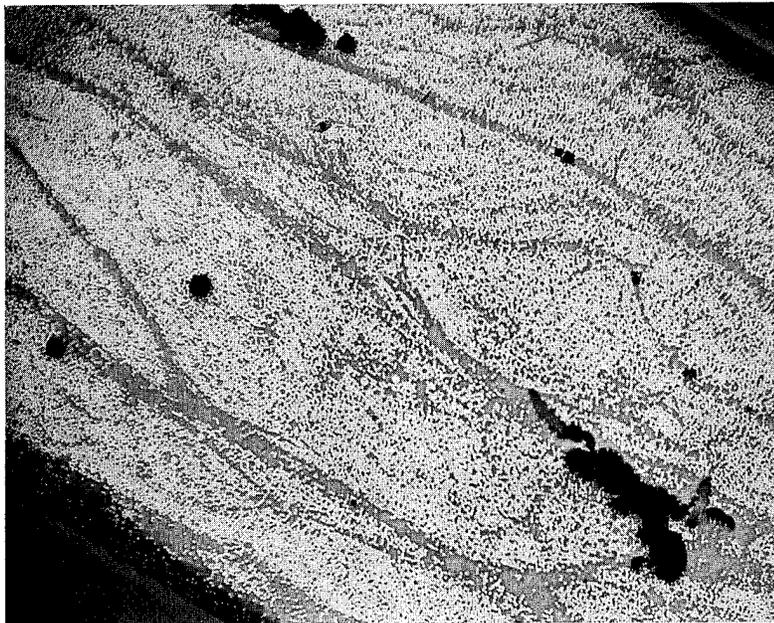
50X

FIGURE 24 CROSS-SECTIONS OF LAMINATE 589-47
(HM-S/PMR-15)



MICRO SECTION B

50X



MICRO SECTION C

50X

FIGURE 25 CROSS-SECTIONS OF LAMINATE 589-51
(HM-S/PMR-15)

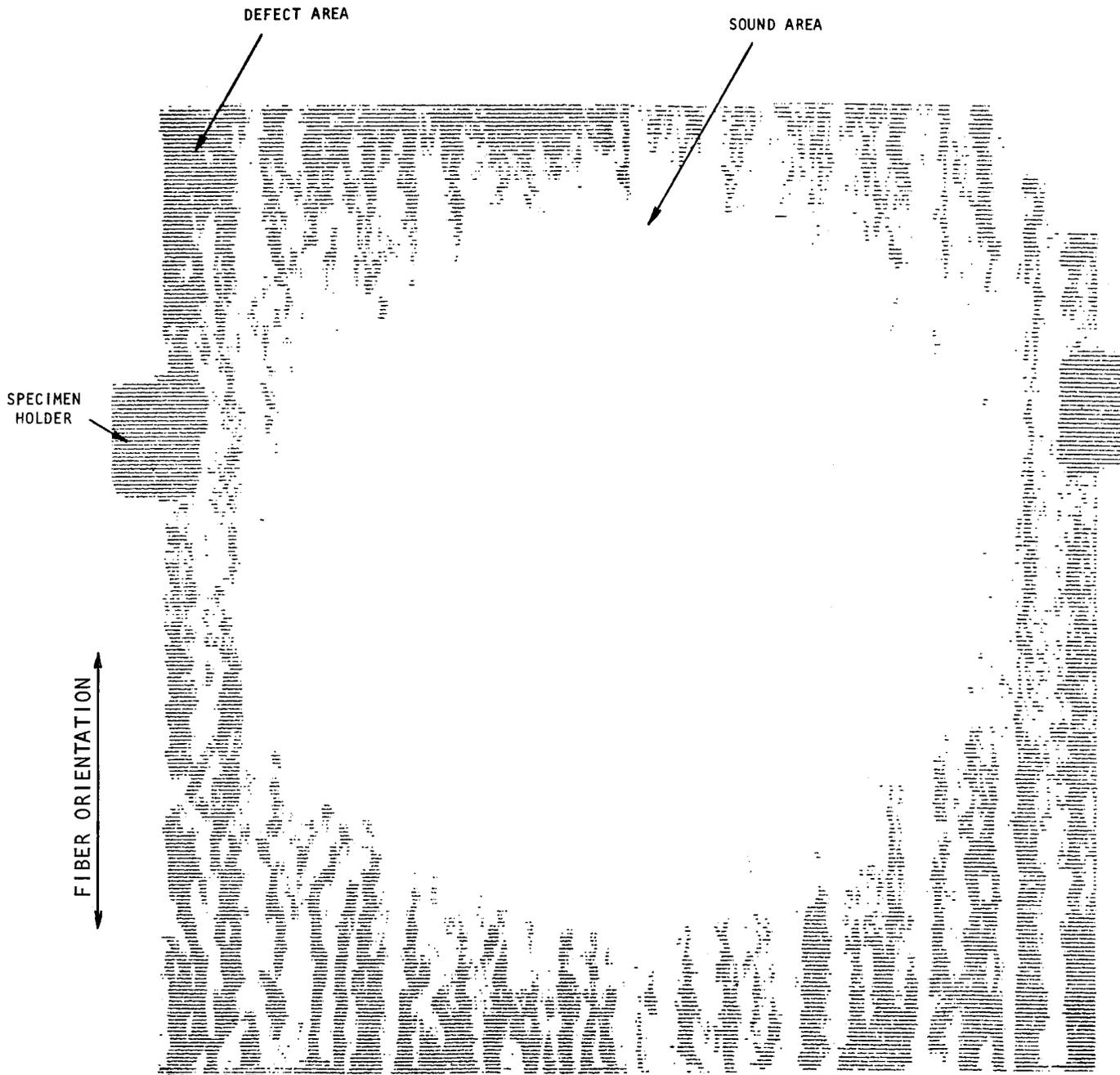
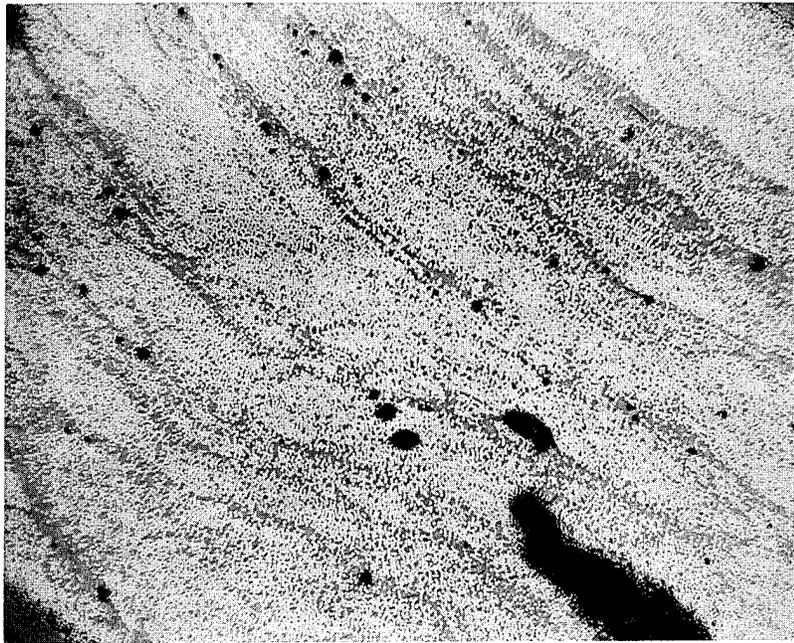
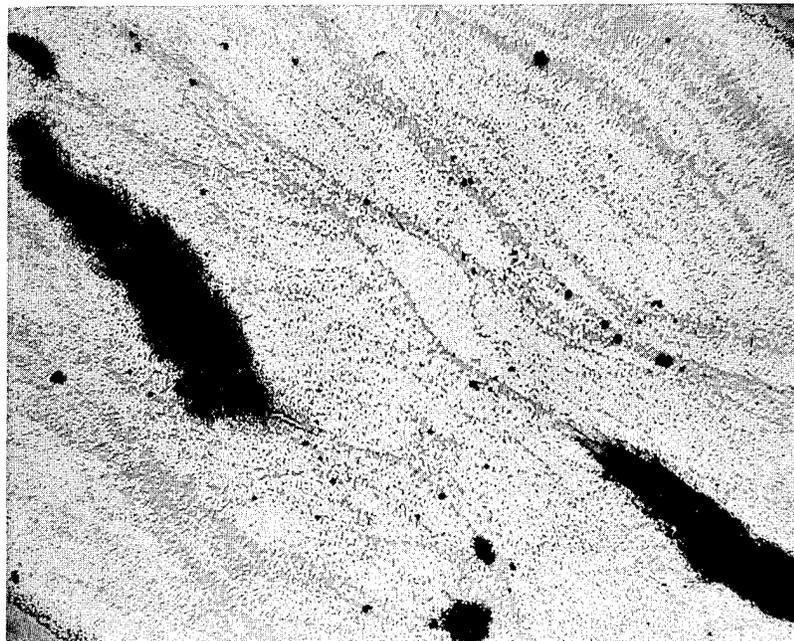


FIGURE 26 SONIC C - SCAN OF LAMINATE 589-44
(PHOTOGRAPHICALLY REDUCED)



50X



50X

FIGURE 27 PHOTOMICROGRAPHS FROM LAMINATE 589-44 SHOWING DEFECTS IDENTIFIED BY SONIC INSPECTION.

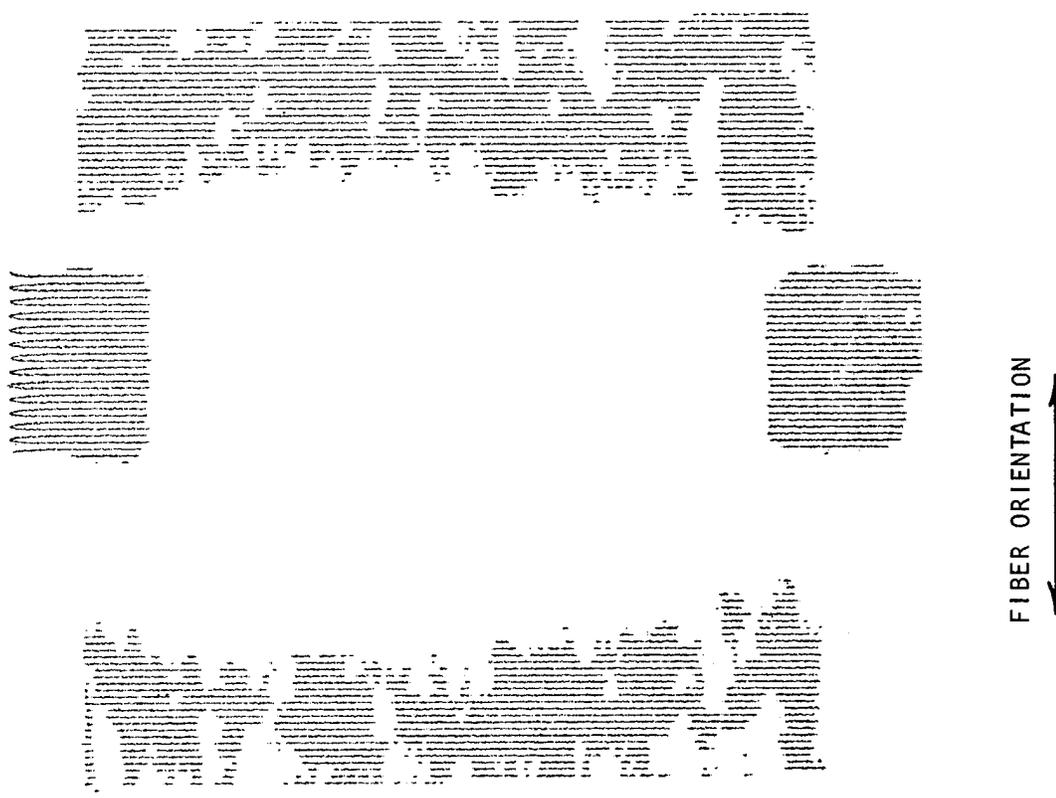
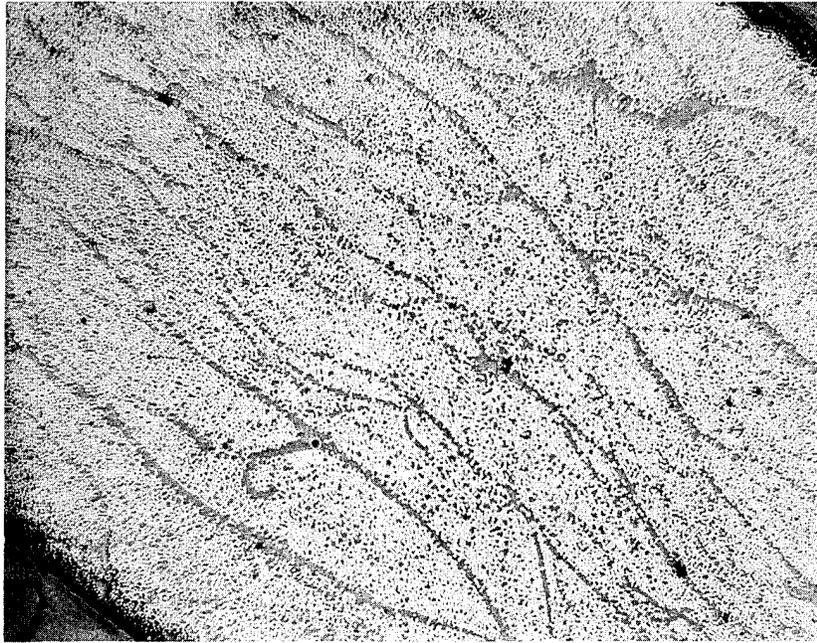
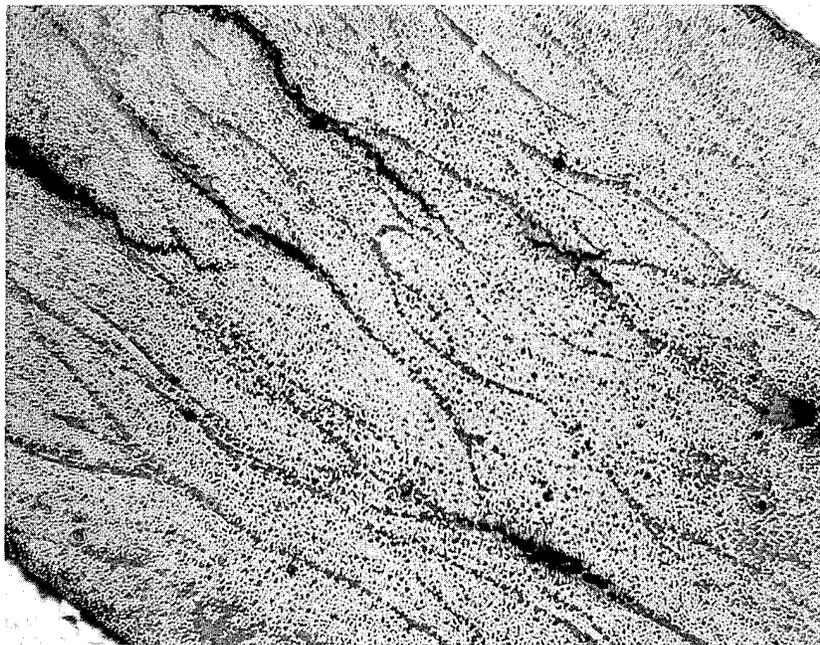


FIGURE 28 SONIC C-SCAN OF LAMINATE 594-31 (10.2cm x 10.2cm).



CENTER AREA

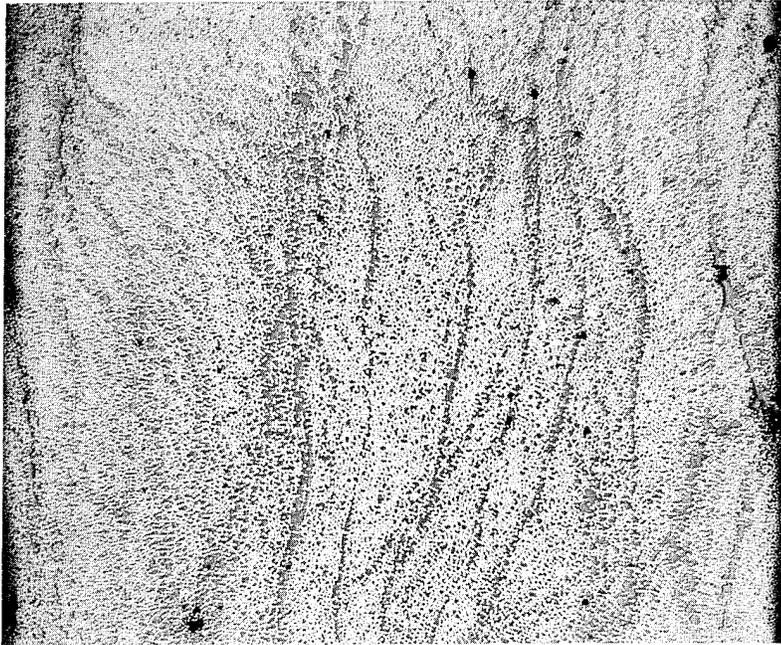
50X



DEFECT AREA

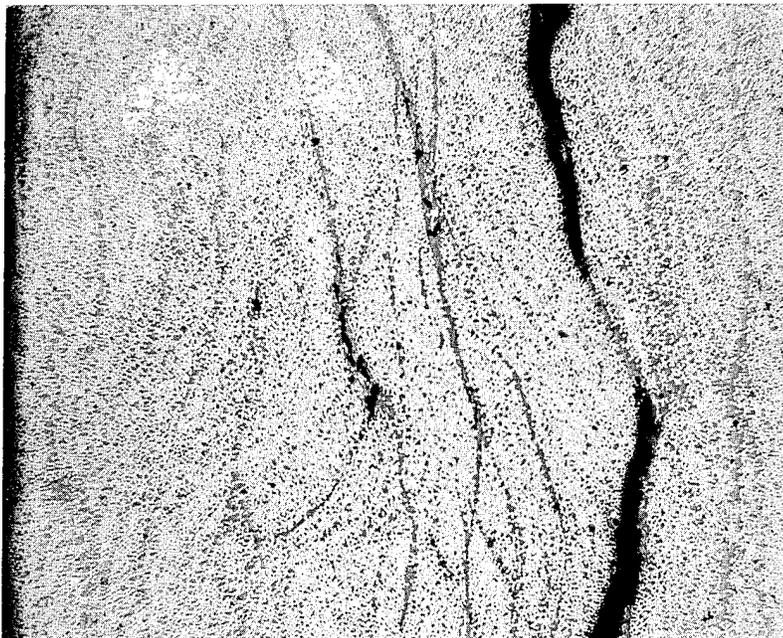
50X

FIGURE 29 CROSS-SECTIONS OF LAMINATE 594-76 (HT-S/PMR-15)



CENTER AREA

50X



DEFECT AREA

50X

FIGURE 30 CROSS-SECTIONS OF LAMINATE 594-80 (HT-S/PMR-15)

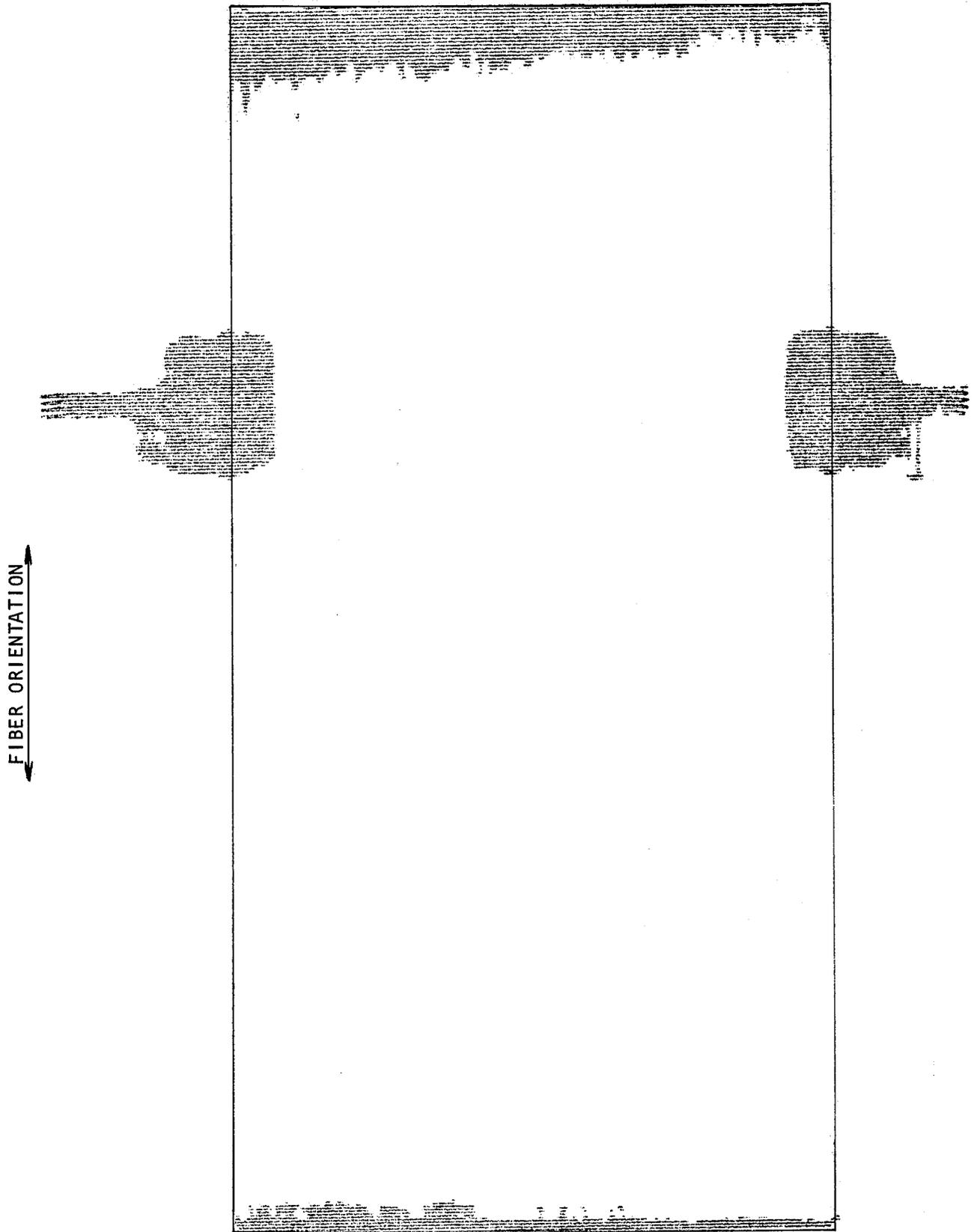


FIGURE 31 C-SCAN OF LAMINATE 669-78 MOLDED WITH STANDARD CYCLE. RESIN SOLUTION PROVIDED BY NASA-LEWIS.



FIGURE 32 ISOTHERMAL EXPOSURE SET-UP SHOWING AIR SOURCE, FLOW METER AND INNER CHAMBER.

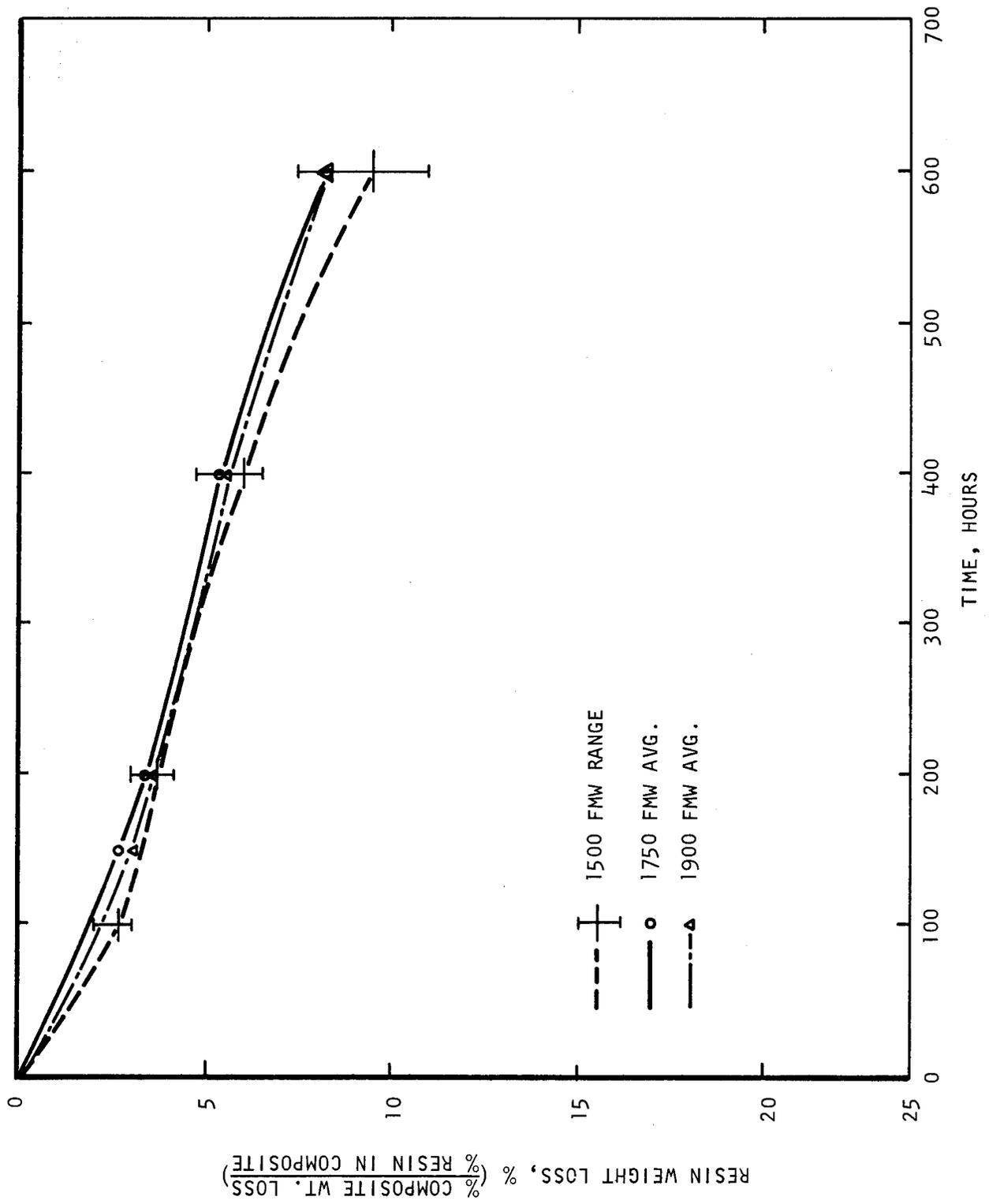


FIGURE 33 WEIGHT LOSS OF PMR/HM-S COMPOSITES IN AIR (100 ml/MIN.) AT 589°K (600°F).

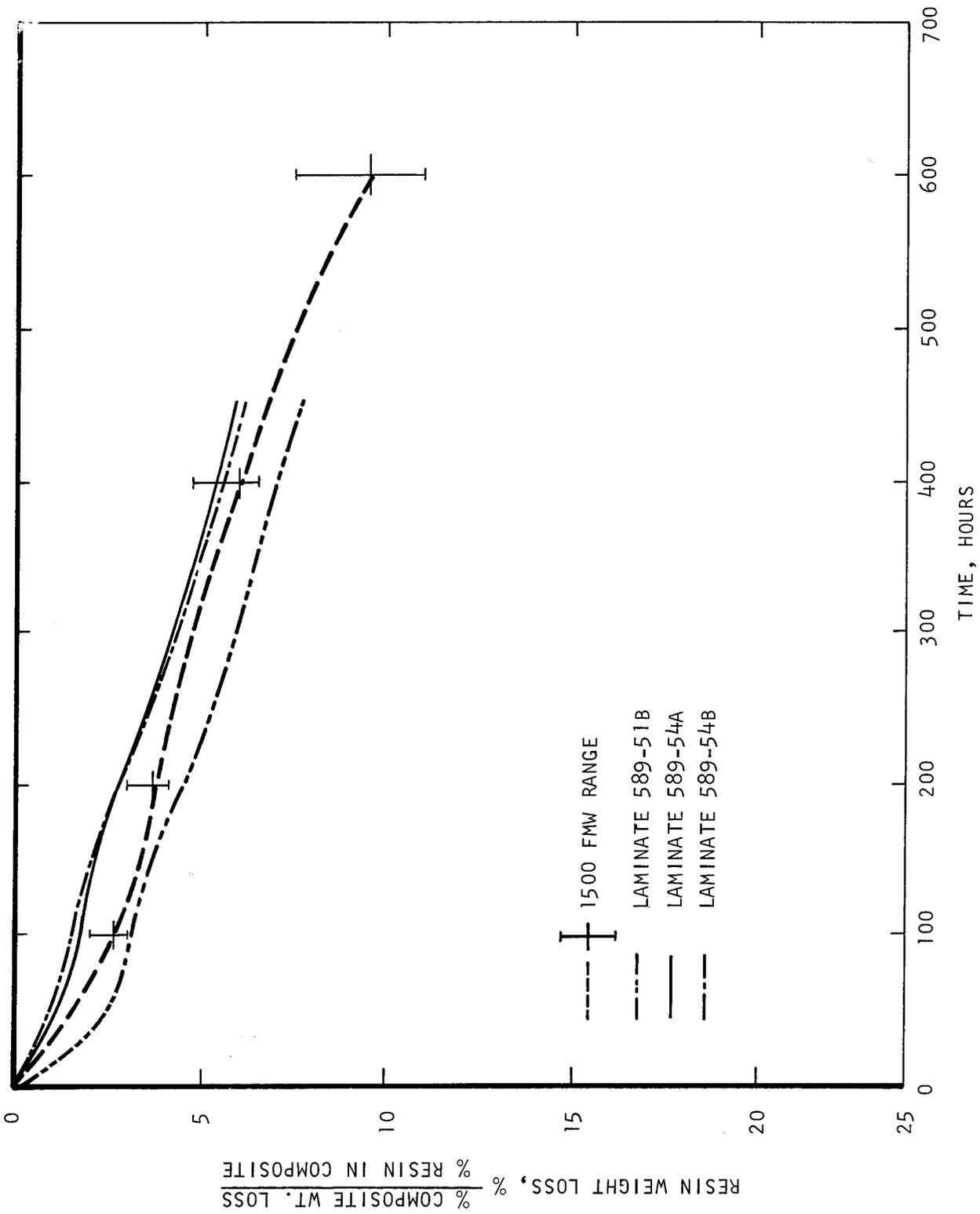


FIGURE 34 WEIGHT LOSS OF PMR/HM-S COMPOSITES IN AIR (100 ml/MIN.) AT 589°K (600°PF).

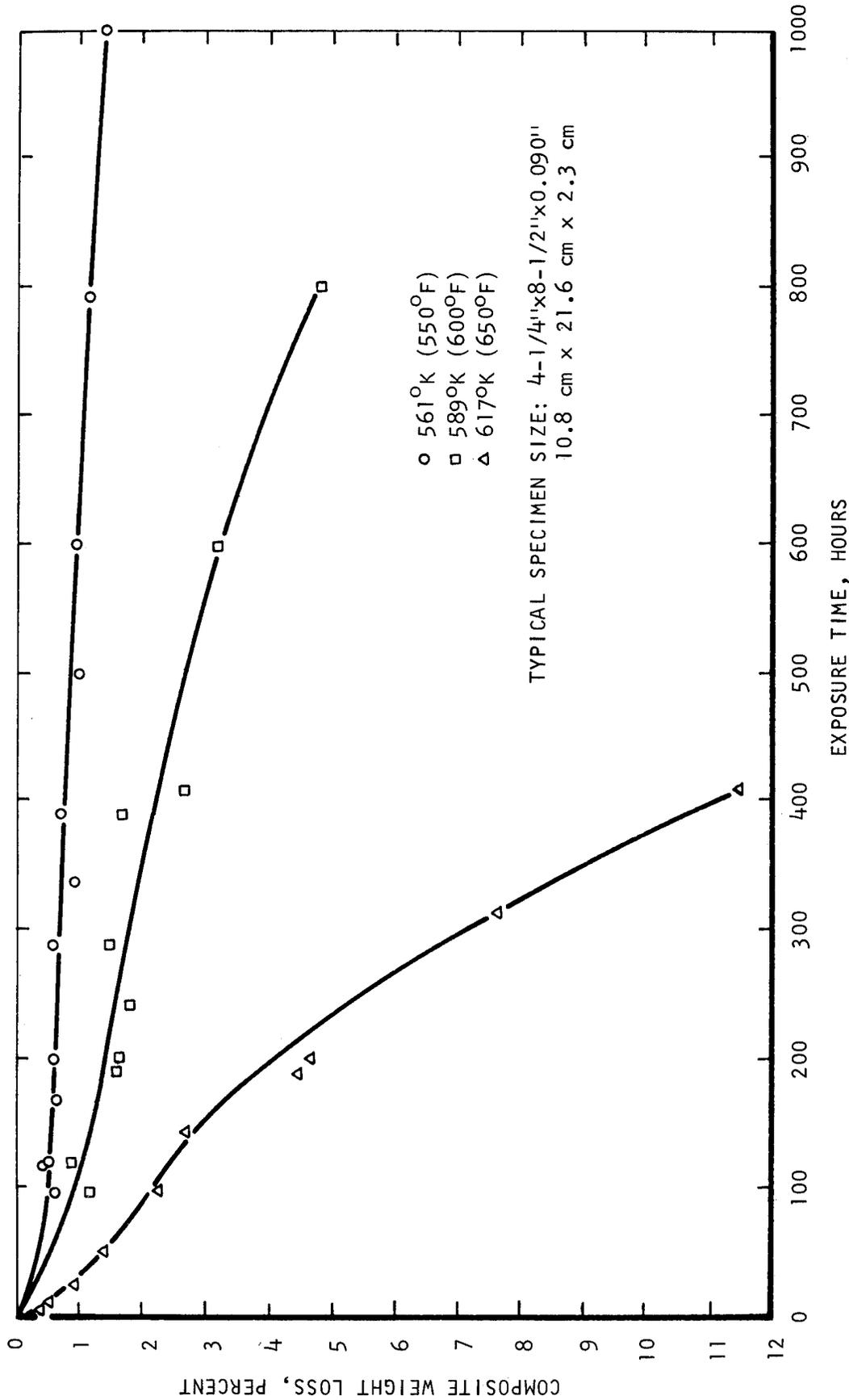


FIGURE 35 35 PERCENT WEIGHT LOSS OF PMR-15/HM-S COMPOSITES EXPOSED TO 100 MI/MIN AIR FLOW AT TEMPERATURE SHOWN.

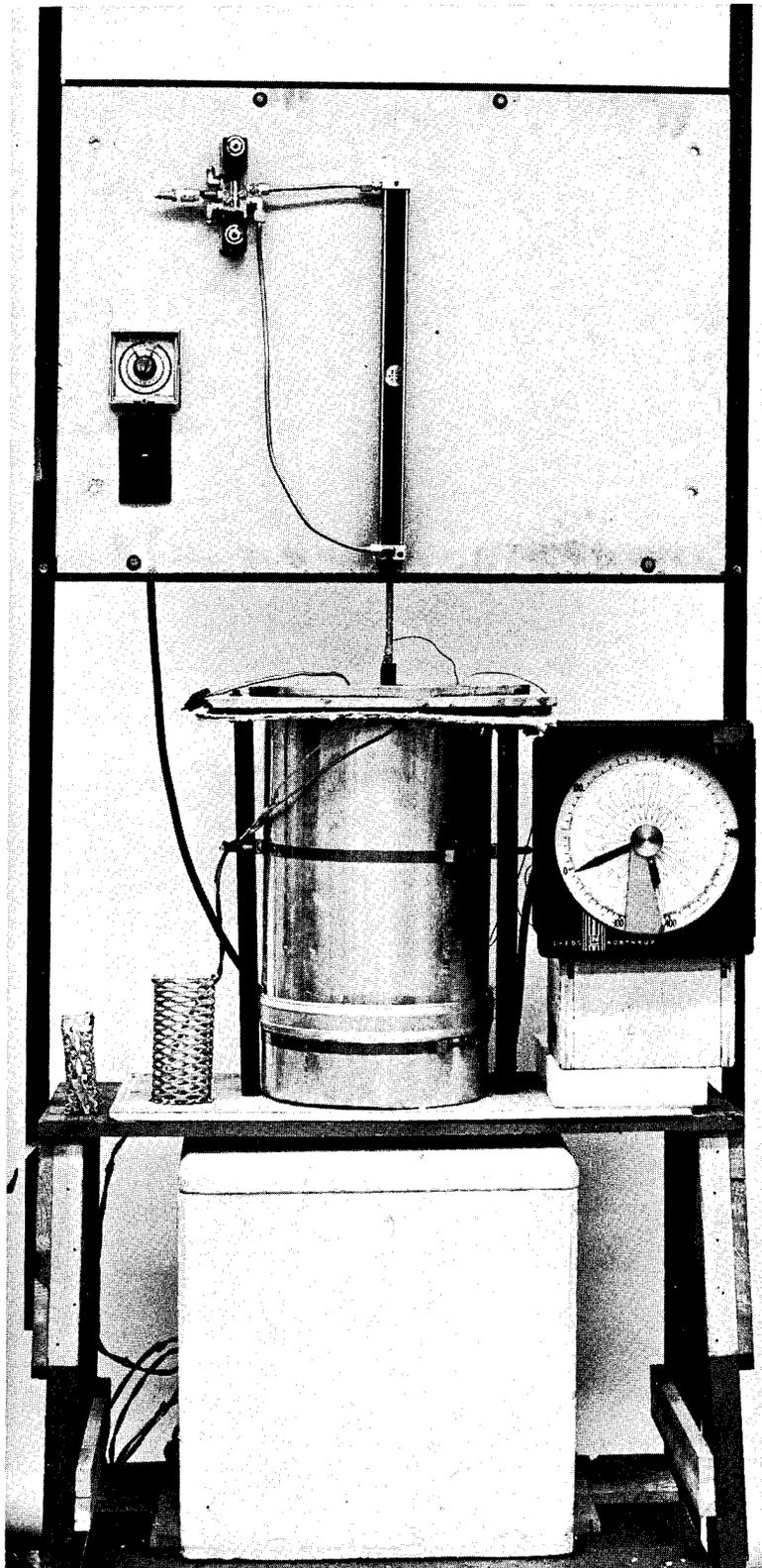


FIGURE 36 PHOTO OF THERMOCYCLING TEST RIG.

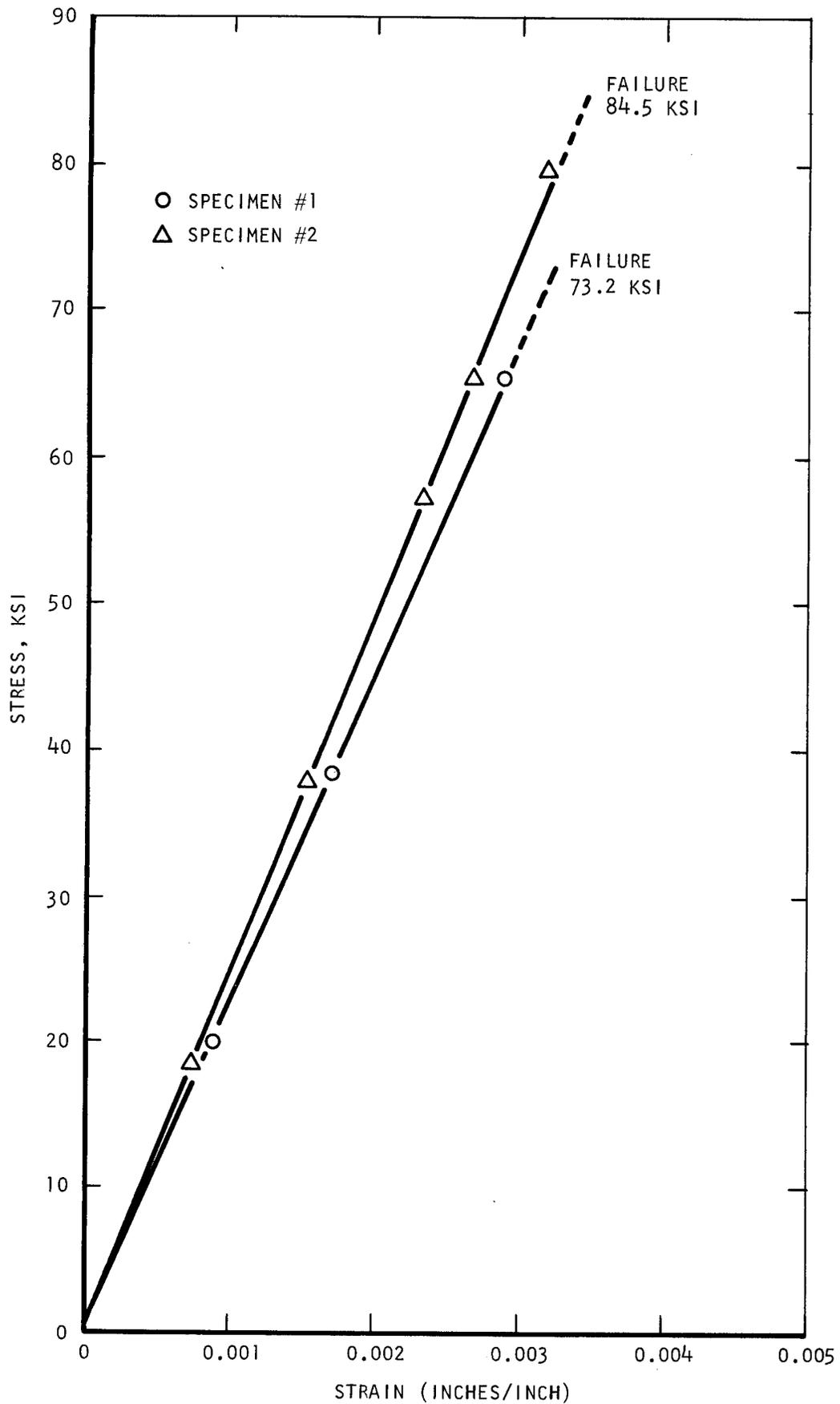


FIGURE 37 STRESS-STRAIN CURVES OF LONGITUDINAL HM-S/PMR-15 TENSILE SPECIMENS AT R.T.

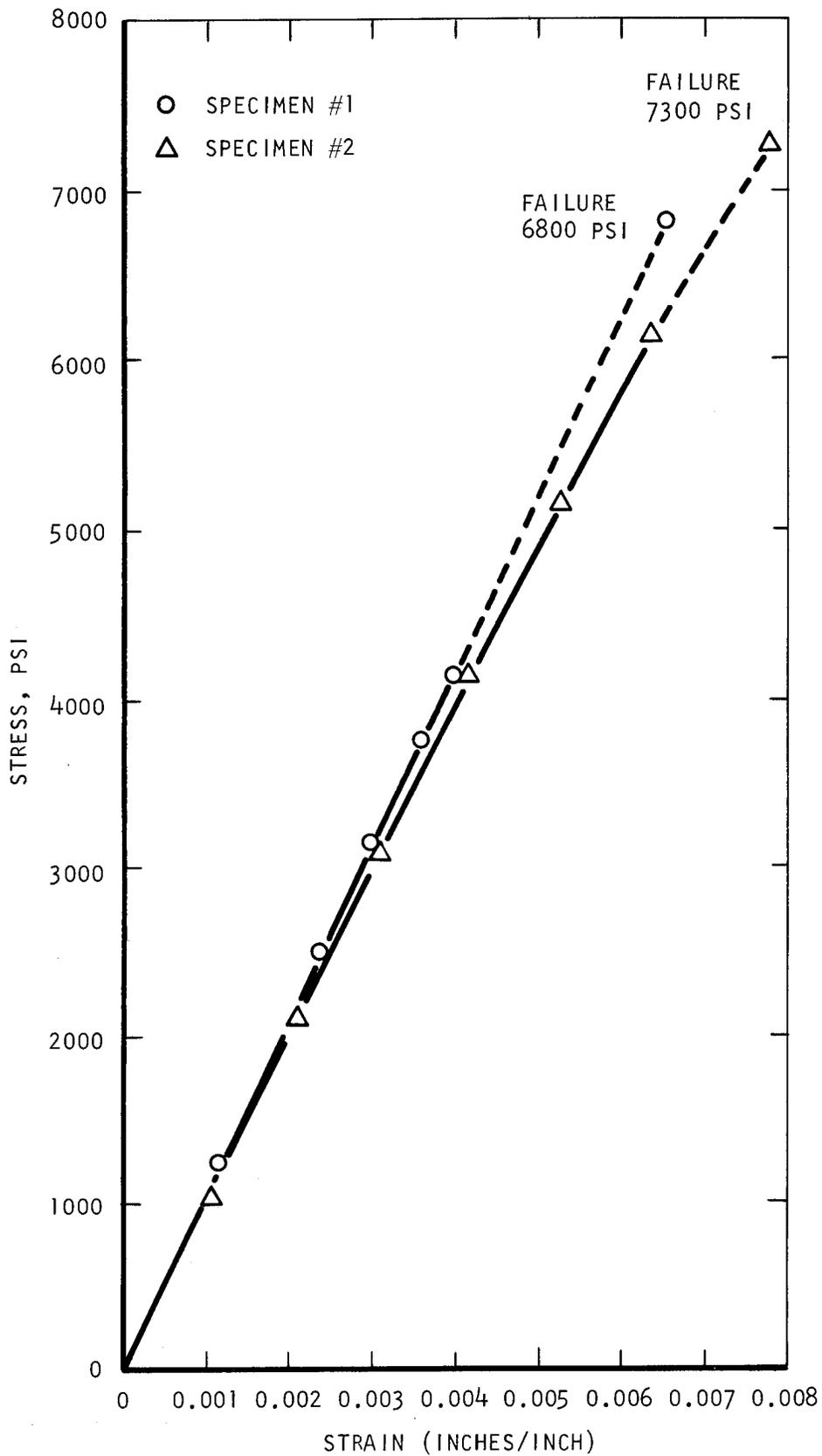
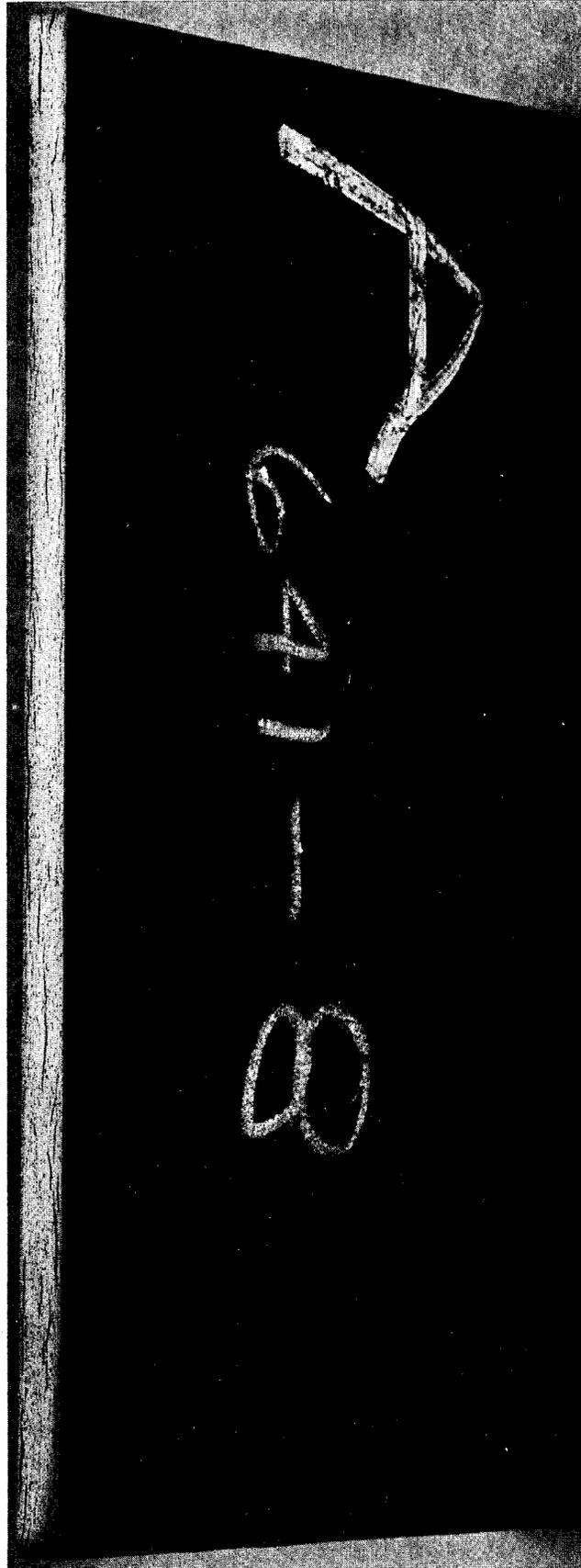


FIGURE 38 STRESS-STRAIN CURVES OF TRANSVERSE HM-S/PMR-15 TENSILE SPECIMENS AT R.T.



(2.5X)

FIGURE 39 CROSS-SECTION OF PMR/HT-S LAMINATE FABRICATED BY THE VACUUM BAG METHOD

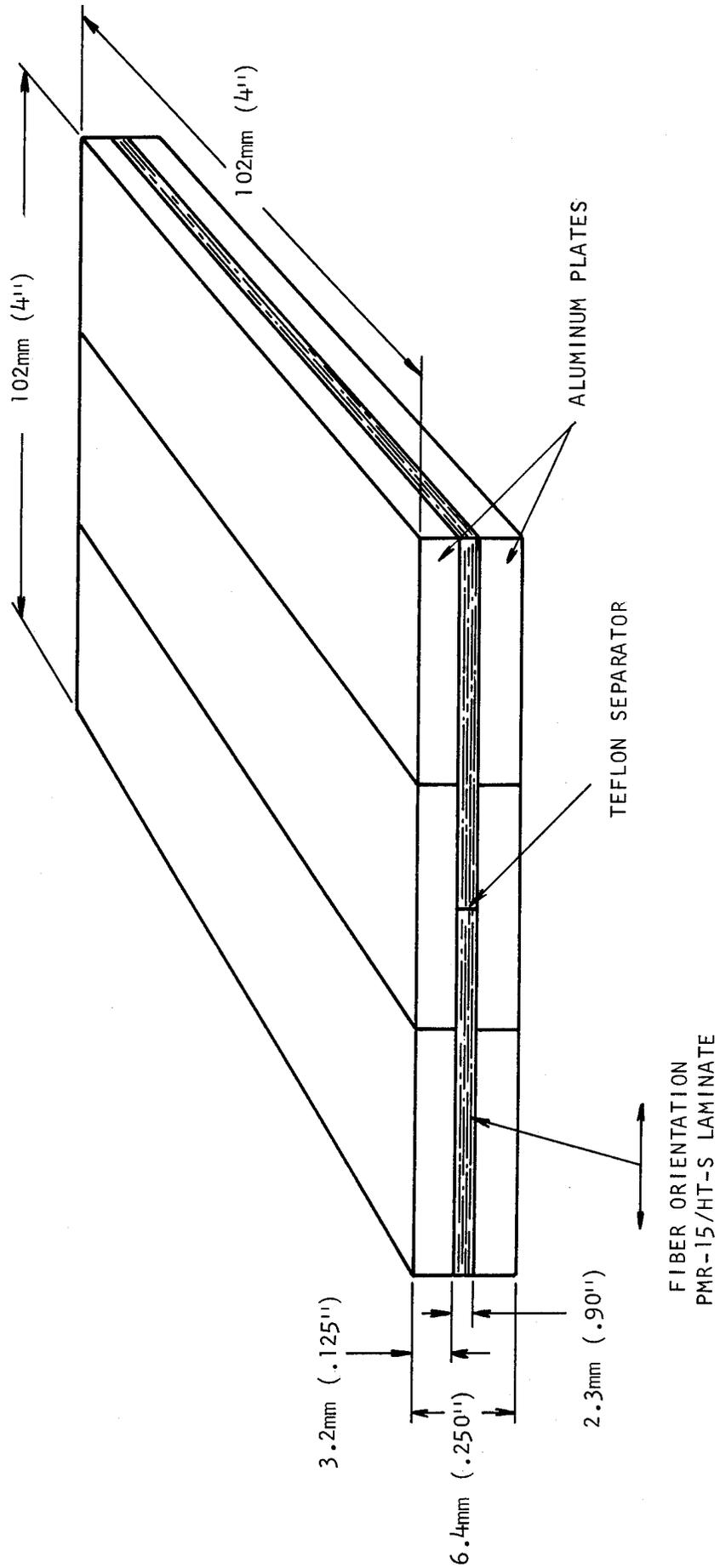


FIGURE 40 ADHESIVE EVALUATION SPECIMEN

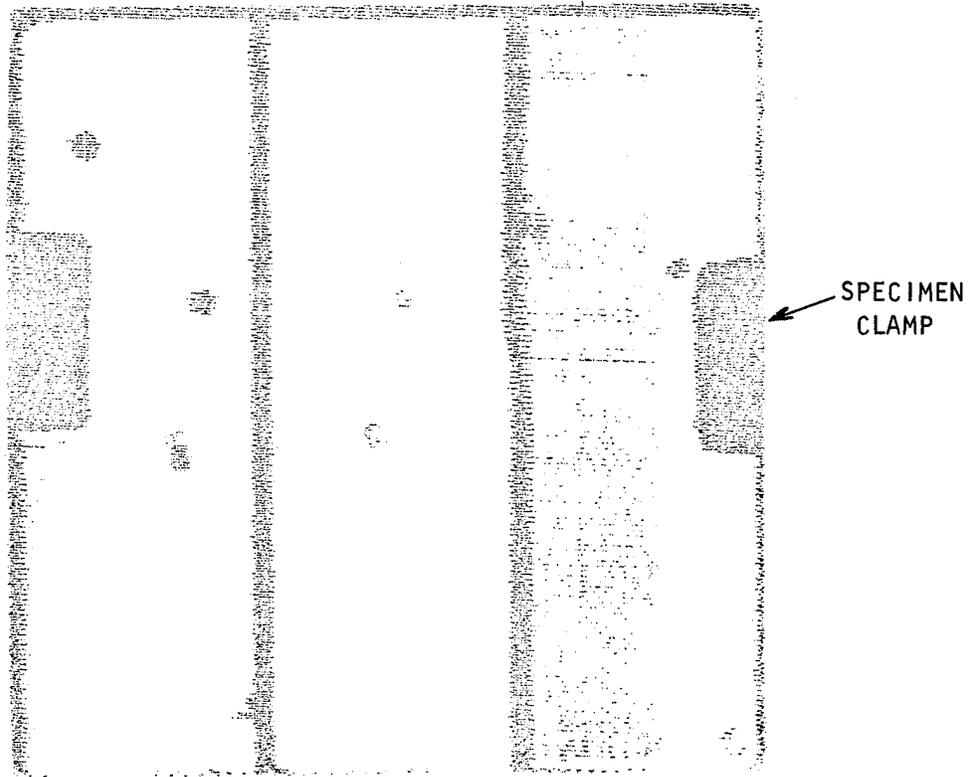


FIGURE 41 C - SCAN OF PRIMER/PMR ADHESIVE SPECIMEN BEFORE POSTCURE

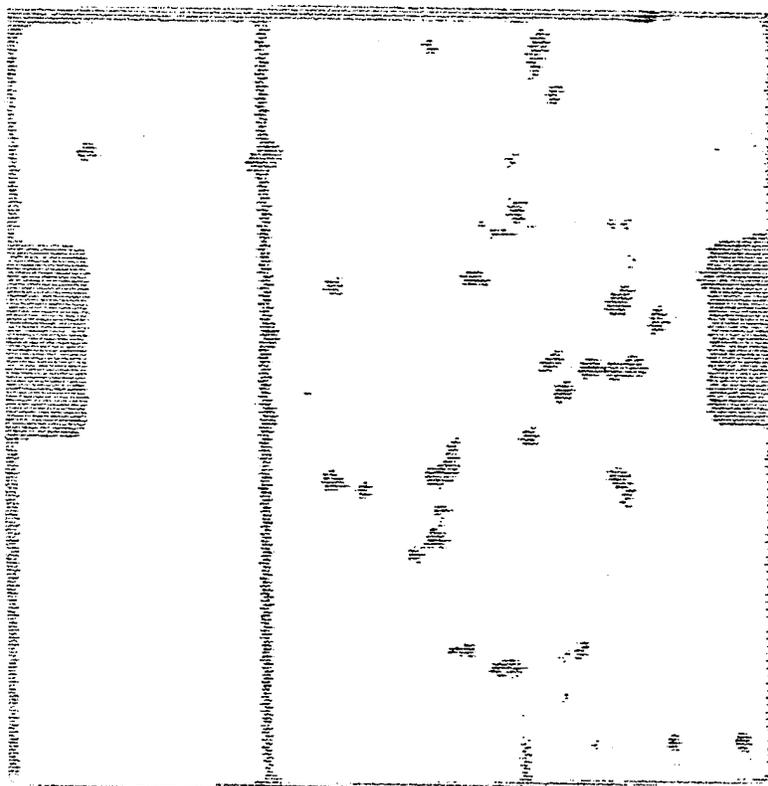


FIGURE 42 C - SCAN OF PRIMER/PMR ADHESIVE SPECIMEN AFTER 617°K POSTCURE

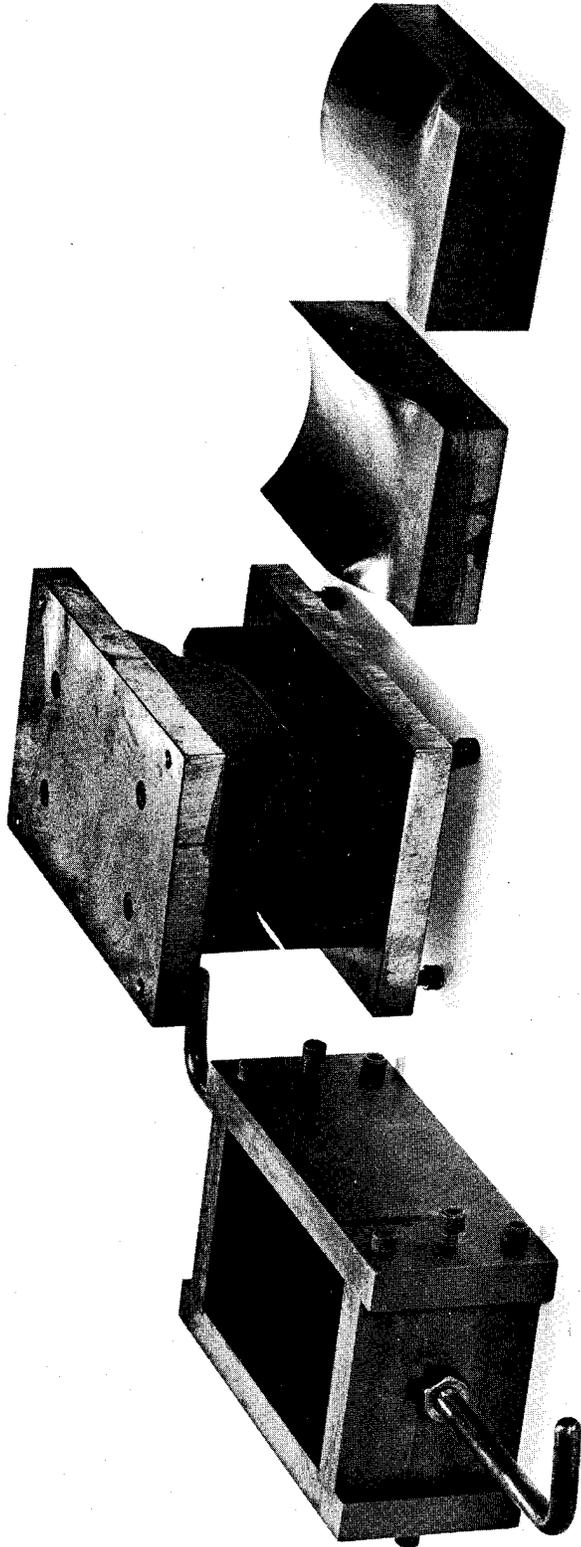


FIGURE 43 COMPOSITE BLADE SPECIMEN PREFORM AND MOLD TOOLING.

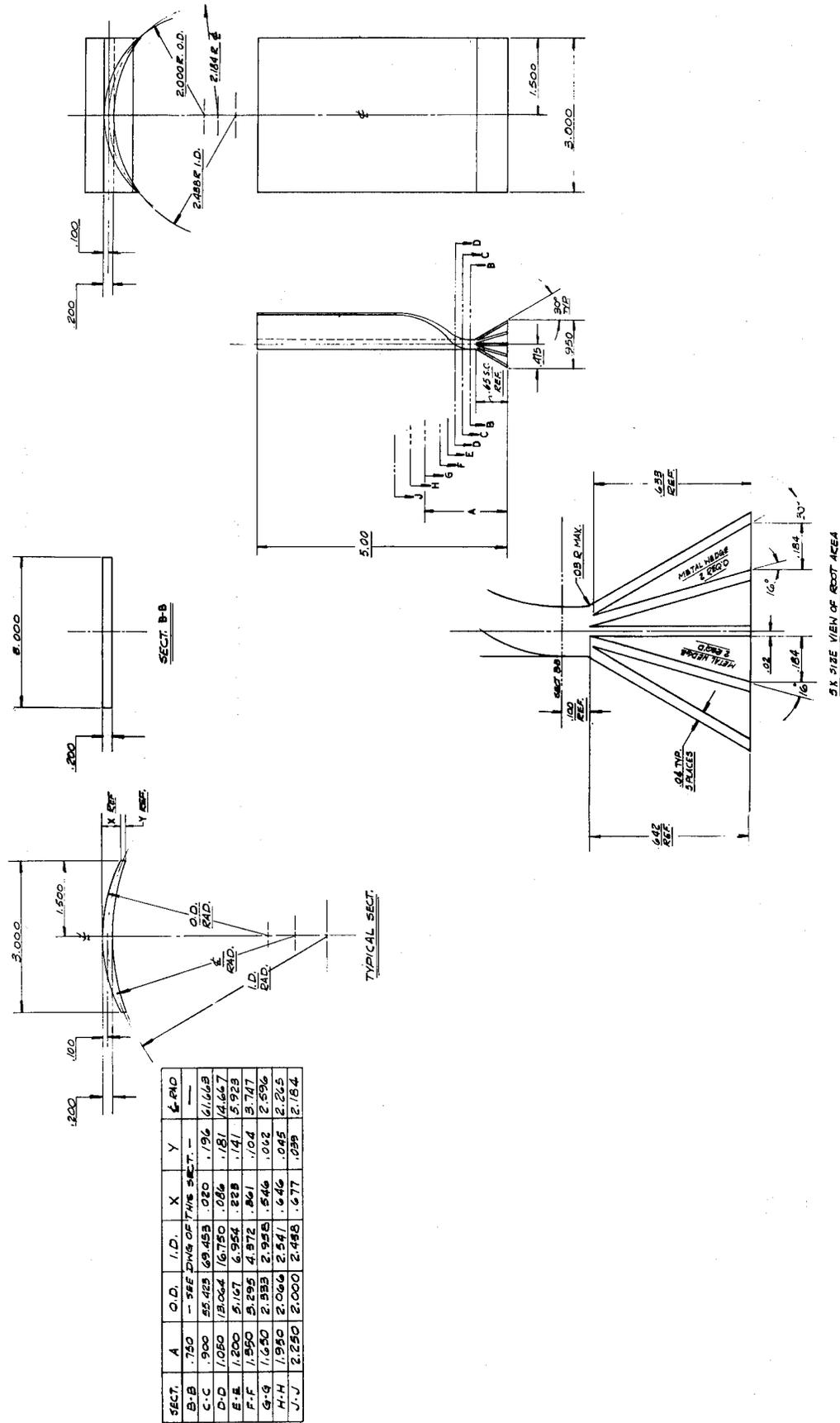
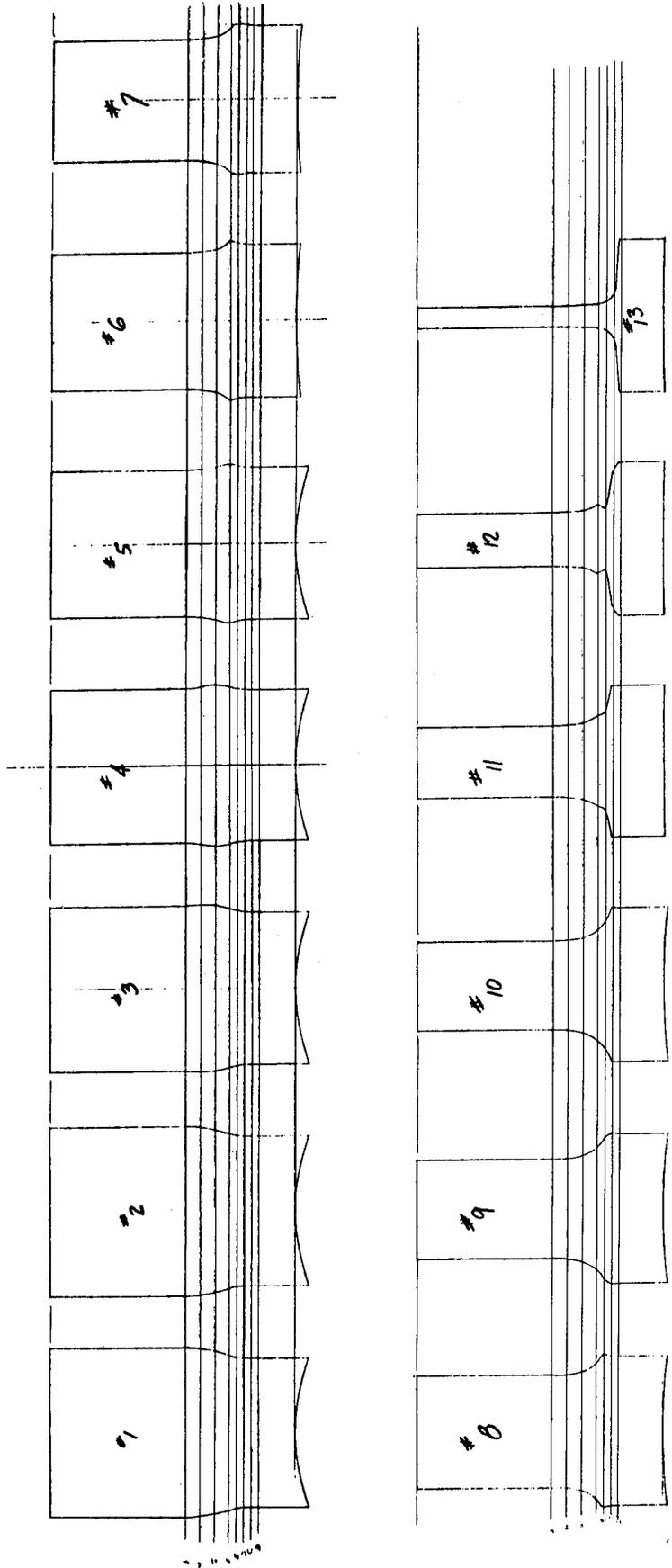


FIGURE 44 COMPOSITE BLADE SPECIMEN DESIGN



SHT 1 OF 2

#1 PLY ~ OD SIDE
 #13 IN CONSECUTIVE ORDER
 #25 PLY ~ ID SIDE

TOP VIEW
 LONGING DRAW ON TIP

FIGURE 45 BLADE SPECIMEN PLY DEVELOPMENT

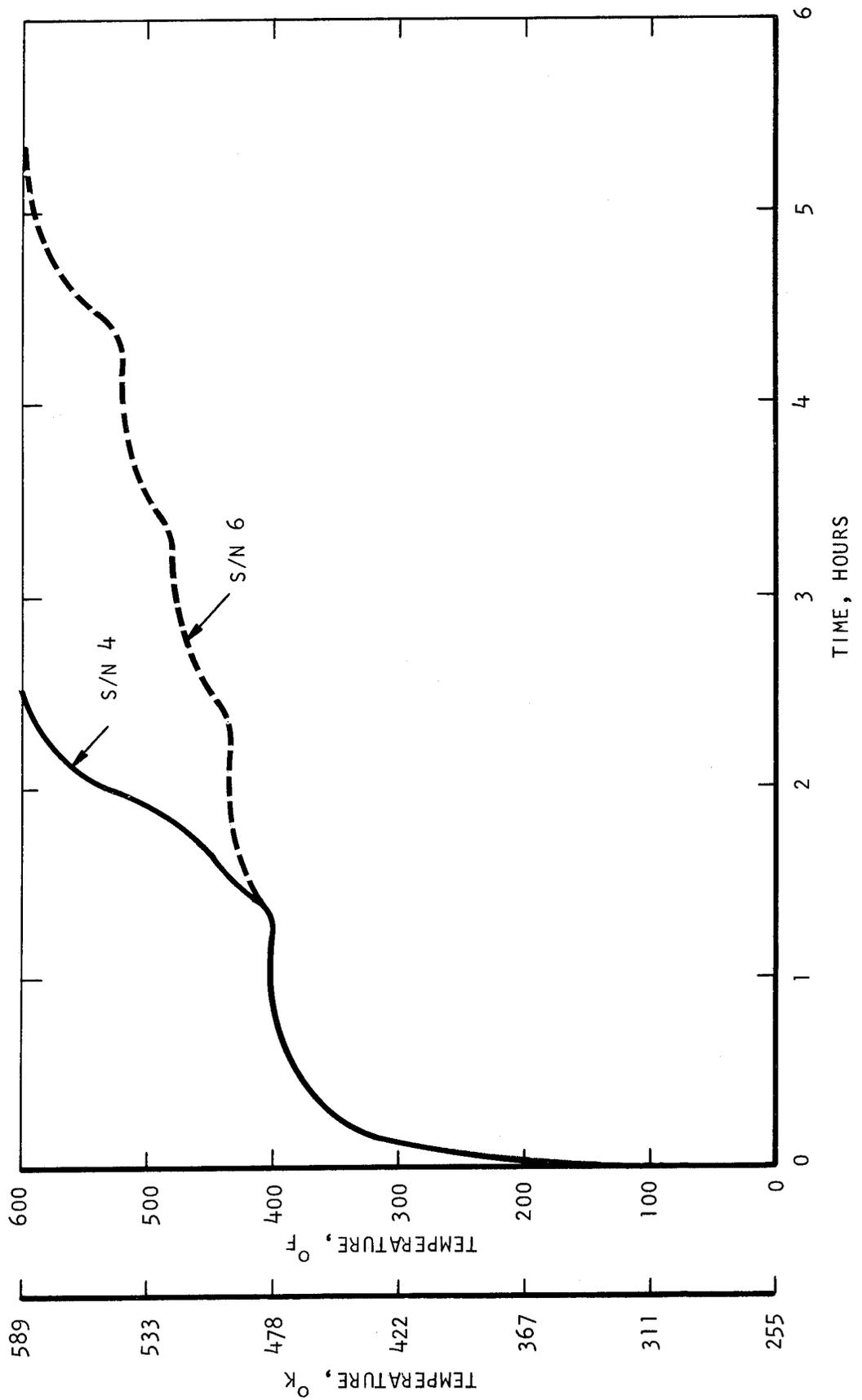


FIGURE 46 AVERAGE TOOL TEMPERATURE DURING HEAT RISE IN MOLDING BLADE SPECIMENS

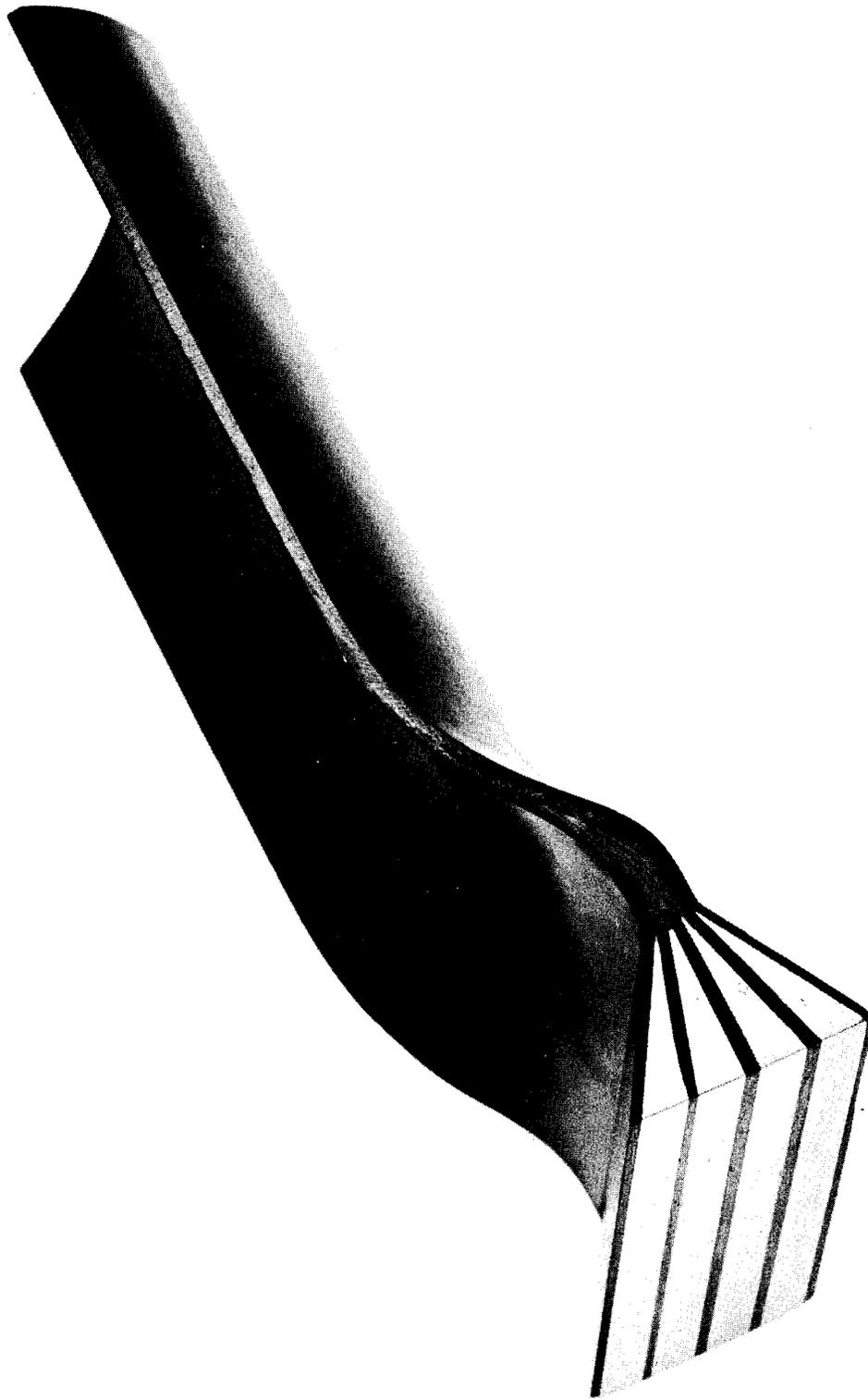
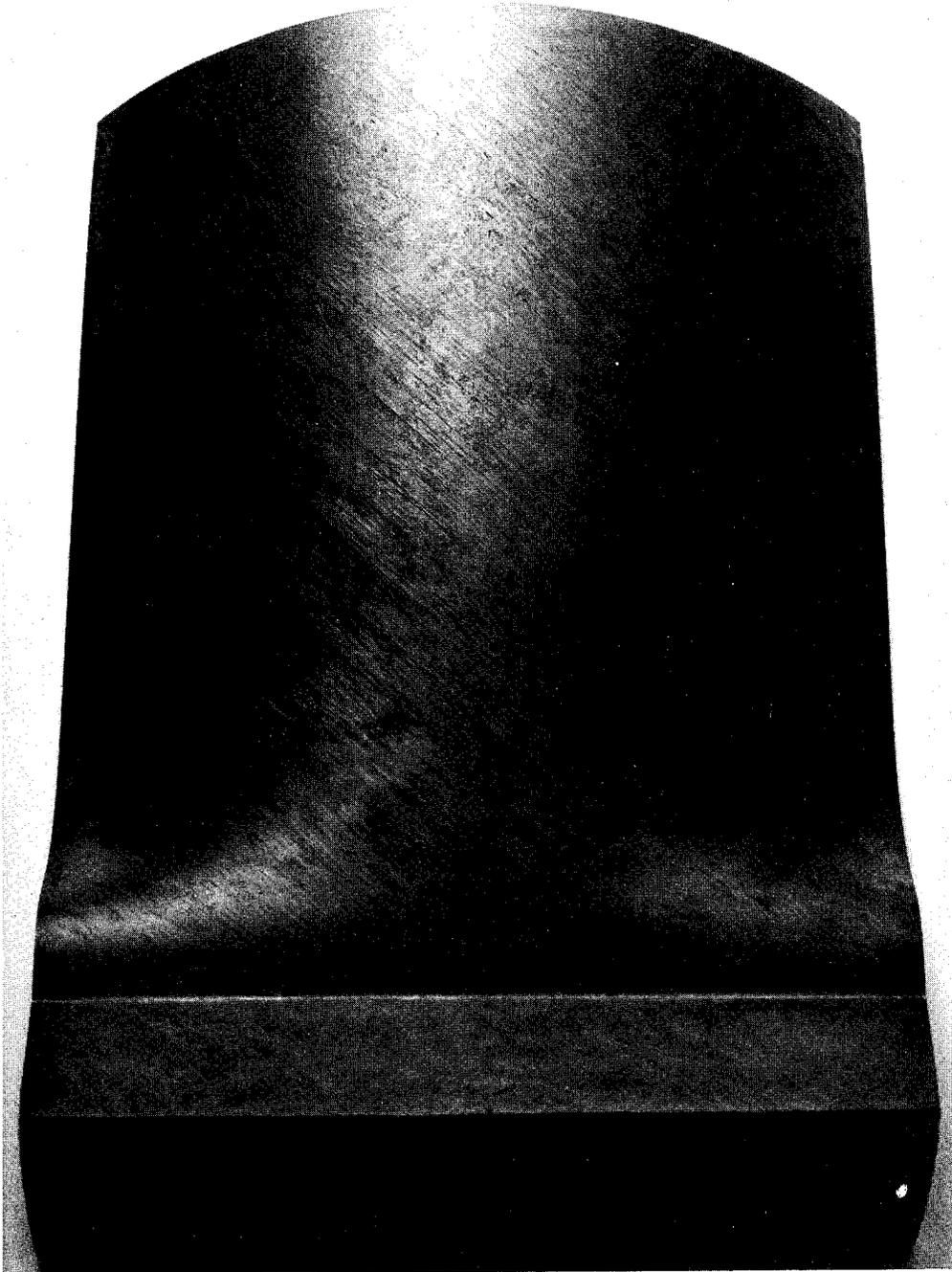
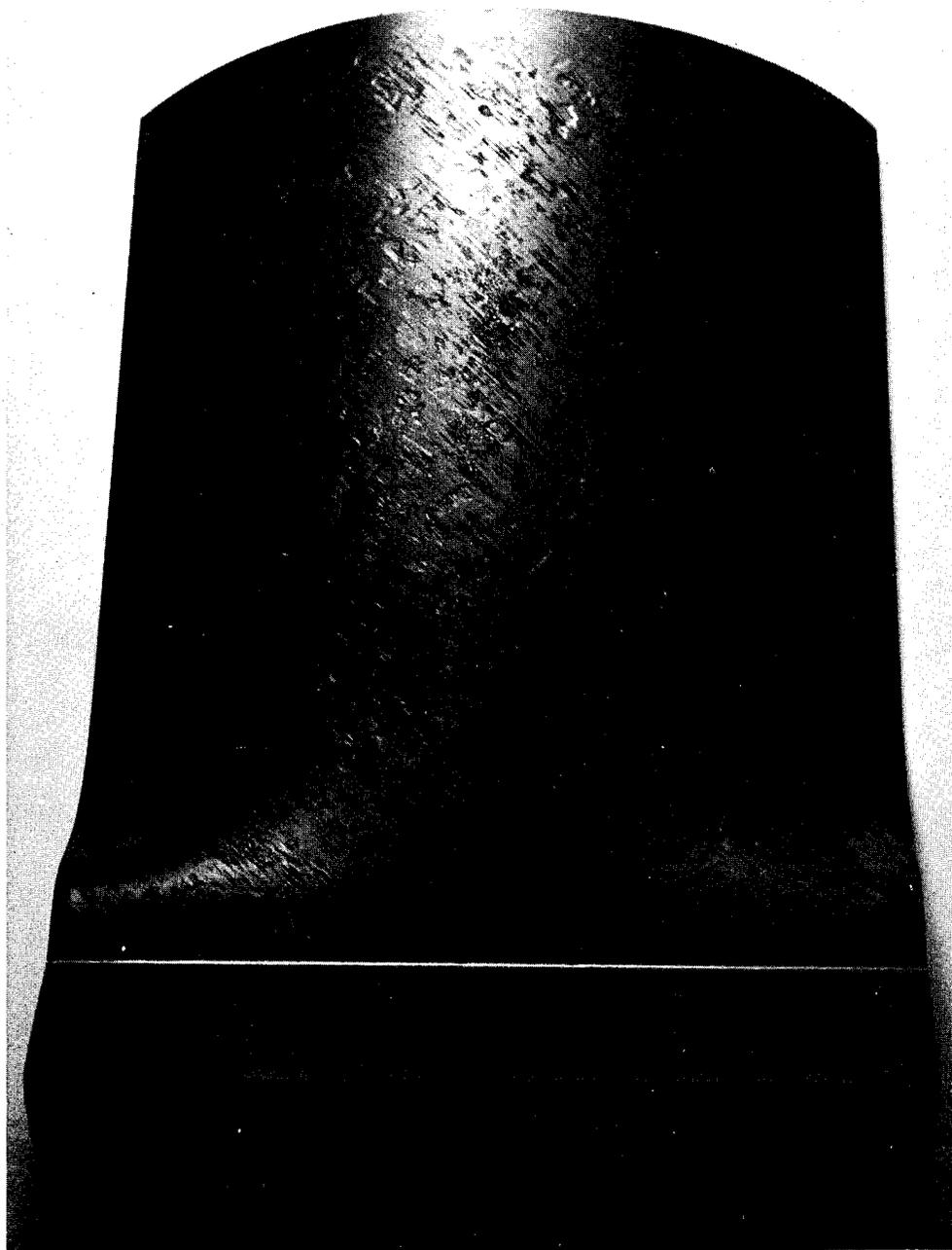


FIGURE 47 COMPOSITE BLADE SPECIMEN.



(1.6x)

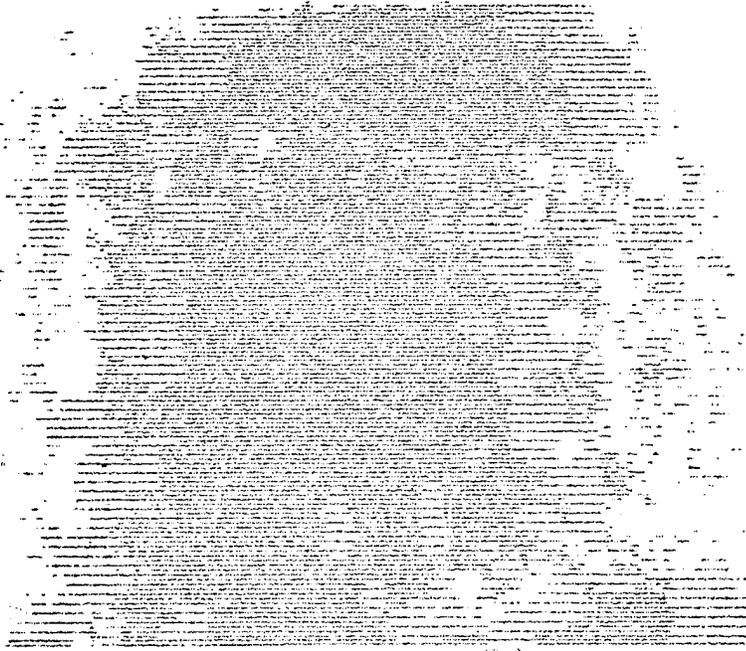
FIGURE 48 SURFACE OF BLADE SPECIMEN S/N 6



(1.6x)

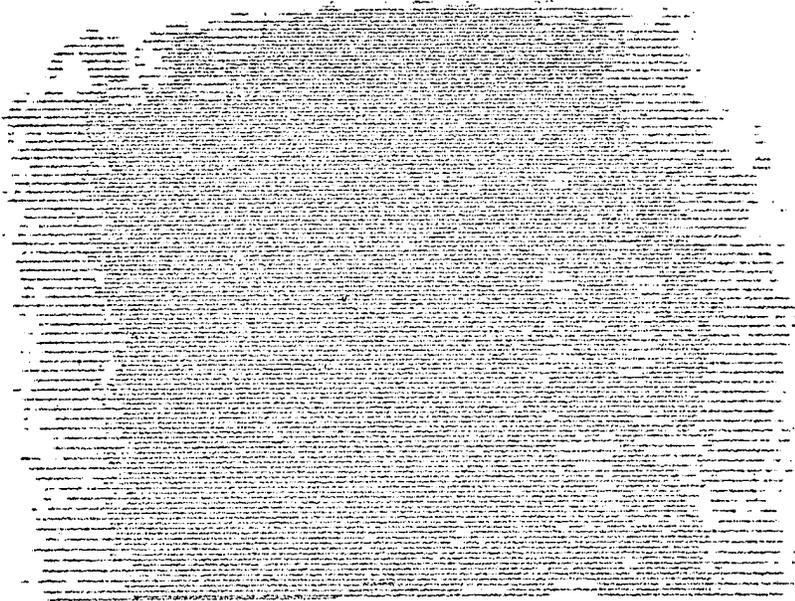
FIGURE 49 SURFACE OF BLADE SPECIMEN S/N 4

TIP



25% SCREEN HEIGHT

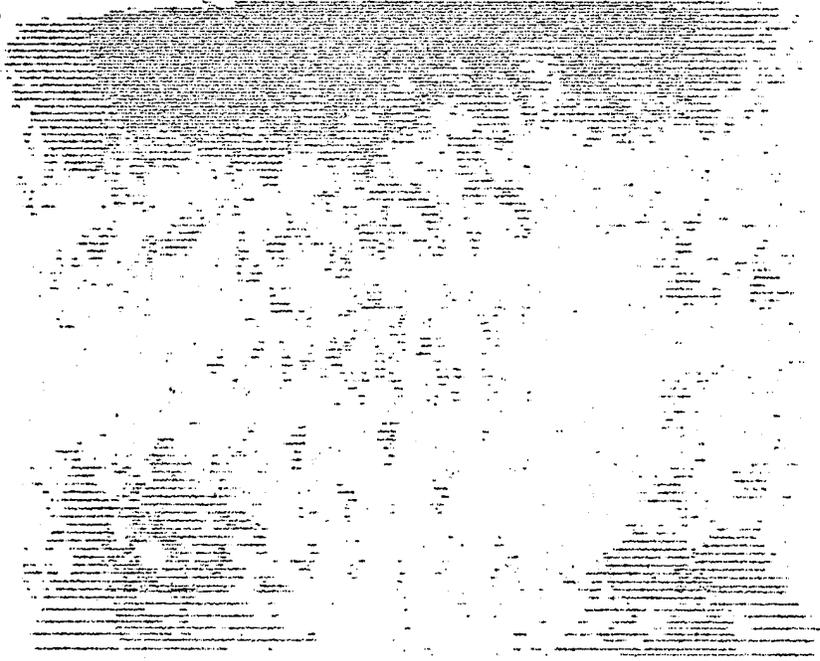
TIP



50% SCREEN HEIGHT

FIGURE 50 C - SCANS OF BLADE SPECIMEN S/N 3

TIP



25% SCREEN HEIGHT

TIP



50% SCREEN HEIGHT

FIGURE 51 C - SCANS OF BLADE SPECIMEN S/N 4

TIP



25% SCREEN HEIGHT

TIP



50% SCREEN HEIGHT

FIGURE 52 C - SCANS OF BLADE SPECIMEN S/N 5



a) TIP CROSS-SECTION 50X



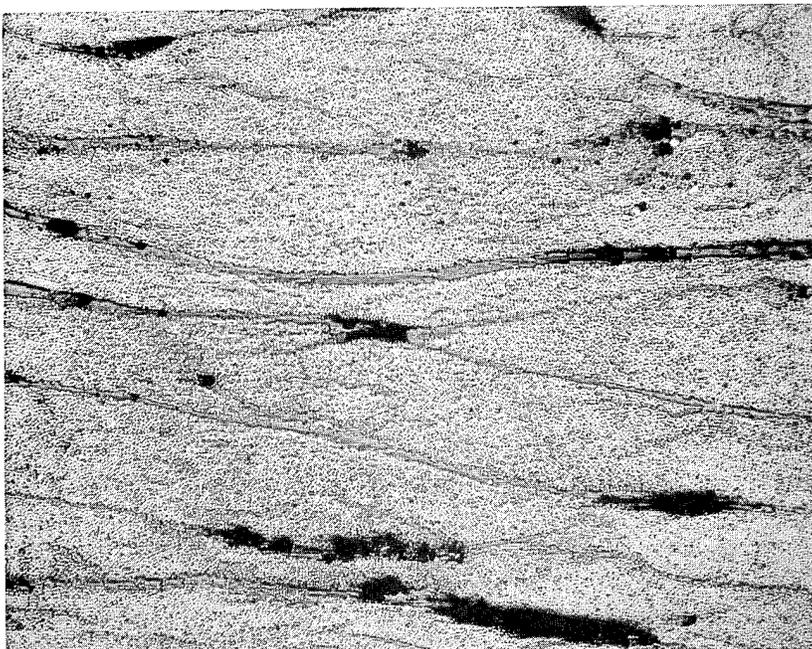
b) CENTER AXIAL SECTION 50X

FIGURE 53 PHOTOMICROGRAPHS OF BLADE SPECIMEN S/N 4



a) CENTER CROSS-SECTION

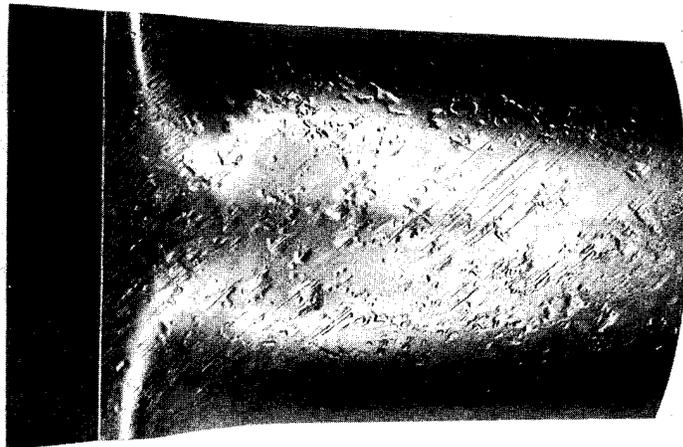
50X



b) ROOT SHELF CROSS-SECTION

50X

FIGURE 54 PHOTOMICROGRAPHS OF BLADE SPECIMEN S/N 4



a) BEFORE POST MOLDING TREATMENT



b) AFTER POST MOLDING TREATMENT

FIGURE 55 SURFACE OF S/N 5 BLADE SPECIMEN BEFORE & AFTER POST MOLDING TREATMENT

APPENDIX A

MECHANICAL TEST SPECIMENS

Special program test methods, such as thermal expansion, thermal cycling, and techniques used to gather strain gage data, are described in the body of the text. Certain frequently used routine mechanical test methods have not been described. These are illustrated in the following Appendix A sketches (Figures A-1 through A-5) with attached notes.

The methods shown in the following pages are widely used and generally accepted. One new test specimen configuration that was used with excellent results was a waisted transverse tensile specimen. This testing method was developed by the NASA Lewis Project Manager and employs two concepts that contribute to its usefulness. These are the reduced gage section and pin gripping; a sketch of the specimen is shown in figure A-1. The reduced gage section insures failure in the gage section rather than at the transition from bonded tab to specimen as is sometimes encountered with other uniform width specimens. Additionally, the use of pin grips reduces specimen mortality in application of the tensile tester holding grips. The machining fixture used to prepare the specimen provides for a drill bushing arrangement so the center line of the specimen is accurately aligned with the pin inserts, thus insuring uniaxial loading.

For room temperature testing, the use of the flat steel washers bonded to the surface on a Teflon bonding fixture was adequate. It was found that, in elevated temperature testing, the addition of a fiberglass cloth tab with a polyimide matrix was required to distribute the load and prevent premature failure through the pin grips. It is recommended that, in the future, a slightly larger area for the specimen "ears" be considered to minimize this type of failure.

Figures A-2 through A-5 illustrate other mechanical test specimens and are self-explanatory.

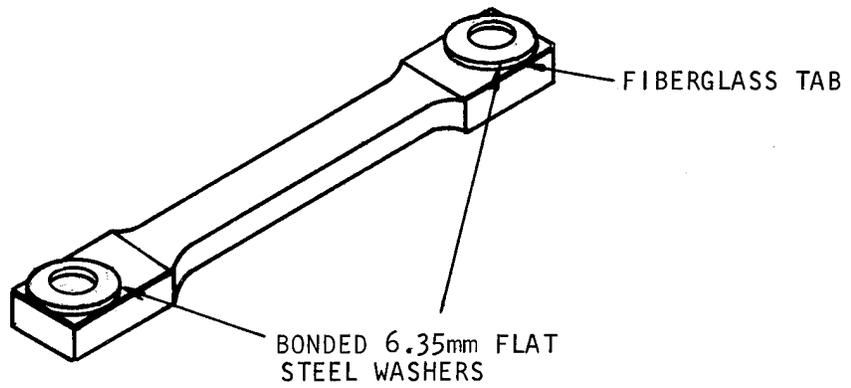
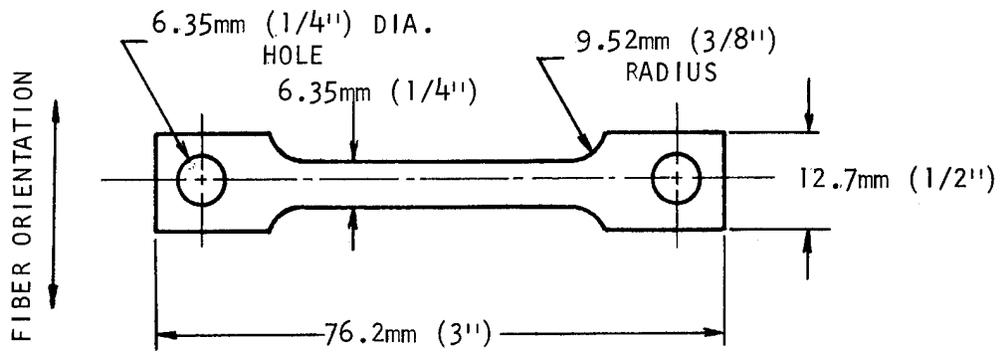
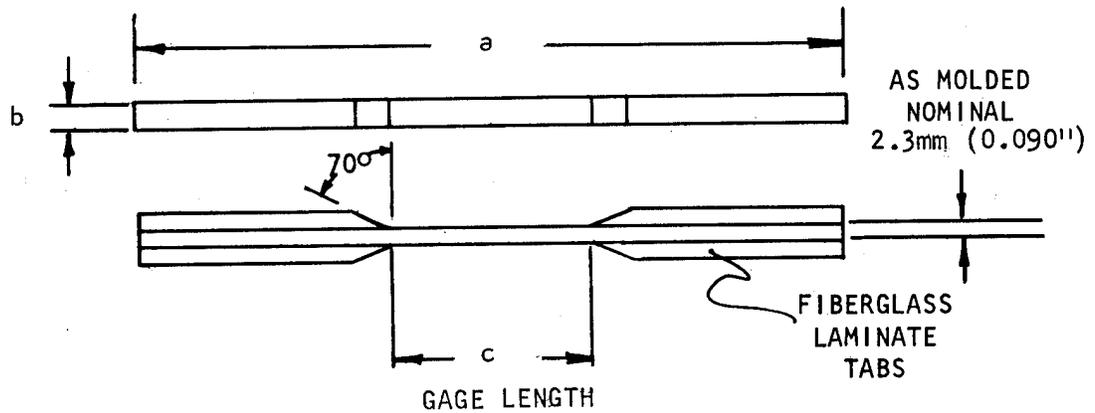


FIGURE A-1 SKETCH OF NEW TRANSVERSE TENSILE SPECIMEN.

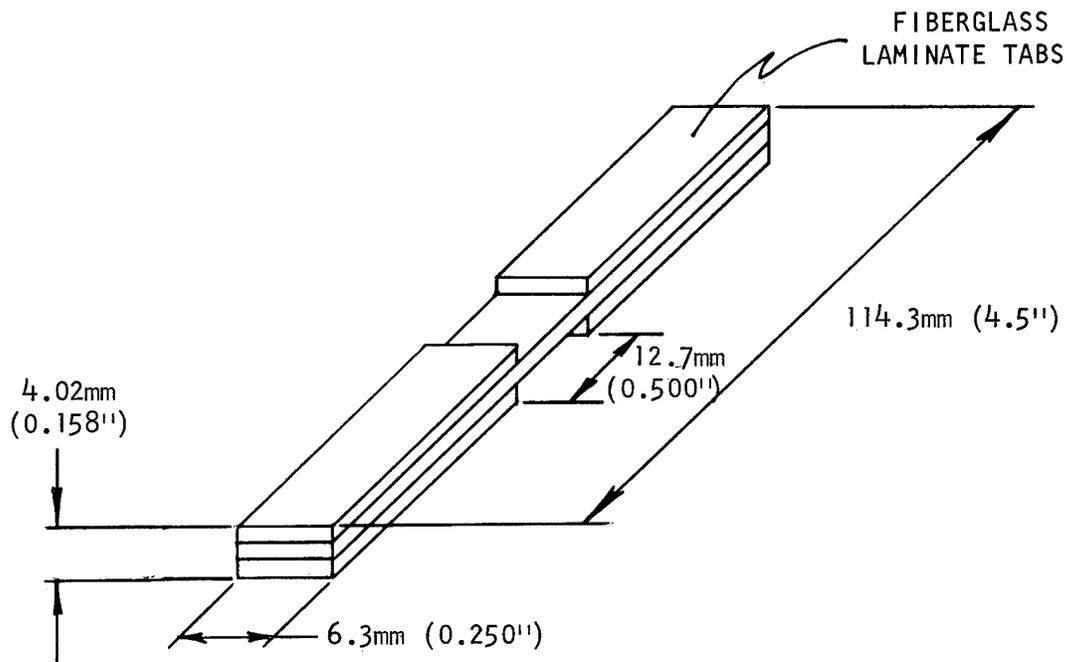


	0°		CROSS-PLY	
	mm	Inches	mm	Inches
a	152.4	6	203.2	8
b	6.3	1/4	19.0	3/4
c	38.1	1.5	88.9	3-1/2

NOTE: FOR ROOM TEMPERATURE TESTING, EPOXY/FIBERGLASS CLOTH LAMINATE TABS BONDED WITH ROOM TEMPERATURE CURING EPOXY ADHESIVE.

FOR ELEVATED TEMPERATURE TESTING, POLYIMIDE/FIBERGLASS CLOTH LAMINATE TABS BONDED WITH HIGH TEMPERATURE STRAIN GAGE ADHESIVE.

FIGURE A-2 CROSS-PLY AND 0° TENSILE SPECIMENS.



NOTE: FOR ROOM TEMPERATURE TESTING, EPOXY/FIBERGLASS CLOTH LAMINATE TABS BONDED WITH ROOM TEMPERATURE CURING EPOXY ADHESIVE.

FOR ELEVATED TEMPERATURE TESTING, POLYIMIDE/FIBERGLASS CLOTH LAMINATE TABS BONDED WITH HIGH TEMPERATURE STRAIN GAGE ADHESIVE.

FIGURE A-3 CELANESE TYPE LONGITUDINAL COMPRESSION SPECIMEN.

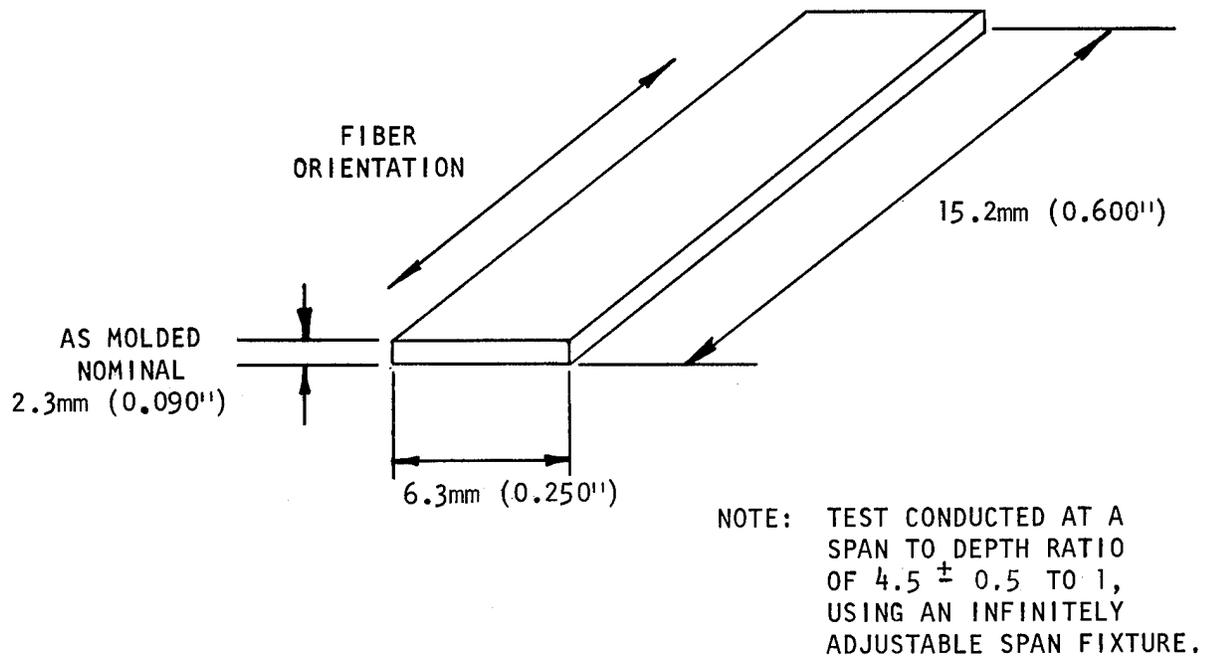


FIGURE A-4 SHORT BEAM SHEAR SPECIMEN

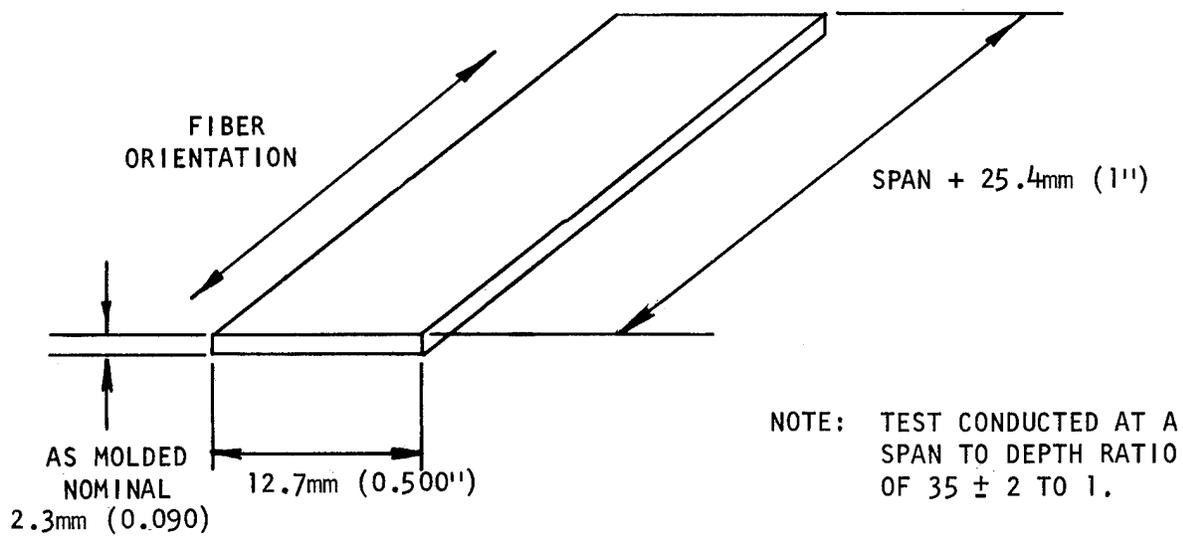


FIGURE A-5 FLEXURE SPECIMEN (THREE POINT)

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