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TRW ER-7396-F

RESIN/GRAPHITE FIBER COMPOSITES

BY

P. J. CAVANO, R.J. JONES AND R.W. VAUGHAN

TRW
EQUIPMENT

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
Contract NAS3-13203

Tito T. Serafini, Project Manager

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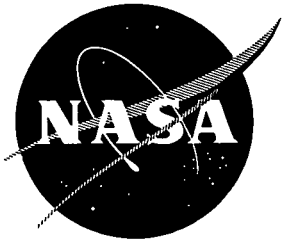

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16. Abstract

Available high temperature resin matrices, suitable for use in advanced graphite fiber composites in jet engine applications were evaluated and a limited number determined as useful for further laboratory examination. A series of planned, sequential screening experiments with resin systems in composite form were performed to reduce the number of candidates to a single A-type polyimide resin that repetitively produced void-free, high strength and modulus composites acceptable for use in the 550°F range for 1000 hours. An optimized processing procedure was established for this system. Extensive mechanical property studies characterized this single system, at room temperature, 500°F, 550°F and 600°F, for various exposure times.

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FOREWORD

This document represents the final report for the work accomplished between 20 June 1969 and 20 April 1971 by TRW Inc., for the National Aeronautics and Space Administration, Lewis Research Center under Contract NAS3-13203 on Resin/Graphite Fiber Composites. This work was conducted under the technical direction of Dr. Tito T. Serafini of the Lewis Research Center, Cleveland, Ohio.

Work on the program was conducted at both TRW Materials Technology of the TRW Equipment, Cleveland, Ohio, and TRW Systems Group, Redondo Beach, California. The development manufacture and synthesis control of A-type polyimide resins was performed by the Chemistry and Chemical Engineering Laboratory of the Science and Technology Division, TRW Systems Group with Dr. E. A. Burns as Project Manager and Dr. R. J. Jones and Mr. R. W. Vaughn as Project Engineers. The remaining development work was accomplished in Cleveland, where Mr. W. E. Winters served as overall Program Manager and Mr. P. J. Cavano acted as Project Manager. Dr. A. P. Sporzynski served as Project Manager during the early part of the program.

The requirements of NASA Policy Directive NPD 2220.4 (Sept. 14, 1970) regarding the use of SI Units have been waived in accordance with the provisions of paragraph 5d of that Directive by the Director of Lewis Research Center.

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SUMMARY

The objective of the program was to develop high modulus graphite fiber composites, using advanced high temperature resin matrices, which would provide usable properties up to 600°F for at least 1000 hours. The primary application considered, during the course of the program, for these composites was for the fabrication of gas turbine engine components, where advantage can be taken of the very high strength and stiffness-to-weight ratios exhibited by these materials. Using these guidelines, the program was devoted to the investigation of a selected number of high temperature resistant resins; the selection and composite optimization of the most promising system; and the characterization of graphite fiber composites, made with the resin, at ambient and elevated temperatures.

Initial candidate resins included two condensation type polyimides, three A-type polyimides, a polyquinoxaline (PQ), a polycarboranesiloxane, a polyimidazopyrrolone (Pyrrone), and a tri-functional silicone resin. The polycarboranesiloxane, the Pyrrone and the PQ were first eliminated on the basis of inferior thermal-oxidative properties. Evaluation of the remaining six systems, in composite form, reduced the number of candidates to two; one commercially available and one recently developed A-type polyimde resin. A statistically designed experiment was utilized to establish optimal processing parameters and to make the final resin selection. The final selection was an A-type polyimide based on the use of nadic anhydride, methylene dianiline, and pyromellitic dianhydride with a formulated molecular weight of 1000 (identified throughout the text as P10P).

The final phase of the program involved an extensive property evaluation of the single selected composite system. Tests were conducted on the material at room temperature, 500°F, 550°F, and 600°F on material both unaged and after exposure at the temperatures given for times up to 1000 hours. Criteria used included the following properties: longitudinal tensile, longitudinal compression, transverse tensile, shear, longitudinal flexure, fatigue, and thermal expansion.

A final review of the collected data indicates that, while the selected A-type polyimide produced composites with excellent short term properties at 600°F, long time use (ca. 1000 hours) would be limited to approximately 550°F range.

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1.0 INTRODUCTION

This document constitutes the final report on Contract NAS3-13203 initiated 20 June 1969 and describes the work performed between 20 June 1969 and 20 April 1971. The principal objective of the program was to develop high modulus graphite fiber composites, using advanced high temperature resistant resin matrices, which would provide usable properties up to 600°F for at least 1000 hours. One application of such composites is for gas turbine engine components where great advantage can be taken of the very high strength and stiffness-to-weight ratios exhibited by these materials. One of the limitations to the use of resin matrix composite materials in jet engines has been the relatively low heat resistance of existing formulations compared to temperatures seen in jet engines, -- ranging from ambient to over 2000°F.

Considerable effort has been and is being exerted in industry and government for the development of more thermo-oxidatively resistant polymers. Several such resins, commercially available or sufficiently advanced in development to warrant evaluation, were investigated. The program was devoted to the investigation of a selected number of high temperature resistant, oxidatively stable resins; the selection and optimization of the most promising system; and the characterization of graphite fiber composites, made with the resin, at ambient and elevated temperatures.

The program was composed of three basic tasks as follows:

TASK I - MATERIAL CANDIDATE SELECTIONS AND MODIFICATION

This Task was devoted to choosing an appropriate reinforcing fiber and up to six high temperature resins suitable for use as matrices in advanced composites. In reviewing suitable systems, it was concluded that an A-type polyimide resin originally developed by the TRW Systems Group, P13N, was a strong contender; this resin was commercially available. Sub-task (I-B) was devoted to the investigation of chemically modified A-type polyimide systems with enhanced thermal-oxidative stability and increased toughness.

TASK II - CANDIDATE SCREENING AND PROCESS DEVELOPMENT

Work in this phase of the program was divided into three sub-tasks. In sub-task II-A, the six selected resins were combined with the chosen reinforcement and the resultant composites graded primarily on the basis of thermal and mechanical properties and tractability. The best two of the systems were carried into sub-task II-C, in which a statistically designed experiment was used to optimize fabrication procedures and select the final matrix candidate. Sub-task II-B, originally designated as a study of the fiber/resin interface, was revised to study the process control involved in synthesizing the A-type polyimide chosen as the single matrix to be characterized.

TASK III - FINAL COMPOSITE SYSTEM CHARACTERIZATION

Unidirectional and bidirectional composites were fabricated using the finally selected resin and the optimized process procedures and evaluated for elevated and room temperature mechanical properties under thermal aging

conditions up to 1000 hours at 500°F, 550°F, and 600°F.

While the ultimate goal of identifying a material for long time use at 600°F was not reached, an A-type polyimide was extensively characterized and determined to be a suitable material for at least 1000 hour use in the 550°F range. Details of the processing techniques employed, evaluation methods and criteria, and final selection procedures are described in the body of the text.

2.0 MATERIAL CANDIDATE SELECTIONS AND MODIFICATIONS (Task I)

The overall objective of this phase of the program was to identify resin and fiber components with the inherent potential of meeting the program goals of long life at elevated temperature when combined in composite form. An initial review of the materials available for candidate matrices indicated that a polyimide resin, PI3N, termed an A-type polyimide, seemed to have considerable merit. Additionally, the unique addition type curing mechanism would not prohibit the modification of the system with regard to chemical composition and structure, molecular weight levels, and additives. It was decided that the TRW Systems Group, inventors of the PI3N resin, should pursue the investigation of increased thermo-oxidative stability and toughness of the A-type polyimides through modification techniques as described above. The reinforcing fiber and other matrix candidates were chosen from the full spectrum available to the industry.

In the following sections, details of the laboratory work involved in selecting materials are given. For convenience, the work was divided into two sub-tasks. Sub-task I-A describes the identification of candidate materials available without development work, and Sub-task I-B discusses the laboratory development work on A-type polyimide variation studies.

2.1 Candidate Selections

2.1.1 Resin Selections

Some of the classes and types of high temperature polymers considered for use are listed below:

A Heterocyclic Polymers

1. Polyimides
2. Polybenzimidazoles
3. Polybenzothiazoles
4. Polyquinoxalines
5. Polyoxadiazoles
6. Polyimidazopyrrolones

B Carbocyclic Polymers

1. Naphthalenediol terpolymer
2. Cross-linkable polyphenylene oxide

C Inorganic or Semi-Inorganic Polymers

1. Polysilazanes
2. Polycarboranesiloxanes
3. Inorganic polymers based on chromium

Through vendor contact and a literature search, and in conference with the NASA Project Manager, preliminary candidates were reduced to nine, using the criteria of high temperature performance, tractability, availability, and price. These were:

1. P13N -- a commercially available polyimide that polymerizes through an addition reaction. The resin system was developed by TRW Systems Group.

2. Skybond 703 -- a condensation type polyimide available from Monsanto Chemical.

3. & 4. Two modifications of the addition-type resin, P10P, developed under NAS3-12412 were to be further developed in the program sub-task 1B.

5. Polyquinoxaline (PQ) -- a thermally stable condensation type available from Whittaker Corporation.

6. Dexil 101 -- a polycarboranesiloxane available from Olin Mathieson Chemical Corporation.

7. Pyrrone -- a polyimidazopyrrolone resin developed by personnel of NASA's Langley Research Center.

8. RS-6228 -- a low flow condensation type polyimide from Monsanto Chemical. Considered to have better thermal resistance than the 703 system. During the course of the program, the identification was changed to Skybond 709.

9. Glass Resin 908 (GR-908) -- a highly cross-linked silicone resin from Owens-Illinois, Inc.

Two of the above systems were rejected as candidates early in the Task. The Dexil exhibited only 4.4% weight loss after 100 hours at 600°F but softened at approximately 500°F. A second system rejected was the pyrrone; in a preliminary screening test at 600°F the pyrrone showed a weight loss of 33% after 180 hours, compared to 23% for the P13N in the same test.

One resin candidate, PQ, proposed for the program was rejected after conducting isothermal weight loss tests at 600°F. This was considered necessary because of the results obtained at TRW with a PQ composite exposed at 600°F in air compared to a P13N composite, both reinforced with treated Modmor II fiber. After 400 hours, weight loss results (normalized to resin loss) were: 50% for the PQ and 20% for the P13N. As a result of this, and performance in isothermalgravimetric analysis (ITGA) of neat resins described below, the PQ was eliminated as a candidate.

The ITGA was conducted as follows: the resins (all supplied as varnishes with the exception of Glass Resin) were placed in aluminum dishes and gradually heated up to 400-450°F to drive off the solvents. The resin samples were then broken up into small pieces and gradually cured to 600°F. Each resin was given a final cure of 1½ to 2 hours at 600°F. Duplicate samples of resins (each weighing approximately 2.5 grams) were used. The cured samples (the size of small gravel) were then exposed to 600°F in an air-circulating oven to determine weight losses after prolonged exposure at that temperature. P13N was used as a control for selection or rejection of resin candidates -- the criterion for

selection of a particular resin being a weight loss lower than P13N.

It should be emphasized that this test was regarded as a preliminary screening test. It was realized that some resins which might perform better than P13N in this test would not necessarily retain their superiority when made into graphite fiber-reinforced composites because of different physical conditions. Despite these limitations, it was thought that the ITGA of cast resins would provide useful information in a relatively short time.

The ITGA test was terminated after completing 1000 hours at 600°F (see figure 1). It can be seen that Skybond 703, 6228 and Glass Resin 908 looked definitely promising as far as weight losses were concerned (22.5%, 13% and 5.8%, respectively, compared to 63.7% for P13N). On the other hand, PQ, after slow initial degradation, deteriorated so rapidly that after 450 hours approximately 80% of the original weight of the samples was lost.

At the conclusion of this portion of the program, the resin candidates to be carried into the next phase were as follows:

1. P13N
2. Skybond 703
3. TRW Systems Modification I
4. TRW Systems Modification II
5. RS-6228
6. GR-908

2.1.2 Reinforcement Selection

The graphite fiber selected to be used originally as the standard high modulus reinforcement on the program was treated Modmor II mid-length tow, distributed in this country by Whittaker Corporation. Selection was based upon availability, ease of impregnation and the unusually high flexural and shear strengths attainable with this material. During the second month of the program, information was received indicating that the Type II fiber might undergo thermal-oxidative degradation at temperatures as low as those being considered as the use temperature on this program, viz. 600°F. To establish the thermo-oxidative stability of Modmor Type II and several other graphite fiber types, an ITGA was performed at 600°F in air.

The results obtained with Modmor II (figure 2) established the susceptibility of the fiber to thermo-oxidative degradation. Weight losses of the fiber at the conclusion of the test (1000 hours at 600°F) were 15.5% and 11.5% (average of 13.5%). Compared to Modmor II, the Modmor I (treated), Celanese, and Great Lakes (Fortafil 5-Y) fibers were only very slightly affected by exposure to 600°F in air, the respective weight losses being 0.9%, 3.1% and 1.8% after 800 hours. It was concluded that the degradation at temperature of Modmor II was excessive and that an alternate fiber had to be selected.

Selection of the replacement for the Modmor II fiber was based on temperature resistance, availability, suitable form for the program, properties, ease of handling, and the conviction that PAN based fibers were superior to rayon based fibers currently available. The fiber selected for use throughout the balance of the program was Great Lakes Research Corporation's Fortafil 5-Y (F5-Y). This was a continuous single ply staple fiber yarn. The yarn was described as having a specific gravity of 1.9 with two twists per inch and a staple fiber length of seven inches. The vendor gave, as nominal property values, a strength of 250,000 psi and a modulus of elasticity of 50 X 10^6 psi. Table I lists the fiber batches received and used throughout the program, along with vendor reported mechanical property data.

Fiber that had been surface treated to improve shear strength, but without a finish was selected. It was felt that it would be impossible to select a fiber finish that would be equally compatible with all six of the resin candidates and changing finishes might bias the composite mechanical performance. Additionally, samples of materials coated with a finish were found to be "springy" and thus more difficult to handle during the impregnation and layup processes.

2.2 A-Type Polyimide Variation Studies

The objective of this sub-task was to 1) identify A-type polyimide formulation modifications possessing both thermo-oxidative stability (ca.600°F) and demonstrating improved toughness (elongations to break $\geq$ 2.5%) and 2) develop preliminary processing methodology for preparation of graphite fiber prepregs and fabrication of reinforced composites using the most promising formulations. The candidate formulations were rated by processing means, thermo-oxidative stability, toughness, graphite composite interlaminar shear strength and flexural modulus and strength. The two formulation modifications having the best combination of properties were to be studied in the subsequent detailed processing characterization studies of Task II.

This activity was conducted in the following two sub elements:

- Selection of the most promising formulations, and
- Preliminary process screening studies,

which are described in detail below.

2.2.1 Resin Synthesis and Characterization

During Contract NAS3-12412 (reference 1) a specific new A-type polyimide resin formulation was identified which offered enhanced thermo-oxidative stability and processibility over that of the commercially available P13N resin. The improved resin formulation consisted of a mixture of nadic anhydride(NA), methylene dianiline (MDA) and pyromellitic dianhydride (PMDA) formulated in proportions sufficient to prepare 1000 molecular weight prepolymer capped with nadic anhydride. Consequently, the emphasis of this program was placed on the use of PMDA and NA constituents which had previously demonstrated enhanced utility.

Technical approaches for enhancing the long term oxidative stability for the resin system consisted of increasing the formulated prepolymer molecular weight, increasing the inherent thermo-oxidative stability of the backbone and utilization of anti-oxidant groups of non-backbone linkage. Aromatic diamine constituents which were selected for study included methylene dianiline, p-phenylene diamine (PPD), benzidine (BZI), and 2,6-diamino pyridine (DAP). Each of these systems was planned for investigation at two FMW's (FMW = Formulated Molecular Weight).

Improvement in the overall toughness of the resin was sought by incorporation of flexible linkages in the polymer backbone. It was anticipated that these formulations could be prepared without significant sacrifice of the thermo-oxidative stability of the resin. Specific diamines investigated, which potentially would provide the flexible linkages, were ethylene dianiline (EtDA), m-phenylene diamine (MPD), and ethylene diamine (EDA).

Resin varnishes were prepared utilizing the diamine constituents identified above: 40 w/o solids resin varnish solutions of amide-acid (A-A) prepolymer in dimethyl formamide (DMF) were prepared. The formulations and formulated molecular weights (FMW) discussed were prepared as amide acid prepolymers according to the following procedure:

> A quantity of diamine was dissolved in DMF and cooled to 20°C with an ice bath. To this solution was added nadic anhydride (NA) in DMF, during which time the temperature was maintained at 30°C by means of an ice bath. This mixture was treated with the addition of an appropriate quantity of pyromellitic dianhydride in DMF. The resulting solution was stirred at ambient temperature for one hour.

Table II lists the specific varnish formulations prepared, their FMW and resultant varnish viscosity. During the varnish synthesis efforts, it was found that prepolymer could not be prepared from ethylene diamine (a "toughness" candidate) due to the formation of a gel from the procedure described.

The varnishes described in Table II were converted to imidized A-type polyimide prepolymer molding powders by the evaporation/drying technique described below:

> The DMF varnish solution was stripped of solvent by evaporation on a rotary evaporator under vacuum at 150°C. The moist A-A residue was then heated in a forced air oven for 10-15 hours at 140°C to give products possessing a desired 2-3% volatile content.

The reduction to volatile contents $\leq$ 3% was necessary to give low void content cured specimens after molding. Each prepolymer was screened for indication of complete imidization by infrared sprectrophotometry.A representative spectrum is shown in figure 3 for 1000 FMW NA/MDA/PMDA. The curve shows no amide absorption in the region of 1650-1700 cm^{-1} which would be present from non-imidized A-A prepolymer.

The imidized prepolymer molding powders were further characterized for hydrolytic stability. The stability results were excellent as indicated by a maximum resin weight loss of 1.7% after a two-hour water boil test.

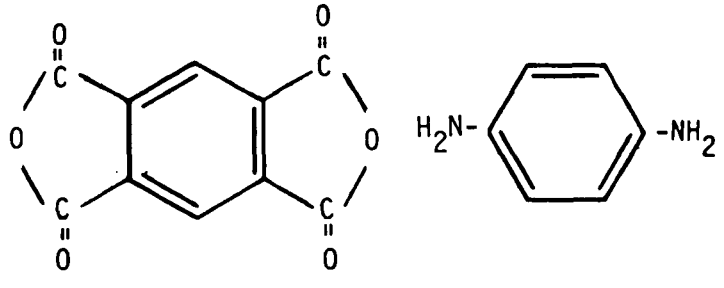
The A-type polyimide modifications given in table II were molded into cured specimens using the processing parameters shown in table III. As can be seen from the data in table III, formulations containing benzidine (BZI), meta-phenylene diamine (MPD), and para-phenylene diamine (PPD) could not be molded into neat consolidated specimens within the range of conditions employed (590-630°F and 500-6000 psi). All of these formulations gave non-dense specimens that crumbled during the determination of Barcol hardness. On the other hand, formulations containing methylene dianiline (MDA) and ethylene dianiline (EtDA) could be molded at reasonable conditions (ca. 580-620°F and 500-800 psi).

Although the data are limited, a tentative theory to the molding (flow and consolidation) behavior of formulations containing PMDA can be expressed at this time. Basing the theory on data arising from this program and previous projects, an interesting trend has been established. All formulations considered employed nadic anhydride (NA) so it will be assumed this species is a constant and does not warrant consideration in the theory. Two dianhydrides were employed in these studies, namely pyromellitic dianhydride (PMDA) and benzophenone tetracarboxylic acid dianhydride (BTDA). Diamines screened to date include MDA, oxydianiline (ODA), thiodianiline (TDA), EtDA, MPD, PPD and BZI. All these monomers fall into definite aromatic structural configurations of which there are three cases; 1) the reactive substituents (dianhydride or diamine groups) are on one phenyl ring, 2) the reactive substituents are located one each on a phenyl ring which is coupled with the exact case through a flexible linkage (such as $-CH_2-$, $-O-$, $-\overset{\overset{O}{\|}}{C}-$, etc.) between the two phenyl rings,

and 3) the same case 2) but without flexible linkage between the rings. These three cases are illustrated below and are summarized with molding data in table IV.

Case I

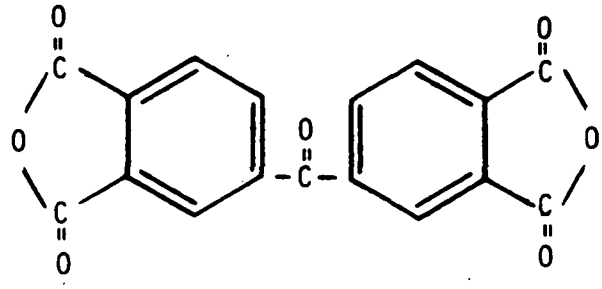
(Substituent Groups on one ring)



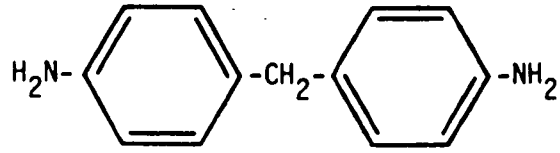
PMDA PPD

Case II

(Substituent Groups located one each on two phenyl rings joined by a flexible linkage)



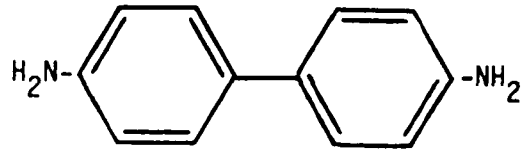
BTDA



MDA

Case III

(Substituent Groups located one each on two-phenyl rings joined directly together)



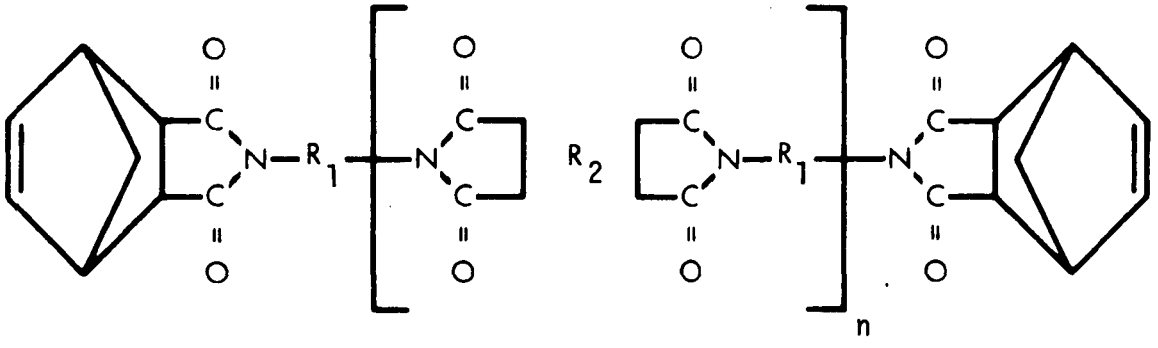
BZI

From the data in table IV it can be seen that PMDA (Case 1) yielded a neat consolidated specimen only when molded at high temperatures (600°F) and only with Case 2 diamines. BTDA (Case 2), on the other hand, gave formulations with Case 2 diamines that processed easily into consolidated specimens, but only with difficulty in formulations containing Case 1 diamines. Under no conditions screened did PMDA give a suitable molded specimen with either Case 1 or Case 3 diamines. Also, PMDA definitely molded more easily with Case 2 diamines when the FMW was decreased as can also be seen in table IV data.

It is believed this behavior is a result of the inherent stiffness of the backbone in A-type prepolymers, which is dependent on the number of imide rings per FMW of the prepolymer in question and on the structure (or Case) of the formulated monomers. Table V compares the number of imide rings per FMW for several selected PMDA and BTDA containing formulations. As can be seen, if

PMDA is formulated with Case 1 (one ring) diamines the number of imide rings increases giving a stiffer prepolymer which does not readily flow or consolidate.

As can be seen from table V, with the exception of NA/BZI/PMDA, a good molded product was achieved if the number of imide rings (i.e., those arising from the reaction of dianhydride R_2 and diamine R_1) in the structure below is maintained at n $\sim$ 3.4. BZI does not contain a flexible linkage between the



aromatic rings and evidently imparts a greater degree of stiffness to PMDA formulations than that obtained with the corresponding Case 2 diamines. This postulate holds true for both BTDA and PMDA containing formulations.

The results obtained in the formulation constituent variation studies have shown that the processibility of A-type prepolymer formulations is directly dependent on interrelationships of:

- The structure of difunctional monomers,
- The formulated prepolymer molecular weight, and
- The number of imide rings in the imidized prepolymer molecule.

The neat resin plugs prepared by the molding studies discussed above were checked for specific gravity, assessed for structure by infrared analysis, and screened for thermo-oxidative stability by thermogravimetric analysis (TGA) prior to isothermal aging.

Formulations prepared that gave consolidated specimens were employed to determine specific gravities by the Westphal balance method (weight in water/weight in air). Typical data are presented below and demonstrate that the variation in cured thermoset A-type polyimide modifications is quite small. The slightly lower specific gravity of the 1000 FMW NA/MDA/PMDA formulation is explained by the higher content of non-aromatic nadic hydrocarbon in the cured polymer.

SPECIFIC GRAVITIES OF A-TYPE POLYIMIDE CURED RESINS

FORMULATION	FMW	SPECIFIC GRAVITY
NA/MDA/PMDA	1000	1.29
	1150	1.32
NA/EtDA/PMDA	1150	1.31
P13N	1300	1.32

An infrared spectrum was determined on all molded (cured) specimens prepared. Each spectrum was very similar and varied only slightly due to the variations of aromatic monomers and substitution employed in the formulations. A typical spectrum is shown in figure 4 for the 1150 FMW NA/MDA/PMDA modification. In this spectrum, the usual carbon hydrogen stretch absorption arising from the nadic species occurs in the region of 2875-300 cm^{-1} and the strong imide absorption occurs in the region of 1700-1780 cm^{-1}.

The cured specimens were all screened for thermo-oxidative stability by TGA determination in air employing a 3°C/minute scan rate at an air flow of 100 ml/minute. All formulations screened by this method gave a TGA tracing very similar to that shown in figure 5 for the 1150 FMW NA/MDA/PMDA. The first weight loss occurred consistently at 450-470°C for each.

All molded specimens were subjected to a two-week (336 hour) isothermal aging exposure in 100 ml/minute flowing air maintained at 600°F and 650°F to assess long term thermo-oxidative stability. As can be seen in figure 6, none of the A-type polyimide formulations prepared offered exceptional stability at 650°F. However, the 1150 FMW NA/MDA/PMDA retained 75% resin weight and looked particularly attractive as a candidate for laminate processing studies. The 1000 FMW NA/MDA/PMDA formulation was definitely inferior to the 1150 FMW material at 650°F, but compared favorably at 600°F. As shown in figure 7, both formulations lost only 3% resin weight after 336 hours of exposure. All other formulations screened were quite labile to oxidation at both 600°F and 650°F. The best non-consolidated specimens produced from the remaining formulations were aged but degraded rapidly in air. This result is believed to have been caused by the many microcracks in the test specimens which provided more surface area and, hence, rapid oxidative degradation.

2.2.2 Investigation of Solid Anti-Oxidants

In order to assess the potential of inorganic anti-oxidants as solid additives to improve the 600°F and the 650°F thermo-oxidative stability of the A-type polyimide formulation modifications, a study was performed using cupric oxide (CuO) as the candidate anti-oxidant. Cupric oxide was added to the 1000 and 1150 FMW compositions of NA/MDA/PMDA and molding studies were conducted as described below.

Neat polymer plugs were molded from the 1000 and 1150 FMW compositions of NA/MDA/PMDA containing 1.0 w/o cupric oxide to investigate the anti-oxidant

potential of this additive. Pertinent molding data are listed below. The products from this molding study appeared to be well consolidated and were subjected to characterization.

NEAT A-TYPE CURED POLYMER MOLDING DATA[a]

FORMULATION	FMW	PRESSURE (psi)	TEMPERATURE (°F)	BARCOL HARDNESS	DWELL (min.)
NA/MDA/PMDA (1% CuO)	1000	1000	630	45	3
	1150	1000	630	41	1

a = All samples were cured for 30 minutes.

To assess the thermo-oxidative stability of NA/MDA/PMDA cured plugs containing CuO, the specimens described above were subjected to an isothermal-gravimetric analysis (ITGA) in air at 600°F and 650°F for 336 hours (two weeks). The resin weight loss data obtained is summarized below.

NEAT RESIN PLUG ITGA DATA AT 600°F and 650°F[a]

FORMULATION	FMW	NEAT RESIN WEIGHT LOSS DATA (%) 600°F	650°F
NA/MDA/PMDA (1% CuO)	1000	15	86[b]
	1150	9	88[b]

a = Aged in air (100 ml/min. flow) for 336 hours.

b = Terminated after 260 hours.

As can be seen from the data, the cupric oxide additive failed to enhance the thermo-oxidative stability of the NA/MDA/PMDA resins. The same resins without CuO exhibited superior thermo-oxidative stability. Evidently incorporation of the solid CuO resulted in the formation of voids during exposure which were responsible for the observed accelerated deterioration as the test progressed.

2.2.3 Other Resin Modifications

The final A-type polyimide formulation modifications investigated in this program were those containing chlorendic anhydride (CA) as the chain terminating end cap group. Such a study was initiated in order to investigate an end cap which potentially may possess enhanced thermo-oxidative stability. One theory for the weak link in the A-type polyimide is the presence of potentially labile aliphatic C-H bonds in the polymeric backbone originating from the pyrolytic polymerization of the nadic end caps. It was believed the C-Cl bonds from the chlorendic cap would produce a backbone with improved thermo-oxidative stability. This approach was initiated after it appeared that the diamine approach to formulation modifications was definitely limited as described previously. Subsequently, four formulated molecular weight

prepolymers of CA/MDA/PMDA were investigated as described below. A-type polyimide formulation modifications were prepared from CA/MDA/PMDA at four FMW's as A-A prepolymers at a 40 w/o solids loading in DMF. The pertinent data associated with these varnishes are listed below. The A-A prepolymers were converted into imidized prepolymer molding powders by vacuum evaporation and drying of the DMF.

VISCOSITIES OF CA/MDA/PMDA VARNISHES

FORMULATED MOLECULAR WEIGHT	VISCOSITY[a] CENTIPOISE/^{o}C
1000	~20 @ 23
1150	30 @ 23
1500	63 @ 25
2000	155 @ 25

a = Brookfield Viscometer Determination

Three molding powders were subjected to molding (curing) studies employing a curing cycle of 30 minutes at temperatures of 600^{o}F-620^{o}F and pressures of 400-1000 psi. The results of these molding studies are listed below. None of the powders molded gave reasonably consolidated specimens. Barcol hardness

CA/MDA/PMDA RESIN MOLDING STUDIES

FMW	DWELL	BARCOL	PRODUCT COMMENT
1150	10 min.	--	Excessive flow. Sample was a black powder.
1500	0	42	Good flow. Sample crumbled in mold.
2000	0	50-52	Little or no flow. Sample cracked in mold.

determinations indicated a slight surface hardening, but the interiors of the specimens were porous. The 1000 FMW prepolymer powder was not molded due to the excessive flow of the 1150 FMW. All samples discolored the mold during cure, strongly suggesting evolution of hydrochloric acid or chlorine gas.

As a result of these findings, further work with chlorendic anhydride was terminated.

2.2.4 Recommendations of A-Type Polyimide Modifications for Process Screening

As discussed above, only three formulations appeared attractive for evaluation as high modulus graphite resin matrices. Specifically, these three

materials were 1000 and 1150 FMW NA/MDA/PMDA and 1150 NA/EtDA/PMDA. Each of these species processed under reasonable conditions into consolidated resin plugs demonstrating good thermo-oxidative stability at 600°F. A summary of key processing conditions and resultant hardness and thermo-oxidative properties of the recommended formulations is given in table VI.

2.2.5 Fabrication Process Screening Studies

Experimental studies were undertaken to assess both the ease of processing the three candidate resin formulations into both Great Lakes Carbon Fortafil 5-Y graphite fiber prepreg and reinforced composites. The findings of this preliminary processing study served as initial reference points for the detailed processing development studies to be conducted subsequently in Task II.

A series of experiments were performed in which impregnating and solvent removal cycles were evaluated. The conditions described below were selected as appropriate for the preliminary screening of varnish formulations after a number of experiments.

Yarn Spacing	- 80 yarns/inch
Impregnation	- Spray Gun Metering
Varnish Resin Solids	- 40 w/o
Yarn Treating Speed	- 25 ft/min.
Drying Cycle	- Heat Lamps - 30 minutes while rotating at 25 ft/min. surface speed on drum.
	- Air Circulating Oven - 10 minutes at 250°F.

Using the parameters given above, a prepreg material was prepared for the evaluation of molding processes and the characterization of mechanical properties of the three following A-type polyimide resin formulations:

- 1000 FMW NA/MDA/PMDA
- 1150 FMW NA/MDA/PMDA
- 1150 FMW NA/EtDA/PMDA

The 1150 FMW NA/EtDA/PMDA varnish precipitated out of solution before it was used to prepare prepreg tapes (approximately 48 hours after varnish preparation). Consequently, tapes were prepared from the precipitated material by applying a slurry of the precipitate to the dry, collimated yarn. The resultant prepreg did not possess integrity and was very difficult to handle; the resinous powder was extremely friable and fell off the yarn when the tape was handled. Characterization of this prepreg was not feasible and, because it was later established that the material was not suitable for molding, further efforts with this resin were curtailed. The physical properties of the two remaining prepregs are listed below.

PHYSICAL PROPERTIES OF PREPREGS

RESIN SYSTEM	VOLATILE CONTENT, w/o	RESIN SOLIDS CONTENT, w/o
1000 FMW NA/MDA/PMDA	18.2	47.3
1150 FMW NA/MDA/PMDA	18.0	51.5

Eleven panels were molded from the prepreg produced with 1000 FMW NA/MDA/PMDA varnish using different processing variables for each panel. These conditions are delineated in table VII together with the properties of each panel. All panels were eight plies thick, 3 inches wide and approximately 3.875 inches long (~3% shorter than the mold cavity, to avoid panel damage during cooling due to the negative coefficient of thermal expansion of the fiber). Flexural properties were determined in triplicate and shear properties were determined in quadruplicate.

Analysis of the tabulated data provided a selection of two sets of molding conditions for further evaluation with all three resin systems during the composite characterization studies. The selected conditions were:

A In Situ Imidization - The 1000 FMW NA/MDA/PMDA amide acid and Fortafil 5-Y yarn prepreg was cut and stacked eight plies thick. This stacked material then was placed into a cold mold which was loaded into a cold press and a pressure of 500 psi was applied. Temperature of the mold then was raised by electrically heating the platens, and when the mold temperature reached 300°F, the pressure was adjusted up to 500 psi. This was necessary since the pressure had dropped as a result of resin flow during heatup. After this the pressure was maintained while the temperature was increased to 600°F. The panels were then cured under these conditions for one hour.

B Imidization of Preform - Prepreg was cut and stacked in the same manner as above. The stacked material was then placed on a steel plate and a silicone rubber dam (high temperature vacuum bag sealing tape) was placed around the periphery of each stack to prevent resin loss and/or fiber washing during processing. A steel plate 0.125 inches thick was placed on top of the material and the complete assembly then was thermally treated in an air-circulating oven for forty hours at 300°F in order to complete imidization of the amide acid. This imidized preform then was loaded into the mold preheated to 600°F and the mold plunger (also preheated to 600°F) was immediately positioned on top of the material. After a total duration of thirty seconds from the first contact of the preform with the 600°F mold surface, a pressure of 500 psi was applied. The panel was then cured for one hour at 600°F under 500 psi.

As a summary of all conditions evaluated, the following comments are provided:

A Imidization of Preforms in Air Circulating Ovens - It was concluded that a 20 hour cycle at 300°F was not long enough to complete imidization thus leaving a high residual volatile content in the preform which resulted in a higher void content of the molded panel (1.64% v/o) than for the panel produced from material imidized for 40 hours at 300°F (-2.1% v/o).

B Imidization of Preforms in Vacuum Ovens - Void contents of panels produced from prepreg imidized in vacuum ovens were considerably higher than for the panels treated in air circulating ovens. Therefore, it was concluded that the air circulating oven treatments were preferable.

C In Situ Imidization of Preforms During the Molding Operation - This process is very dependent upon operator skills.

D Dwell Cycles, Cure Times and Molding Pressures - Variations in properties obtained while evaluating these conditions were not great enough to draw conclusions on their specific effects.

Using the two selected molding techniques discussed above, duplicate panels were molded from each of the two candidate resin systems. Because of the poor quality of the prepregs using the 1150 FMW NA/EtDA/PMDA resin formulation, only one panel was prepared using each molding condition. As a result, a total of ten 0.080-inch thick panels approximately 3 inches by 4 inches were prepared.

Five longitudinal flexural specimens were cut from each panel plus either one transverse flexural specimen or eight short beam shear specimens. Half the number of specimens was used for mechanical testing at room temperature and the remainder were used for 650°F testing after a 30 minute exposure at 650°F. A discussion of the molded panels and analysis of their physical and mechanical properties, as shown in table VII, follows.

Panels molded from both the amide acid and imidized 1150 NA/EtDA/PMDA prepregs were not consolidated and indicated that very little resin flow had occurred. Further evaluation of these panels was not performed.

Panels molded from both the 1000 FMW and 1150 FMW NA/MDA/PMDA prepregs provided comparable mechanical properties when molded from either the amide acid or imidized prepreg. The panels molded from the amide acid preforms had excessive flow and resulted in low resin content. This low resin content is believed to be a contributory factor for the relatively high void content for Panels 3, 4, and 7 (see table VIII). The results obtained in this study do not indicate any strong preference for either resin system.

In evaluation of the two molding processes employed in this study, it is apparent that molding the amide acid prepreg requires more operator skill than is required for molding the imidized prepreg. For example, Panel 8 was unsatisfactory because of an operator misjudgement while molding and Panels 3, 4 and 7 all had excessive resin flow. The process recommended for use with these systems consists of:

- Imidization of the stacked prepreg for 40 hours at 300°F, and then
- Molding in a 600°F preheated mold.

The room temperature properties of composites obtained with these A-type formulations compare very favorably with reported properties for epoxy/ Fortafil 5-Y composites. The high transverse flexural strengths are an indication of excellent resin adhesion to the graphite. Elevated temperature testing at 650°F indicates excellent strength retention for short term exposures at 650°F. From the tabulated results, it appears a minimum of 75% property retention is obtained from both resin systems at this test condition.

2.2.6 Selection of Most Promising Formulation Modification

The results of the activities described in Section 2.2 were reviewed and the following two resin varnish formulations were selected for use in detailed processing characterization in Task II:

1000 FMW NA/MDA/PMDA

1150 FMW NA/MDA/PMDA

For convenience in documenting, these two resin systems were designated P10P and P11.5P, respectively.

2.2.7 Sub-Task Conclusions

Summarized below are the conclusions reached during this sub-task effort study to develop improved A-type laminating resins.

1. Neat resin studies, employing NA and PMDA as fixed ingredients to prepare twelve A-type polyimide modifications by varying diamine components and/or formulated molecular weight (FMW), have identified limitations in processibility of these formulations. It was concluded that one ring aromatic diamines (e.g. meta- or para-phenylene diamine) and/or FMW combinations that give an average of 3.6 imide rings per repeat unit impart intractability to the A-type polyimide modifications that makes them unsuitable for high modulus graphite composite resin matrices at fabrication limits of 650°F and 1000 psi.

2. Formulation modifications in which chlorendic anhydride (CA) was substituted for NA did not cure to consolidated specimens. It was concluded that such formulations evolve gaseous hydrochloric acid at cure temperature (ca. 600°F) and CA is unsuitable for use as the monoanhydride component of A-type polyimide formulations.

3. A-type formulation modifications prepared from NA/MDA/PMDA demonstrated the best combination of thermo-oxidative stability and processibility suitable for meeting the objectives of this program. The two selected for further evaluation in the following program phase were:

NA/MDA/PMDA - 1000 FMW (P10P)

NA/MDA/PMDA - 1150 FMW (P11.5P)

4. Molding processes were evaluated for both 1000 FMW and 1150 FMW NA/MDA/PMDA - Fortafil 5-Y prepreg tapes. The process which produced the best end properties with the greatest reproducibility was that in which the stacked prepreg was imidized first in an air circulating oven at 300°F for 40 hours. The imidized preform was then dropped into a preheated mold at 600°F and cured for one hour at 500 psi.

5. From evaluation studies of composites formed from 1000 MFW and 1150 FMW NA/MDA/PMDA and 1000 FMW NA/EtDA/PMDA, it was concluded that the 1000 FMW NA/EtDA/PMDA resin system was not suitable for use in composite resin matrices due to its storage instability. Mechanical properties of the resultant composites using the other two resin systems provided properties at room temperature equivalent to or better than the the best reported data for epoxy/Fortafil 5-Y composites. Evaluated temperature testing at 650°F indicated excellent strength retention for short term exposures at 650°F (over 75% property retention).

6. The work to develop a tougher A-type polyimide by employing three specific diamine candidates (ethylene dianiline (EtDA), m-phenylene diamine (MPD), and ethylene diamine(EDA)) containing flexible linkages was unsuccessful. The EDA containing system yielded an unusable gel in the standard synthesis procedures. The MPD system could not be consolidated, even in the unreinforced form. The EtDA exhibited a prohibitive storage instability in the varnish form.

3.0 CANDIDATE SCREENING AND PROCESS DEVELOPMENT (Task II)

The objective of this task was to use the fiber and resin candidates selected in Task I in fabricating composites which were to be screened on the basis of mechanical properties and thermal resistance so that the final preferred system could be identified for characterization in Task III. This work was divided into a sub-task in which the six initial candidates were reduced to two; a process optimization and final selection sub-task; and a small sub-task which was devoted to a synthesis control study of the finally selected A-type polyimde resin.

3.1 Resin Candidate Screening

Each of the initial six resin candidates were to be evaluated in composite form through the four following steps:

a. Collimation and impregnation

b. Staging for solvent removal to develop handleability

c. Cure cycle development

d. Property evaluation

3.1.1 Skybond 703

As was the case with each of the systems studied, impregnation studies were carried out on the laboratory collimator pictured in figure 8. The primary parameters to be controlled in achieving target resin solids were resin varnish concentration and viscosity (both controlled in processing by specific gravity), drum speed and yarn per inch (YPI) fiber count. The tubular staging chamber shown in the photograph was eliminated after the first early work with the Modmor II fiber. In all subsequent work the staging was accomplished in oven cycling.

With a goal of a prepreg resin content of 45%, a number of experiments were conducted with the Fortafil 5-Y fiber and the 703 resin. After several runs final limits were set at the following parameter levels:

Varnish Concentration	-	45 w/o
Varnish Specific Gravity	-	1.120
Yarns/Inch	-	64
RPM (20" diameter drum)	-	10

Variations in staging conditions included prepreg coverings, exposure times, temperatures, and the use of air circulating and vacuum ovens. The final technique selected included both an air circulating and vacuum oven treatment. First the flat prepreg was covered with a fine copper screen to maintain flatness and staged for one hour at 175°F. This produced a handleable prepreg with good tack and drape. Then a 13-ply 4" x 4" stack of material was subjected to two hours at 165°F in a vacuum oven at 28" Hg; this latter operation reduced the volatile content to 12-18%.

The achievement of sound laminates with this condensation type of polyimide is very difficult since chain extension and ring closure occur simultaneously with an accompanying viscosity increase. In the case of the 703 system, the high boiling solvent, N-methylpyrrolidinone (B.P. 394°F), further adds to the problem since the bulk of this also must be removed from the laminate before final cure takes place.

The staged prepregs were molded in a 4" x 4" closed die. Three different curing schedule approaches were used to establish molding conditions.

A. Increasing temperature (from 250°F to 300°F) at constant pressure (contact to 15 psi).

B. Increasing pressure at constant temperature (250°F).

C. Constant temperature (set at the gel point of the resin, 325°F) with steady increase in pressure.

The results of the first two techniques were not completely satisfactory. The last curing schedule involving a long staging cycle at the gel temperature of the resin (325°F) produced satisfactory composites. The precise cycle used was as follows:

TEMPERATURE	PRESSURE, psi	TIME, Minutes
320°F	Contact	12
320°F	250 then back to Contact	2-3
400°F	250	30

The typical characteristics of sound laminates before postcure were very consistent:

Laminate Thickness (typ.)	0.088 inches
Thickness, per ply	6.3 mils
Transverse shrinkage	0.7%
Specific Gravity	1.65 - 1.66

The test laminates were postcured up to 650°F prior to test. The postcuring cycle (recommended by Monsanto) consisted of four steps: four hours each at 400, 500, 600 and 650°F. There was a marked decrease of specific gravity of all of the laminates due to high weight losses experienced during postcure, accompanied by a slight increase in thickness. The averaged data are summarized as follows.

CHANGES OF 703/FORTAFIL 5-Y COMPOSITES IN POSTCURE UP TO 650°F

	BEFORE POSTCURE	AFTER POSTCURE	PERCENT CHANGE
Thickness/Ply	6.3 mils	6.6 mils	5% Increase
Transverse Direction	3.632 inches	3.637 inches	0.14% Increase
Specific Gravity	1.65-1.66	1.51-1.52	8.5% Decrease

The mechanical test results of the 703 laminates are shown in table IX. The room temperature values for flexural strength and modulus were acceptable but shear strength was low. There was a dramatic decrease in mechanical strength properties at 650°F indicating a considerable softening of the resin matrix at that temperature.

Photomicrographs of laminates before and after postcure are shown in figure 9. The upper photograph illustrates a laminate that had a void content of 4.2% before postcure and 11.6% after postcure.

The isothermal weight loss characteristics of the 703 composites in air at 600°F are shown in figure 10, a summary of the final thermal aging of all composites examined in this sub-task.

3.1.2 P13N

P13N is an A-type polyimide resin system which cures by a pyrolytic addition reaction. Polymerization, chain extension or crosslinking of P13N molecules occurs during final cure after imidization. This factor is responsible for the low void content of P13N laminates. The planned elimination of the postcuring operation for P13N resin offered another real advantage over other commercial polyimides.

The high temperature (550-600°F) required for curing P13N composites presents some processing difficulties. Tooling and equipment must be designed to withstand higher operating temperatures, and the curing schedule (time/temperature/pressure cycle) is important because of the very fast rate of polymerization.

Initial prepregs were made using the following parameters.

Varnish Concentration - 35%
Varnish Specific Gravity - 1.075
YPI - 60
RPM (20" diameter drum) - 10

These conditions produced resin starved laminates. Later, varnish concentration was raised to 40% (specific gravity = 1.100) to increase resin content above 30% in the laminates and YPI was lowered to 56 to eliminate

overlaps in the prepregs. These changes produced laminates with an acceptable appearance.

Various staging procedures were used to remove some of the volatile materials and still retain handleability of the prepregs. The following procedure was finally selected: a sheet of collimated, resin-impregnated fiber was covered with a copper screen (using perforated Mylar film on the bottom for support) to keep the prepreg flat and allow uniform evaporation of the solvent. After a short staging in an air-circulating oven at 80°C to impart better integrity to the prepreg, the prepreg was made into several 12 ply, 4" x 4" layups, and further staged for varying lengths of time in a vacuum oven at 74°C to remove additional volatile material. The parameters selected were as follows:

(1) 30 minutes in the 80°C oven

(2) 15 minute soak of the stacked layup in the 74°C oven

This produced material with a volatile content of 30% (determined by a 30 minute exposure at 600°F). Subsequent molding work indicated that material of this volatile content produced sound laminates with proper molding procedures.

Various curing cycles were investigated to produce composites with satisfactory appearance and low void content. The initial procedure was as follows: after a short staging cycle (the final sequence described above), the prepregs were laid up in a 4" x 4" die (12 plies) and placed at contact pressure in a press with platen temperature held at 550°F. The dwell time (time at contact pressure) was varied from 5 to 15 minutes, then full pressure (250 psi) was applied for 1 hour at 550°F.

This procedure was not satisfactory and a series of experiments yielded the method described below.

1. Hold prepreg stack at contact pressure for 6 minutes at 650°F (platen temperature).
2. Close press to 0.083" stops (0.003" greater than laminate).
3. Relieve pressure to remove 0.003" shims.
4. Apply full pressure (250 psi) directly to laminate.
5. Reduce mold temperature to 550°F.
6. Hold one hour at 550°F and 250 psi.
7. Cool under pressure.

The molded characteristics of these three P13N composites molded with the technique given were as follows:

- Laminate thickness (typ.) - 0.080 inches
- Thickness per ply - 6.4-7.1 mils
- Transverse shrinkage - 0.7-0.9%
- Specific gravity - 1.57-1.60

Photomicrographs of two laminates produced by this process are shown in figure 11. Although the process had not been optimized the mechanical properties at both room and elevated temperatures (table IX) were quite acceptable. Composite weight loss behavior at 600°F is shown in figure 10.

3.1.3 Glass Resin 908

Glass Resin 908 was introduced into the program because of its excellent thermo-oxidative performance in the 600°F isothermal weight loss test on the cured resins. Since 908 resin looked like a potential candidate at the very beginning of the program, prepreg was made and a laminate molded using Modmor II fiber just after the program inception. The results were quite encouraging, flexural strength and modulus were 142,600 psi and 20.8×10^6 psi.

During this phase of the program, work was started with Great Lakes fiber to establish collimation and staging conditions. After a series of preliminary trials, it was established that prepregs with good handleability could be made using the following parameters:

Varnish Concentration	45%
Varnish Specific Gravity	1.025
Yarns Per Inch	60
RPM (20" diameter drum)	10

The typical varnish formulation was as follows:

100g 908 Resin
60g Toluene
60g Xylene

Two staging cycles were evaluated, 15 minutes and 30 minutes in 74°C vacuum oven using 12 ply stacked up layups. Both cycles brought prepreg volatile contents into the 3% range, which was thought to be quite satisfactory. Coupled with appropriate molding conditions, described below, good quality laminates were produced.

Several composites were made using different curing cycles in an attempt to mold acceptable laminates. Most prepregs were staged for a short time at 400°F in the press and molded at 500°F and 250 psi. In early experiments, it was found that 400°F was too low to adequately cure the resin, therefore, molding temperature was increased from 500°F to 600°F. Almost all the laminates had one or more longitudinal cracks. It was surmised that shrinkage of the resin matrix under pressure in the cooldown step contributed to cracking. In order to alleviate or eliminate the cracking problem, the molding procedure was modified by releasing pressure immediately after completing the curing cycle, and the fibers were cut .050 inches shorter than the length of the mold to reduce the tendency of the composites to bow due to thermal expansion in the longitudinal direction. These two approaches produced very satisfactory laminates with no evidence of cracking. The final cycle used is described below:

TEMPERATURE, °F	PRESSURE, psi	TIME, Minutes
450	Contact	15
550	250	60

The molded characteristics of laminates (12 plies each) produced by this technique were as follows:

Laminate Thickness (typ.)	0.081 inches
Thickness Per Ply	6.6 mils
Transverse Shrinkage	2.4%
Specific Gravity	1.56-1.58

Prior to high temperature testing, the laminates were postcured as follows:

400°F - 4 hours
500°F - 4 hours
600°F - 4 hours
650°F - 4 hours

The mechanical test values for the GR-908 composites are shown in table IX. It can be seen that the composites performed reasonably well in the 650°F flexural test. The values were not exceptional, but only lost 32% of flexural strength and 20% in modulus from room temperature levels. However, the shear strength values were disappointing. Because of the outstanding thermo-oxidative resistance, illustrated in figure 10, a small supplemental program was conducted at TRW in an attempt to enhance the shear strength of the silicone resin composites with Fortafil 5-Y. A number of approaches were tried, including the use of specialty fiber finishes. No significant improvement was achieved and the effort was discontinued.

Figure 12 shows typical cross sections of a laminate used for test (after postcure). In comparing the appearance of the voids with those in the polyimide composites, it can be seen that the voids are fewer in number and generally much larger.

An example of a "hollow" fiber can be seen in the photo at 500X in the lower center of figure 12B. The cause of the "hollow" fibers is unknown, but these have been observed in PAN precursor fibers from other companies.

Two other items of interest can be seen in figure 12B. First, in the upper center, an area of resin appears lighter in color. Examination of the mount under binoculars, using reflected light, shows in similar areas to this patterns which resemble stress concentrations in birefringent resin materials.

No attempt was made to determine the connection between these patterns and actual stress concentration around fibers, if any, but as can be seen in figure 12B, there are a number of what appear to be microcracks in the resin. Since the laminates were postcured, it seems logical to hypothesize that residual stresses do exist in the resin and may be related to the apparent stress patterns shown in the glassy, translucent 908 resin.

3.1.4 RS-6228

This sytem was retained as a viable candidate because of its excellent thermo-oxidative stability and its use of lower boiling solvents than the Skybond 703. While impregnating and staging presented some few difficulties, the molding portion of the study required an extensive effort.

In the impregnation investigation, several dilution solvents were used, including 3A, 2B denatured ethanol, n-butyl alcohol and isopropyl alcohol. Ultimately, best results were obtained with the use of 200 proof (completely water free) ethyl alcohol. One bad batch of resin slowed efforts, but the final prepregging limits to achieve a target 42% resin content were set as follows:

Varnish Concentration	- 40%
Varnish Specific Gravity	- 1.010
RPM on 20" dia. drum	- 15-20
Yarns Per Inch	- 56 & 64 (Equipment Improvement)

A series of staging tests indicated that the most reasonable conditions were represented by a 10 minute exposure in a vacuum oven at 180°F. This yielded a 18±1% volatile content in the prepreg and produced material with good to fair handling characteristics.

Initial studies of gel and flow behavior versus staging conditions were performed with glass cloth reinforcement. With these data, 13 experiments were completed with the graphite reinforcement in a series of straightforward molding trials at 350°F, 475°F, and 600°F. Results were disappointing and a series of tests with closed die procedures supplemented with the use of vacuum venting were tried. Typically, laminates were found to be extremely porous or of a texture that indicated resin polymerization before the release of the volatile material.

Another approach sometimes used during molding to permit volatile removal is a process of alternating application and release of pressure at a given temperature; this is referred to as "breathing" or "bumping" the laminate. A glass laminate produced by "bumping" at 400°F over a four minute period at one minute intervals yielded a laminate with a specific gravity of 2.01 (calculated theoretical density 2.07, void content 2.9%). Employing this bumping technique, a series of ten RS-6228/F5-Y laminates were prepared.

Table X describes, in sequence, the processing used to mold the prepregs. The table is, for the most part, self-explanatory and the data are presented in the order in which the laminates were molded.

As can be seen from the relatively small changes made in processing parameters, the method is extremely sensitive. Very precise control of temperature is required and, as is noted, processing steps were timed in seconds. As will be noted from table X, laminates selected for postcure and evaluation were molded at platen set temperatures of 400°F, 425°F, and 410°F.

The recommended molding cycle, therefore, was as follows:

Collimate with care to avoid any gaps in the prepreg to obtain the highest YPI count possible. Improve integrity of the prepreg by squeezing individual sheets between rubber sheets at approximately 150°F. Cut plies approximately 3% shorter than length of die and reduce volatile content range to 18 ± 1% by staging for 10 minutes under full vacuum at 180°F. Stack plies carefully and compact at 100 psi and room temperature. Center preform on thin plates (0.025") and place sandwich into die at 415°F ± 5°F(accurately controlled) and apply kiss pressure (less than 10 psi) and bump every 30 seconds for 3.5 minutes and then apply 500 psi in a press/die set up with controlled parallel surfaces. Hold 30 minutes at 415°F and cool slowly under kiss pressure. Postcure for four hours at the temperature at which the laminate is to be used.

As can be seen from table IX, even though the laminates had relatively high void contents, mechanical property values were acceptable. Figures 13 and 14 illustrate the variability of the laminates and the different response to postcure observed in two of the test moldings. Figure 10 shows the 600°F isothermal weight loss behavior of the RS-6228 composites compared to other candidate systems.

3.1.5 P10P (NA/MDA/PMDA 1000 FMW)

The processes by which the two development A-type polyimide systems were synthesized and selected are discussed in Section 2.2. The first of these to be evaluated was the 1000 FMW, P10P. The first quart of P10P was received only two days after manufacture, and all prepregs made immediately. The batch had a resin solids content of 40% and a viscosity of 85 cps at 24°C.

Three prepreg runs were made using the resin dip tank method, using the varnish as received (specific gravity of 1.085). Using a target resin solids of 35-40%, 64 YPI, and a speed of 20 and 25 RPM on the 20 inch diameter drum, prepregs showed a volatile content of 35 to 42%.

After winding, while the prepreg was still on the drum, two 250 watt infrared lamps were placed on 8 inch centers and at a distance of 9 inches from the drum surface. The drum was rotated at two RPM for 30 minutes or 45 minutes. Both conditions produced material with good handleability. The 30 minute IR lamp cycle dropped the volatile content from 39.9% to 33.5%; the 45 minute exposure dropped the volatile content from 40% to 26.3%. A subsequent 10 minute exposure of the material in a 250°F air circulating oven reduced the remaining volatile content to approximately 13%. This material had limited handleability.

Using the recommended molding approach developed in sub-task I-A, preforms were prepared by laying the plies (4 x 3.88 inches) in a molding die. Three preforms of 12 plies each were stacked with separators in the same die and then exposed to a 40 hour cycle in a 300°F, air circulating oven. Typical weight losses experienced during imidization were 6 to 9%. Even though a 1/2 pound weight was placed on top of the preforms, no preform consolidation was observed at the end of the 40 hour cycle. A test ply, exposed to the same 40 hour cycle,

had a volatile content of 3.7% after imidizing.

The molding cycle employed was as follows: place preform, sandwiched between thin steel plates (0.025 inches), into 600°F die (press platens at 600°F), and apply 500 psi molding pressure after 30 seconds. The thirty second count was started as soon as the preform contacted the hot die. At the end of one hour, pressure was reduced to kiss and the die cooled slowly. No postcure was used. This cycle produced dense, sound laminates of very reproducible quality. Cross sections of two typical laminates can be seen in figure 15.

All laminates had a heavy flow bead and exhibited good appearance. Thicknesses were 0.083 inches on laminates tested. In five difference laminates, molded from two different impregnation runs, analytically determined resin solids values were 35-44%.

Storage of the unused resin varnish was at room temperature, under a blanket of dry nitrogen, as recommended. On the morning of the eleventh day after manufacture, both the unused 40% varnish and that retained, in a separate container, from the impregnation dip tank were observed to have precipitated. While all work for this task had been completed, the precipitation, in the 40% varnish form, reflected a problem in storage stability.

As can be seen from table IX, the mechanical test values at both room temperature and 650°F were quite acceptable. Isothermal aging behavior at 600°F is illustrated in figure 10.

3.1.6 P11.5P (NA/MDA/PMDA 1150 FMW)

The second developmental A-type polyimide to be evaluated was the 1150 FMW, P11.5P. One quart of the P11.5P resin was prepared on March 10, 1970. Solids content was 40% and the viscosity was 88 cps at 24°C. The prepreg runs were made immediately after receipt of the resin.

Processing of the material was much the same as P10P material described above. Volatile content of the material after winding and rotating at room temperature for one hour was 28.6%, volatile content dropped to 21.2% after a 30 minute exposure to the IR lamps. Volatile content after 10 minutes at 250°F was 7.3 and 9.0% on the two runs. Preforms were imidized for 40 hours at 300°F; volatile loss on the preforms (approximately 35 grams apiece) ranged from 9.6 to 5.9% with an average loss of 7.8%. Volatiles remaining in two sample plies checked after two imidization runs were 1.5% and 0.7%.

Moldings were prepared in exactly the same manner as the P10P. Three laminates had thicknesses ranging from 0.075 inches to 0.079 inches. Two differences were observed in comparing the P10P and P11.5P moldings: the resin flash observed on the longitudinal ends of the P11.5P laminates was reduced to a very small bead, and approximately 1/4 inch on each side of the laminate was unusable due to inadequate consolidation. Both these differences can be attributed to lower resin flow resulting from the higher starting formulated molecular weight.

Figure 16 shows typical cross section of two of the P11.5P laminates molded. No explanation is available for the fissures observed in laminate R2/L2.

Table IX displays all test data generated. As can be seen, the short beam shear values for the laminate with voids is significantly lower. It should also be noted that in testing the 650°F short beam shear specimens, all those specimens from this laminate (R2/L2) and three specimens from R2/L3 showed indistinct failure points, which resulted in carrying the load application to specimen bottoming in the fixture. All specimens from R2/L1 were clear cut breaks. The values for the P11.5P/F5-Y looked reasonable but experienced a greater drop-off with temperature than the P10P system.

Figure 10 displays the 600°F isothermal weight loss behavior.

3.1.7 Candidate Comparisons and Selection

At the end of this sub-task, the collected data and evolved laboratory experience were intensively reviewed and several meetings were held with all personnel involved. During the course of these discussions, a decision was reached on the resin systems to be carried into Task IIC, Process Optimization and Final Selection.

Of the six resin systems considered, it was decided to optimize two polyimide materials that employ the unique addition type curing reaction, namely, P13N and P10P. While many factors were considered in making the decision, the basic reasoning was that the achievement of reproducible low void content laminates, by a reasonably straightforward process, outweighed the apparent lower isothermal losses experienced by other polyimides at 600°F. It is expected that the economical operating temperature range for organic matrix composites in jet engines will for some years be fixed at the 500 ± 50°F level with limited, short-term excursions into the 600°F range. For this reason, sustained performance at 600°F was not considered as the only criterion.

In considering each of the systems individually, the GR-908 silicone resin was felt to have potential based on thermo-oxidative stability, but the poor shear strength detracted from the attractiveness of the system. Since the program did not specifically provide for further investigation of this system, a small IR&D program was undertaken to aid in making the final decision on this material. Improved processing significantly improved the flexure strength of composites but did little for the shear strength. Therefore, the GR-908 was rejected as being deficient in usable shear strength for the program.

The 703 polyimide was difficult to process and exhibited softening in short term elevated temperature tests. The Monsanto 6228 polyimide resin exhibited good property values and weight retention in 1000 hours at 600°F, but was extremely difficult to process, even under laboratory conditions, and yielded much higher void content laminates (see table IX) than the addition type polyimides.

Of the three addition type polyimides evaluated, the commercially available P13N was chosen because of its excellent mechanical properties at both room temperature and 650°F. In a choice between the developmental P10P and P11.5P, the P10P was selected for its high property values and slightly better processing characteristics than the P11.5P. Even though the isothermal weight loss curves show the P11.5P being slightly superior in thermo-oxidative resistance, on a theoretical basis, if thermal performance is predicted on the

number of imide rings, the difference is only slight. For example, the P10P contains 4.68 imide mols/gram and the P11.5P contains 4.76 imide mols/gram.

The improved performance of the P13N material over the P10P and P11.5P systems shown in the isothermal curves in figure 10 represented a departure from anticipated theoretical behavior and that shown on early isothermal tests on unreinforced molded resin plugs. The use of pyromellitic dianhydride (PMDA) in the P10P and P11.5P instead of the benzophenone tetracarboxylic acid dianhydride (BTDA) used in P13N should increase the thermal oxidative stability due to the elimination of the -C=O- bond in the BTDA.

In a review of the synthesis procedures used on the development quantities of the P10P materials, it became clear that many variables existed in the process. It was, therefore, decided that the batches of P10P used in the following tasks would be prepared under rigidly controlled conditions. Careful control procedures were to be followed to eliminate the possibility of hydrolysis reactions, raw materials were to be purified, and analytical methods were to be employed to check such things as molecular weight distribution and active end group content before shipment and use of the resin. It was expected that these procedures would result in a material that met anticipated performance standards and would permit a fair comparison of the PMDA and BTDA bearing materials.

The results of the special preparation techniques of the P10P resin and accompanying analysis are discussed below.

3.2 Characterization of P10P Manufacture

The objective of this sub-task was to provide process control and documentation for the manufacturing of the P10P A-type polyimide which was selected for more detailed study in the previous sub-task. This effort was initiated as a result of the considerable variation noted in the P10P batches prepared. In addition, it was observed that the 40 w/o solids varnish was unstable and precipitated from solution. It was felt that the study might give some indication of the phenomena involved.

It was noted that all P10P samples prepared on this contract and those prepared for independent evaluation since November 1969 consistently gave Brookfield viscosity readings of 80-100 centipoises (cps) at 24-25°C, and lower subsequent high modulus graphite reinforced composite flexural properties than 180 cps P10P varnish evaluated previously.

It was decided that the higher viscosity varnish was most desirable to obtain optimum or improved composite properties from P10P A-type polyimide resin. Consequently, a study was undertaken to investigate the reproducible preparation of higher viscosity P10P varnish as well as to obtain documentation on the purity of starting monomers and characterize the chemical species existing in the varnish intermediates.

3.2.1 Preparation and Characterization of P10P Ingredients

Prior to initiation of this sub-task, all monomers were recrystallized before use but, due to program limitations, the only criterion used to discern

purity of monomers was a reasonable (ca. 1-2°C) melting point range within that reported in the literature. The dimethyl formamide solvent was used as-received. In this sub-task, the nadic anhydride (NA),methylene dianiline (MDA) and pyromellitic dianhydride (PMDA) monomers were recrystallized, stored under nitrogen and then characterized for purity and specific chemical species which might affect storage life. The as-received dimethyl formamide (DMF) was analyzed and found to have low level impurities which were not deemed to be significantly high enough to cause or initiate instability, therefore, the DMF was not distilled prior to use. Details are presented below.

The dimethyl formamide was analyzed for water content, refractive index, free acid and/or free base content, significant impurities by gas chromatography and nuclear magnetic resonance, and dissolved gases. The results of these determinations are presented below.

CHARACTERIZATION OF PURIFIED DIMETHYL FORMAMIDE

DETERMINATION	BATCH 1	2	3	4	5
Water Content, w/o	0.019 0.020	0.019 0.019	0.019 0.019	0.15 0.15	0.024 0.026
Acid Content, μeq/g	0.1 0.1	0.1 0.1	0.1 0.1	0.1 0.1	0.1 0.1
Base Content μeq/g	1.8 3.2	1.5 1.5	1.1 1.4	2.3 2.3	2.0 1.5
Refractive Index	1.42839	1.42839	1.42839	1.42816	1.42812
Dissolved Total Gases, cm^3(STP)/g	0.040	0.070	0.072[a]	0.079[a]	0.072[a]
Impurities, G.C.	b	b	b	b	b
Impurities, NMR	c	c	c	c	c

[a]Composition (v/o) of dissolved gases: Batch 3 19.4% O_2, 80.6% N_2
Batch 4 20.5% O_2, 77.0% N_2
Batch 5 20.5% O_2, 80.4% N_2

[b]No detectable organic impurities at level greater than 0.002%

[c]No detectable impurities

The maximum quantity of dissolved oxygen, 0.016 cm^3 (STP)/g DMF, corresponds to only a 0.0021 w/o or 0.0066 M oxygen content. A water content of 0.18 w/o is equivalent to 0.01 M H_2O in DMF; Batch 4 was rejected because of its high water content. In all PIOP batches prepared the water content of DMF was 0.025% or less.

Methylene dianiline was recrystallized from isopropyl alcohol and analyzed for amine content by both a direct titration and an acetylation technique, water content and melting point by differential scanning calorimetry (DSC). The results of these tests are listed below.

CHARACTERIZATION OF RECRYSTALLIZED METHYLENE DIANILINE

DETERMINATION	VALUES	
Assay, % MDA	100.8	101.9
Water Content, w/o	0.12	0.09
Melting Point, °C	94.3	

NA was recrystallized from benzene and was analyzed for anhydride content, free acid content, maleic content by nuclear magnetic resonance, water content and melting point by DSC. The results of these tests are given below. It is interesting to note that the recrystallization removes essentially all of the maleic species known to be in the impure NA (~6%).

CHARACTERIZATION OF RECRYSTALLIZED NADIC ANHYDRIDE

DETERMINATION	VALUES	
Assay, % NA	94.9	94.9
Free Acid Content, meq/g	0.45	0.42
Water Content, w/o	0.02	0.02
Maleic Acid (NMR)	Nil	
Melting Point, °C	168.3	

PMDA was recrystallized from a 1:1 mixture of acetone-benzene. The recrystallized product was analyzed for anhydride content, free acid content, water content, and melting point by DSC. The results of these determinations are presented below.

CHARACTERIZATION OF RECRYSTALLIZED PYROMELLITIC DIANHYDRIDE

DETERMINATION	VALUES	
Assay, % PMDA	98.3	98.2
Free Acid Content, meq/g	0.115	0.121
Water Content, w/o	0.02	0.02
Melting Point, °C	94.3	

3.2.2 Varnish Synthesis Methodology

A review of resin varnish requirements indicated a need for a laboratory synthesis scheme suitable for preparing reproducible batches of PIOP in one gallon quantities. Because water introduced during preparation by sorption from the air was considered to be one of the most potentially dangerous sources

of product degradation in situ (due to possible hydrolysis of NA and PMDA as well as amide acid prepolymer), nitrogen purge and blanketing were employed during all monomer dissolution and subsequent synthesis (mixing) operations. The previously defined monomer addition sequence for all A-type amide acide prepolymer formulating, including P13N, which involved addition of NA to MDA followed by addition of PMDA, was employed for the studies.

The standard A-type formulation methodology was subject to a rate of addition study of a slurry of NA in DMF to a solution of MDA in DMF (adjusted to 25°C). A slower than previously employed, but practical, rate of addition of NA that gave negligible ($\leq 2^{\circ}C$) solution heat-up rise (monitored by a thermocouple) was defined for the desired one-gallon ingredient quantities. Similar experiments defined a suitable rate of addition for treatment of NA/MDA adduct solution in DMF with a slurry of PMDA in DMF. Stirring times after additions were defined that gave products in solution demonstrating an equilibrium or constant viscosity as a function of time at 25°C. The procedure ultimately selected and used to synthesize P10P, amide acid varnish solution at 40% solids loading in DMF at the desired high viscosity (ca. 300 cps), is described below.

A 5-l round bottomed flask equipped with mechanical stirrer, nitrogen inlet, dropping funnel, and a thermocouple was purged with nitrogen then 725.02 g of recrystallized MDA in 1400 ml of DMF (dissolved under nitrogen) was added as a solution through the dropping funnel. The temperature was adjusted to $\leq$ 25°C, then 513.17 g of NA slurried in 400 ml of DMF was added with stirring over a period of 12 minutes, during which time the temperature was controlled between 20°C by external cooling with an ice bath. After this addition, the reaction mixture was allowed to stir under nitrogen for 22 minutes at $\sim$ 24°C, then 456.66 g of recrystallized PMDA slurried in 896 ml of DMF was carefully added over a period of 38 minutes, during which time the temperature was controlled between 19.5°C and 25°C by external cooling. After this addition, the mixture was allowed to stir at 25°F for two hours under nitrogen. The resulting 40 w/o solids loaded varnish produced from this procedure was light brown in color and had a Brookfield viscosity of 325 at 24°C. The varnish was carefully bottled and stored under nitrogen prior to shipment and use.

3.2.3 Characterization of P10P Varnish and Intermediate

The 40 w/o P10P varnish was analyzed both during (after adding NA to the excess MDA) and at conclusion of its preparation. Details of this characterization are reported below.

The solution resulting after addition of NA-DMF solution to MDA-DMF solution in concentrations used for the P10P varnish was analyzed. Specific analyses performed were intrinsic viscosity, amine content, anhydride content, and water content. The results of these tests are presented below.

CHARACTERIZATION OF NADIC ANHYDRIDE-METHYLENE DIANILINE MIXTURES

DETERMINATION	VALUES	
Intrinsic Viscosity [η]	0.155	
Amine Content, meq/g	5.2	4.7
Anhydride Content, meq/g	0.473	0.499
Water Content, w/o	0.31	0.32

The prepared P10P varnish was analyzed for specific characteristics to serve as reference quality control properties. Specific analyses performed were Brookfield viscosity, intrinsic viscosity, solids content, water content, specific gravity and molecular weight distribution by gel permeation chromatography. The results of these tests are listed below.

PROPERTIES OF P10P VARNISH

DETERMINATION	VALUES	
Brookfield Viscosity, cps	230	
Intrinsic Viscosity [η]	0.0497	
Water Content, w/o	0.43	0.43
Solids Content, w/o	39.6	40.0
Density, g/ml	1.0962	

During the period of this sub-task only one batch of P10P was prepared and, hence, comparative data were not obtained. The procedure for making the P10P did result in the desired high viscosity.

The apparent molecular weight distribution of high viscosity P10P resins, prepared by the improved methodology described above, was determined using gel permeation chromatography (GPC). A typical GPC curve determined on the P10P resins at a 0.25% concentration employing a Waters ALC-GPC-301 unit is shown in figure 17. The GPC column consisted of a series of five columns, each filled with styrogel, having molecular weight exclusion limits ranging from 1×10^6 to 500. As can be seen in this curve, the major fraction of the prepolymer is distributed in two major overlapping peaks centered in the area of calibration numbers 33 to 36. It is possible that these fractions correspond to prepolymers of n = 1 and n = 2. The curve also contains a sizable low molecular weight fraction centered at calibration numbers 40-45, which most probably is the simple bis(nadic) adduct of MDA (e.g., n = 0). The application of GPC methodology to analysis of A-type polyimide products is in its infancy and, therefore, quantitative relationships of peak height or molecular weight cannot be stated.

3.2.4 Analysis of Anomalous Resin Batch

Subsequently, during the attempted use of the second lot prepared by the techniques described above, unusual behavior was observed in both varnish and prepreg. First, a gradual precipitation started in the varnish 20 days after

manufacture; the precipitate was flocculent in nature rather than granular, as previously observed, and occurred very slowly rather than all at once. Second, it was impossible to fabricate sound laminates using a technique already established as acceptable. The laminates were extensively blistered and some exhibited a "burned" appearance.

The varnish was re-examined, and imidized prepregs were compared to similar prepreg from acceptable lots. The varnish and prepreg yielded essentially standard infrared spectra and the varnish showed no significant degradation or change in molecular weight distribution. It was concluded that the differences were not attributable to prepolymer chemistry, per se, but were probably related to more subtle differences associated with polymer physical properties. Since the specific cause could not be identified, the varnish lot and all laminates produced from it were discarded.

3.2.5 Summary of Characterization of P10P Manufacture

Methods were developed for purifying and analyzing the ingredients used in the synthesis of the P10P varnish; these are detailed above. The synthesis procedure described above did yield the higher viscosity resin previously deemed to produce higher property laminates. Both the final varnish and NA/MDA intermediate were characterized and the data reported above. Data of this type should be useful in beginning to establish limits for subsequent work with these types of polyimides.

3.3 Composite Process Optimization and Final Resin Selection

The objective of this sub-task was to identify optimized process parameters for the two resins under study, P10P and P13N, and, from the mechanical test values obtained, select the superior of the two resins.

The commercial P13N and the P10P prepared with improved control methods were used in this sub-task to optimize processing. Careful study was directed to the imidizing, molding, and postcure of the test laminates made with Fortafil 5-Y fiber. Experiments were performed to examine the effect of preform compaction, the ambient environment during imdization (e.g., air or vacuum), and imidization temperatures at various times to achieve complete imidization. In the molding study, temperatures, pressures, and molding times were evaluated. Postcure times in two environments (air and nitrogen) were examined. Performance was judged on mechanical properties at room temperature and 600^{o}F. Details of this effort are described in the following sections.

3.3.1 Experimental Approach

In considering the processing of the A-type polyimides, it was apparent that eight factors or variables were important in influencing the final performance of the composites. It can be seen that in investigating these eight factors at two levels (see table XI) a full test matrix would demand 256 trials. If two resins were to be examined, the number of trials would double. This amount of testing was beyond the task planned effort, and consequently, a more efficient method of study was sought.

A number of statistical plans were considered, and finally, a fractional factorial experiment was chosen. The particular experimental plan chosen was a 1/4 replication of eight factors in two blocks. This type of experimental design was possible since some past experience was available with both resin systems for choosing factor levels. The selection of this form of experiment design reduced the total number of trials to be performed to 64. An experiment of this design has another outstanding advantage besides cost reduction; it permits the identification of variable interactions which might well be missed in the single factor at a time approach.

The experimental design selected provided a statistically significant statement about: (1) the preferred resin (P10P or P13N); (2) main effects of factors, (table XI); and (3) first order interactions (interactions of two variables or factors). The design was taken from a National Bureau of Standards booklet (ref. 2). A schematic of this plan, adapted to the composite optimization of the current program, is shown in figure 18.

A single laminate was molded for each of the 64 conditions represented in figure 18. From each of these laminates, two flexure specimens and two short beam shear specimens were machined. Each specimen was tested at ambient or elevated temperature and the results constitute the six responses considered in the interpretation of the statistical analysis. These included:

Ultimate flexure strength at Room Temperature
Ultimate flexure strength at 600°F
Short beam shear strength at Room Temperature
Short beam shear strength at 600°F
Flexural modulus at Room Temperature
Flexural modulus at 600°F

The use of a single test specimen for each of the conditions was a statistically acceptable technique owing to the large number of tests run in gaining comparative data between factor levels. For instance, in comparing the two levels of factor "A" (compaction vs. no compaction), a total of 32 values were collected to represent each condition. Although these values represent the incorporation of multiple variables, the balanced statistical design averages out the effects of the other variables, so that, in essence, a comparison over any one factor can be thought of as being an independent experiment designed for testing only that factor.

Prepregging the commercially available P13N material was relatively straightforward. A 200 gram quantity of the 40% varnish was diluted with 50 grams of DMF (reagent grade) to yield a varnish with a specific gravity of 1.060 and a viscosity of 70 cps. Four 18 inch wide prepregs were made on a 20 inch diameter drum at 15 RPM at 64 YPI using the standard dip tank method.

To average resin solids content in the final laminates, three or four plies were taken from each sheet of prepreg for every 15 ply laminate. Analytical determinations on the first four laminates molded showed a resin content of 37.1, 36.4, 37.3 and 37.8%, a very narrow range, that compared well with the average prepreg resin content values of 37.8%.

After the prepregging operation, the impregnated material was allowed to rotate for an hour (no heat application) to permit some solvent to evaporate so that the prepreg could be taken off the drum (on Mylar backing) without loss of collimation. Pieces 18 inches wide by about 16 inches long were staged at 180°F in an air circulating oven for one hour. The top cover of Mylar was removed during oven treatment. At the end of this oven treatment the prepregs had a total volatile content (600°F determination) ranging from 14.3 to 16.6%. While this material seemed initially "dry", after storage for a day or two the material had good tack due to volatile stabilization throughout the ply thickness.

In cases where preforms were required for molding, a pressing for 5-10 minutes at 100°F and 50 psi was adequate to achieve a handleable preform with good integrity, adequate bulk and no resin loss.

Weight loss in the various cycles was quite uniform. They were as follows: 300°F/Air, 14.6%; 300°F/vacuum, 14.6%; 400°F/Air, 15.4%; 400°F/ Vacuum,14.1%. Each condition represents an average of eight specimens.

A technique for molding low cost test coupons (2 in. x 4 in.) for the process optimization studies in this task was developed. Essentially, the method involved eliminating the closed die and substituting a stainless steel foil wrap over the laminate, which is first sandwiched between thin steel plates. Since a large number of laminates were required in this task, the use of a more massive die, that needed to be heated and cooled for each molding cycle, would have severely limited the speed with which laminates could have been produced. The substitution of the foil wrap method during molding circumvented this difficulty.

Molding cycles were as prescribed by the experiment design. Volatiles loss of the 32 laminates during molding ranged from 0.5% to 1.0%. Flash loss, due to flow ranged from 0.5% up to 4.0%. The flow values, due to the narrow range and difficulty of precisely measuring flow, are not felt significant for comparison of various cycles.

The first lot of the PIOP resin to be used in this phase of the program, prepared by the special techniques discussed in Section 3.2, exhibited some unusual storage behavior. As received, the material was a thickened, clotted fluid. Additionally, over a period of time, the viscosity displayed a drop from the as-manufactured value of 240 cps to final value of 125 cps just before precipitation. Details of the varnish storage behavior are listed in table XII.

Check laminates, made with the material during this period, exhibited good specific gravity, appearance, and were found to be essentially void free in microscopic examination. The clotted appearance was attributed to cold temperatures experienced in shipment. However, after a review of all of the available data, no firm hypothesis could be found which accounted for the progressive viscosity drop. One interesting phenomenon was noted during the continued observation of the varnish. The 40% material (stored under dry nitrogen at room temperature) precipitated after 10 days from manufacture; the material that had been diluted to approximately 22% and stored under the same conditions did not precipitate over the observation period up to 90 days.

At this time, a laminate was prepared from this material. The laminate had a good appearance, was essentially void free and had excellent mechanical properties. It was concluded from this that storage stability was, at least in part, dependent on concentration level, and that the observed changes had only a limited effect on composite properties.

Once the proper viscosity and concentration levels were reached, the prepregging proceeded much as usual. Conditions were maintained as for P13N, i.e., 15 RPM, 64 YPI, and a target resin solids content of 35%. Staging at 180°F was the same and retained volatile content after oven exposure was again in the 15% range.

Imidizing and molding were carried out according to the experimental plan. Total weight losses experienced in all four imidization cycles ranged from 12.5 to 13.0%.

Representative composite specimens from each resin series were selected for resin solids determination. Since laminates for each resin series were prepared by mixing plies from each of four prepreg runs, it is felt that these values reflected conditions for the entire series. The P13N (Block 1) series ranged (17 specimens) from 33.6% to 41.7% with an average of 37.0%. The P10P (Block 2) series ranged (14 specimens) from 31.2% to 36.6% with an average of 34.7%. Considering fiber weight variability and experimental error in processing and analysis, it was felt that the values fell within normal good practice and made direct comparisons of material properties valid.

3.3.2 Results and Data Analysis

Figures 19 through 24 display all response values for each of the six criteria employed, e.g., ultimate flexural strength, modulus, etc. All data collected were ordered and then analyzed on a high speed digital computer. A computer program was written for this specific experimental analysis in the generalized Fortran IV language. The program performed the Yates method of analysis of variance of a 1/4 replication of a 2 to the 8th factorial experiment in two blocks. Conclusions from this analysis are given below. A detailed description of the statistical techniques and interpretation used are given in Appendix A.

3.3.3 Sub-task Summary and Conclusions

From a systematic review and interpretation of the data collected, the following statements can be made about the materials studied.

Both resin systems generally yielded high quality composites, showing a fairly narrow range in property spreads, considering the variable processing used, and a reasonable tolerance to processing parameters. While some initial difficulties were encountered with the specially prepared P10P system, subsequent processing in this phase with both systems was relatively straightforward. Work with the P10P in a later task where multiple batches were handled revealed certain inconsistencies; however, it is felt that the use of the statistically designed experiment was an economical and effective tool and that sound conclusions were reached based on the data collected.

Clearly, the P10P was the preferred choice between the two resins evaluated. Two statistically strong statements as well as two of lesser significance were made which support the selection of P10P. With regard to optimized processing, the following cycle was selected: Imidization of a compacted preform which is imidized in an air circulating oven for one hour at 400°F and molded at 650°F for one hour at 1000 psi, followed by a postcure in an air atmosphere for 16 hours.

4.0 SELECTED SYSTEM COMPOSITE CHARACTERIZATION (Task III)

The objective of this phase of the program was to characterize the finally selected resin system, in composite form, by a series of mechanical tests conducted at various temperatures on specimens previously aged at elevated temperatures. The complete test matrix is displayed schematically in figure 25. As can be seen, a variety of mechanical and physical tests were to be performed from room temperature up to 600°F on specimens aged for periods up to 1000 hours. Details of this effort are described in the following sections.

4.1 Panel Fabrication

Using the experience gained in the previous sub-task, the P10P/F5-Y prepreg was prepared with a target of 31-35% resin solids; the goal was a 55-60 v/o of fiber volume in all panels molded. Although received in a 40% varnish, the varnish was cut to a 20-25% w/o concentration range for use throughout all the impregnation runs.

During the course of this Task, three lots of the specially prepared P10P resin were received. Table XIII lists the viscosity and specific gravity determination recorded over the various time periods and gives notes describing events observed. In brief, as can be deduced from table XIII, three problems were encountered; progressive viscosity drop, precipitation of the varnish, and a high rejection rate on panels.

The first lot handled in this phase exhibited a progressive drop in viscosity and the 40% varnish (small quantity retained for observation) began to precipitate on the twentieth day after manufacture. While no precipitation was noted in the 25% varnish material, no sound laminates could be molded using the technique recommended in the previous Task, or by modifications to the molding method including changes in imidization time and molding temperature. Additionally, infrared spectra were run on both varnish and prepreg and no irregular responses could be noted. As was noted in Section 3.2.4, in which this particular lot is discussed, the material was rejected.

The second lot also showed a drop in viscosity with time, but 71% of the 8½"x 8" laminates molded by the technique developed in the process optimization phase were sound. The third lot, received in a 25% varnish form instead of the standard 40%, showed only a minor viscosity change but yielded only 50% acceptable laminates. With this latter lot, molding difficulty seemed to increase with time. The last five out of six large laminates were badly blistered. Dropping down to a laminate size of 2 inches by 6 inches seemed to minimize the blistering observed. In an examination of IR spectra from the three resin varnish lots (in DMF), no discernible differences could be noted.

As indicated, the molding cycle used throughout the whole of this task was developed in the process optimization phase (Task IIC). This included preforming the laminate stack, imidizing for one hour at 400°F and placing the preform into a die preheated to 650°F. At the end of 30 seconds hold time (started from the time the preform contacted the die), 1000 psi pressure

was applied. Pressure was maintained for one hour and the laminate cooled under contact pressure. All panels were postcured for 16 hours in an air circulating oven at 650°F.

Although some sub-size panels (2 inches x 6 inches) were molded, the bulk of the laminates were made in a 8½ inch die. In the case of the unidirectional panels, the preforms were cut ½ inch short. This allowed for the growth of the laminate upon cooling and was a convenient size for material utilization of the prepreg sheet.

Tables XIV and XV represent summaries of the characteristics of all laminates manufactured during this phase of the program. As can be seen, criteria used for monitoring processing variation, e.g., weight loss in imidizing, shrinkage, weight loss in molding, indicate no significant differences between good and bad laminates. Prepregging and flow during molding were obviously quite uniform; fiber volume (with a target of 55-60 v/o) ranged from a low of 55.1 v/o to a high of 60.2 v/o.

At the bottom of the table, information is provided about the disposition of the given laminate and quality measurements. Note the low level and the consistency of the calculated void content (based on difference between measured and theoretical specific gravity). Photomicrographs were made of every laminate used on the program. Figures 26 and 27 show only three chosen at random for presentation; these clearly support the low calculated void contents shown in the table. Figure 28 shows a photomicrograph of a 0/90° cross plied laminate(used in fatigue testing). The multiple cracks are quite clear and result from the residual stresses encountered in molding. The crack appearance was not unexpected and, in fact, is typical of any high modulus graphite fiber composite with any known graphite fiber composite with any known resin molded at this orientation.

One laminate (#48) was molded to a thickness of 0.480 inches for machining into thermal expansion and torsion rod specimens. The same cycle (drying, imidizing, molding and postcure) was employed as was used for all other laminates in this phase. Figure 29 shows an end view of this thick laminate as molded; the characteristic minimum flow experienced can be seen around the edges. Figure 30 displays the polished end of the same laminate. In this photograph, the macrocracks observed after molding (before postcure) can easily be seen. Figure 31A is a photomicrograph (at 50X) showing a magnified view of the cracks. The areas not cracked were found to be void free; this is illustrated in figure 31B. In the machining of test specimens, the non-cracked areas were carefully selected for use.

The void free character of this thick laminate was encouraging but the presence of the large cracks in this unidirectional panel was unexplained. Only the single thick composite was made, so no firm conclusions could be drawn about the cause.

4.2 Thermal Exposure

In preparing material for testing, three different air circulating ovens were used; one set at 500°F, one at 550°F, and one at 600°F. Large panels were used as is, or perhaps cut into two pieces. These were stacked between plies

of coarse glass cloth to permit air circulation, and the entire stack covered with a final ply of glass cloth and a steel plate 1/8" thick. Periodically, samples were withdrawn for weight loss checks, and at 150 hours and 300 hours for the 600°F exposure, and at 740 hours, 840 hours, and 1000 hours for the 500°F and 550°F exposures, the laminates were withdrawn for subsequent machining and test.

Figure 32 is a graphic presentation of the weight loss behavior of the test laminates at the three temperatures. The marked difference in performance between 600°F, and 550°F can be clearly seen. Without intermediate data, it would have to be assumed that 550°F would represent an upper limit for these materials.

Using the same isothermal data, an Arrhenius plot of composite weight loss was drawn. This is shown in figure 33. Using this set of curves, projections can be made on the number of hours in which similar composites could be expected to lose either 1.5% or 4.5% weight at various temperatures. It should be noted that before firm judgements were made of this type, considerably more work would have to be done to determine variability between lots of resin, processing techniques, oven air flow influences, and test specimen configuration contributions.

4.3 Test Techniques

Following thermal exposure, the panels were machined into the specific test specimen configurations desired, figures 34 through 40 show schematics of all the specimens used. While certain difficulties were encountered in specimen preparation and test, a review of current literature reveals that these were not unique. The basic problem in mechanical testing of advanced fiber-resin matrix composites is that the high loads required to fracture the unidirectional specimens are difficult to transfer into composite from the specimen fixture due to the relatively low composite strength in the other axes.

Many of the specimen types required a tab material bonded to the specimen in the gripping area. In all cases the tab material employed was a woven glass cloth reinforced polyimide laminate (0.035"-0.040" thick). Selection of the adhesive for bonding the tab material represented a problem because of the high test temperatures planned. For room temperature specimens a tough, room temperature curing epoxy was used without difficulty. Three different adhesive systems were evaluated for the high temperature work. These included 350°F curing polyimide/glass adhesive prepreg, a formulated glass supported polyimide adhesive with a minimum curing temperature of 500°F, and a high temperature liquid epoxy strain gage adhesive. The latter system was found to be most useful because of its liquid state (which helped bonding to the specimen heat affected surfaces) and its low cure temperature (350°F). Poor bonds were obtained with both the other adhesives.

As might be expected, little difficulty was experienced in performing the flexure and short beam shear tests at either room or elevated temperature. Failures were appropriate and the data closely grouped. In tensile testing (both longitudinal and transverse) difficulty was encountered in reproducibly obtaining failures in the gage length. Although some number of longitudinal tensile failures were obtained in the gage length, the bulk were at the tab

end or at the end of the gripping fixture. The majority of transverse tensile failures were in the gage section, but many failed at the end of the bonded tab. Another difficulty with this latter specimen was the extreme delicacy required in mounting the specimen in the test machine to avoid premature specimen fracture.

The most plaguing problem experienced was in the longitudinal compression testing. The Celanese fixture was chosen because it eliminates two problems normally encountered with this type of testing, end brooming and buckling in the gage length. The fixture is shown in figure 42; a mounted specimen is shown to the right and the complete fixture is represented by the three subassemblies shown at the left. The basic problem with this system is encountered at high temperatures. All load into the specimen must be transferred through the tab and the adhesive bond; hence, the limiting factor is the elevated temperature shear strength of available adhesives.

The adhesive system chosen is recommended by the vendor for short time use over 700°F. However, tab slippage was experienced at 550°F and 600°F. Because the system gave no difficulty in tensile testing of the same specimens at the same temperatures, careful attention was given to the fixture. Some modifications were made but the conclusion was that less normal support load (due to the mating tapered cylinders) was applied in the compression fixture than in the tensile wedge grips (where the same adhesive was used without difficulty). In certain cases, specimens were retested after tab slippage by machining a radius in each side of the test specimen, to reduce the width from 0.250 inches to approximately 0.170 inches, and rebonding new tabs. In this way, all specimens were tested.

Torsion specimens were run on a modified lathe shown in figure 43; a closeup of the specimen in the holding fixtures is shown in figure 44. The equipment, with modification, has been used successfully on both metallic and graphite/resin composites, yielding accurate, closely-grouped values in repetitive tests. Allowances are made in the equipment for axial movement during test, and the unit shows a linear relation in dead weight calibration through the load range used. A loading range of 60 degrees/minute was used and both load and deflection curves were plotted autographically on a Visicorder strip chart.

Calculations of torsional shear strength and tangent shear modulus were calculated with the following relations used by Hanna and Steingiser (ref. 3).

τ_u = torsion shear strength

M_T = maximum applied torsional moment (lb-in)

D = rod diameter (inches)

J = polar moment of inertia (inches)

$$J = \frac{D^4}{32} \quad \text{for a rod}$$

$$\tau_u = \frac{M_T D}{2J}$$

G = torsional tangent shear modulus

L = gage length of rod (inches)

$\Delta\theta$ = change in angle of twist corresponding to the applied M_T (radians)

$$G = \frac{\Delta M_T L}{J\Delta\theta}$$

A number of methods were originally considered for running the fatigue experiments, including an air excitation method and four point bending. The method chosen was a constant amplitude deflection in first mode resonance of a cantilever beam. Specimen excitation was through an electrodynamic shaker. Details of this method are given in Appendix B, including photographs of equipment, specimen failure definition, and calculation methods.

The thermal expansion testing was subcontracted to Dynatech R/D Company, Cambridge, Massachusetts. Two single specimens 2 inches x 1/4 inch x 1/4 inch with fiber orientations of 0° and 90° were run in duplicate from room temperature through $572^{\circ}F$.

Before testing, the initial length of the sample was measured with an accuracy of ± 1 micron. It was then placed together with a temperature measuring platinum-platinum 10% rhodium thermocouple in the fused quartz measuring head of a Netzsch Electronic Automatic Recording Dilatometer. The system was placed inside a protection tube and placed in the center of a furnace. After a period of stabilization, the furnace was turned on and programmed to heat the sample to the maximum temperature desired at a rate of $2^{\circ}C$ per minute, and to allow it to cool at the same controlled rate after reaching the maximum temperature. The change in the sample length and the sample temperature were recorded continuously throughout the test. On completion, the sample length was again measured. The above procedure was then 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.

Standard techniques were employed in preparing and testing the specimens requiring strain gages. Gages were bonded on after tab attachment using elevated temperature adhesives as required. Testing was done in the Instron test unit using a SR-4 calibration unit and a switching and balancing unit to sequentially provide the multiple gage input to the Instron strip recorder. Data, used to plot the stress-strain diagrams discussed subsequently, were taken from these curves.

4.4 Test Results and Discussion

Figure 25 illustrates the test plan fulfilled in this phase of the program. In considering the order in which specific tests were to be conducted, a number of options were available. The method chosen, i.e., the use, for the most part, of a single laminate in testing each different type of specimen at a given temperature, provided a significant advantage. A real comparison of

material performance was gained between different temperatures in that the comparisons were made between different laminates. The alternative to this would have been the selection of one laminate to be used for one type of test, transverse tensile for example, in which portions of this single laminate were aged as required and tested. The method chosen, it is felt, represented a higher degree of "randomization". In point of fact, using this technique the data did reveal a considerable difference between performance of various laminates despite being exposed to temperature at the same time and the care taken in panel manufacture.

This variability is not surprising since, as is noted earlier, some differences were observed in the performance of the various batches of resin. The variability encountered was not unique to this program. Data published in March of 1971 by Jones, et al (ref. 4),confirms this observed behavior. Using the P10P resin and Courtaulds HMS graphite fiber, a series of 12 panels were molded and tested in flexure at room temperature. The strength distribution recorded is shown in figure 45. As can be seen considerable variation was noted.

Fiber properties also played a large part in laminate variation. While the fiber quality improved over the course of the program both in weight/unit length consistency and strength properties, considerable variation (see table 1) was noted. The tensile strength of the fibers ranged from 191,000 psi to 245,000 psi and the modulus from 48 to 55 million psi. Using all the values provided, the average fiber tensile strength was 228,000 psi and the standard deviation was 18,500 psi. It is obvious that a spread of values of this magnitude would contribute heavily to variation of the finished panel mechanical properties.

As a check on variation within test replicate groups, data (five replicates) representing each condition were treated statistically. In the tables individually listing data collected for each type of test, the mean, standard deviation, standard error and range are shown. These data were obtained by the use of a computer and a prepared statistical program.

Before the data were subjected to this treatment, the replicate groups were examined for outlying values using the Dixon Criterion described by Natrella (ref.5). The object was to determine the advisability of discarding certain results showing a relatively large deviation from the mean. With the probability or risk of rejecting an observation that really belonged in the group set at 98 or 99%, none of the values observed was rejectable. It was, therefore, concluded that the data within groups represented a reasonable spread.

The data collected from work performed in this phase are discussed below. Table XVI is a summary of all static mechanical test values collected during this phase of the program. Subsequent tables display individual values determined in each different type of test.

4.4.1 Longitudinal Tensile

Table XVII displays all the longitudinal tensile values collected. As can be seen, the short time temperature exposures, even at 600°F, do not indicate a strength decay. It is not until the 300 hour exposure at 600°F that any real loss in strength is shown. This is not surprising, considering that, in this type of test, the bulk of the load is taken up by the longitudinally oriented fibers.

4.4.2 Longitudinal Compression

Table XVIII shows the longitudinal compression results. The footnotes reflect the difficulties encountered in testing which were discussed in the section on Test Techniques. Here the 600°F data show a considerable falloff from lower temperature tests. The longer time exposures at 550°F also show some strength reduction although the values are still at a respectable level. The more rapid decay of strength vs. temperature is understandable since in the compression test the strength of the matrix plays a larger role than in tensile loading.

4.4.3 Flexure

All flexure strength and modulus values are shown in table XIX. As can be seen, there is almost no change in the modulus figures. Again, the 600°F strength numbers do show some degradation although the values are still quite high.

4.4.4 Transverse Tensile

Table XX shows all of the transverse tensile results collected. In general, the level of these values was disappointing. Epoxy matrices show perhaps 2000 psi higher room temperature values. It was expected, with the high level of short beam shear experienced indicating a good bond of fiber to resin, that this number would be higher. The rapid drop in strength shown with temperature was not felt to be unusual since the prime contributor to strength in these tests is the matrix. For this reason, the long term exposures at 550°F show a significant drop. The trend of strength loss is felt to be compatible with the results of the isothermal weight loss measurements.

4.4.5 Short Beam Shear

The short beam shear data shown in table XXI display a surprising consistency at temperature. This test is generally felt to reflect resin matrix characteristics quite strongly. As can be seen, while some small reduction is noted with temperature, the values indicate a very good retention of shear strength with time and temperature.

4.4.6 Torsional Strength and Modulus

The torsional shear strength values shown in table XXII were quite disappointing. In a direct comparison with the room temperature short beam shear, the values are almost twice the torsionally determined numbers. No explanation

is available since no specific correlation between the two test methods has been established at TRW. The modulus values show a higher modulus than is observed in most epoxies -- in the neighborhood of 400,000 psi.

4.4.7 Strain Gage Testing

The test plan required a number of static test specimens to be strain gaged. Table XXIII displays a summary of all data gathered during this series of tests. Items of special interest in the table are the low strain to failure indicated by the longitudinal tensile tests (a characteristic of the fiber) and the Poisson's ratio values. The Poisson's ratio determined at elevated temperature appears quite high which indicates a high transverse strain during extension. This behavior is understandable when it is considered that the resin is less brittle at temperature. While theoretically a value over 0.5 is not possible, the difference is attributed to experimental error and the value reported to demonstrate the trend shown.

Figures 46 through 48 (stress-strain curves) graphically illustrate the behavior of the specimens during loading. The four longitudinal tensile specimens exhibited a linear relationship up to failure. This response, coupled with the low strain to failure shown in table XXIII, characterizes the material as being brittle. While two of the transverse tensile curves and the compression curve do display a small plastic range on the upper end, it is obvious that the material cannot be classified as a tough system.

4.4.8 Thermal Expansion

The thermal expansion data collected are listed in table XXIV and are displayed graphically in figure 49. For purposes of comparison, curves are also shown for an HM-S/P13N composite characterized under an IR&D program. The values shown for the 90° orientation are relatively low when compared to epoxies, which are generally found to range in the 30 to 40 X 10^{-6} in/in-$^{\circ}$F region.

4.4.9 Fatigue

Four S-N curves are shown in figures 50 through 53. In the first two, specimen failure was identified as the first change in slope of resonant frequency. The latter two curves are plots of the same specimens that were permitted to run until a 5% change in frequency was noted. Although it is felt that the first change in slope reflects first specimen damage and should be used to characterize the material, both techniques have been observed in the literature in reporting data.

While limited polyimide data are available for comparison, it is felt that the curves display the good fatigue life generally shown with the graphite reinforced composites. For example, the unidirectional material exhibited a life of 54% stress retention after 10 million cycles. The linearity of the $0^{\circ}/90^{\circ}$ material curve is probably due to the highly cracked condition observed before test, and shown quite clearly in the photomicrographs of this material (figure 28). Despite this cracked condition an average modulus, determined from the natural frequency as shown in Appendix B, figure B-6, was

14.5×10^6 psi. The unidirectional material modulus, determined the same way, was 24.9×10^6 psi, which compares well with statically determined values.

4.5 Composite Characterization Summary

A review of the results of this phase of the program reveals a number of facts that should be emphasized. In panel fabrication for program requirements, a number of batches of resin and fiber were used; both fiber and resin displayed a wide variation in properties and behavior. While the fiber consistency and quality improved over the course of the program, it was apparent that certain unknowns exist in the preparation and control of the development A-type resin. Further work in understanding this system is required.

Despite the variations discussed above, impregnation and molding techniques yielded over 30 laminates with a determined fiber volume variation of only ± 2.6%. While panel rejection rate was quite high, this was attributed primarily to the resin problems discussed earlier.

Thermal aging tests indicated that the inherent thermo-oxidative stability of the resin used in this portion of the program limits the use of composites of this nature to a life of about 1000 hours in the 550°F range. The Arrhenius plots provided should permit projection of acceptable time-temperature limits for various conditions.

Mechanical test difficulties encountered during the course of this phase were not new to the field of advanced composites. While specimens did not always break in gage length sections, the data were reasonably closely grouped. Statistical data were provided for confirmation of these judgements. The only test method used that seems unsuitable for high temperature work was the Celanese method of compression testing. The limiting factor was the elevated temperature shear strength of the specimen-tab bond.

An examination of the collected mechanical test data indicate a material with a typically brittle stress-strain curve and only a 0.33% strain to failure. The composite material exhibited useful life in fatigue tests out to 10 million cycles. The upper temperature limit as noted above was shown to be about 550°F for extended times; the only property that showed significant drop before the 1000 hour period at 550°F was the transverse tensile which began to drop off at the 840 hour period at this temperature.

While numerical goals were originally set for this program, they were cast in terms of an English high strength fiber (Modmor II). The alternate fiber selected because of the weight losses exhibited in the English fiber at 600°F produced composites with quite respectable specific strength and modulus. The program target values and those obtained are listed below:

	TARGET	OBTAINED
Shear Strength, at RT (psi)	10,000	10,000
Specific Tensile Str., at RT (inches)	3×10^6	$1.5\text{-}1.8 \times 10^6$
Specific Mod., at RT (inches)	300×10^6	461×10^6

It can be seen that the specific tensile value obtained is short of the target goal. However, this is easily understood when the respective vendor data on raw fiber material are compared. The raw English fiber is advertised as having a specific tensile strength of 5.6 to 6.3 million inches; the Fortafil 5-Y vendor data gives a nominal specific tensile of only 3.6 million inches.

5.0 PROGRAM CONCLUSIONS

Specific conclusions on such things as processing details, test techniques, and rejected candidates were presented in the body of the text following descriptions of work done in each phase. The itemized conclusions below represent those major statements that summarize the overall findings of the program.

1. A specific A-type polyimide, based on a synthesis of nadic anhydride, methylene dianiline and pyromellitic dianhydride with a formulated molecular weight of 1000, was determined on a mechanical property basis to be superior to the commercially available P13N and suitable for applications in long time (1000 hours) use at temperatures up to 550°F in composite form.

2. Processing of multiple batches of the experimental polyimide revealed that the material must still be considered a developmental system and further work is required to fully define critical parameters before the material is ready for extensive commercial application.

3. A process, free of operator judgement factors, was defined for molding the A-type matrix composites that repetitively produced low void containing, high quality laminates.

4. High frequency fatigue studies established that the P10P/F 5Y composites have a usable life out to 10 million cycles with a minimal degradation. A fatigue limit of 54% or room temperature ultimate stress was determined after 10 million cycles.

5. An examination of the total performance of the resin candidates studied indicated that the A-type polyimide appears best suited for application to complex jet engine components.

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6.0 RECOMMENDATIONS

The recommendations made below follow from a review of the information collected on the program.

1. Further studies should be performed to identify the critical parameters that influence the variable performance and storage stability characteristics of the developmental A-type polyimide. A synthesis method should be developed that combines the monomers in a reproducible manner so that the high temperature performance and processing qualities of this system can be more completely utilized.

2. Since the inception of the program, improved graphite fibers have become available which are superior to the staple yarn used. The resin system utilized in this program should be evaluated with these improved reinforcements.

3. Additional composite isothermal weight loss studies,employing standardized techniques, should be made using multiple batches of resin and composite panels to fully define thermo-oxidative stability over a wide range of temperatures.

4. Additional composite development studies should be pursued with thick laminates, various orientations, and various configurations to confirm the practicality of the processes selected.

5. Time dependent properties such as creep, stress-rupture, high temperature fatigue, and environmental fluid effects should be determined to extend the characterization of the composite system for practical applications.

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TABLE I
GREAT LAKES FORTAFIL 5-Y
VENDOR CERTIFICATION DATA

Order Date	Amount	Fiber Tensile, Ksi	Modulus, Msi	Weight gm/in Avg/Min/Max.	Epoxy Composite Short Beam Shear, Avg., Psi	Lot & Spool Numbers
12-18-70	3 lbs.	235	51	.00164 .00158 .00174	N/A	Lot 1537, Spool 16 Lot 1539, Spools 1,2,3,4,6,7,8,9
12-8-70	0.3 lbs.	235	51	.00160	8,170	Lot 1537, Spool 15
11-4-70	3 lbs.	243	50	.00162 .00151 .00168	8,950	Lot 1537, Spools 6,7,8,9,10,11,12, 13,14
9-11-70	2 lbs.	245	52	.00164 .00159 .00173	9,150	Lot 1536,Spools 3,4,5 Lot 1537, Spools 1,2,5
7-7-70	2 lbs.	230	50	.00159 .00154 .00168	10,700	Lot 1535, Spools 12, 13, 14,15,18,19
3-31-70	0.7 lbs.	240	50	.00167 .00167 .00168	N/A	Lot 1529, Spools 1,2
3-18-70	2 lbs.	235	55	.00165 .00158 .00168	8,780	Lot 1527, Spool 2 Lot 1528, Spools 2,3, 4,5,7
2-12-70	2 lbs.	230	55	.00161 .00143 .00175	9,080	Lot 1523, Spool 228 Lot 1524, Spools 1,2, 3,4,5
12-16-69	5 lbs.	191	49	.00186 .00159 .00214	10,670	Lot 1515, Spools 8,10,11 Lot 1516, Spool 2 Lot 1517, Spool 2 Lot 1518, Spools 1,2,3 Lot 1519, Spools 2,5,6,7,11
10-22-69 10-15-69 10-8-69	4 lbs.	198	48	.00194 .00157 .00220	9,330	Lot 1512, Spools 9,10,11,12,13 Lot 1513, Spools 1,2,3,4,7 Lot 1514, Spools 1,2

TABLE II
A-TYPE POLYIMIDE - ACID VARNISH SYNTHESIS DATA

Diamine Monomer Employed	Prepolymer Formulation Code	Formulated[a] Molecular Weight	Varnish[b] Viscosity (cps)
Methylene Dianiline	NA/MDA/PMDA	1000	107
		1150	142
Benzidine	NA/BZI/PMDA	1000	>1000
para-Phenylene Diamine	NA/PPD/PMDA	1000	140
		1150	650
2,6-Diaminopyridine	NA/DAP/PMDA	1000	c
		1150	45
meta-Phenylene Diamine	NA/MPD/PMDA	1150	240
		1150	253
		1150	510
		800	520
Ethylene Dianiline	NA/EtDA/PMDA	1150	142
Ethylene Diamine	NA/EDA/PMDA	1150	Gel

[a]Prepared at 40 w/o solids loading in DMF

[b]Determined with a Brookfield Viscometer at 24°C

[c]Insufficient varnish volume for viscosity measurement

TABLE III
NEAT A-TYPE CURED POLYMER MOLDING DATA[a]

Formulation	FMW	Pressure (psi)	Temperature (°F)	Barcol Hardness	Remarks
NA/MDA/PMDA	1000	500	590	42	Consolidated
	1150	500	620	47	Consolidated
NA/BZI/PMDA	1000	500-6000	590-620	b	No consolidation
NA/PPD/PMDA	1000	500-6000	580-620	b	No consolidation
	1150	500-6000	590-630	b	No consolidation
NA/MPD/PMDA	1150	500-6000	590-620	b	No consolidation
NA/EtDA/PMDA	1150	800	620	38	Consolidated

[a]Molded with 0 to 30 second dwell time and 30 minute cure

[b]All samples crumbled on attempted determination of Barcol hardness

TABLE IV
MOLDING BEHAVIOR OF A-TYPE POLYIMIDES AS A FUNCTION OF PHENYL RINGS PRESENT IN REACTANTS

Dianhydride/ Case	Diamine/ Case	Formulated Case	Formulated Molecular Weight (FMW)	Processing Conditions Temp (°F) Pres (Psi)	Highest Barcol Hardness
BTDA/2	MDA/2	NA/MDA/BTDA	1300	540/500	53
	ODA/2	NA/ODA/BTDA	1300	540/1000	52
	EtDA/2	NA/EtDA/BTDA	1300	600/800	40
	MPD/1	NA/MPD/BTDA	1300	630/800	63
PMDA/1	MDA/2	NA/MDA/PMDA	1000	590/500	50
			1150	590/500	47
			1300	620/500	40
			1500	620/1000	--
	ODA/2	NA/ODA/PMDA	1300	590/1000	--
	EtDA/2	NA/EtDA/PMDA	1150	620/800	38
	PPD/1	NA/PPD/PMDA	1000	500-600/580-620	--
	MPD/1	NA/MPD/PMDA	1150	500-6000/590-620	--
			800	400-1000/580-630	--
	BZI/3	NA/BZI/PMDA	1000	500-6000/590-620	--

TABLE V
IMIDE RINGS IN A-TYPE POLYIMIDES AS A FUNCTION OF MONOMER COMBINATIONS AND FORMULATED MOLECULAR WEIGHTS

Formulation	Molecular Weight	Monomer Cases (Dianhydride-Diamine)	Average[a] Number of Imide Rings	Molded Products[b] Characteristics
NA/MDA/BTDA (P13N)	1300	2-2	3.4	Good
NA/ODA/BTDA	1300	2-2	3.4	Good
NA/MDA/PMDA	1000	1-2	2.6	Good
	1150		3.4	Good
	1300		4.2	Medium-Poor
	1500		5.4	Poor
NA/PPD/PMDA	1000	1-1	4.2	Poor
	1150		5.2	Poor
NA/MPD/PMDA	1150	1-1	5.2	Poor
NA/BZI/PMDA	1000	1-3	2.8	Poor

[a] Average number of imide rings resulting from reaction of dianhydride and diamine.

[b] Based on Barcol hardness; Good = >45, Medium = <45, Poor = None

TABLE VI
SUMMARY OF KEY PROPERTIES OF THREE A-TYPE POLYIMIDE MODIFICATIONS RECOMMENDED FOR PROCESSING STUDIES

Formulation	Formulated Molecular Weight	Processing Variables for Cure[a] Temp. (°F)	Pressure (psi)	Barcol Hardness	Thermo-Oxidative Stability at 600°F (%)[b]
NA/MDA/PMDA	1000	590	500	42	97
	1150	620	500	47	97
NA/EtDA/PMDA	1150	624	800	38	91

[a] Employing a 0-30 second dwell time and 30 minute cure

[b] Reported as % resin weight retention after aging for 336 hours in air (100 ml/min flow)

TABLE VII
SUMMARY OF SCREENING MOLDING PROCESS VARIABLES

Molding Pressure Psi	Dwell Time Secs.	Imidizing Cycle	Loading Conditions	Cure Time at 600°F Hrs.	Flexural Strength Ksi	Flexural Modulus Msi	Short Beam Shear Strength Ksi	Thickness[a] Ins.	Specific Gravity	Resin Content w/o	Fiber Volume v/o	Void Content v/o
500	40	None	600°F	1	105	20	8.4	0.097	1.62	40.4	50.81	-1.2
500	80	None	600°F	1	80	19	9.1	0.080	1.56	40.0	49.26	2.7
200	40	None	600°F	1	61	12	8.7	0.090	1.53	48.6	41.38	1.4
500	40	None	600°F	4	59	12	7.0	0.077	1.55	49.5	41.19	-0.2
500	40	None	600°F	8	62	15	6.3	0.073	1.53	45.0	44.28	2.8
500	0	None	Mold 70°F Press 600°F	1	119	26	7.5	0.085	1.58	33.6	55.21	3.9
500	0	None	Mold 70°F Press 70°F	1	128	24	7.5	0.064	1.60	39.9	50.61	0.28
500	30	20 hrs at 300°F in air	600°F	1	104	17	9.1	0.076	1.58	39.6	50.22	1.64
500	30	40 hrs at 300°F in air	600°F	1	107	22	9.3	0.076	1.58	49.4	42.07	-2.1
500	30	20 hrs at 300°F in vacuum	600°F	1	76	25	8.8	0.082	1.53	46.2	43.31	2.3
500	30	0.5 hrs at 300°F in vacuum	600°F	1	90	18	7.0	0.083	1.53	42.9	45.97	3.5

[a]All panels were eight plies thick

TABLE VIII
EVALUATION OF CANDIDATE RESINS IN COMPOSITES

Panel No.	Resin System	Preform Condition	Specific Gravity	Resin Content w/o	Fiber Volume v/o	Void Content v/o	Thickness in.	Longitudinal R.T. Flexural Strength Ksi	Longitudinal R.T. Flexural Modulus Msi	Transverse R.T. Flexural Strength Ksi	Shear Strength at R.T. Ksi	Longitudinal 650°F Flexural Strength Ksi	Longitudinal 650°F Flexural Modulus Msi	Shear Strength at 650°F Ksi
1	1150 NA/EtDA/PMDA	(1) Amide-acid	(3)											
2	1150 NA/EtDA/PMDA	(2) Imidized	(3)											
3	1000 NA/MDA/PMDA	(1) Amide-acid	1.59	25.5	62.34	6.3	0.065	120.0 130.3 126.0	28.6 26.4 24.5		5.6 6.2 6.4	127.9 127.9	19.2 22.2	4.6 4.1 4.8
4	1000 NA/MDA/PMDA	(1) Amide-acid	1.51	22.5	61.58	12.1	0.063	115.8 120.0 118.9	26.7 23.5 28.6	(4)		111.2 93.5	21.0 22.2	
5	1000 NA/MDA/PMDA	(2) Imidized	1.55	45.7	44.29	0.9	0.087	94.0 102.8	16.7 17.1	6.4		116.7 109.7	(6) (6)	
6	1000 NA/MDA/PMDA	(2) Imidized	1.58	39.6	50.22	1.1	0.076	106.6 110.8 111.1	21.2 20.2 18.2		7.4 8.8 8.4 8.8	120.8 122.5	18.2 16.7	6.7 6.6 6.6 6.6
7	1150 NA/MDA/PMDA	(1) Amide-acid	1.53	31.4	55.23	7.8	0.063	98.1 113.0	19.4 23.0	6.9		118.2 111.7 125.7	18.5 19.0 22.2	
8	1150 NA/MDA/PMDA	(1) Amide-acid	(5)											
9	1150 NA/MDA/PMDA	(2) Imidized	1.59	38.7	51.29	1.1	0.077	90.5 105.2 101.0	20.9 19.3 21.2		9.0 8.1 8.7 8.5	116.7 120.9	19.0 20.0	7.4 7.5 7.2 6.9
10	1150 NA/MDA/PMDA	(2) Imidized	1.58	38.6	51.05	1.6	0.076	93.8 100.0	18.0 19.0	6.8		108.9 108.4 102.3	17.4 19.0 15.8	

(1) Stacked unimidized prepreg was loaded into a cold mold and cold press. Pressure of 500 psig was applied and the temperature raised to 300°F. At this time the pressure was adjusted to 500 psig (pressure drop occurred due to resin flow). The temperature was then raised to 600°F and the part was cured for one hour at 600°F under 500 psig.

(2) Stacked prepreg was imidized in an air circulating oven at 300°F for 40 hours. The imidized preform was then dropped into a preheated mold at 600°F and cured for one hour at 500 psig.

(3) Panels were not consolidated and unsuitable for test.

(4) Specimen broke during machining.

(5) Pressure was adjusted too late resulting in a non-consolidated molding which was not suitable for test.

(6) Tests did not provide reliable stress/strain plots.

TABLE IX
SUMMARY OF LAMINATE SCREENING PROPERTIES

MATERIAL/LAMINATE		FIBER VOLUME % BEFORE/AFTER POSTCURE	VOID CONTENT BEFORE/AFTER POSTCURE	AVG. RT FLEX, KSI (NO. OF SPEC.) SPAN/DEPTH	AVG. 650°F FLEX, KSI (NO. OF SPEC.) SPAN/DEPTH	AVG. RT FLEX MODULUS MSI (NO. OF SPEC.)	AVG. 650°F FLEX MOD. MSI	AVG. RT SHORT BEAM SHEAR, PSI (NO. OF SPEC.) SPAN/DEPTH	AVG. 650°F SHORT BEAM SHEAR, PSI (NO. OF SPEC.) SPAN/DEPTH	600°F WT. LOSS % 500 HRS/ 1000 HRS	LAMINATE SPECIFIC GRAVITY AS MOLDED/ POSTCURED	TRANSVERSE MOLD SHRINKAGE %	POSTCURE TRANSVERSE WIDTH CHANGE %	POSTCURE WT. LOSS %
703	L6+	65.5/59.9	4.2/11.6	120 (2) 34:1	31 (1) 35:1	21 (2)	9 (1)	5,200 (2) 4.6:1	2,500 (2) 4.1:1	1.8 4.5	1.65 1.51	0.7	+0.14	5.5
	L7+	65.5/59.9	4.2/11.6	119 (1) 39:1	22 (2) 34:1	21 (1)	7 (2)	5,800 (2) 4.6:1	2,900 (2) 4.1:1	2.6 5.4	1.65 1.51	0.7	+0.14	5.5
GR 908	L15+	49.4/N.C.	3.1/N.C.	-	61 (3) 25:1	-	15 (3)	4,100 (6) 5:1	-	0.6 0.9	1.56 1.56	2.4	No Significant Change in Thickness or Weight	
	L16+	48.6/48.4	0.6/1.2	88 (3) 24:1	-	18 (3)	-	-	2,700 (6) 4.0:1	0.6 0.8	1.58 1.57	2.4		
RS 6228	R8L4	49.4/N.C.	4.0/N.C.	95 (2) 37:1	-	20 (2)	-	-	-		1.61 1.61	-	-2.8	4.3
	R9L1	49.5/N.C.	6.0/N.C.	99 (2) 33:1	107 (2) 30:1	20 (2)	15 (3)	9,400 (3) 4.3:1	5,500 (3) 4.5:1		1.59 1.59	-	-3.5	4.2
	R10L2	47.8/45.3	7.3/12.1	95 (3) 33:1	-	17	-	-	-		1.53 1.45	-	-2.6	3.2
	R12L1	55.5/53.0	4.8/8.8	112 (2) 31:1	63 (3) 31:1	23 (2)	18 (3)	8,300 (3) 4.0:1	4 200 (4) 4.0:1		1.61 1.54 1.61	0.4	-2.0	2.8
P10P	R2L1	48.5 *	-0.6 *	101 (2) 36:1	97 (2) 36:1	22 (2)	19 (2)	9,100 (3) 4.0:1	4,800 (4) 4.0:1		1.59 *	1.0	*	*
	R2L3	50.4 *	0 *	101 (2) 36:1	95 (2) 36:1	23 (2)	18 (2)	9,700 (4) 4.0:1	5,600 (4) 4.0:1		1.60 *	1.0	*	*
P11.5P	R2L1	55.2 *	0.6 *	104 (2) 31:1	87 (3) 31:1	25 (2)	18 (3)	9,800 (3) 4.0:1	4,000 (4) 4.0:1		1.63 *	1.0	*	*
	R2L2	56.0 *	0.6 *	110 (2) 33:1	61 (3) 33:1	25 (2)	15 (3)	7,800 (3) 4.0:1	3,000 (4) 4.0:1		1.64 *	-	*	*
	R2L3	55.9 *	0.6 *	106 (2) 32:1	74 (3) 32:1	25 (2)	17 (3)	9,500 (3) 4.0:1	3,900 (4) 4.0:1		1.64 *	-	*	*
P13N	L12+	54.0 *	2.4 *	117 (1) 25:1	122 (2) 37:1	23 (1)	22 (2)	7,500 (5) 4.8:1	5,400 (5) 4.1:1	5.1 13.0	1.60 *	-	*	*
	L13+	59.7 *	6.5 *	101 (1) 27:1	113 (1) 27:1	22 (1)	17 (1)	7,800 (5) 5.3:1	6,200 (5) 4.1:1	4.7 12.6	1.58 *	-	*	*
	L15+	50.6 *	3.1 *	89 (1) 23:1	-	19 (1)	-	8,500 (5) 4.5:1	6,200 (5) 4.1:1	- -	1.57 *	-	*	*

*NOT POSTCURED

+BASED ON CALCULATED RESIN SOLIDS

TABLE X
RS6228/FORTAFIL 5-Y MOLDING SUMMARY

LAMINATE CODE	MOLDING CYCLE	STAGING CONDITIONS	SPECIFIC GRAVITY	RESIN SOLIDS, %	PLY THICKNESS MILS/PLY	VOID CONTENT %	v/o FIBER %	LAMINATE QUALITY	SHRINKAGE %
8/4	Die at 400°F. Bump at 1 minute intervals for 3.5 minutes. Hold 30 minutes at 500 psi. Cool under full pressure.	Vacuum oven 10 min/176°F	1.61	41.7 Determined	6.8	2.7	50.7	Dark reddish brown. One crack.	NA
9/1	As above	As above	1.59	40.8 Determined	6.4	4.1	51.7	Reddish black. Two cracks. Non-Post-cured: Flex = 99,200 psi (Avg. 2) Mod = 20×10^6 psi (Avg. 2) SBS = 9,400 psi (Avg. 3)	NA
9/2	As above	As above	1.46	40.0 Calculated	6.6-7.8	12.2	52.5	No cracks. 0.012" taper in 4"x4" laminate	NA
10/1	As above except cool under kiss pressure.	Vacuum oven 10 min/160°F	1.60	40.4 Calculated	7.0	3.6	52.1	Color pronounced - reddish brown - no cracks.	NA
10/2	As above except 425°F and 3 minutes.	Vacuum oven 10 min/176°F 17.9% vols left remaining	1.53	40.6 Determined	6.4-8.1	7.8	51.9	Tapered. Color light in thick portion, darker in thin portion of laminate. No cracks.	NA
11/1	As above except 415°F and 3 minutes	Vacuum oven 10 min/180°F +10 min/180°F +5 min at 275°F +8 min at 300°F in air circ. oven.	1.50	36.5 Calculated	8.7	10.8	56.2	Surface rough. No cracks.	0.6
11/2	As above except 2 min. bump period forced cool under kiss pressure.	Vacuum oven 10 min/180°F Remaining vols.: 17.0%	1.56	38.5 Calculated	6.9	6.6	54.1	One crack. Good surface	NA
9/3	As above except total bump period 2 min: 45 sec and bump every 30 sec.	As above	1.49	44.0% Calculated	6.2-7.8	9.3	48.4	One crack	NA
11/3	Die at 410°F. Bump every 30 sec. for 3.5 minutes. Hold 30 min. at 500 psi. Cool under kiss pressure.	As above	1.53	40.5 Calculated	7.2	7.8	52.0	No cracks. Color good. Surface generally good.	1.0
12/1	As above	As above Vols.: 18.7%	1.61	34.5 Determined	6.6	4.8	58.3	As above	0.4

TABLE XI

FACTORS AND LEVELS SELECTED FOR INVESTIGATION

	FACTOR	LEVEL LOWER	LEVEL UPPER
A.	Precompaction	No	Yes
B.	Imidizing Temperature	300°F/40 Hours	400°F/1 Hour
C.	Imidizing Environment	Air	Nitrogen
D.	Mold Pressure	500 Psi	1000 Psi
E.	Mold Temperature P13N P10P	 550°F 600°F	 600°F 650°F
F.	Mold Time	30 Minutes	60 Minutes
G.	Post Cure Environment	Air	Nitrogen
H.	Post Cure Time	0 Hours	16 Hours

Note 1: Experiment design in two blocks of a 1/4 replication of 8 factors. Block 1 represents P13N resin and Block 2 represents P10P resin.

Note 2: Post Cure temperature used was 50°F above mold temperature except in the case of P10P molded at 650°F. In this case, a 650°F post cure was used.

TABLE XII
P1OP VARNISH STORAGE BEHAVIOR (1ST IMPROVED LOT)

Time Elapsed Days	Event	Viscosity cps	Specific Gravity	Dilution to w/o	Diluted Viscosity cps	Diluted Specific Gravity	Comments
0	Resin Synthesis	240					
1	Resin received - clotted	400	1.115				
3	Varnish stirred 90 minutes - Clots eliminated	170		22.8 21.3		1.020 1.018	Used for Prepreg
7	Unopened container-no clots	125		22.2	30		Used for Prepreg
9	Unopened container-no clots	125		21.9		1.018	Used for Prepreg
10	Remaining 40% solids solution precipitated						
56	22.5% Solids solution - no precipitation						
90	22.5% solids solution - no precipitation						Laminate molded. Good values.

TABLE XIII
SUMMARY OF P1OP LOTS USED IN TASK III

Task III Lot No.	Time Elapsed Days	Concentration* w/o	Viscosity cps	Specific Gravity	Comments
1	0	40	293		
	8	40	168		
	18	25	29	1.010	
	20	40			Flocculent precipitate noted.
	22	25	37	1.030	Lot rejected - poor laminates.
2	0	40	272		
	2	40	248	1.100	
	5	40	148	1.090	
	6	40	130		
	12	40			Precipitated.
	13	25	29	1.030	
	16	25	27	1.030	
	16	25			One quart out of three precipitated.
	33				No precipitation on two remaining quarts. All non-precipitated material used.
3	0	25	14		
	4	25	40	1.025	
	10	25	30		
	31	25	26	1.028	
	54	25	26	1.032	
	74	25			No precipitation observed.

*Data listed chronologically. The 40% values refer to material as received or retained at 40% for observation. The 25% varnish was used in the impregnation process.

TABLE XIV
TASK III - SUMMARY OF 8-1/2" X 8-1/2" LAMINATE CHARACTERISTICS

LAMINATE IDENTIFICATION / CHARACTERISTIC	31[2]	32	33	34	35	36	37	39	40	41	43	44	45	46
DATE IMPREGNATED DATE MOLDED	11-9-70 11-10-70	11-11-70 11-12-70	11-11-70 11-12-70	11-13-70 11-16-70	11-13-70 11-16-70	11-17-70 11-18-70	11-17-70 11-18-70	11-20-70 11-23-70	11-20-70 11-23-70	11-24-70 11-24-70	11-24-70 11-25-70	11-30-70 11-30-70	12-1-70 12-2-70	12-2-70 12-2-70
FIBER BATCH/ROLL	1537-9	1527-9 1528-5 1535-14 1535-19 1536-5	1537-12	1536-3 1537-6 1537-12	1537-6	N/A	1537-10	1537-13	1537-13	Composite of Prepreg from Runs 34,35,36, 37,39,40	1537-11	1537-7	1535-15	1537-8
RESIN BATCH	5112-38	5112-38	5112-38	5112-8	5112-38	5112-38	5112-38	5112-38	5112-38	5112-38	5112-38	5112-38	5112-38	5112-38
WT. LOSS IN IMIDIZING, %	16.6	14.9	17.1	15.7	14.9	15.0	15.5	14.5	14.9	13.3	13.3	14.0	14.7	14.4
WT. LOSS IN MOLDING, %	0.5	0.2	0.3	1.2	1.5	0.4	0.5	1.4	1.5	1.0	1.3	0.7	1.4	1.5
MOLD SHRINKAGE, %[1]	1.3	1.3	1.3	N/A	N/A	N/A	1.2	1.3	1.5	N/A	1.3	1.3	N/A	1.3
THICKNESS (4 LOCATIONS), MILS	84-84 84-84	80-85 80-84	87-82 88-82	83-87 83-84	80-81 80-82	N/A	N/A	75-80 80-85	75-79 79-81	85-80 82-78	87-87 81-81	76-76 79-79	82-79 79-77	85-83 90-87
SP. GR. AFTER MOLDING	1.64	1.64	1.64	1.63	1.65	1.65	1.64	1.65	1.64	1.65	1.64	1.67	1.64	1.65
WT. LOSS IN POST CURE, %	0.4	0.3	0.4	0.8	0.5	0.6	0.6	0.4	0.5	0.6	0.5	0.5	0.7	0.6
SP. GR. AFTER POST CURE	1.64	1.64	1.64	1.63	1.64	1.65	1.64	1.65	1.64	1.65	1.65	1.67	1.64	1.65
RESIN SOLIDS, w/o	33.2	33.6	35.2	32.9	33.8	32.2	32.2	32.5	34.8	34.0	32.7	32.5	36.2	30.5
FIBER VOLUME, v/o	57.6	57.2	55.8	57.6	57.1	58.7	58.4	58.6	56.3	57.3	58.4	59.3	55.1	60.3
VOID CONTENT, v/o	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6
APPEARANCE AFTER MOLDING	Good	Good	Good	Burned Blistered Cracked	Good. A Few Yellow Streaks on Surface	Good	Good	Good	Multiple Blisters in 1 Quadrant	Good	Good	Good	Good	Good
QUALITY 50X MICRO AFTER POST CURE	Good	Some Voids, Microcracks	Some Voids	High Void Content	Good	Good	Good	Good	Good	Good	High Voids. Good 2nd Micro	Good	Good	Good
DISPOSITION	600°F Soak	Scrap. Poor Appearance after 600°F Soak	Scrap. Poor Appearance after 600°F Soak	Scrap	500°F Soak	550°F Soak	550°F Soak	550°F Soak	Scrap	500°F Soak	Scrap	500°F Soak	600°F Soak	600°F Soak

[1] Percent Shrinkage in Width (Hot Die to Cold Parts), [2] Refers to Laboratory Notebook Page

TABLE XIV
TASK III - SUMMARY OF 8-1/2" X 8-1/2" LAMINATE CHARACTERISTICS (CONT.)

CHARACTERISTIC \ LAMINATE IDENFIFICATION	47	48	49	50	51	53	54	55	56	57	58	59	60	62
DATE IMPREGNATED DATE MOLDED	12-3-70 12-3-70	N/A 12-8-70	N/A 12-7-70	12-7-70 12-7-70	12-8-70 12-9-70	12-15-70 12-16-70	1-4-71 1-5-71	1-5-71 1-5-71	1-5-71 1-7-71	1-8-71 1-8-71	1-8-71 1-13-71	1-15-71 1-15-71	2-3-71 2-4-71	N/A 2-5-71
FIBER BATCH/ROLL	Composite of Prepreg from Runs 41,43,44, 45,46,47	From Previous Impregnations	From Previous Impregnations	1519-7	1519-7 1519-11	1537-15	1539-9	1539-1	1539-1 1539-9 1539-2	1539-2	1539-3	1539-6	1539-3 1539-6	From Previous Impregnations, Lot 1539
RESIN BATCH	5112-38	5112-38	5112-38	5112-38	5112-48	5112-48	5112-48	5112-48	5112-48	5112-48	5112-48	5112-48	5112-48	5112-48
WT. LOSS IN IMIDIZING, %	N/A	N/A	14.1	13.1	13.6	12.8	14.2	14.6	14.4	N/A	13.7	14.7	14.4	N/A
WT. LOSS IN MOLDING, %	N/A	2.0 Includes Fiber Loss	1.3	0.6	0.4	1.0	0.4	1.0	1.3	2.5	0.9	1.2	1.3	1.0
MOLD SHRINKAGE, %	1.3	N/A	0°/90° Laminate	0°/90° Laminate	1.2	1.2	1.3	N/A	1.3	1.3	N/A	1.3	1.4	1.3
THICKNESS (4 LOCATIONS), MILS	82-81 84-83	479-482 477-482	68-70 70-70	76-79 75-78	85-90 88-93	76-83 78-83	80-81 80-80	86-88 90-90	88-75 89-76	77-81 76-82	82-83 82-82	89-85 85-81	85-80 88-77	
SP. GR. AFTER MOLDING	1.64	1.69	1.60	1.60	1.63	1.66	1.68	1.65		1.67				
WT. LOSS IN POST CURE, %	0.5	N/A	1.8	1.4	0.4	0.8	0.7	0.5		0.4				
SP. GR. AFTER POST CURE	1.64	1.64	1.63	1.62	1.63	1.66	1.67	1.65						
RESIN SOLIDS, w/o	32.4	32.8	31.8	29.6	32.3	32.7	31.4	35.2						
FIBER VOLUME, v/o	58.3	59.7	58.4	60.0	58.0	58.8	60.2	56.2						
VOID CONTENT, v/o	0.6	0.0	1.2	3.0	1.2	0.0	0.0	0.0						
APPEARANCE AFTER MOLDING	Good	Good Longitudinal Cracks	Good	Good 1 Blister	Good	Good	Good	Good	Multiple Dispersed Blisters	Good except for Low Density Strip-in Center	Multiple Blisters in one corner. Low Density Strip-up Center.	Multiple Dispersed Blisters. A few Yellow Streaks on Surface	Multiple Dispersed Blisters	Multiple Dispersed Blisters
QUALITY 50X MICRO AFTER POST CURE	Good	Good	Multiple Cracks	Good	Good	Good	Few Isolated Voids	Good	N/A	Voids in Center. Remainder Good.				
DISPOSITION	R.T. Fatigue	Torsion-Thermal Expansion	Scrap. Excessive Kiss Time in Molding	R.T. Fatigue	R.T.Test	Test at 500°F & 600°F	High Temperature Fatigue	550°F Test	Scrap	550°F Fatigue	Scrap	Scrap	Scrap	Scrap

TABLE XV
SUMMARY OF 2 X 6 INCH LAMINATE CHARACTERISTICS

CHARACTERISTIC \ LAMINATE IDENTIFICATION	63A	63B	64A	64B	67A	67B	67C	67D	67E*
DATE IMPREGNATED	2-9-71	2-9-71	2-12-71	2-12-71	2-12-71	2-12-71	2-12-71	2-12-71	2-12-71
DATE MOLDED	2-9-71	2-9-71	2-12-71	2-12-71	2-18-71	2-18-71	2-18-71	2-19-71	2-19-71
LAMINATE ORIENTATION	0°	0°	0°	0°	0°/90°	0°/90°	0°/90°	0°/90°	0°/90°
FIBER BATCH/ROLL	1537-15	1537-15	1539-8	1539-8					
RESIN BATCH	5112-48	5112-48	5112-48	5112-48	5112-48	5112-48	5112-48	5112-48	5112-48
WEIGHT LOSS IN IMIDIZING, %	10.7	9.2	9.9	9.3					
WEIGHT LOSS IN MOLDING, %	1.1	0.5	N/A	N/A					
MOLD SHRINKAGE, %	N/A	-	N/A	N/A					
THICKNESS, MILS	83	79	84	80	71	71	72	69	72
SP. GR. AFTER MOLDING	N/A	-	N/A	N/A					
WEIGHT LOSS IN POST CURE, %	1.0	-	0.9	1.1					
SP. GR. AFTER POST CURE	1.65	-	1.66	1.67					
RESIN SOLIDS, w/o	34.2	-	34.2	32.1					
FIBER VOLUME, v/o	57.1	-	57.5	59.7					
VOID CONTENT, v/o	0.0	-	0.0	0.0					
APPEARANCE AFTER MOLDING	Good	Yellow Streaks on Surface	Good	Good	Blistered	Good	Blistered	Blistered	Good
QUALITY 50X MICRO AFTER POST CURE	Good	-	Good	Good					
DISPOSITION	600°F Test	Hold	600°F Test	600°F Test	Hold	Hold	Hold	Hold	Hold

*MOLDED AT 600°F INSTEAD OF 650°F USED ON ALL OTHERS.

TABLE XVI
TASK III MECHANICAL TEST DATA SUMMARY

Exposure & Test Temperatures Exposure Time (Hours)	RT	500°F				550°F				600°F		
		0	740	840	1000	0	740	840	1000	0	150	300
Short Beam Shear, psi	10,000	5800	6300	6200	6600	5500	5900	5000	4700	4600	5600	5100
Flexure Strength, Ksi	115.2	135.4	120.8	124.7	117.6	115.9	122.6	114.5	104.7	119.4	78.7	94.0
Flexure Modulus, Msi	23.6	25.3	25.0	27.2	25.3	25.5	25.2	24.7	24.6	24.4	22.2	23.0
Longitudinal Tensile, Ksi	91.0	110.9	107.3	98.0	94.2	99.0	92.5	104.3	105.5	92.4	93.5	58.4
Longitudinal Compression,Ksi	103.9	96.1	88.3	103.9	90.4	77.7	102.0	89.6	82.8	77.2	81.2	77.6
Transverse Tensile, psi	2900	1200	1000	1000	1000	1200	1000	600	600	--	--	--
Torsional Shear Strength,psi	5600											
Torsional Shear Modulus, Msi	0.51											

TABLE XVII
TASK III DATA COMPILATION - LONGITUDINAL TENSILE STRENGTH

Test & Exposure Temperature / Exposure Time (Hours)	Spec.No.	RT	500°F				550°F				600°F		
			0	740	840	1000	0	740	840	1000	0	150	300
Tensile Strength, Ksi	1	85.5	81.6	-	106.5	102.8	106.1	82.1	104.1	93.0	93.2	97.0	58.4
	2	90.4[A]	114.3	109.1	99.6	102.2	99.9	88.9	103.3	105.0	85.8	95.1	52.8
	3	102.7[A]	120.8	111.4	100.9	95.7	97.7	100.0	102.3	110.9	88.8	103.9	59.1
	4	93.7[A]	116.6	100.6	110.9	92.0[A]	91.6	98.3	105.4	108.0	93.5	77.1	66.8
	5	82.6[A]	121.0	108.2	72.3	78.5[A]	99.8	93.3	106.5	110.5	100.9	94.5	54.7
Mean		91.0	110.9	107.3	98.0	94.2	99.0	92.5	104.3	105.5	92.4	93.5	58.4
Standard Deviation		7.8	16.6	4.7	15.1	9.9	5.2	7.3	1.7	7.4	5.7	9.9	5.4
Standard Error		3.5	7.4	2.3	6.7	4.4	2.3	3.3	0.7	3.3	2.6	4.4	2.4
Range		20.1	39.4	10.8	38.6	24.3	14.5	17.9	4.2	17.9	15.1	26.8	14.0

FOOTNOTE: A = Strain gaged specimen

TABLE XVIII
TASK III DATA COMPILATION - LONGITUDINAL COMPRESSIVE STRENGTH

Test & Exposure Temperature	Spec.No.	RT	500°F	500°F	500°F	500°F	550°F	550°F	550°F	550°F	600°F	600°F	600°F
Exposure Time (Hours)		--	0	740	840	1000	0	740	840	1000	0	150	300
Ultimate Compressive Strength (Ksi)	1	104.2[A]	B	86.8	95.1	79.4[C]	67.3[E,CD]	127.2	88.8	B	78.2[CDE,DE]	78.8[CD]	51.2[CD]
	2	95.5	96.8	97.8	115.2	88.5[C]	80.7[CD]	85.2	94.3	94.7	67.7[DE]	78.4	65.6[CD]
	3	104.6	98.9	84.9	94.9	B	71.5[CD]	90.0	79.9	78.6	69.7[DE]	86.4[CD]	90.6[CD]
	4	109.1	95.2	79.1	119.3	89.7	81.1[CD]	85.3	84.1	76.7	77.2[DE]	81.3	96.9[CD]
	5	106.1	93.4	92.7	95.2	103.8	78.3[E]	122.5[CD]	100.8	81.2	71.2[DE]	B	83.8[CD]
Mean		103.9	96.1	88.3	103.9	90.4	77.8	102.0	89.6	82.8	77.2	81.2	77.6
Standard Deviation		5.1	2.3	7.2	12.2	10.1	5.4	21.0	8.3	8.1	--	3.7	18.8
Standard Error		2.3	1.2	3.2	5.5	5.3	3.1	9.4	3.7	4.1	--	1.8	8.4
Range		13.6	5.5	18.7	24.4	24.4	9.6	42.0	20.9	18.0	--	8.0	45.7

FOOTNOTES:
A = Specimen strain gaged
B = Specimen run - value invalid
C = Specimen tested previously --- Tab slippage encountered before failure. Tabs rebonded and specimen tested with resultant value shown.
D = Gage section of specimen reduced in width by 0.040"/side on 0.8 inch radius.
E = No specimen failure --- Tab slippage -- Specimen bore stress shown before tab slip. Values not included in average.

TABLE XIX
TASK III DATA COMPILATION - FLEXURAL STRENGTH AND MODULUS

Test & Exposure Temperature / Exposure Time (Hours)	Spec.No.	RT	500°F				550°F				600°F		
			0	740	840	1000	0	740	840	1000	0	150	300
Flexure Strength, Ksi	1	115.1	132.9	123.3	124.5	121.3	113.3	120.5	111.9	103.0	123.1	79.1	93.0
	2	117.9	135.5	120.4	124.9	115.1	117.8	129.1	115.9	109.0	115.7	78.8	93.8
	3	111.6	138.7	125.6	123.6	118.7	115.0	120.4	116.2	105.7	96.5[A]	81.0	95.8
	4	118.5	132.6	116.9	122.8	114.0	114.6	122.9	114.0	104.6	118.7	76.8	94.5
	5	112.0	137.3	117.9	127.9	119.0	118.7	120.3		101.4	120.0	78.0	92.9
Mean		115.0	135.4	120.8	124.7	117.6	115.9	122.6	114.5	104.7	119.4	78.7	94.0
Standard Deviation		3.2	2.7	3.6	1.9	3.0	2.3	3.8	2.0	2.9	3.1	1.5	1.2
Standard Error		1.4	1.2	1.6	0.9	1.3	1.0	1.7	1.0	1.3	1.5	0.7	0.5
Range		6.9	6.1	8.7	5.1	7.3	5.4	8.8	4.3	7.6	7.4	4.2	2.9
Flexure Modulus, Msi	1	23 0	25.3	24.3	27.2	25.3	25.2	25.2	24.5	24.2	23.5	21.9	23.2
	2	24.0	24.9	25.2	27.4	25.1	25.6	25.0	24.9	25.1	23.6	21.6	22.4
	3	23.0	25.5	25.4	27.2	25.4	25.8	25.2	24.5	24.5	23.6[A]	22.6	23.4
	4	24.4	25.1	25.3	26.9	24.9	25.7	25.4	24.8	24.6	25.2	21.7	22.7
	5	23.7	25.8	25.0	27.4	25.6	25.4	25.1	--	24.6	25.2	23.3	23.1
Mean		23.6	25.3	25.0	27.2	25.3	25.5	25.2	24.7	24.6	24.4	22.2	23.0
Standard Deviation		0.6	0.3	0.4	0.2	0.3	0.2	0.1	0.2	0.3	1.0	0.7	0.4
Standard Error		0.3	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.5	0.3	0.2
Range		1.4	0.9	1.1	0.5	0.7	0.6	0.4	0.4	0.9	1.7	1.7	1.0

FOOTNOTE: A = Failed in shear, not used in average.

TABLE XX
TASK III DATA COMPILATION - TRANSVERSE TENSILE STRENGTH

Test & Exposure Temperature / Exposure Time (Hours)	Spec.No.	RT	500°F				550°F			
			0	740	840	1000	0	740	840	1000
Tensile Strength, psi	1	3280	1240	A	950	920	1430	1210	460	780
	2	3010[B]	1270	A	920	1080	870	1010	790	560
	3	2997[B]	A	950	1010	1230[B]	990	1100	500	430
	4	2896[B]	1210	A	1380	929[B]	1740	710	840	650
	5	2472[B]	1150	A	660	A	1080	1160	600	550
Mean		2931	1217	950	984	1039	1222	1038	638	594
Standard Deviation		293	51	--	250	146	356	197	170	130
Standard Error		131	25	--	115	73	159	88	76	58
Range		808	120	--	720	310	870	500	380	350

FOOTNOTES: A = Broken in handling
B = Strain gaged specimen

TABLE XXI
TASK III DATA COMPILATION - SHORT BEAM SHEAR STRENGTH

Test & Exposure Temperature / Exposure Time (Hours)	Spec. No.	RT	500°F				550°F				600°F		
			0	740	840	1000	0	740	840	1000	0	150	300
Individual Values, psi	1	9,560	5,670	5,990	5,980	6,380	5,430	6,560	4,750	5,240	4,500	5,630	5,480
	2	9,190	5,880	6,330	6,150	6,780	5,440	5,620	5,130	4,260	4,590	5,480	5,310
	3	10,690	5,700	6,430	6,230	6,320	5,650	5,620	4,990	4,800	4,640	5,640	5,110
	4	10,140	5,920	6,610	6,370	6,490	5,500	5,860	4,950	4,640	4,630	5,750	4,290
	5	10,200	6,030	6,120	6,500	6,820	5,700	5,820	5,020	4,720	4,470	5,430	5,190
Mean		9,956	5,840	6,296	6,246	6,558	5,554	5,896	4,968	4,732	4,566	5,586	5,076
Standard Deviation		586	152	246	200	229	123	387	138	351	77	129	460
Standard Error		262	68	110	89	102	55	173	62	157	34	58	206
Range		1,500	360	620	520	500	270	940	380	980	170	320	1,190

TABLE XXII
ROOM TEMPERATURE
TORSIONAL SHEAR STRENGTH AND MODULUS

Specimen Number	Shear Strength, psi	Shear Modulus, X 10^5 psi
1	5026	6.0
2	5313	6.0
3	5042	5.5
4	5816	3.4
5	6948	4.8
Average	5629	5.1

TABLE XXIII
SUMMARY OF DATA FROM STRAIN GAGED MECHANICAL TESTS - TASK III

SPECIMEN	Exposure Temperature & Time	Test Temp.°F	Loading Rate in/min	Ultimate Strength Ksi	Failure Strain %	Modulus Msi	Poisson's Ratio
#1 Longitudinal Tensile Laminate 51	None	Room	0.050	102.7	0.36	28.9*	N/A
#2 Longitudinal Tensile Laminate 51	None	Room	0.050	93.7	0.33	27.6	0.40
#3 Longitudinal Tensile Laminate 51	None	Room	0.050	82.6	0.29	27.6	0.42
#1 Longitudinal Compression Laminate 51	None	Room	0.050	104.2	0.48	23.4	0.43
#1 Transverse Tensile Laminate 51	None	Room	0.010	3.0	0.26	1.1	0
#2 Transverse Tensile Laminate 51	None	Room	0.010	2.9	0.27	1.1	0
#3 Transverse Tensile Laminate 51	None	Room	0.010	2.5	0.23	1.1	0
#1 Longitudinal Tensile Laminate 41	1000 hours at 500°F	500	0.050	78.5	0.27	25.5	0.52
#1 Transverse Tensile Laminate 41	1000 hours at 500°F	500	0.002	0.9	0.15	0.6	0

* Tensile moduli determined by extensometer on three other specimens from this laminate. Values were:

27.1×10^6 psi
25.8×10^6 psi
26.3×10^6 psi

TABLE XXIV
COEFFICIENT OF THERMAL EXPANSION OF PIOP/FORTAFIL 5-Y COMPOSITE

Temperature Interval		$\alpha \times 10^{+6}$			
		Longitudinal		Transverse	
Deg C	Deg F	Deg C^{-1}	Deg F^{-1}	Deg C^{-1}	Deg F^{-1}
20-60	68-140	0.5	0.3	25.8	14.3
60-100	140-212	0.5	0.3	28.6	15.9
100-140	212-284	0.5	0.3	31.4	17.4
140-180	284-356	0.5	0.3	34.2	19.0
180-220	356-428	0.5	0.3	36.9	20.5
220-260	428-500	0.5	0.3	39.5	22.0
260-300	500-572	0.5	0.3	42.0	23.4

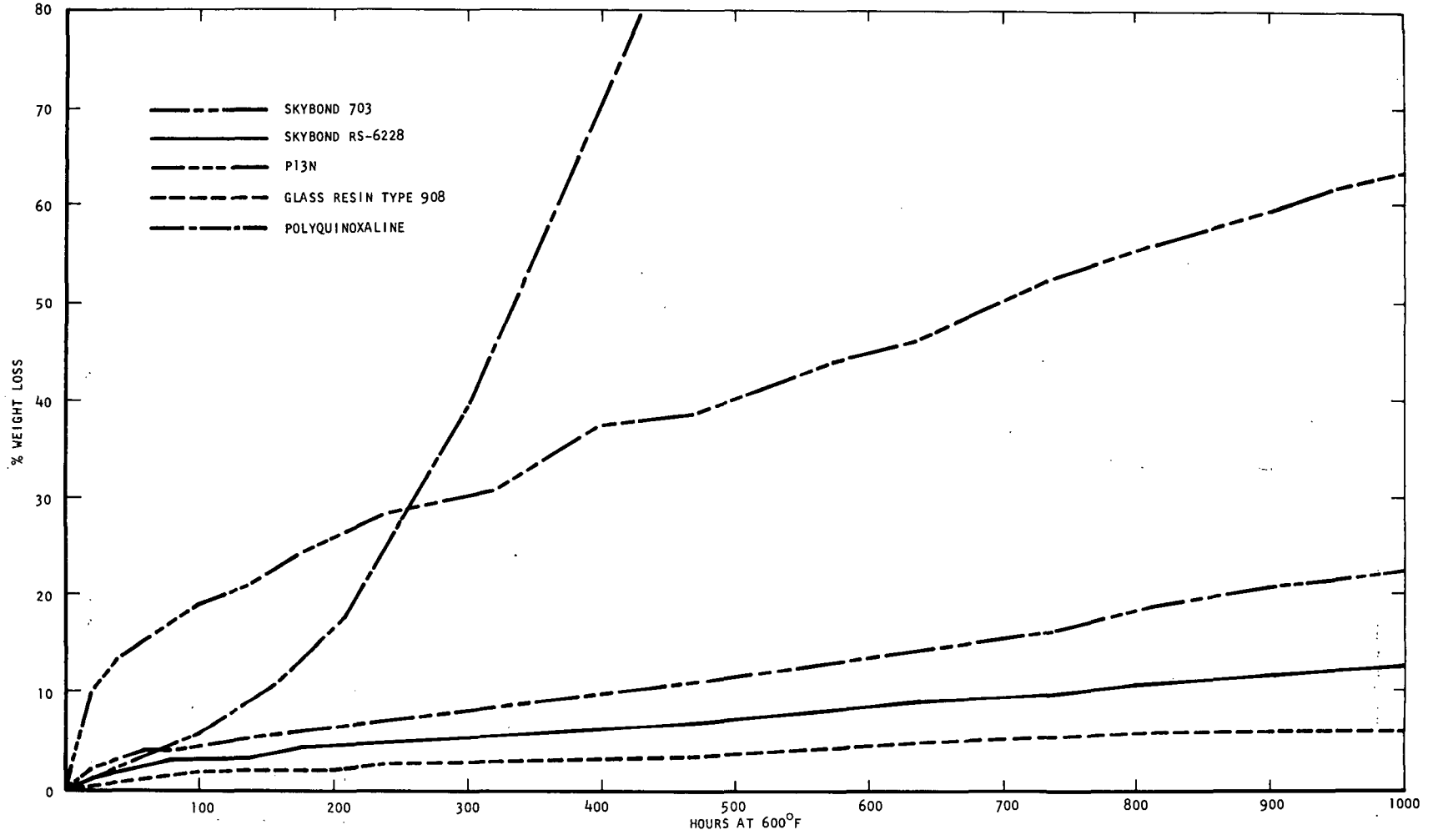


FIGURE 1 ISOTHERMALGRAVIMETRIC ANALYSIS IN AIR AT 600°F OF SEVERAL UNREINFORCED RESIN CANDIDATES

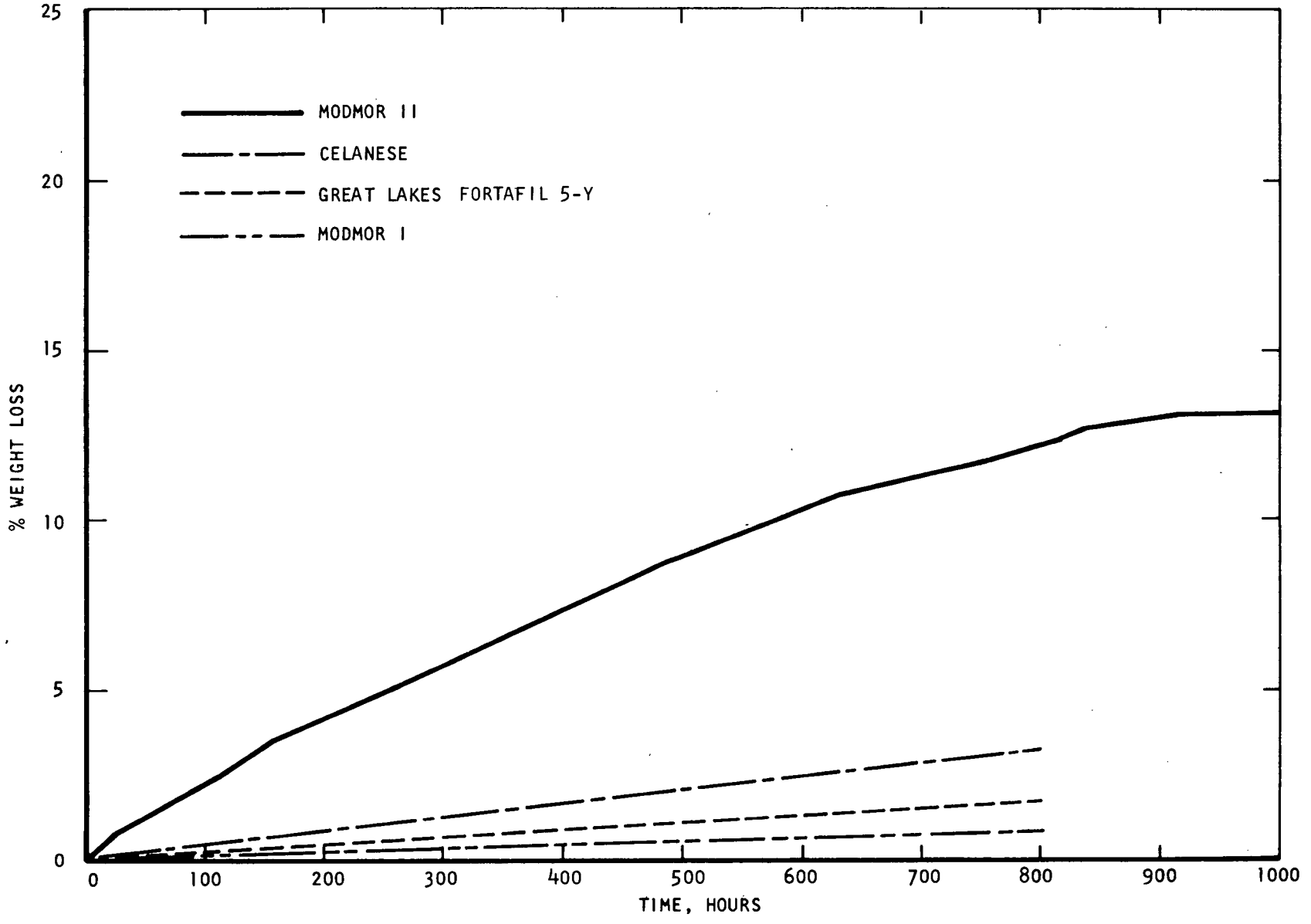


FIGURE 2 ISOTHERMALGRAVIMETRIC ANALYSIS OF SEVERAL CANDIDATE REINFORCING FIBERS IN AIR AT 600°F

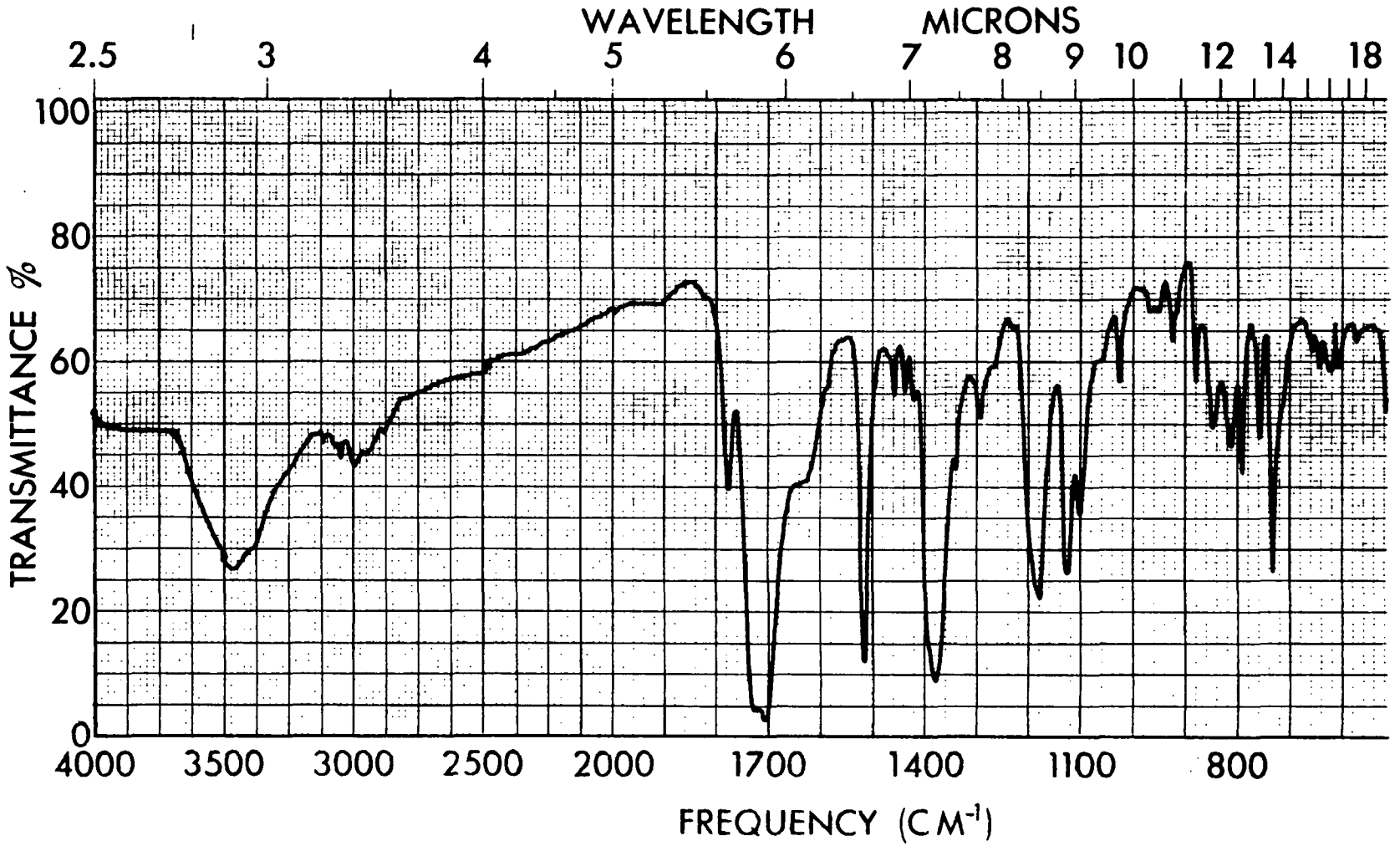


FIGURE 3 INFRARED SPECTRUM OF NA/MDA/PMDA 1000 FMW
IMIDIZED PREPOLYMER (KBr)
CONCENTRATION: 3.5 mg/g KBr

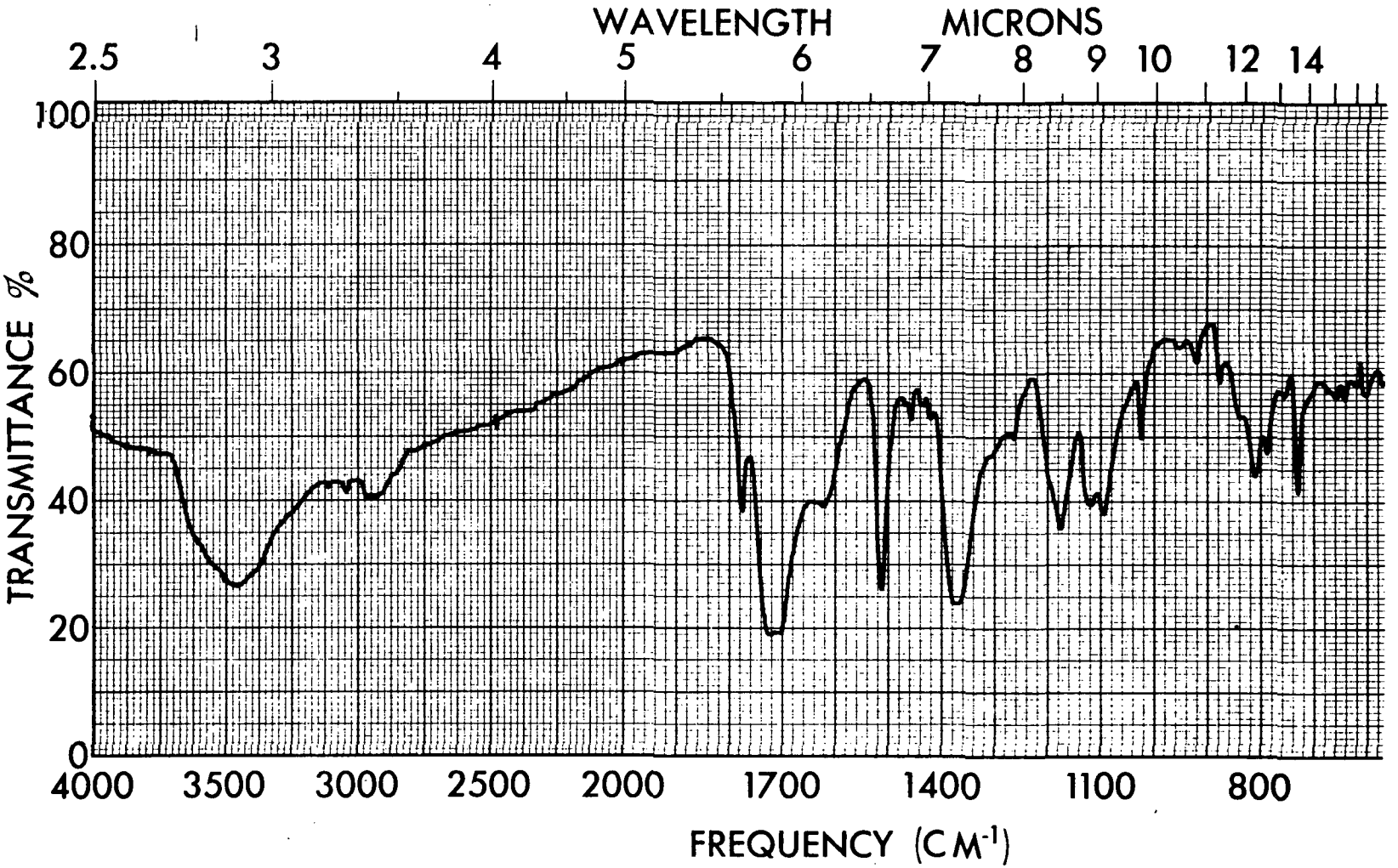


FIGURE 4 INFRARED SPECTRUM OF 1150 FMW NA/MDA/PMDA CURED POLYMER (KBr)
CONCENTRATION: 4.8 mg/g KBr

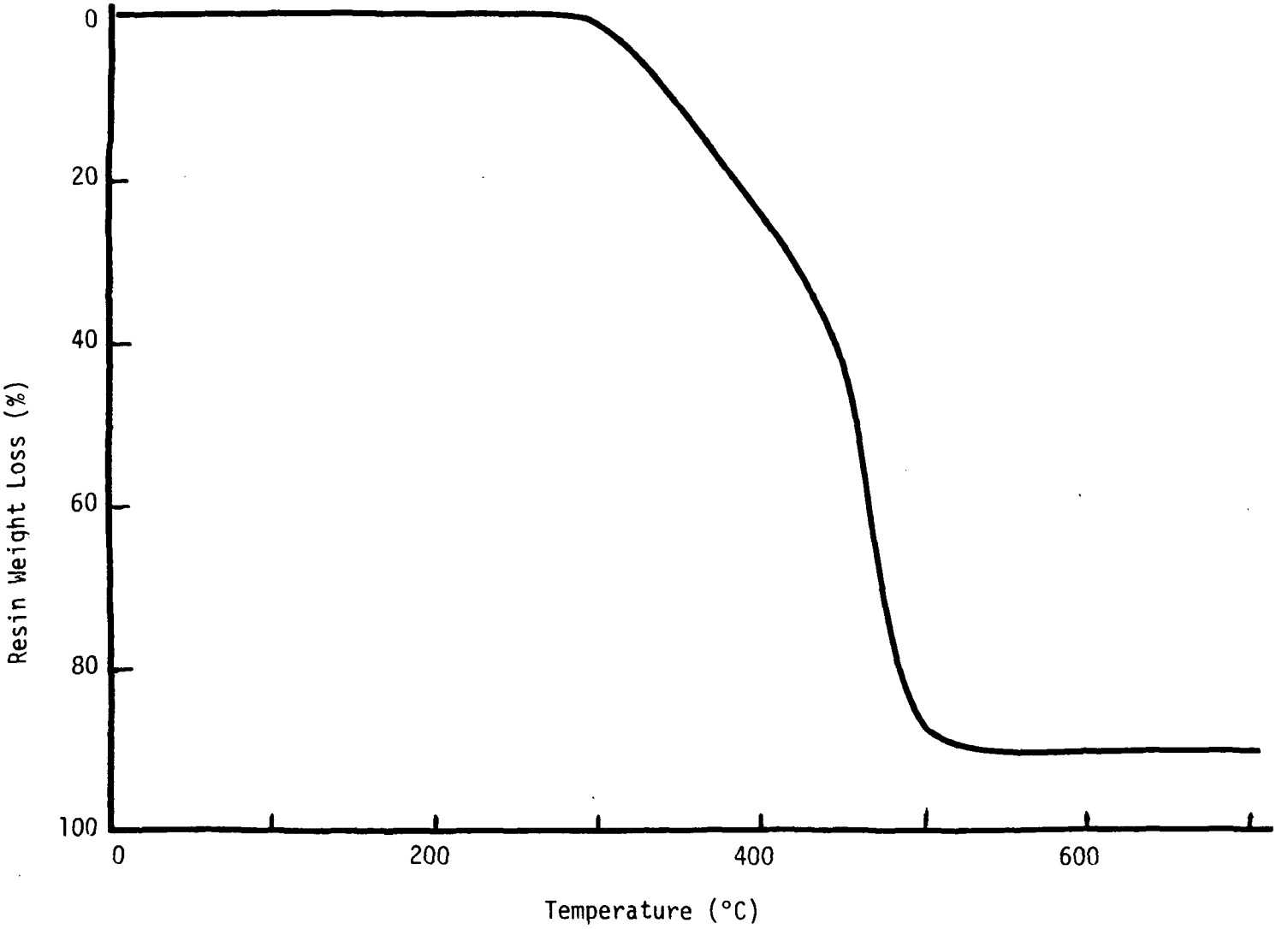


FIGURE 5 THERMOGRAM OF 1150 FMW NA/MDA/PMDA CURED POLYMER IN AIR
SCAN RATE: 3°C/MIN. FLOW: 100 cc/MIN.

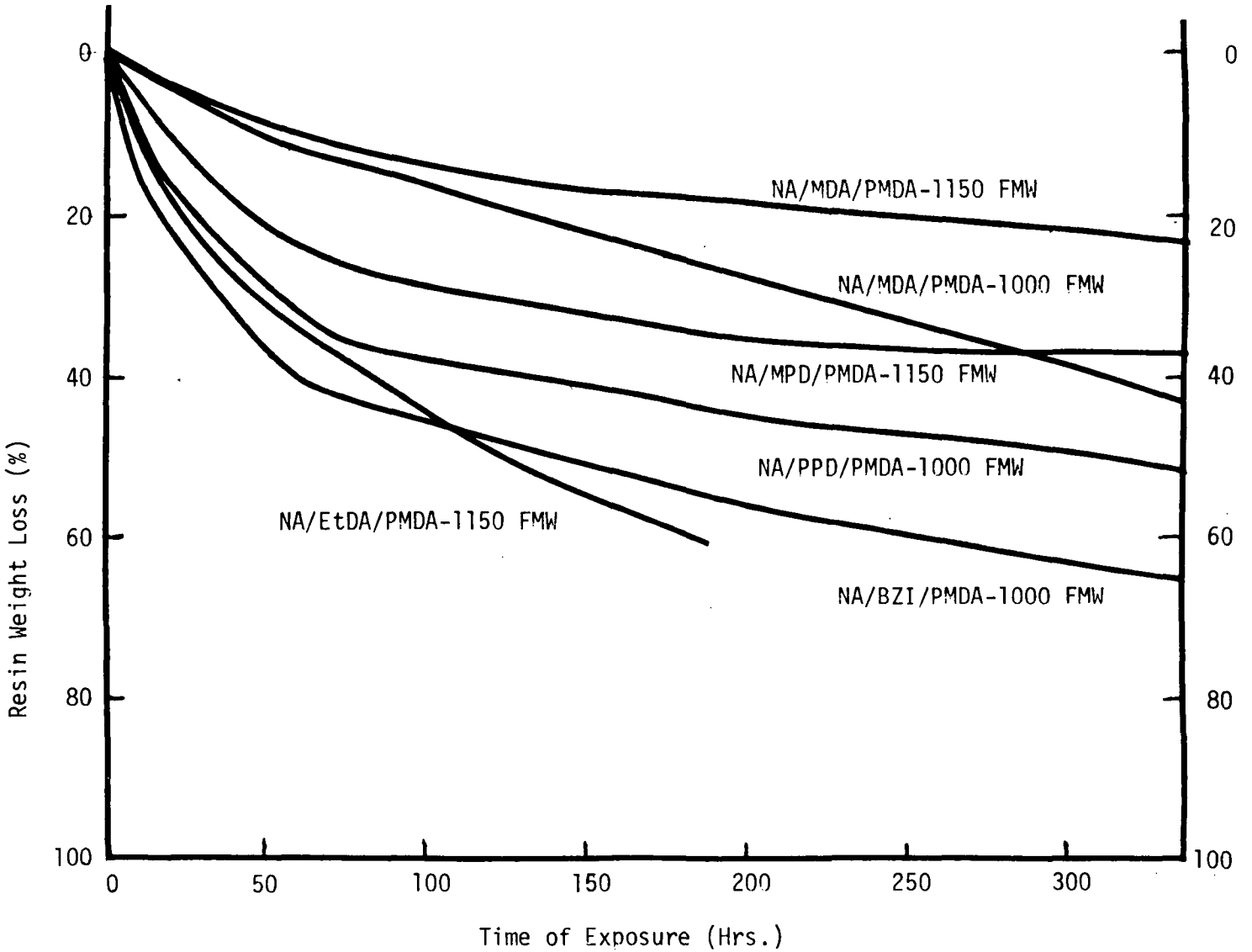


FIGURE 6 PLOT OF RESIN WEIGHT LOSS AS A FUNCTION OF ISOTHERMAL EXPOSURE AT 650°F IN AIR (100 cc/MIN. FLOW)

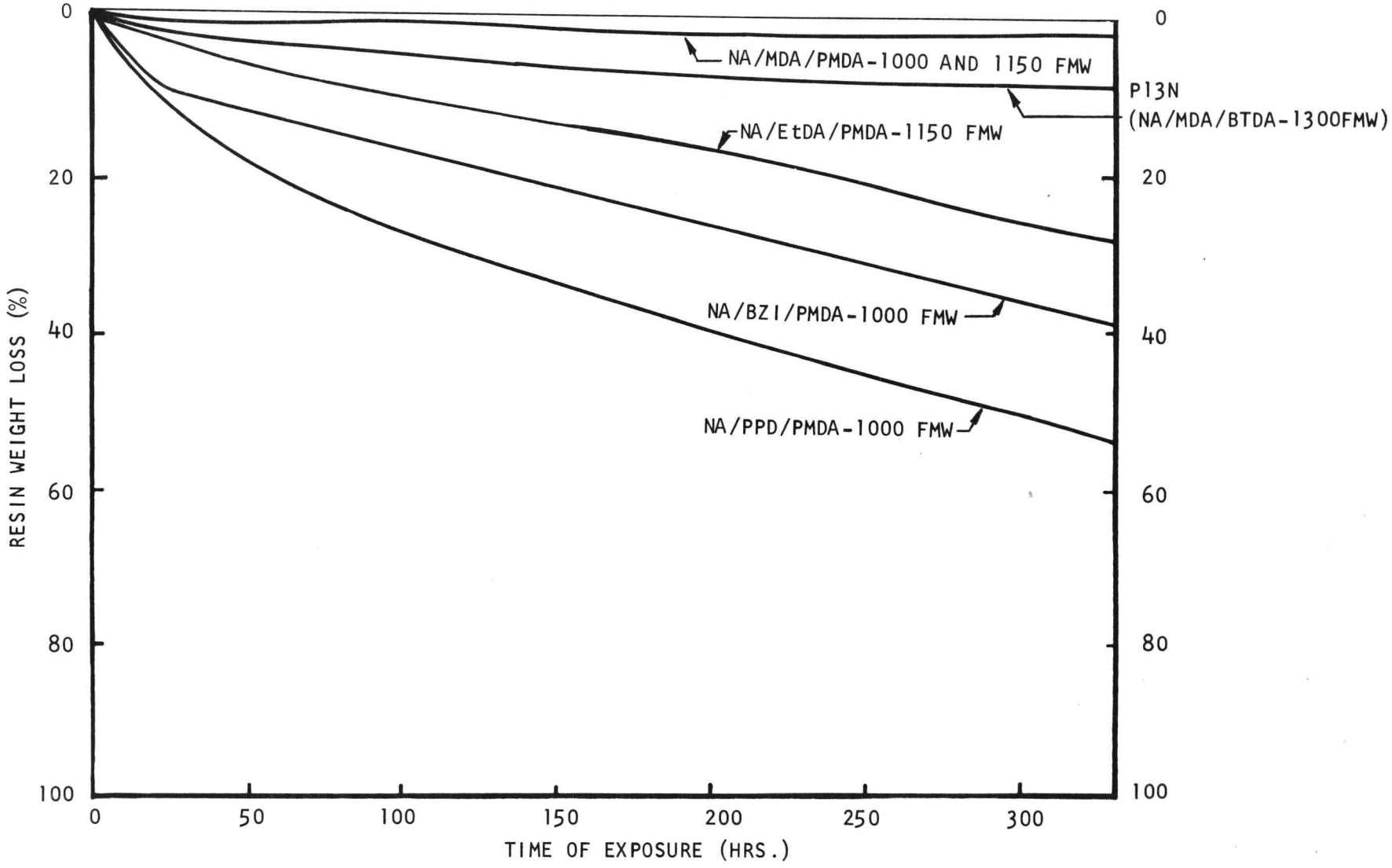


FIGURE 7 PLOT OF RESIN WEIGHT LOSS AS A FUNCTION OF ISOTHERMAL EXPOSURE AT 600°F IN AIR (100 cc/MIN FLOW).

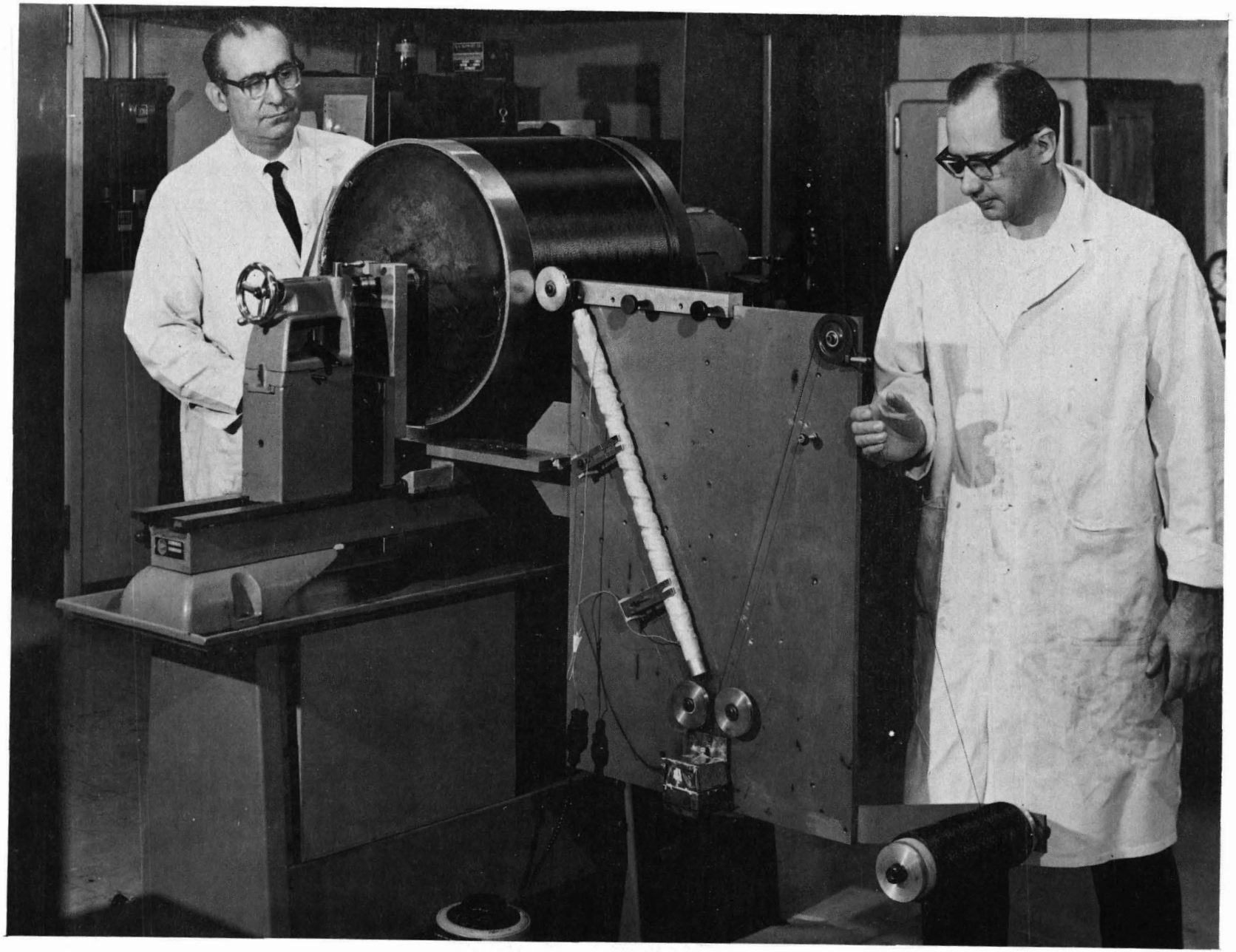
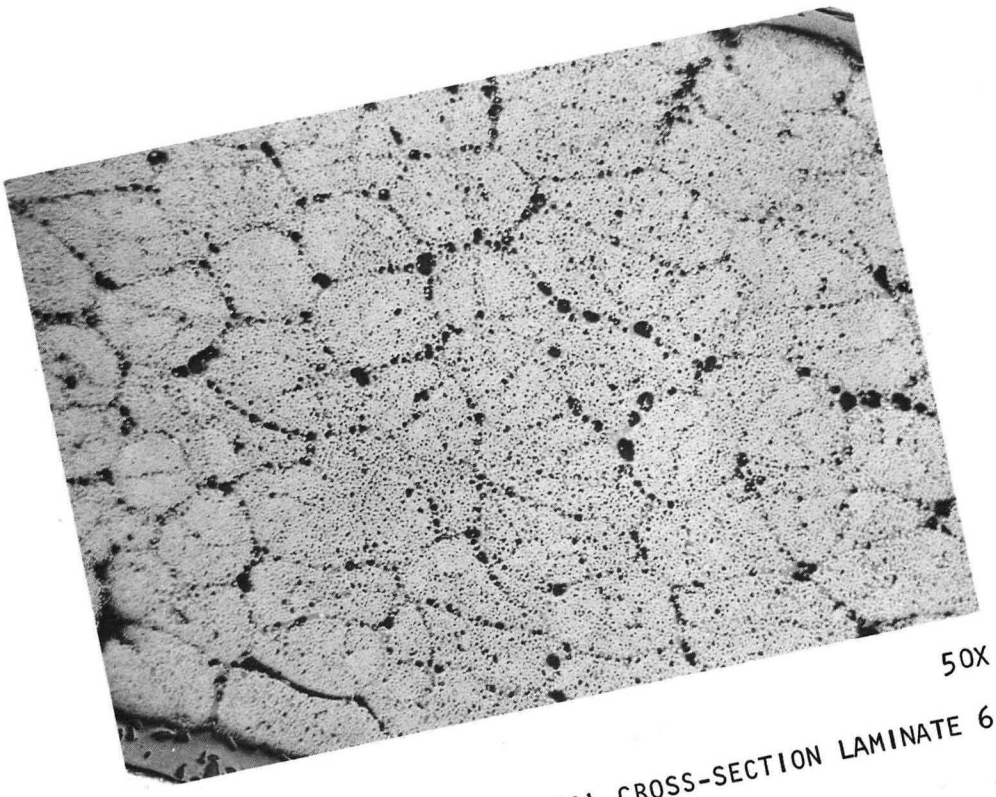
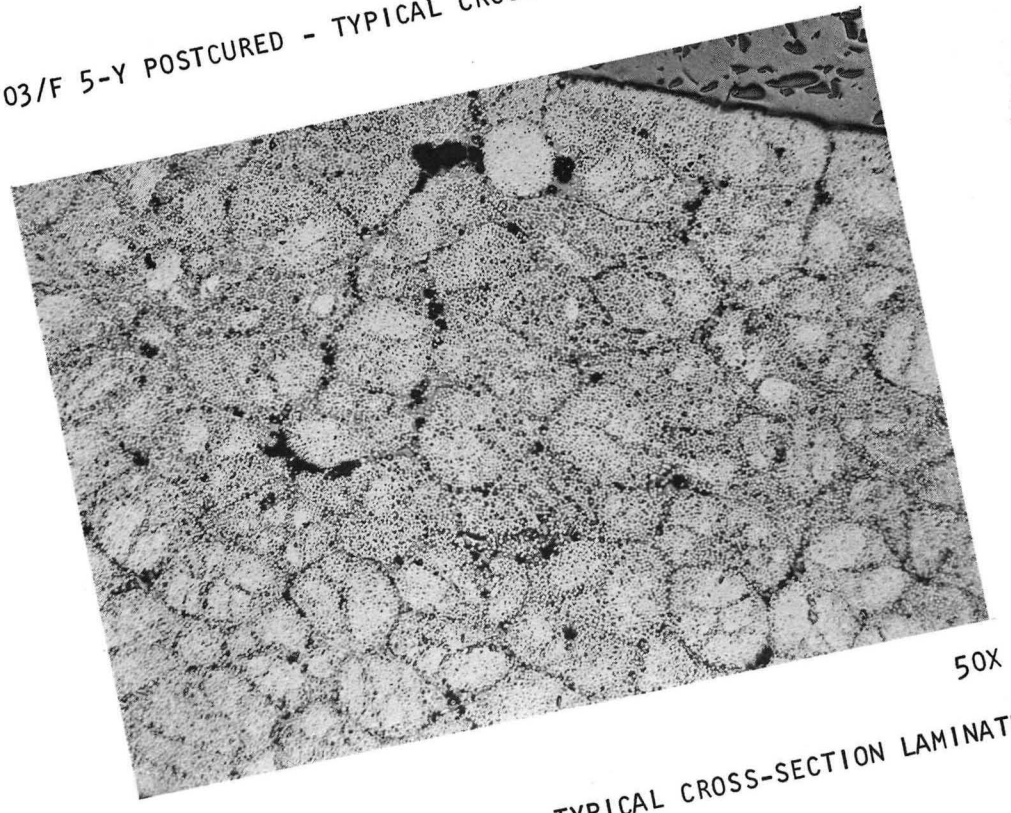


FIGURE 8 DRUM WINDING APPARATUS



50X

703/F 5-Y POSTCURED - TYPICAL CROSS-SECTION LAMINATE 6



50X

703/F 5-Y NOT POSTCURED - TYPICAL CROSS-SECTION LAMINATE 5

FIGURE 9 PHOTOMICROGRAPHS OF 703/F 5-Y COMPOSITES

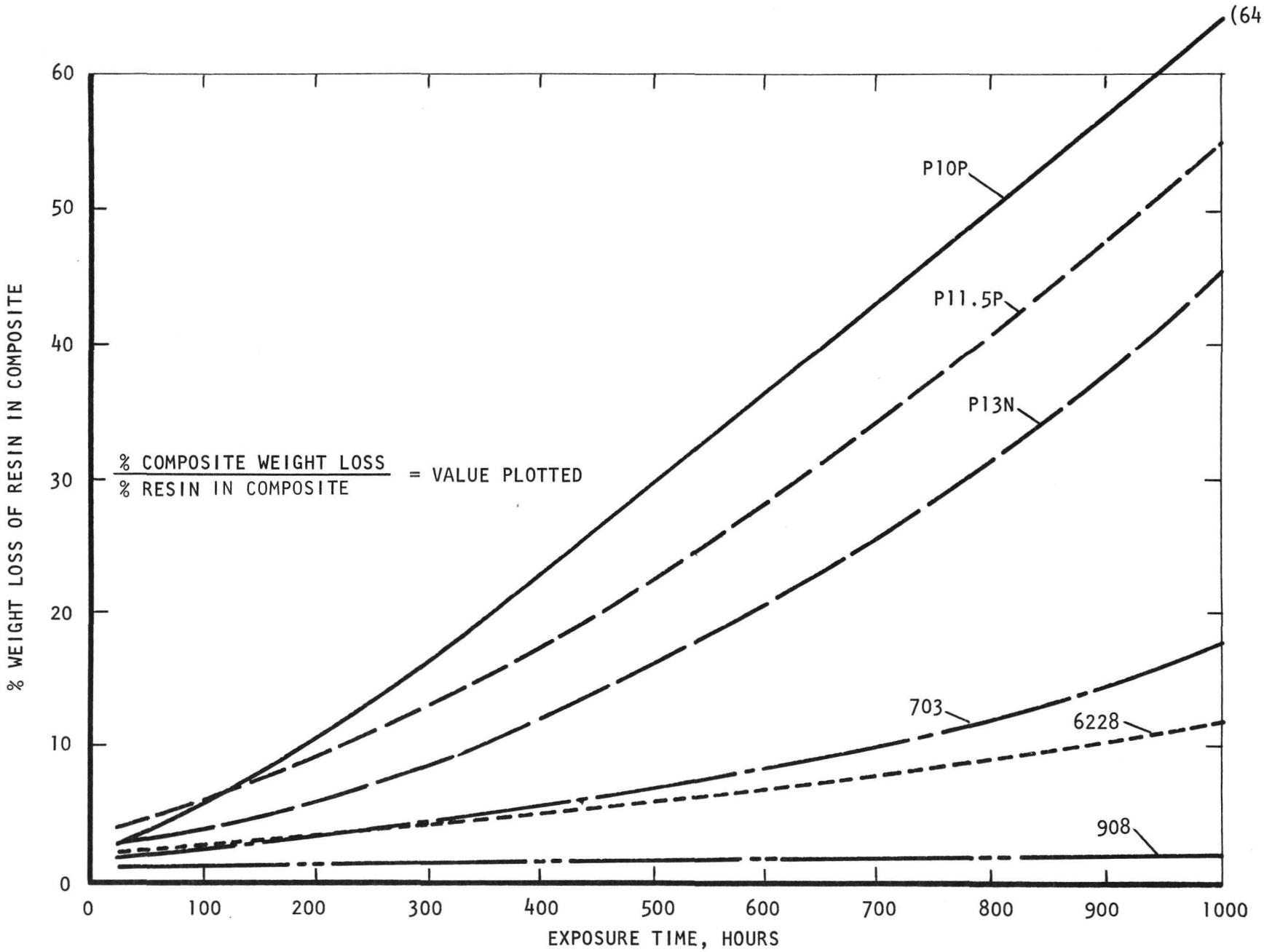
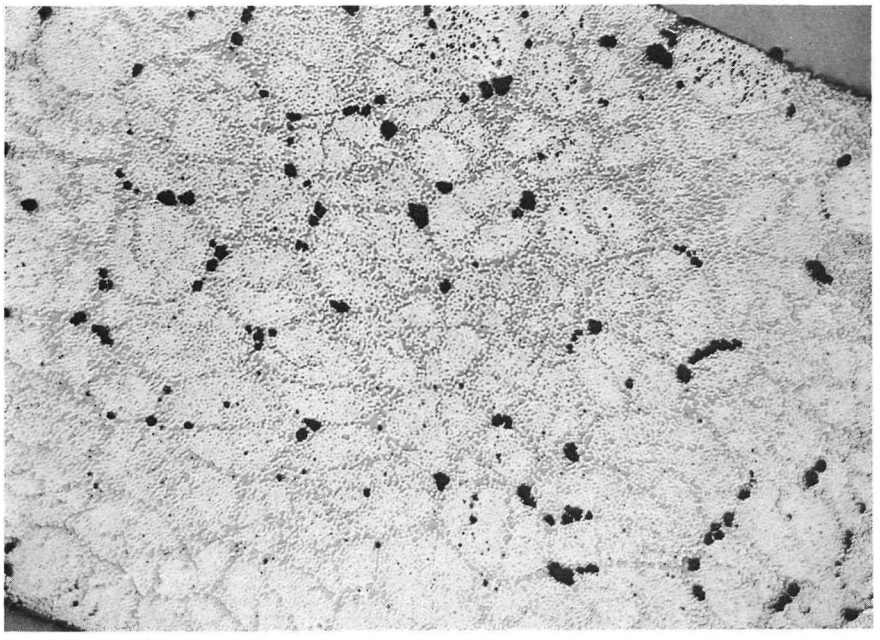


FIGURE 10 600°F ISOTHERMAL COMPOSITE EXPOSURE IN AIR



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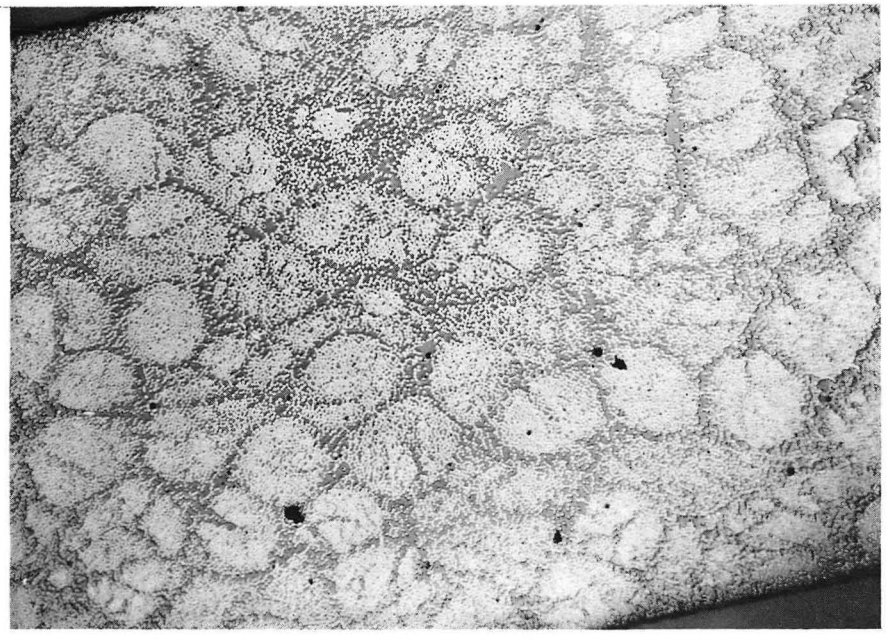
P13N/F 5-Y NOT POSTCURED - TYPICAL CROSS-SECTION LAMINATE 12



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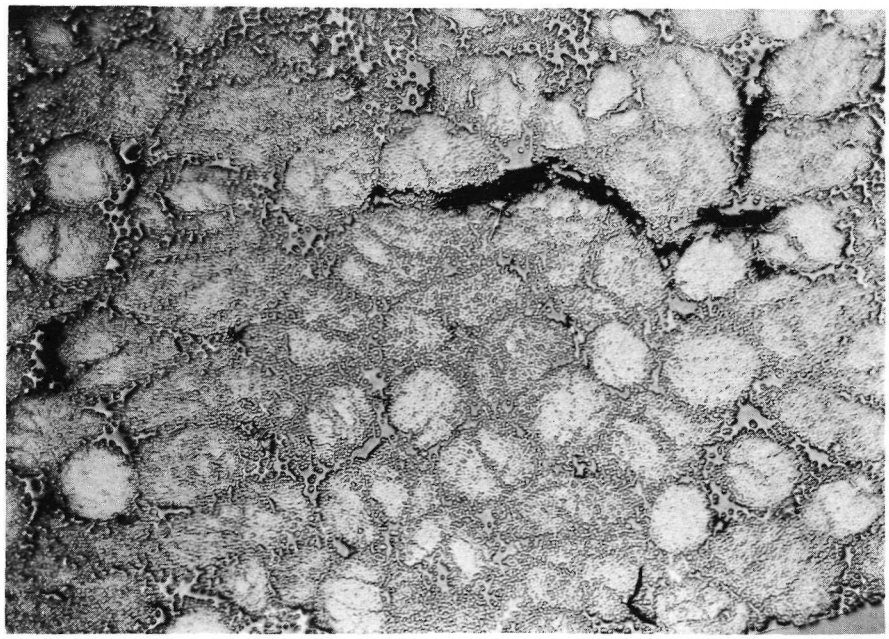
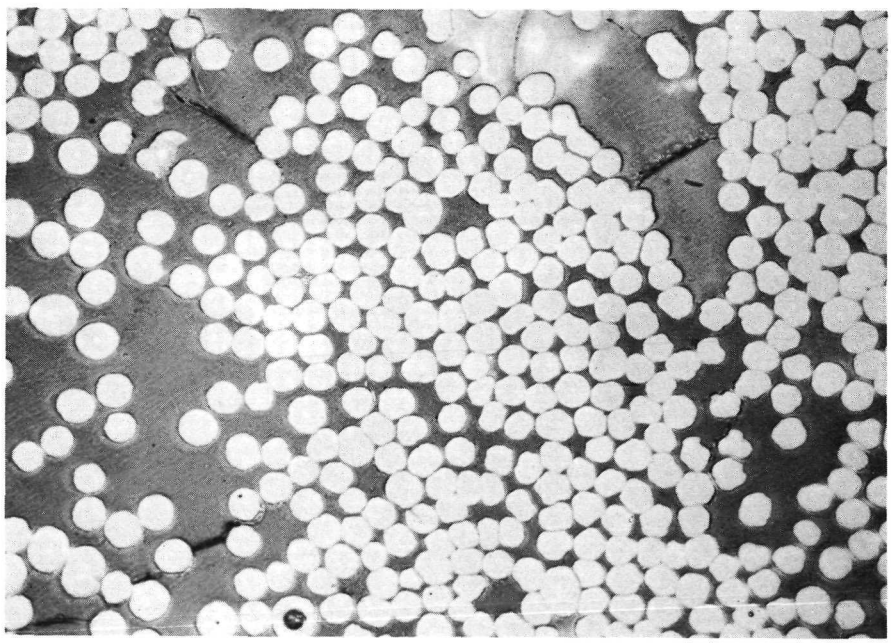
P13N/F 5-Y NOT POSTCURED - TYPICAL CROSS-SECTION LAMINATE 13

FIGURE 11 PHOTOMICROGRAPHS OF P13N/F 5-Y COMPOSITES



50X

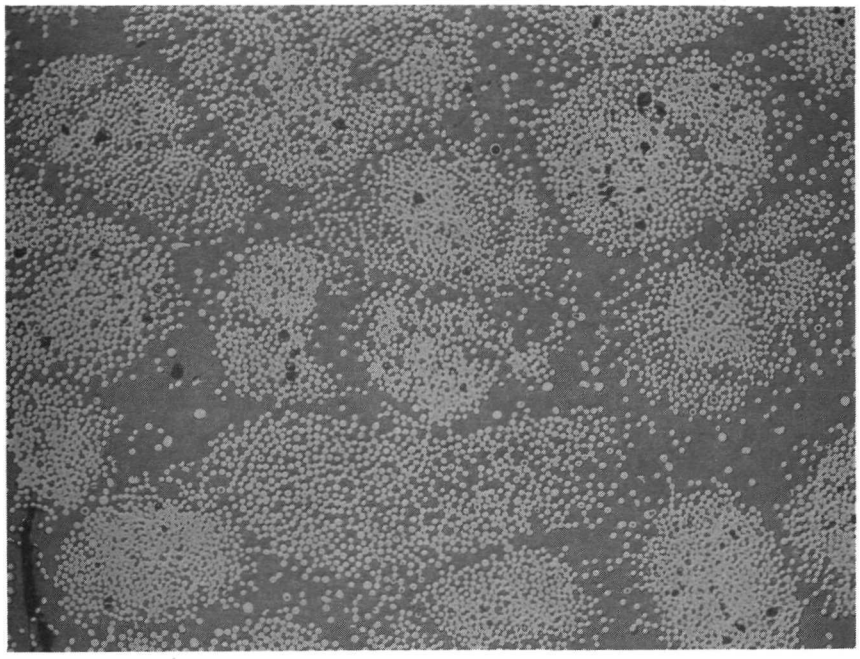
FIGURE 12A GR-908/F 5-Y POSTCURED
TYPICAL CROSS-SECTION LAMINATE 16



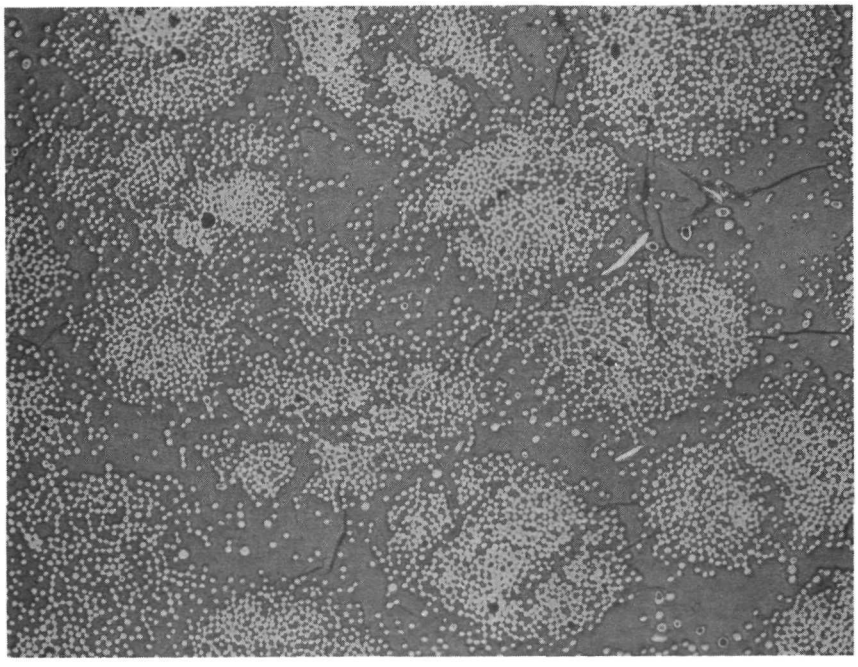
500X

FIGURE 12B GR-908/F 5-Y POSTCURED LAMINATE 16

FIGURE 12 PHOTOMICROGRAPHS OF GR-909/F 5-Y COMPOSITES

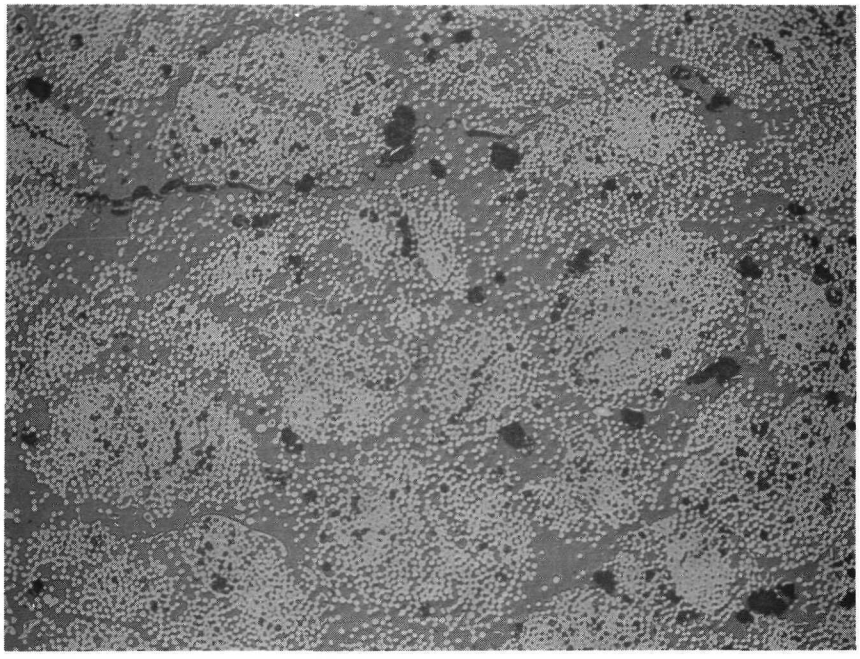


AFTER POSTCURE 100X

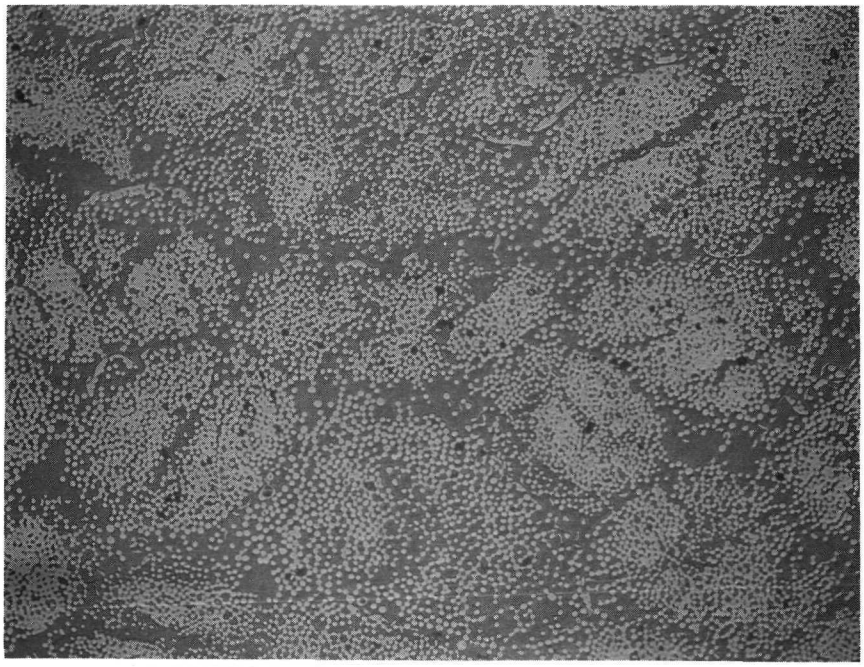


BEFORE POSTCURE 100X

FIGURE 13 RS6228/F5Y TYPICAL CROSS-SECTION OF LAMINATE 8/4

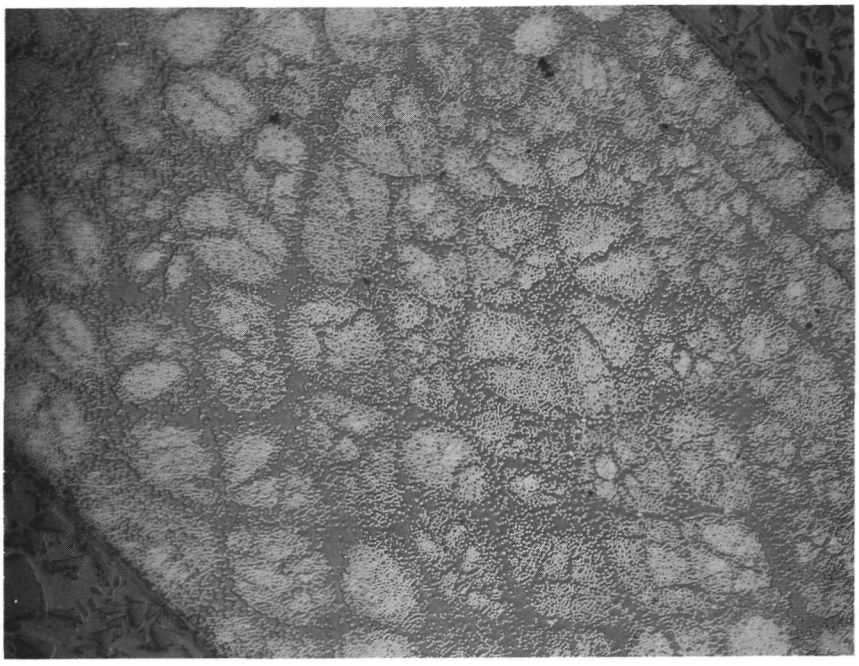


AFTER POSTCURE 100X



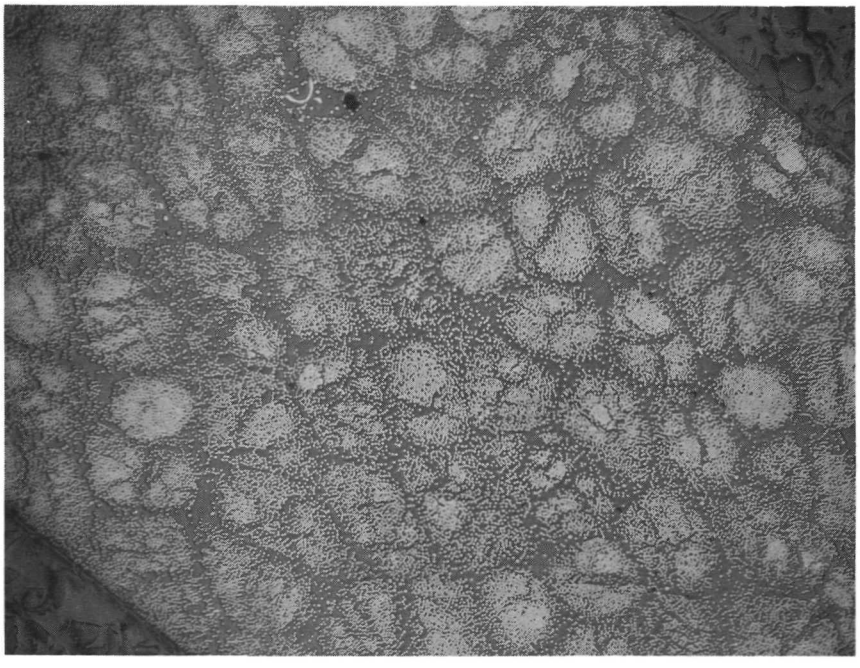
BEFORE POSTCURE 100X

FIGURE 14 RS6228/F5Y TYPICAL CROSS-SECTION OF LAMINATE 12/1



50X

P10P/F5Y TYPICAL CROSS-SECTION OF LAMINATE R2/L1



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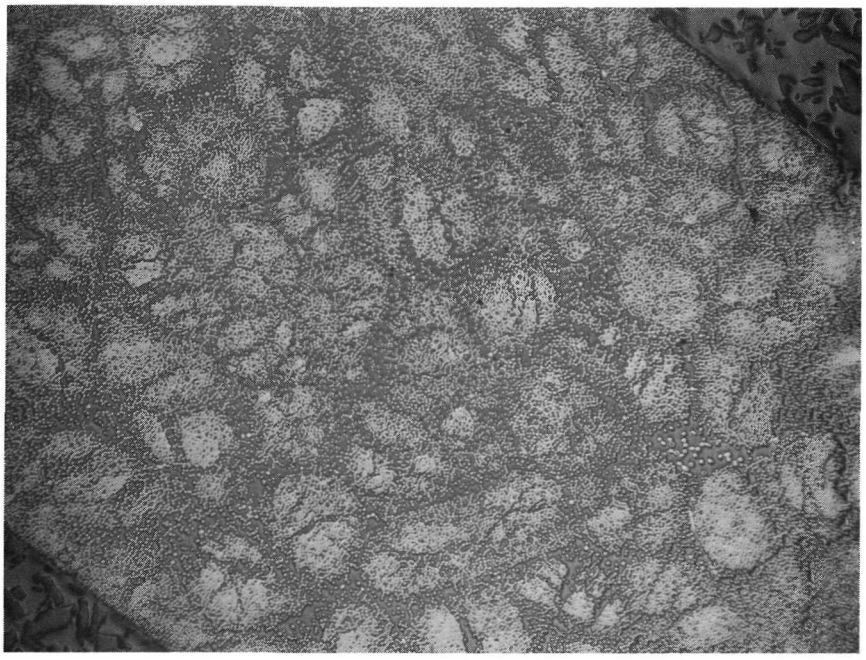
P10P/F5Y TYPICAL CROSS-SECTION OF LAMINATE R2/L3

FIGURE 15 PHOTOMICROGRAPHS OF P10P/F5Y LAMINATES



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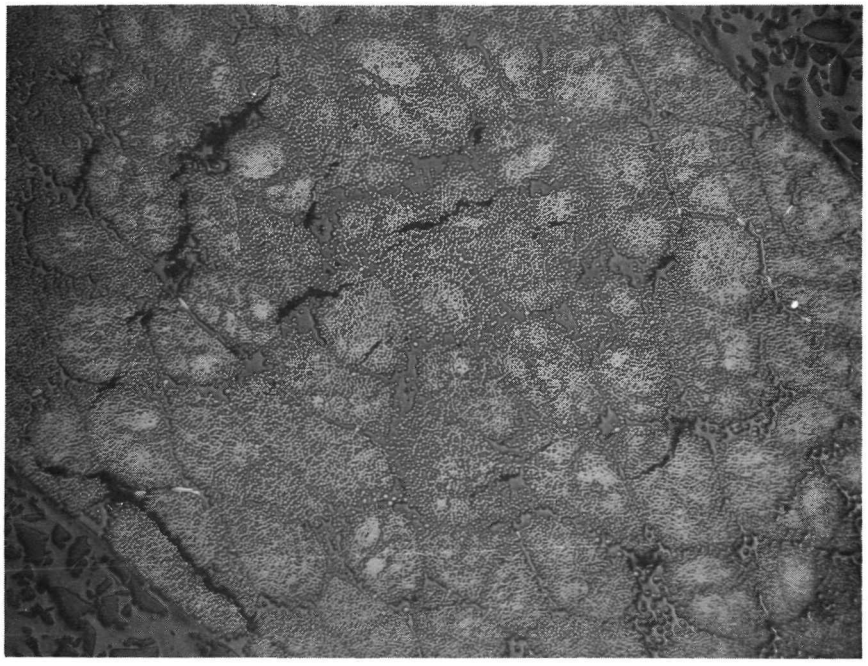
P11.5P/F5Y TYPICAL CROSS-SECTION OF LAMINATE R2/L1



50X

P11.5P/F5Y TYPICAL CROSS-SECTION OF LAMINATE R2/L2

FIGURE 16 PHOTOMICROGRAPHS OF P11.5P/F5Y LAMINATES

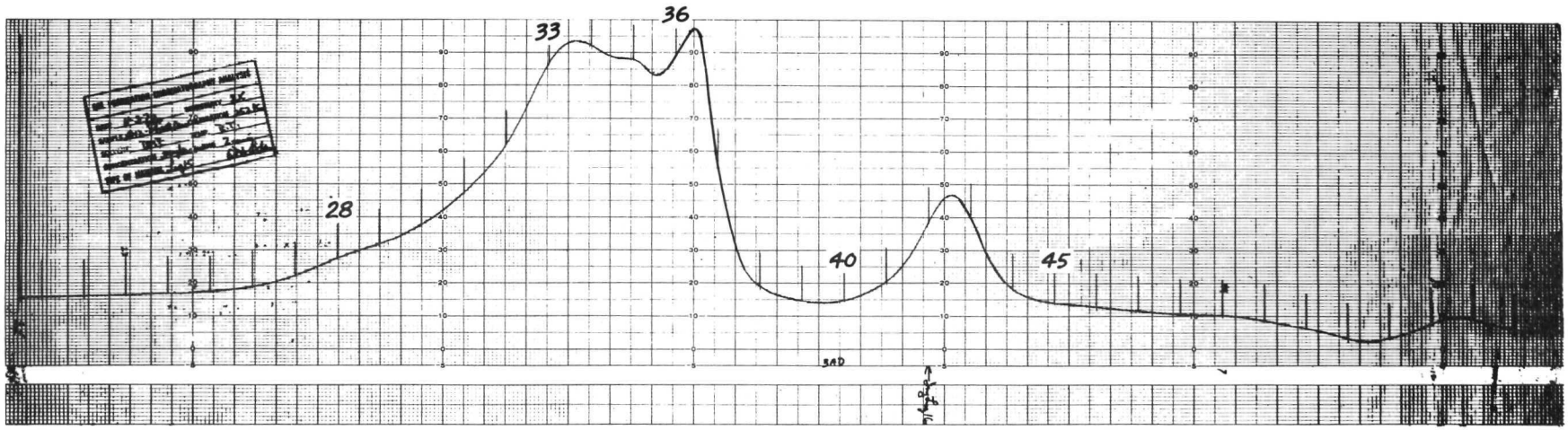


FIGURE 17 GPC TRACING OF PIOP AMIDE-ACID VARNISH

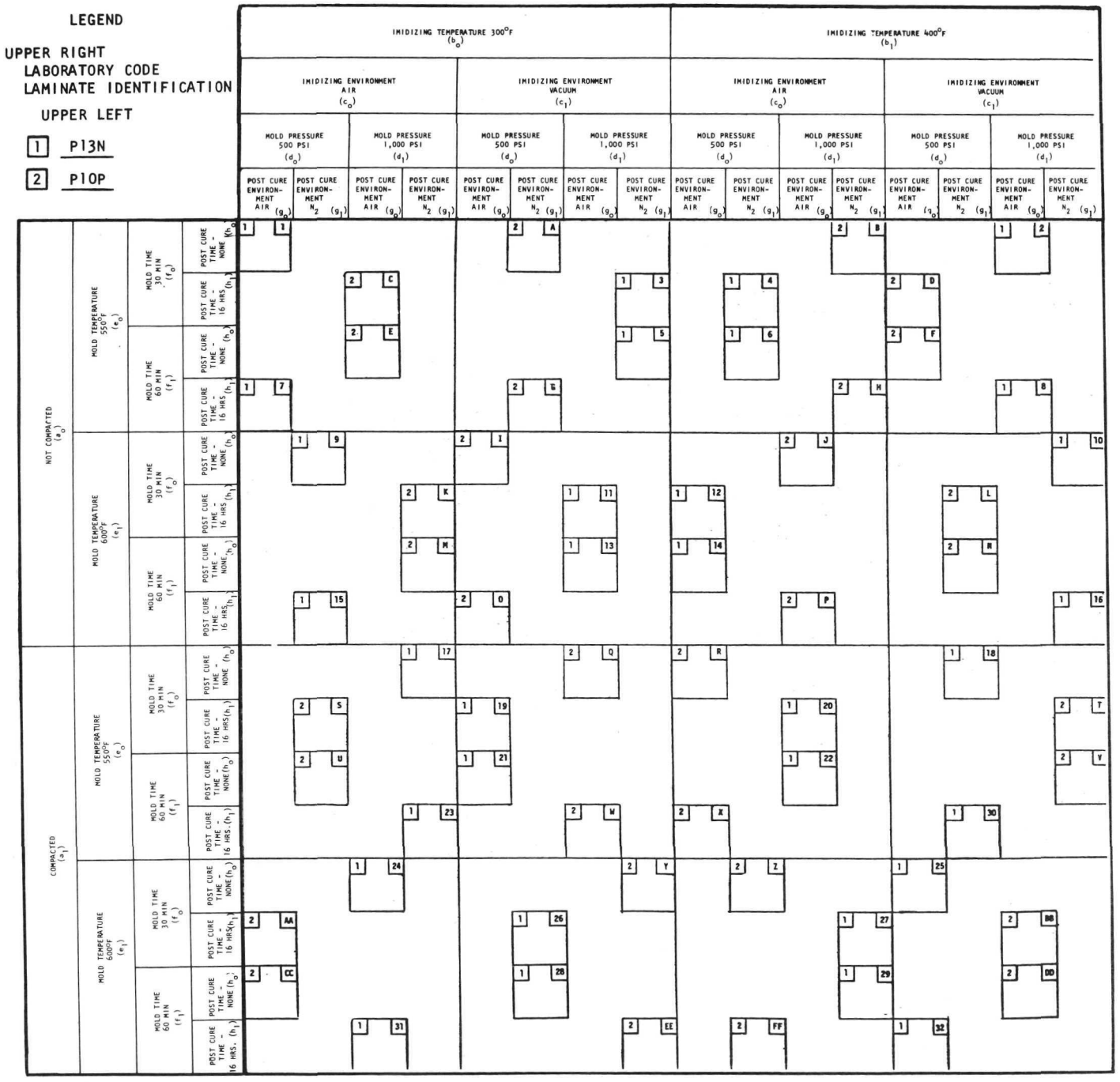


FIGURE 18 SCHEMATIC OF FRACTIONAL FACTORIAL EXPERIMENT

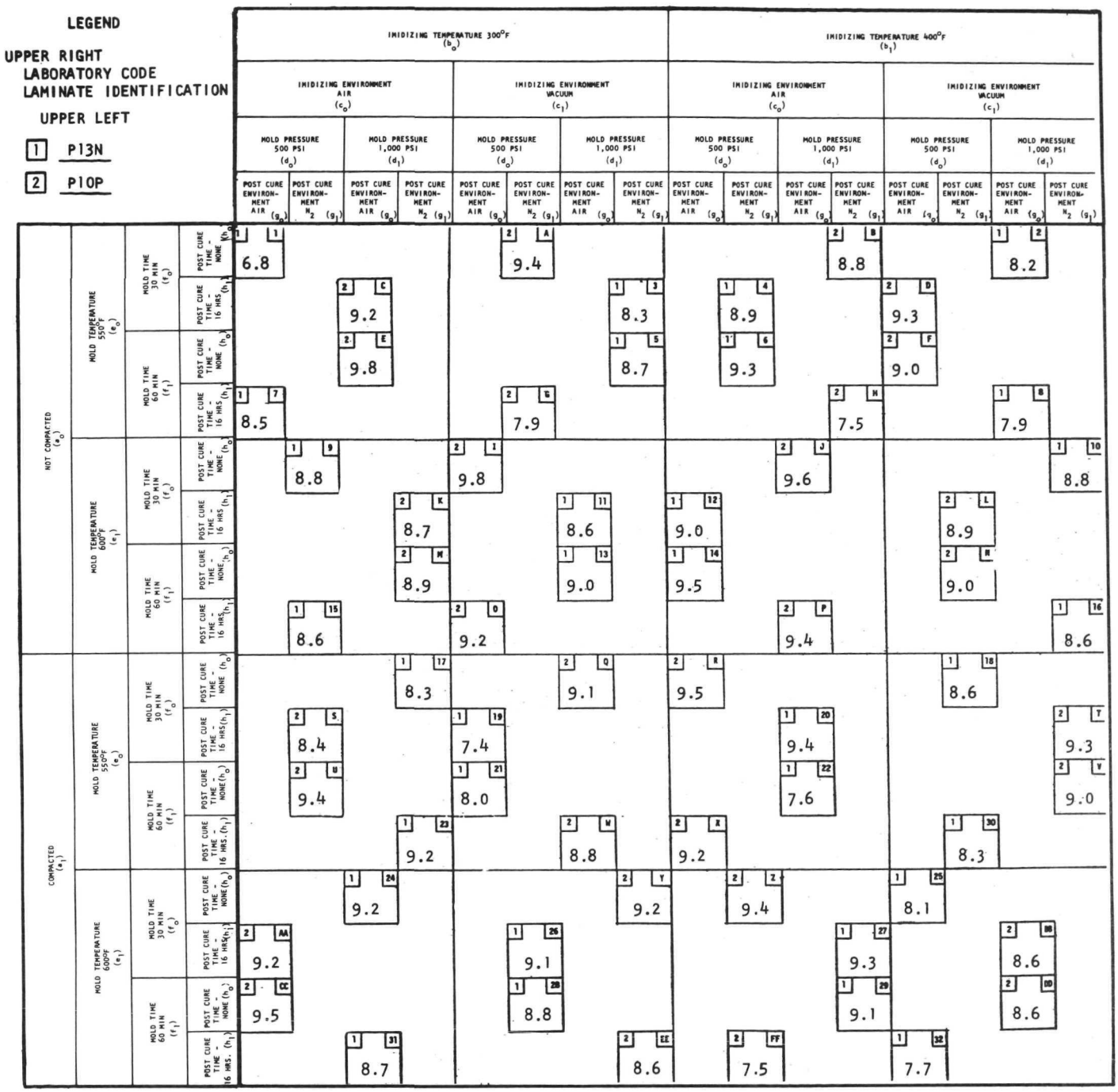


FIGURE 19 SHORT BEAM SHEAR STRENGTH AT ROOM TEMPERATURE (KSI)

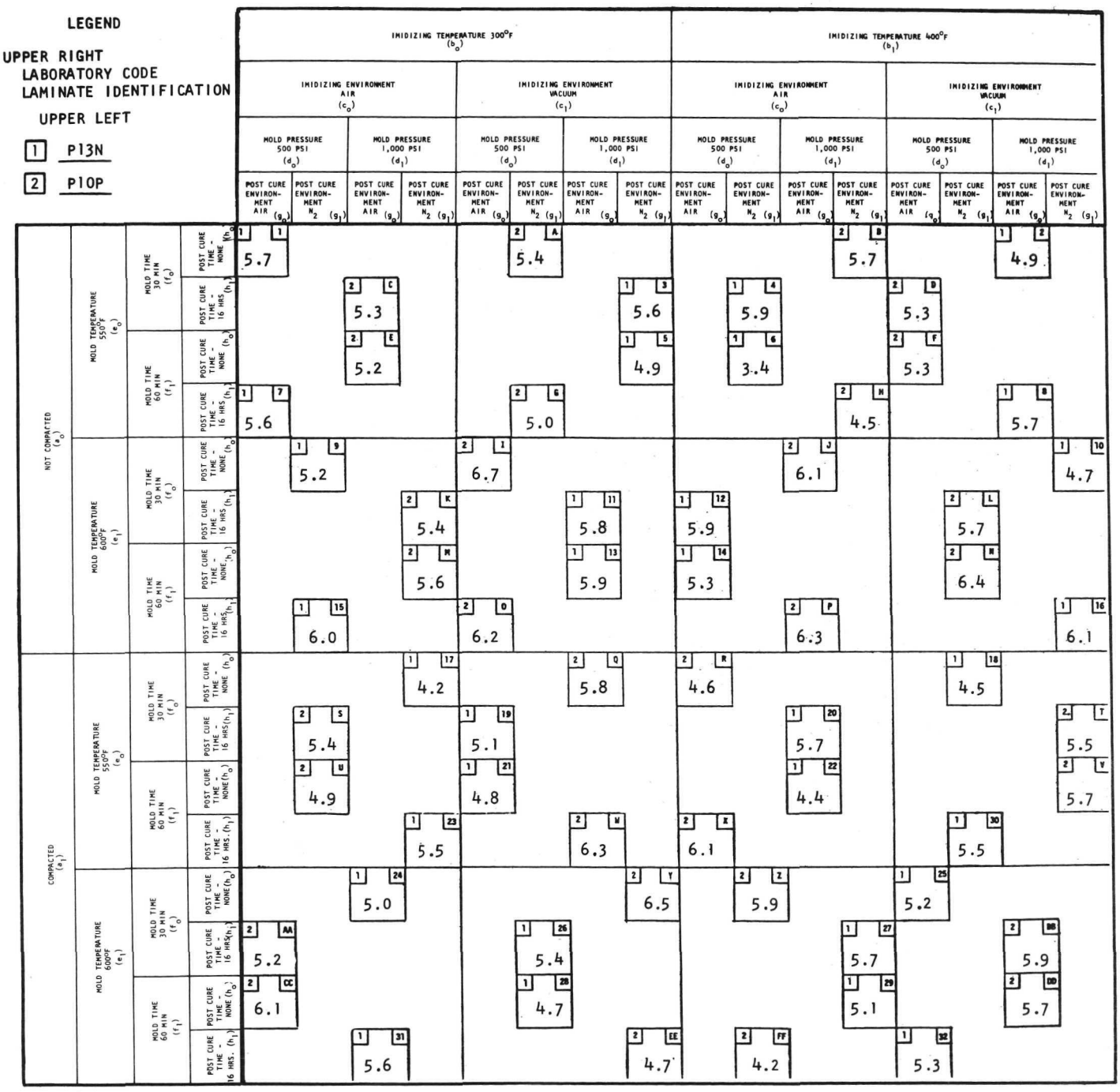


FIGURE 20 SHORT BEAM SHEAR STRENGTH AT 600°F (KSI)

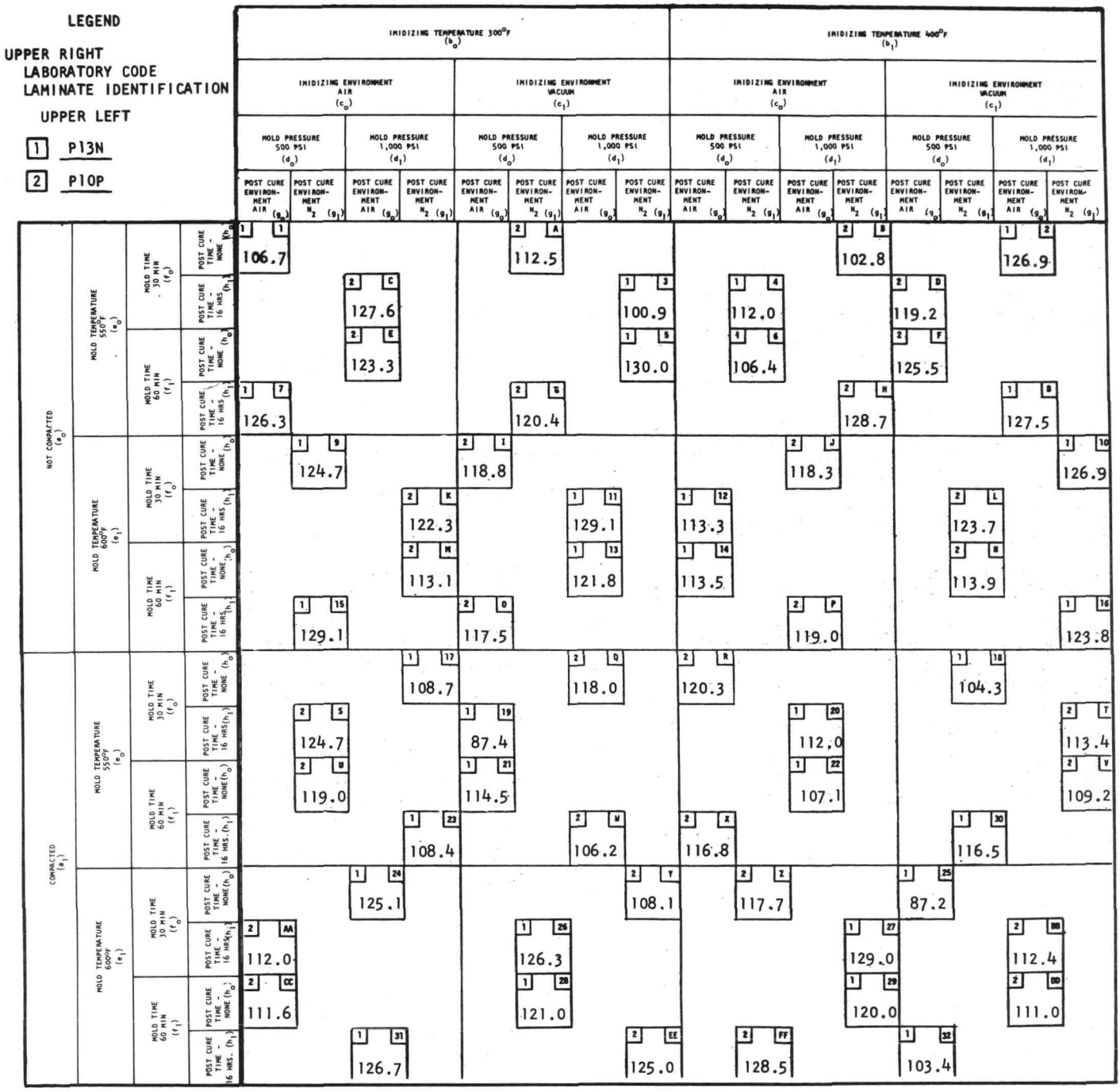


FIGURE 21 ULTIMATE FLEXURE STRENGTH AT ROOM TEMPERATURE (KSI)

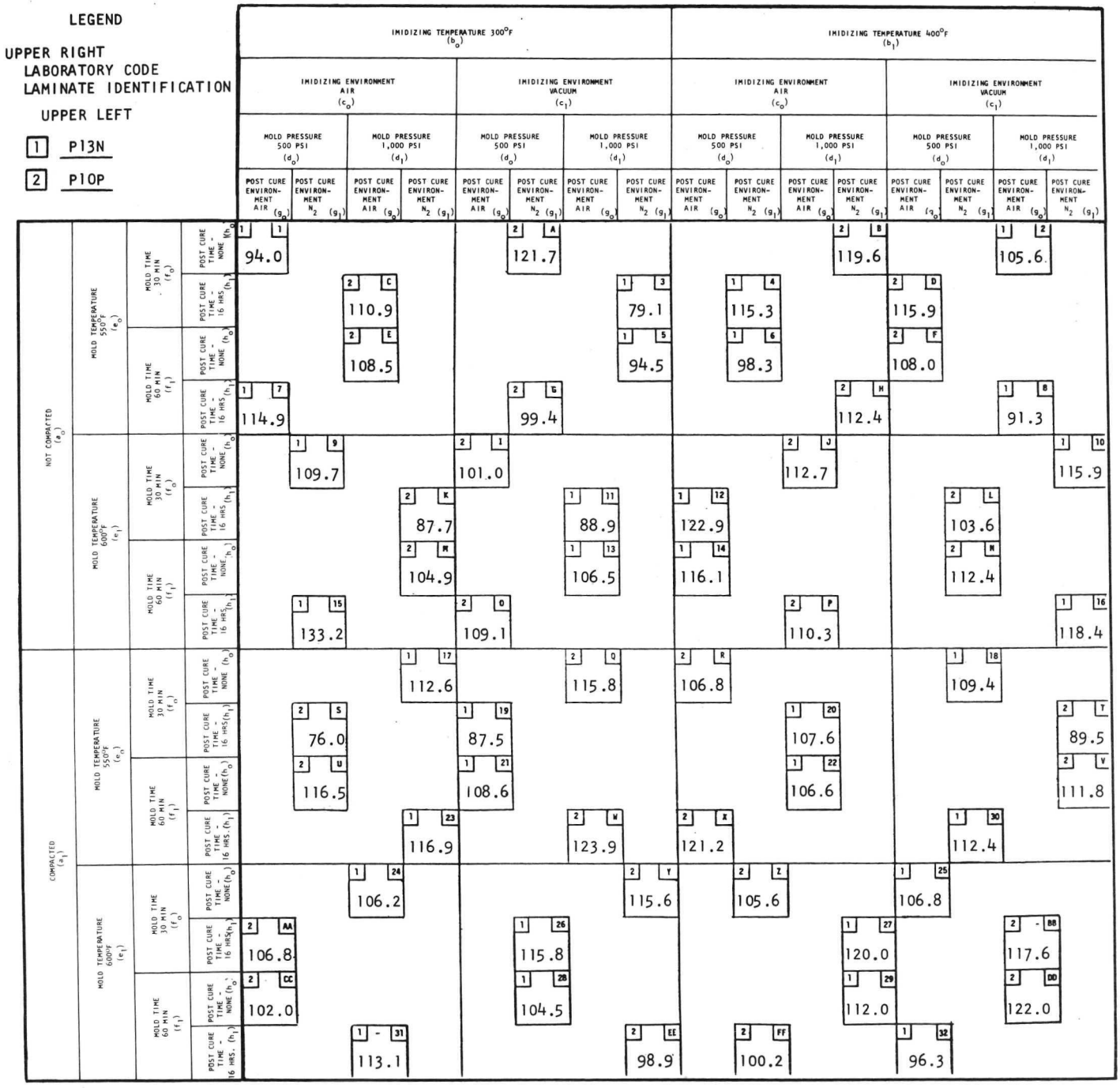


FIGURE 22 ULTIMATE FLEXURE STRENGTH AT 600°F (KSI)

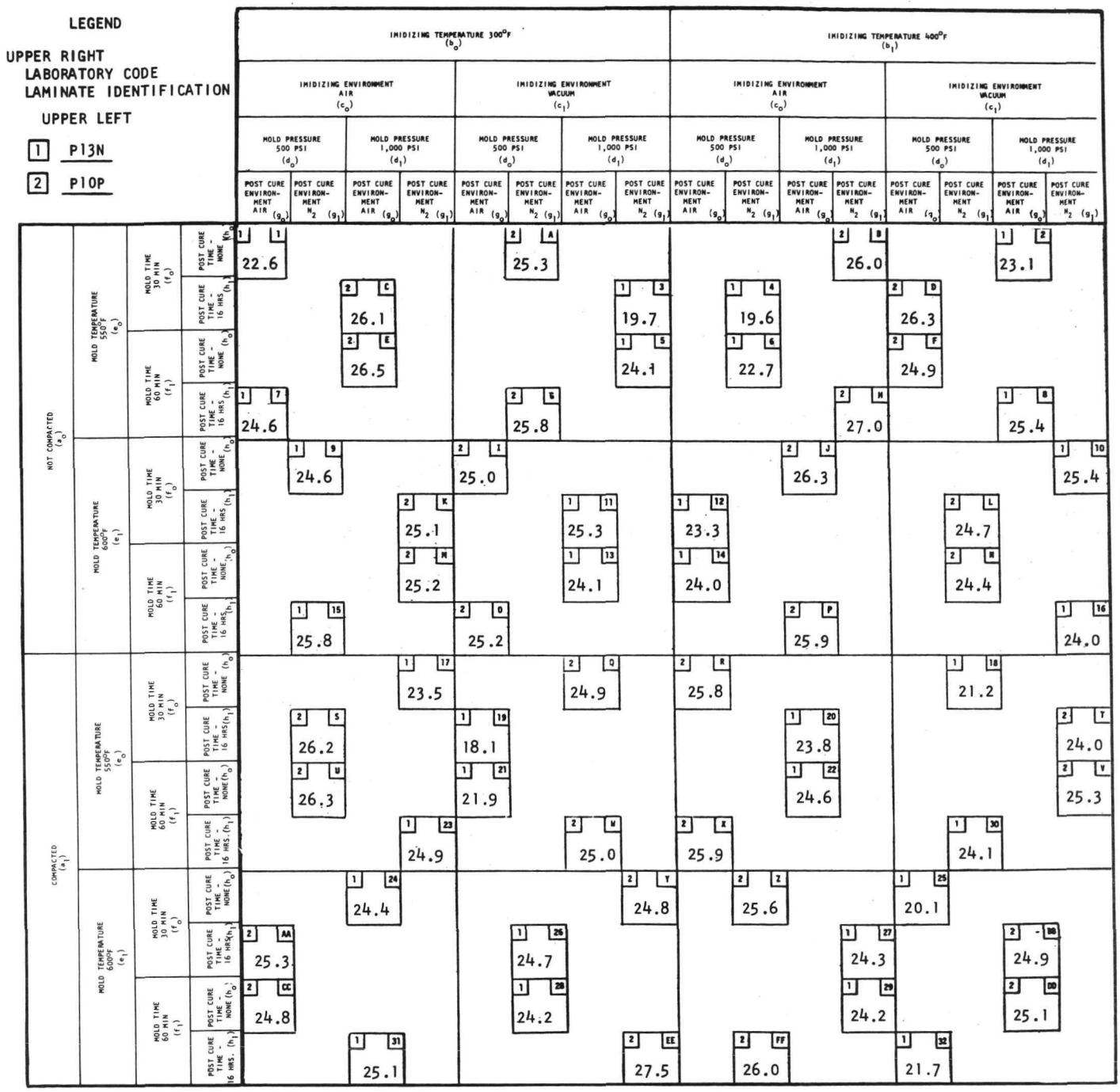


FIGURE 23 FLEXURE MODULUS AT ROOM TEMPERATURE (MSI)

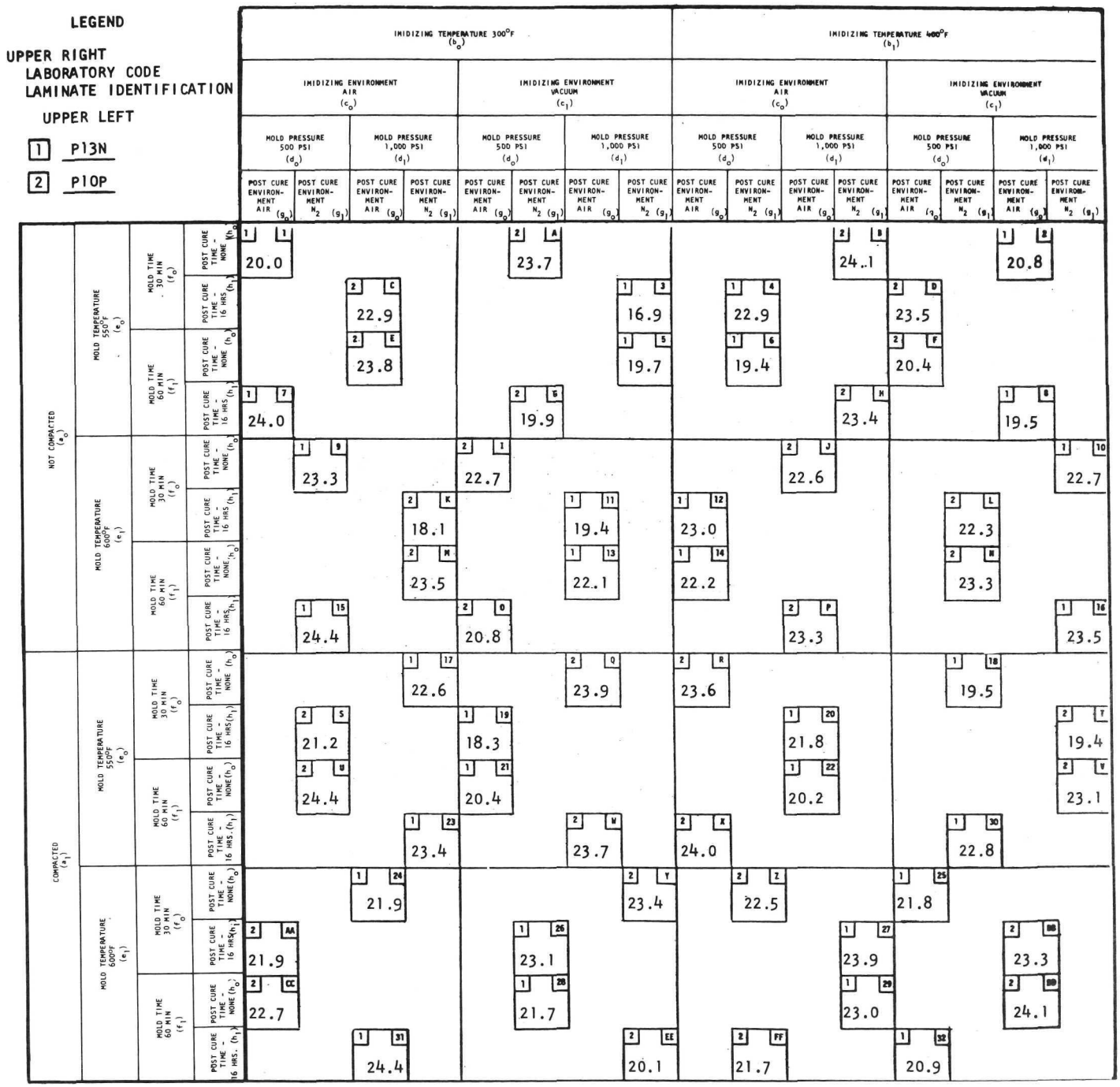


FIGURE 24 FLEXURE MODULUS AT 600°F (MSI)

FIGURE 25

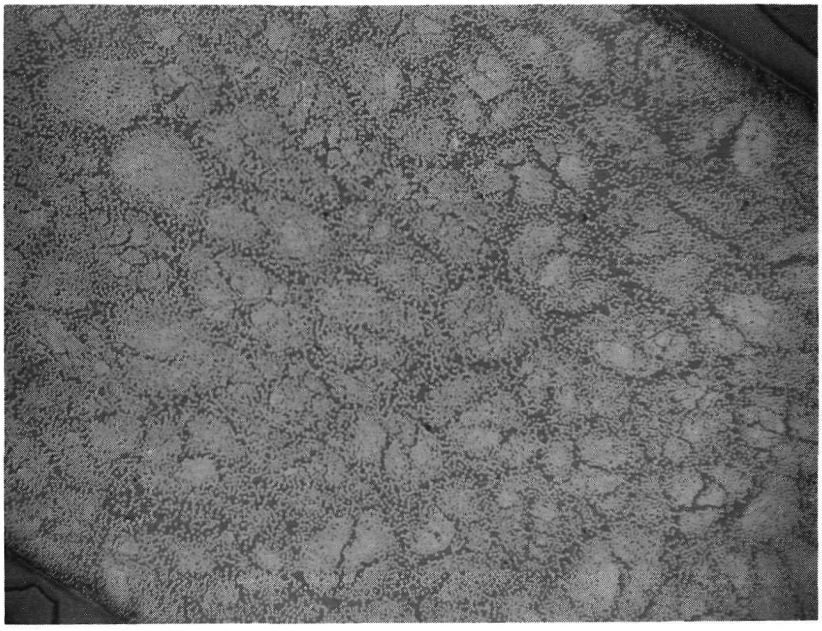
TASK III COMPOSITE CHARACTERIZATION TEST PLAN

TEST TEMP. °F	EXPOSURE TIME HOURS	LAMINATE NUMBER	LONGITUDINAL TENSILE	LONGITUDINAL COMPRESSION	TRANSVERSE TENSILE	SHEAR	THERMAL EXPANSION	LONGITUDINAL FLEXURE	FATIGUE	
									LONGI.	0/90
75	--	51	5[1] (3/3)[2]	5 (1/3)	5 (3/3)	5 Torsion 10 SBS(3)		5	12 (Lam.#47)	12 (Lam.#50)
500	0	53	5	5	5	5 SBS		5		
	740	35	5	5	5	5 SBS		5		
	840	44	5	5	5	5 SBS		5		
	1000	41	5 (1/3)	5	5 (1/3)	5 SBS				
550	0	55	5	5	5	5 SBS		5		
	740	36	5	5	5	5 SBS		5		
	840	37	5	5	5	5 SBS		5		
	1000	39	5	5	5	5 SBS		5		
600	0		5 (Lam. #64A)	5 (Lam. #64B)		5 SBS (Lam.#63A)	2 at 0° 2 at 90°	5 (Lam.#63A,53)		
	150	46	5	5	---	5 SBS	(Lam.#48)	5		
	300	45	5	5	---	5 SBS		5		

[1] Total number of individual specimens to be tested.

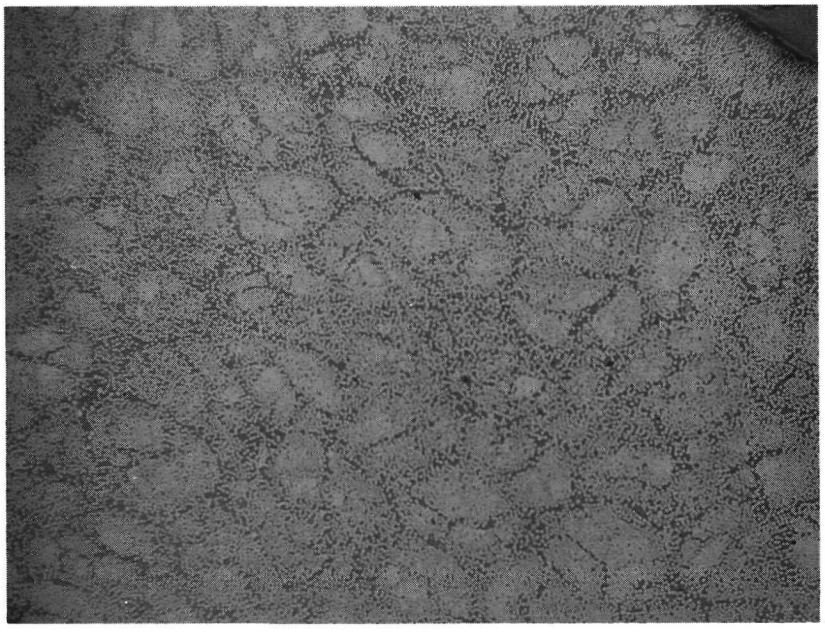
[2] Figures in parenthese refer to the selected specimen to be strain gaged; e.g. (3/3) indicates three specimens with three strain gages each.

[3] SBS = Short Beam Shear



50X

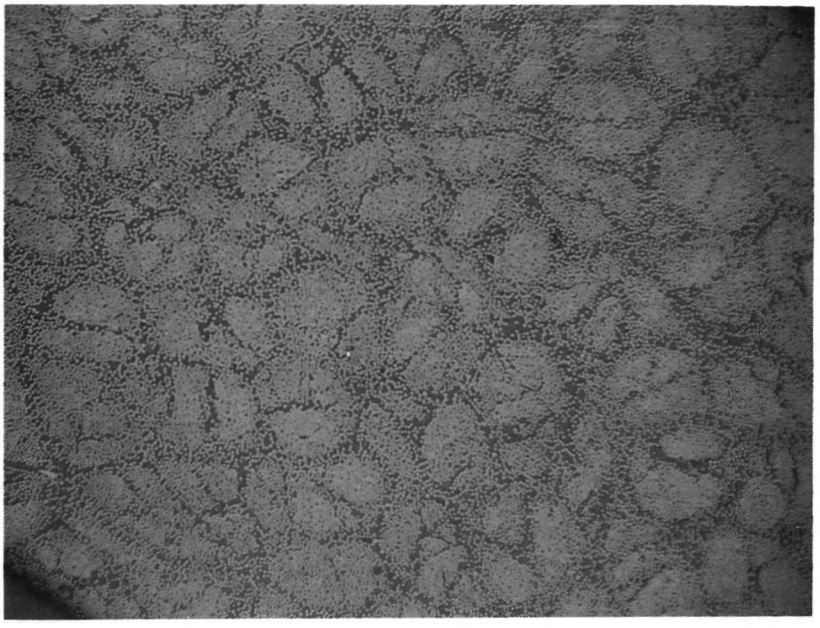
LAMINATE 45



50X

LAMINATE 46

FIGURE 26 PHOTOMICROGRAPHS OF CROSS-SECTION OF UNIDIRECTIONAL P10P/F 5-Y LAMINATES



LAMINATE 51 50X

FIGURE 27 PHOTOMICROGRAPH OF CROSS-SECTION OF UNIDIRECTIONAL P10P/F 5-Y LAMINATE

LAMINATE 50 50X

FIGURE 28 PHOTOMICROGRAPH OF CROSS-SECTION OF $0^{o}/90^{o}$ CROSS-PLIED P10P/F 5Y LAMINATE

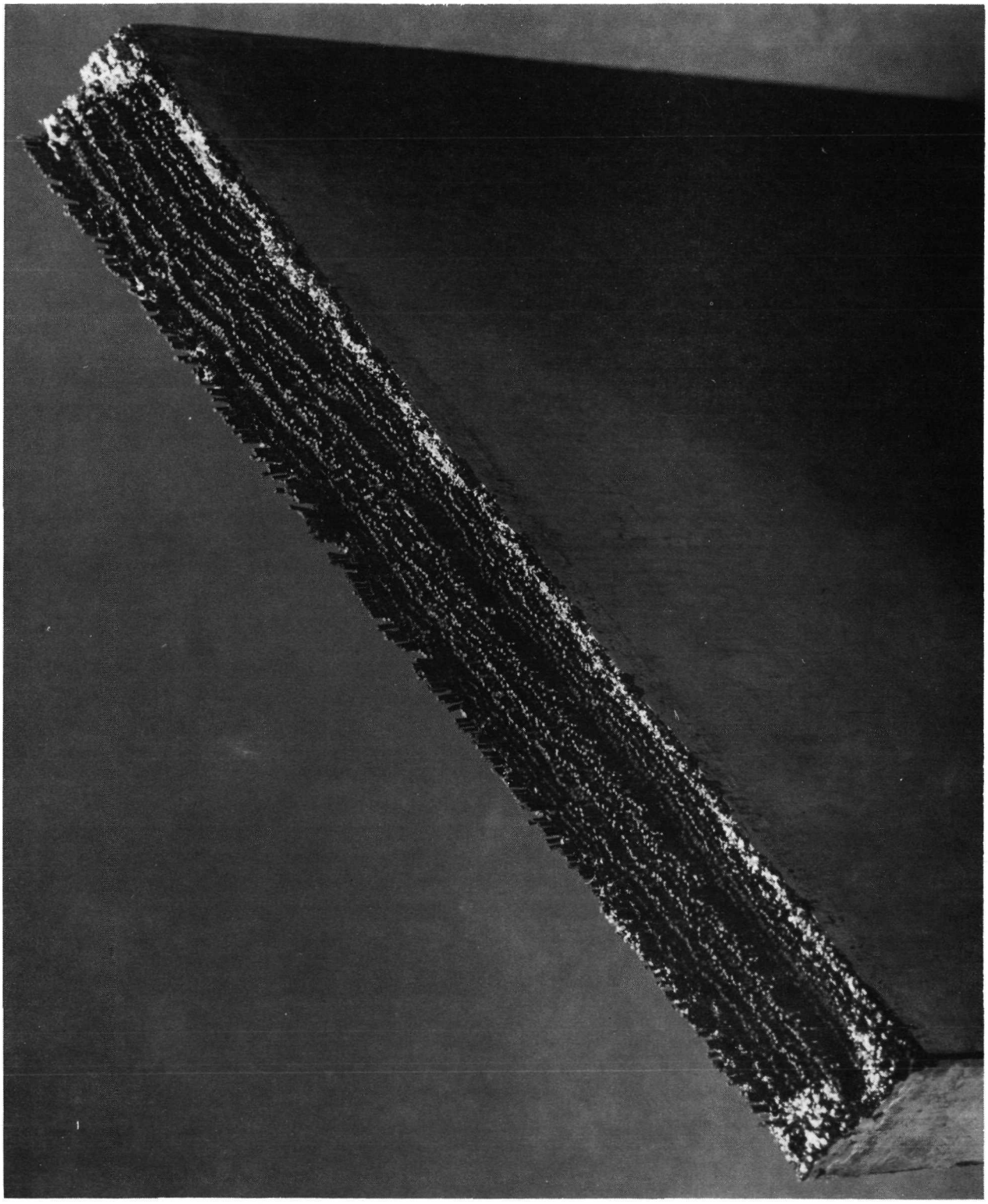


FIGURE 29 AS MOLDED END-VIEW OF 4" x 4" x 0.480" P10P/F 5-Y LAMINATE

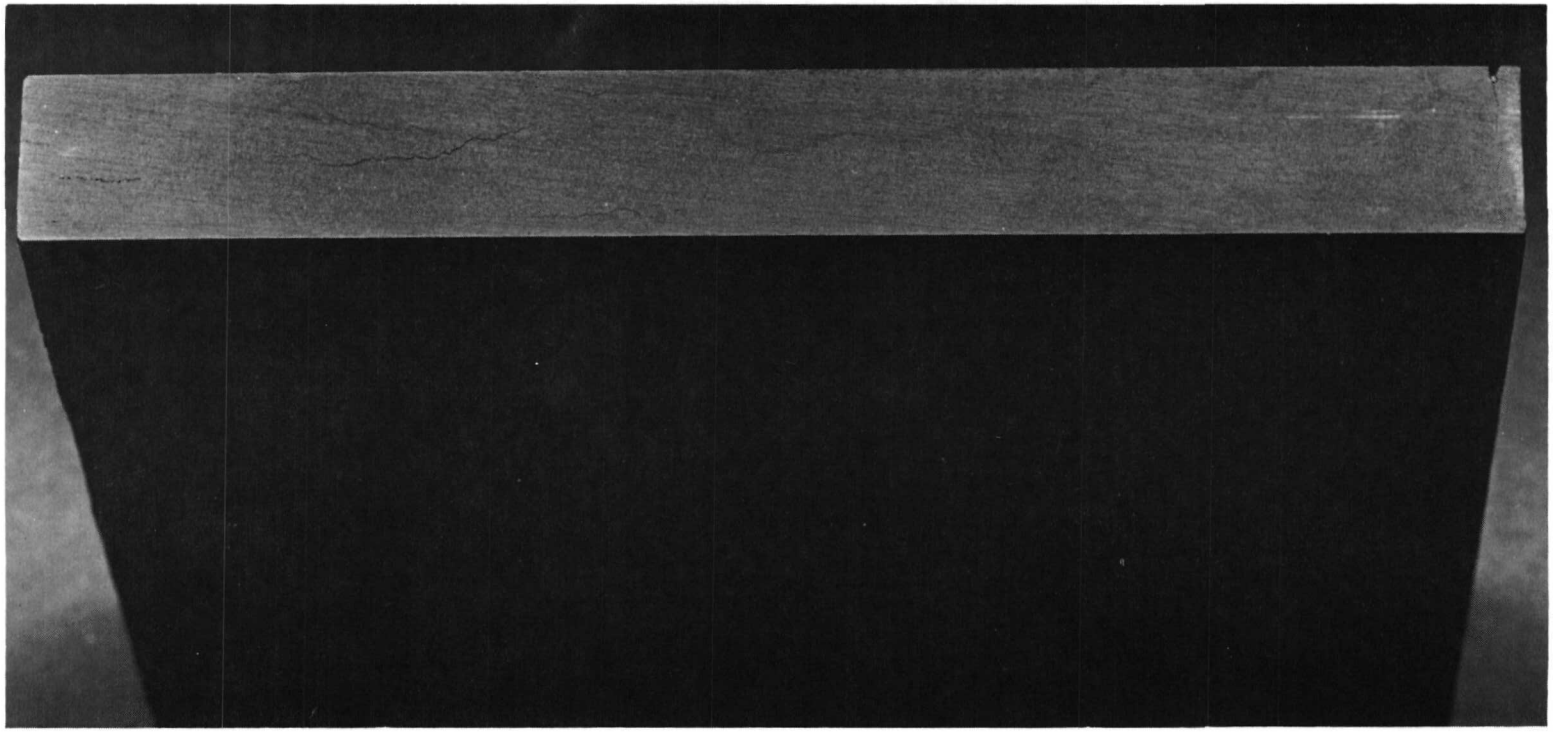
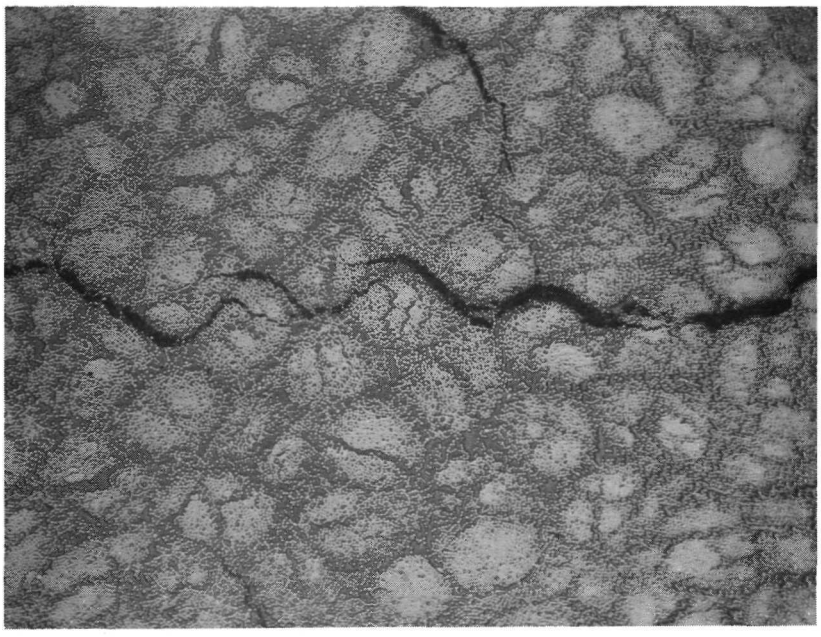
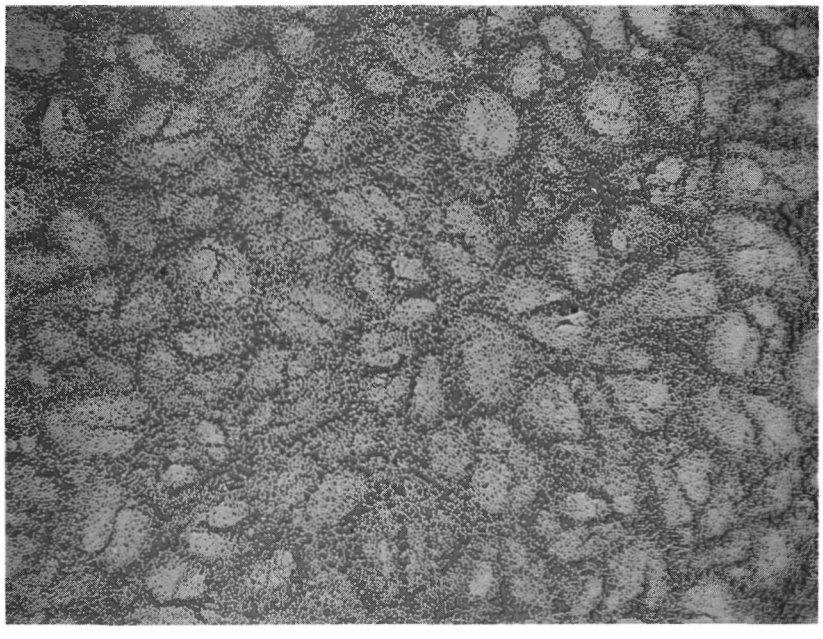


FIGURE 30 POLISHED END VIEW OF 4" x 4" x 0.480" P10P/F 5-Y LAMINATE SHOWING MACRO CRACKING.



(a) 50X



(b) 50X

FIGURE 31 PHOTOMICROGRAPHS OF 4" x 4" x 0.480" LAMINATE SHOWING (a) MACROCRACKS & (b) VOID-FREE APPEARANCE IN NON-CRACKED AREAS.

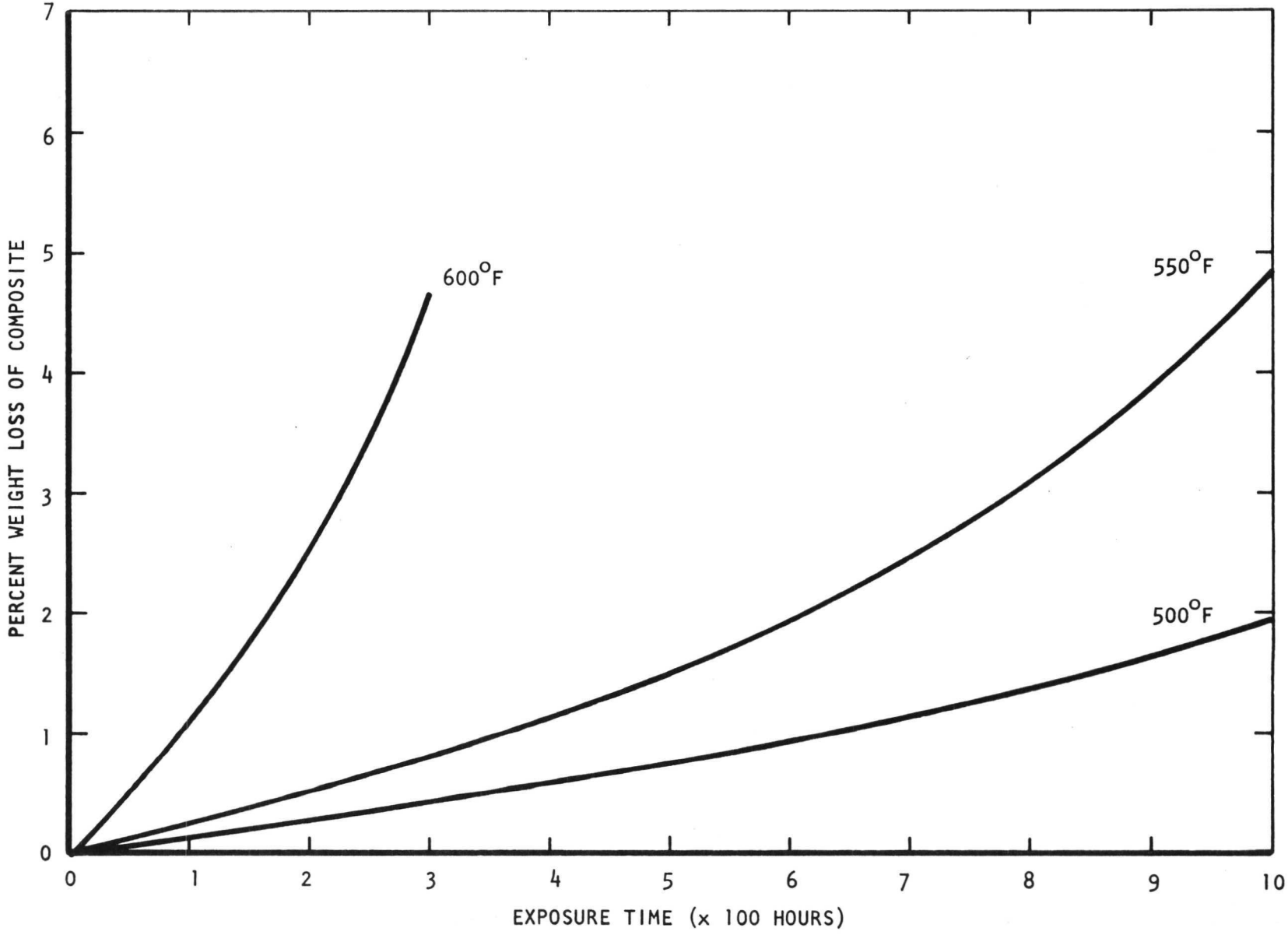


FIGURE 32 ISOTHERMAL WEIGHT LOSS CURVES P10P/FORTAFIL 5-Y IN AIR

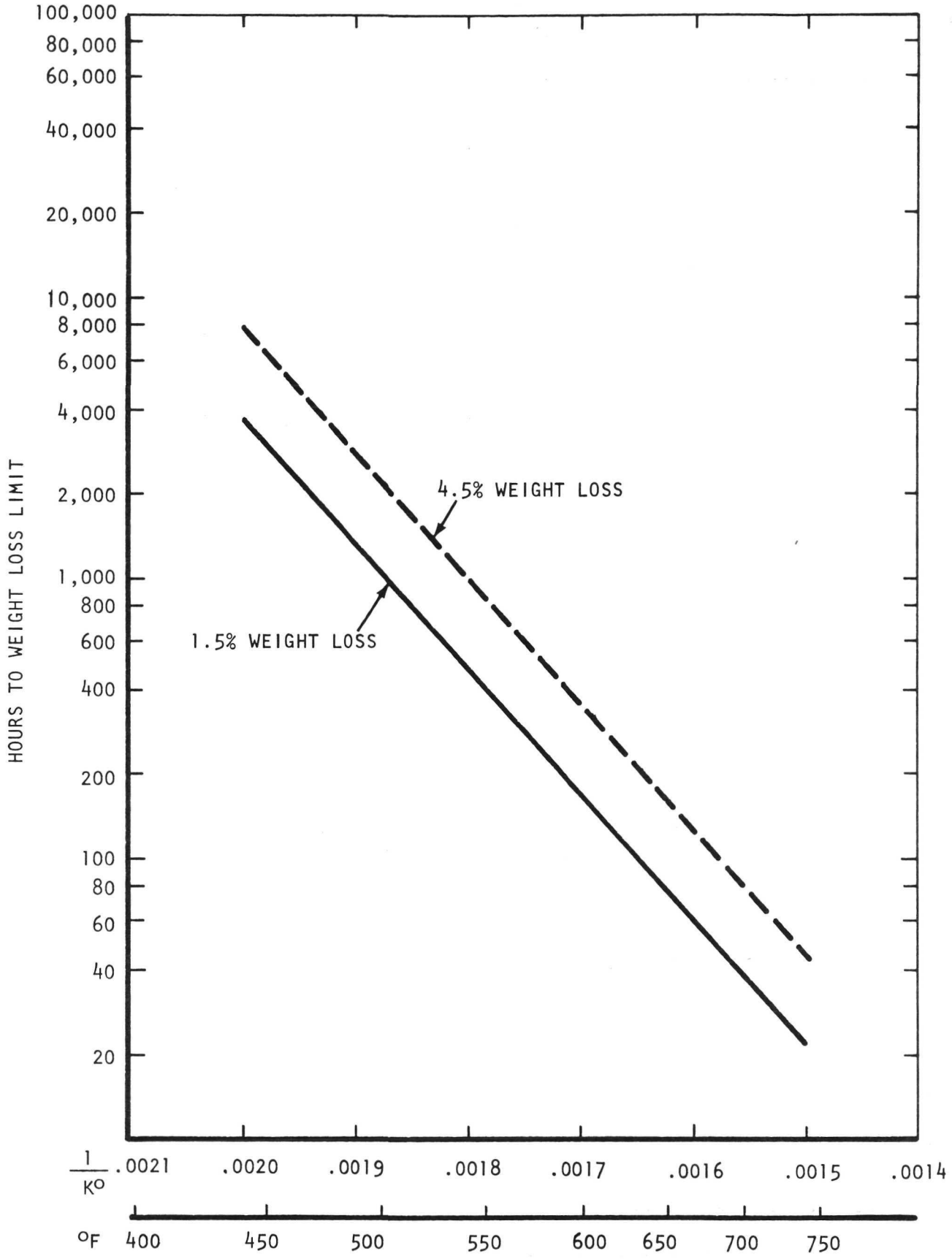
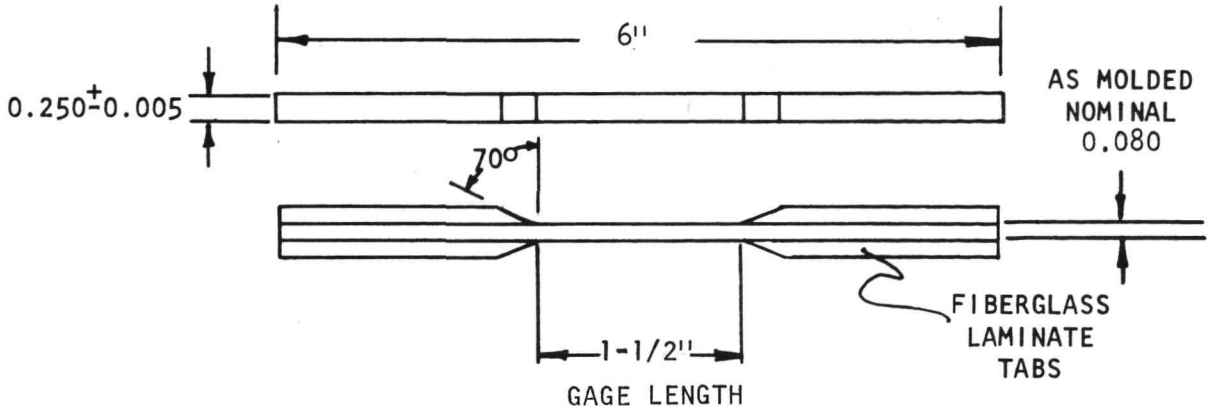


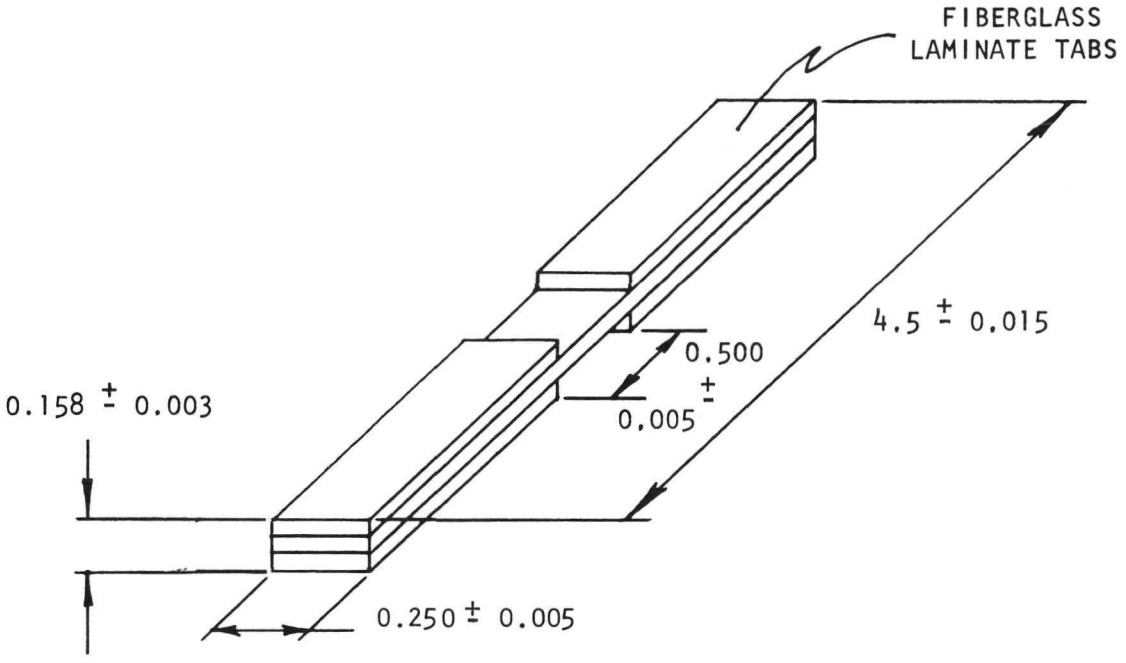
FIGURE 33 ARRHENIUS PLOT OF COMPOSITE WEIGHT LOSS (P10P/F 5-Y)



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.

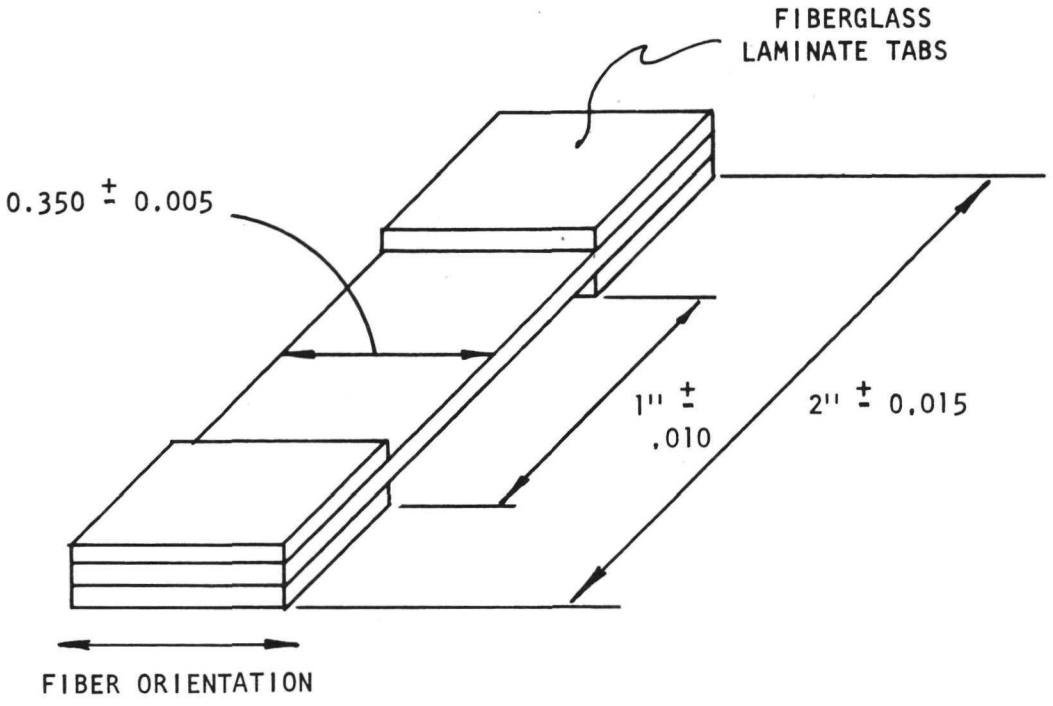
FIGURE 34 LONGITUDINAL TENSILE SPECIMEN



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.

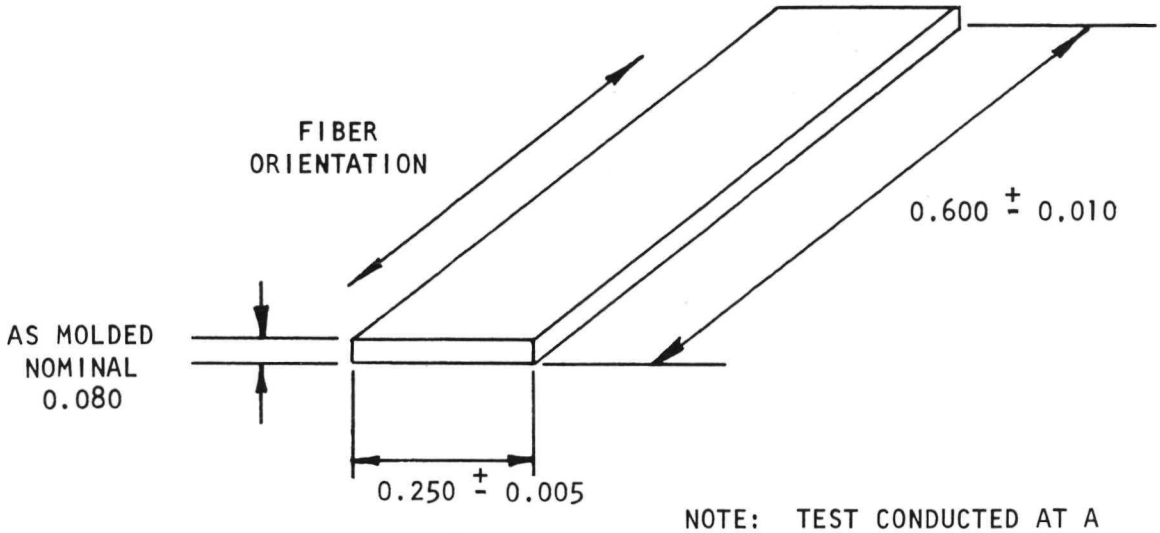
FIGURE 35 LONGITUDINAL COMPRESSION SPECIMEN



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

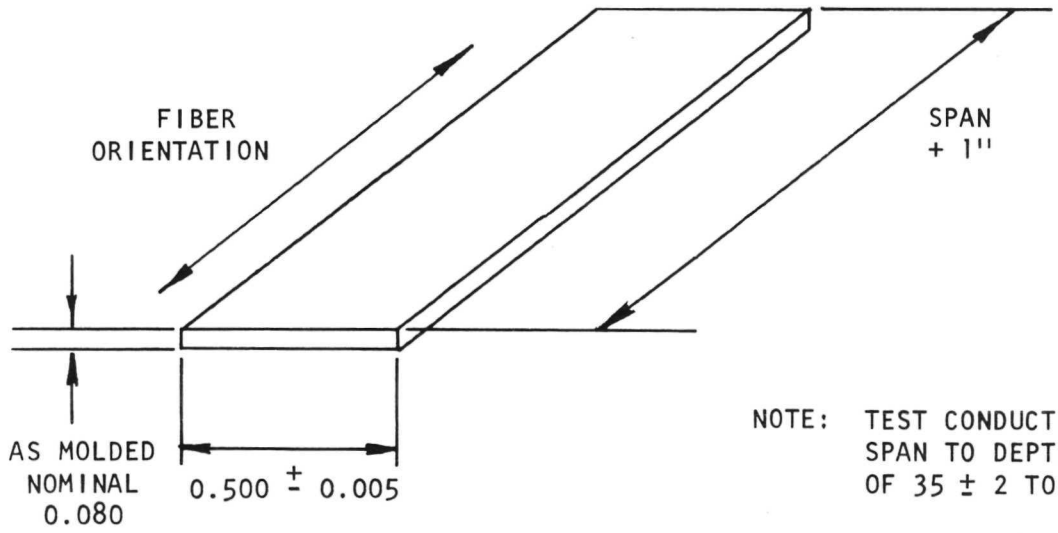
FOR ELEVATED TEMPERATURE TESTING, POLYIMIDE/FIBERGLASS CLOTH LAMINATE TABS BONDED WITH HIGH TEMPERATURE STRAIN GAGE ADHESIVE

FIGURE 36 TRANSVERSE TENSILE SPECIMEN



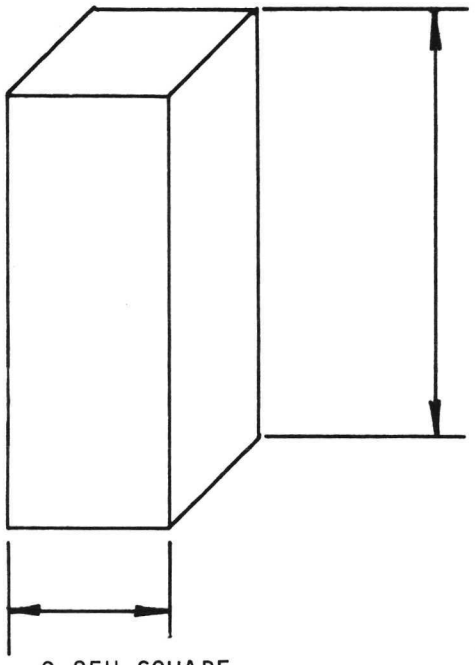
NOTE: TEST CONDUCTED AT A SPAN TO DEPTH RATIO OF 4.5 ± 0.5 TO 1, USING AN INFINITELY ADJUSTABLE SPAN FIXTURE.

FIGURE 37 SHORT BEAM SHEAR SPECIMEN



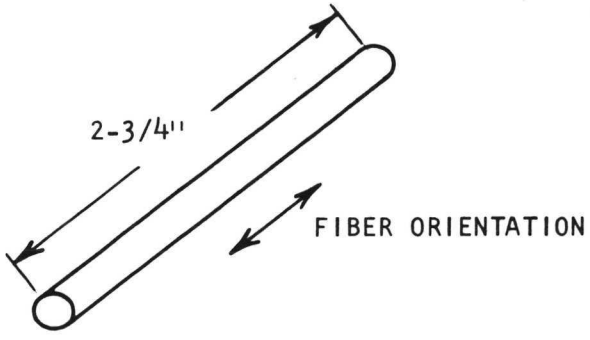
NOTE: TEST CONDUCTED AT A SPAN TO DEPTH RATIO OF 35 ± 2 TO 1.

FIGURE 38 FLEXURE SPECIMEN (THREE POINT)



NOTE: DIMENSIONS ARE NOMINAL

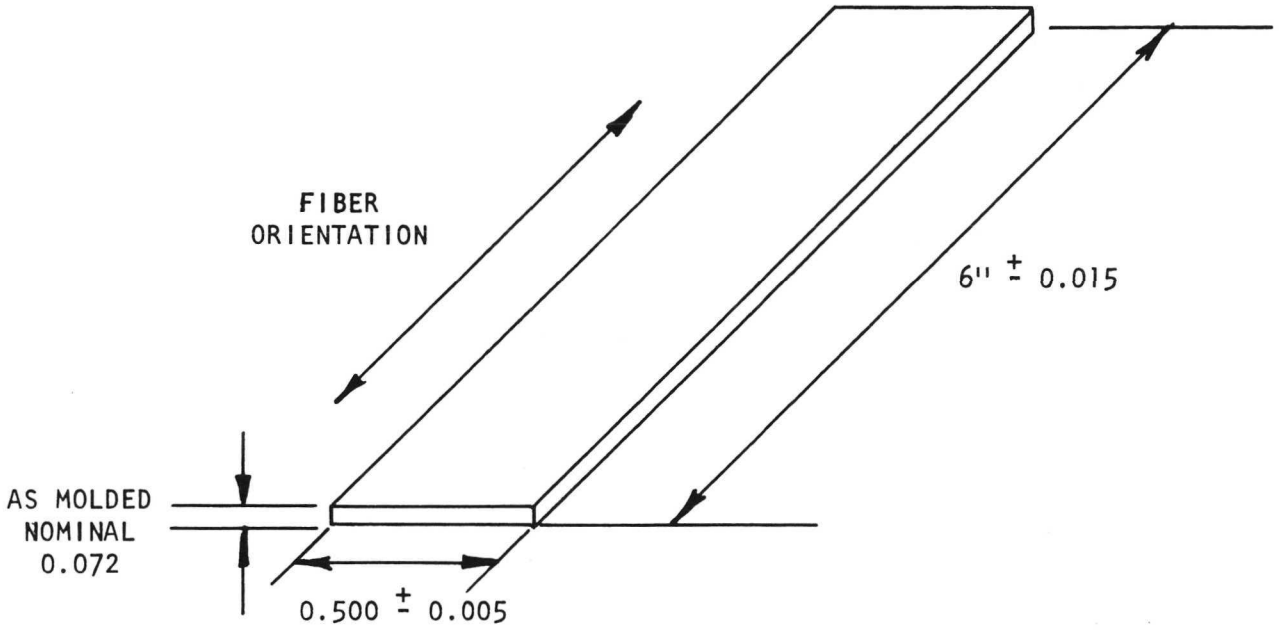
FIGURE 39 THERMAL EXPANSION SPECIMEN



0.250 DIAMETER

NOTE: DIMENSIONS ARE NOMINAL

FIGURE 40 TORSION ROD SPECIMEN



NOTE: PLY STACKING SEQUENCE
FOR 0°/90° SPECIMENS

0
90
0
90
0
90
90
0
90
0
90
0

FIGURE 41 FATIGUE SPECIMEN

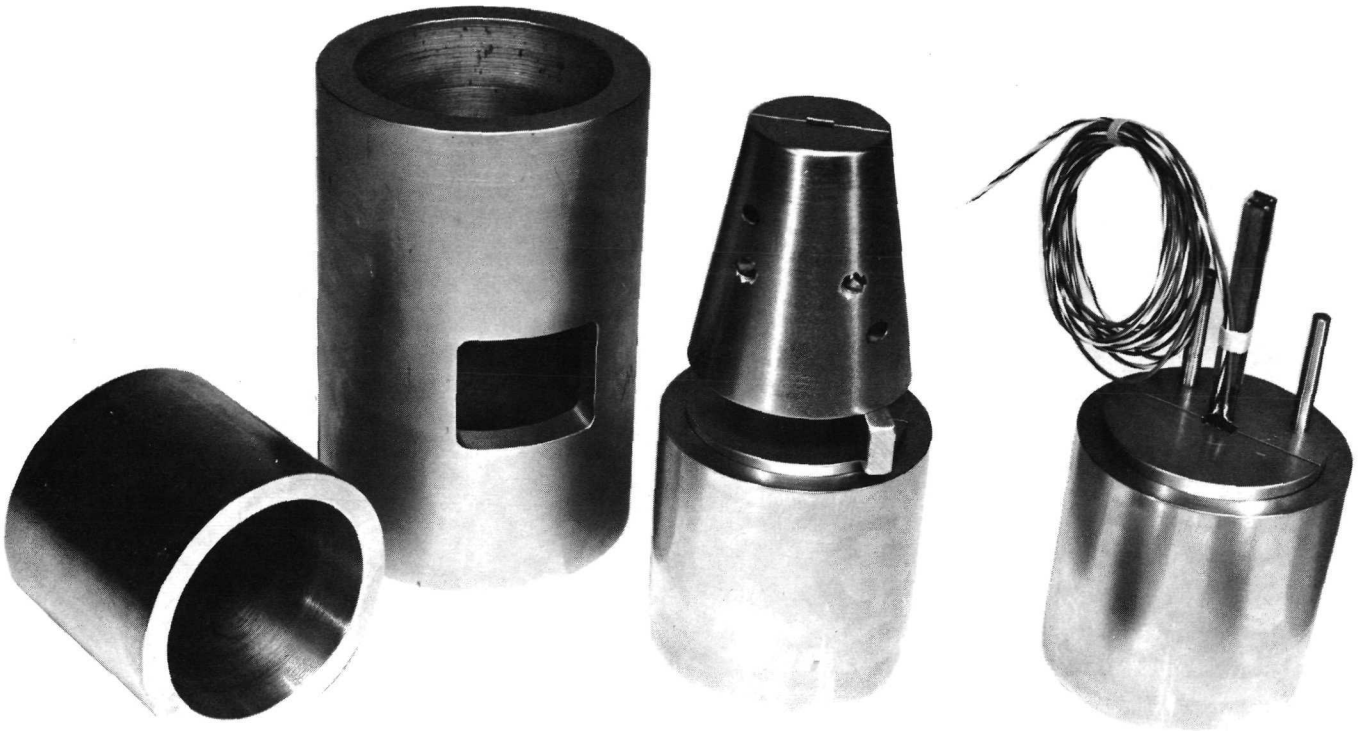


FIGURE 42 COMPRESSION TEST FIXTURE

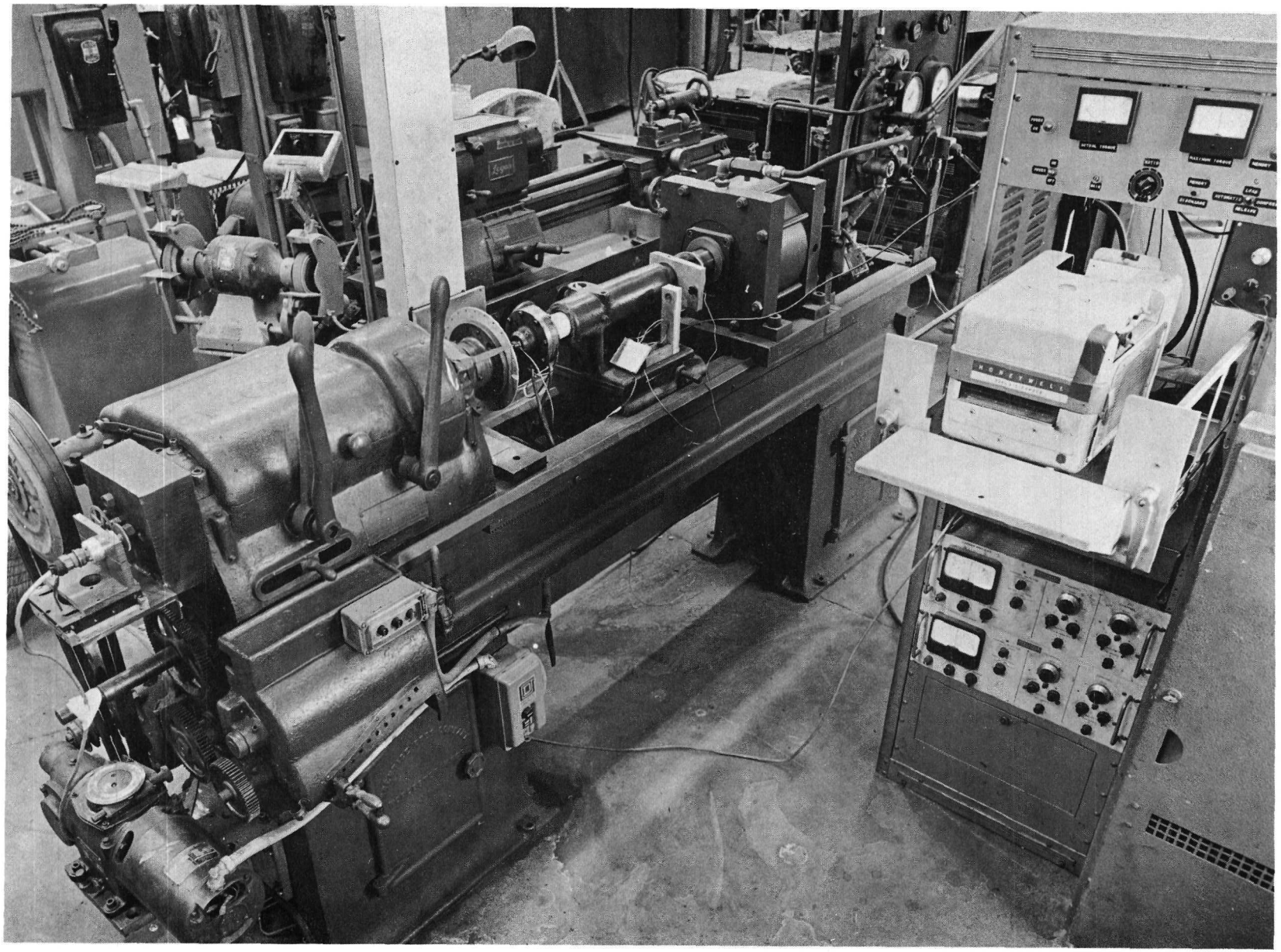


FIGURE 43 TORSION TEST UNIT AND RECORDING INSTRUMENTATION

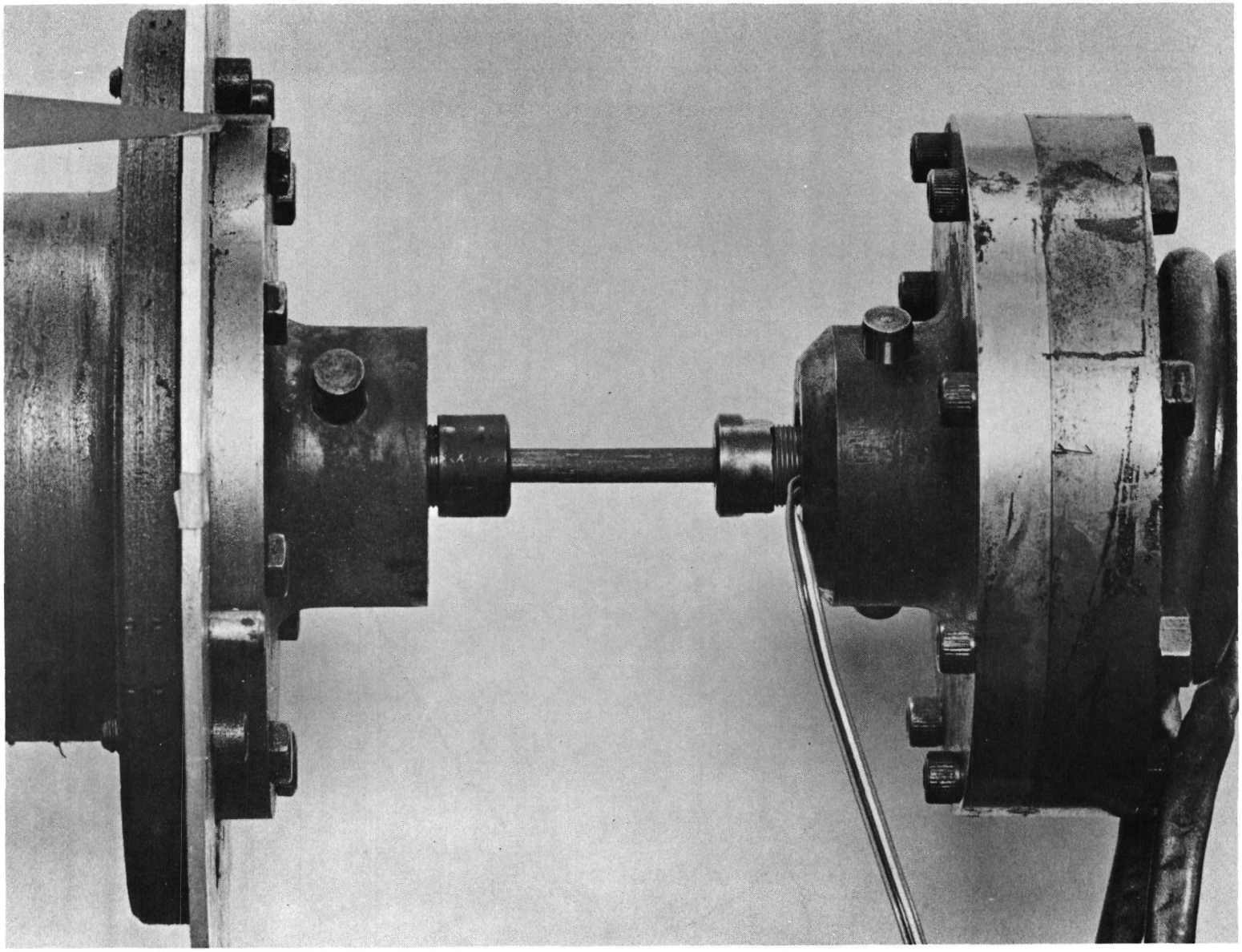


FIGURE 44 CLOSE-UP OF TORSION ROD SPECIMEN IN TEST GRIPS

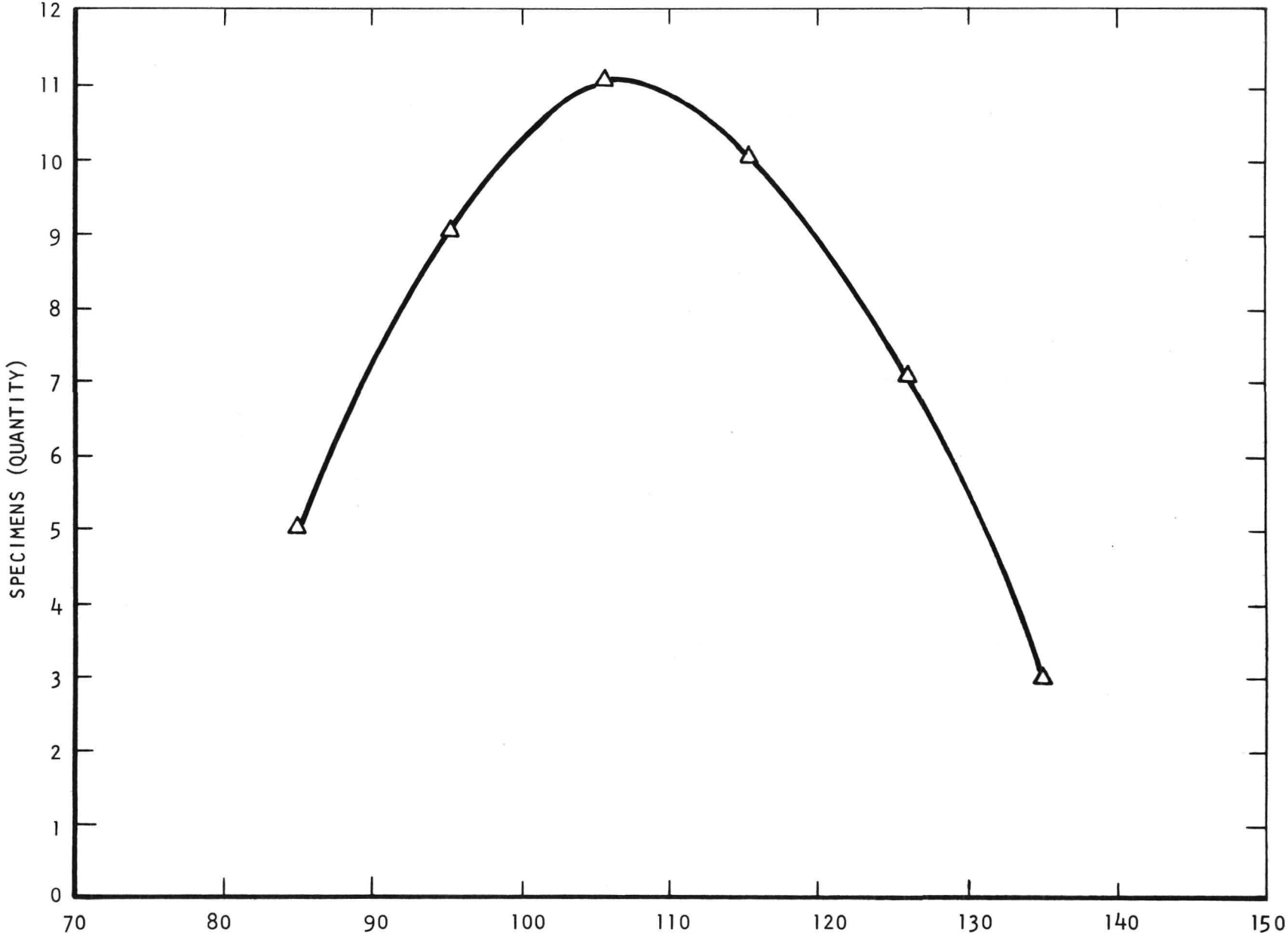


FIGURE 45 FLEXURAL STRENGTH DISTRIBUTION FOR P10P/F 5-Y LAMINATES

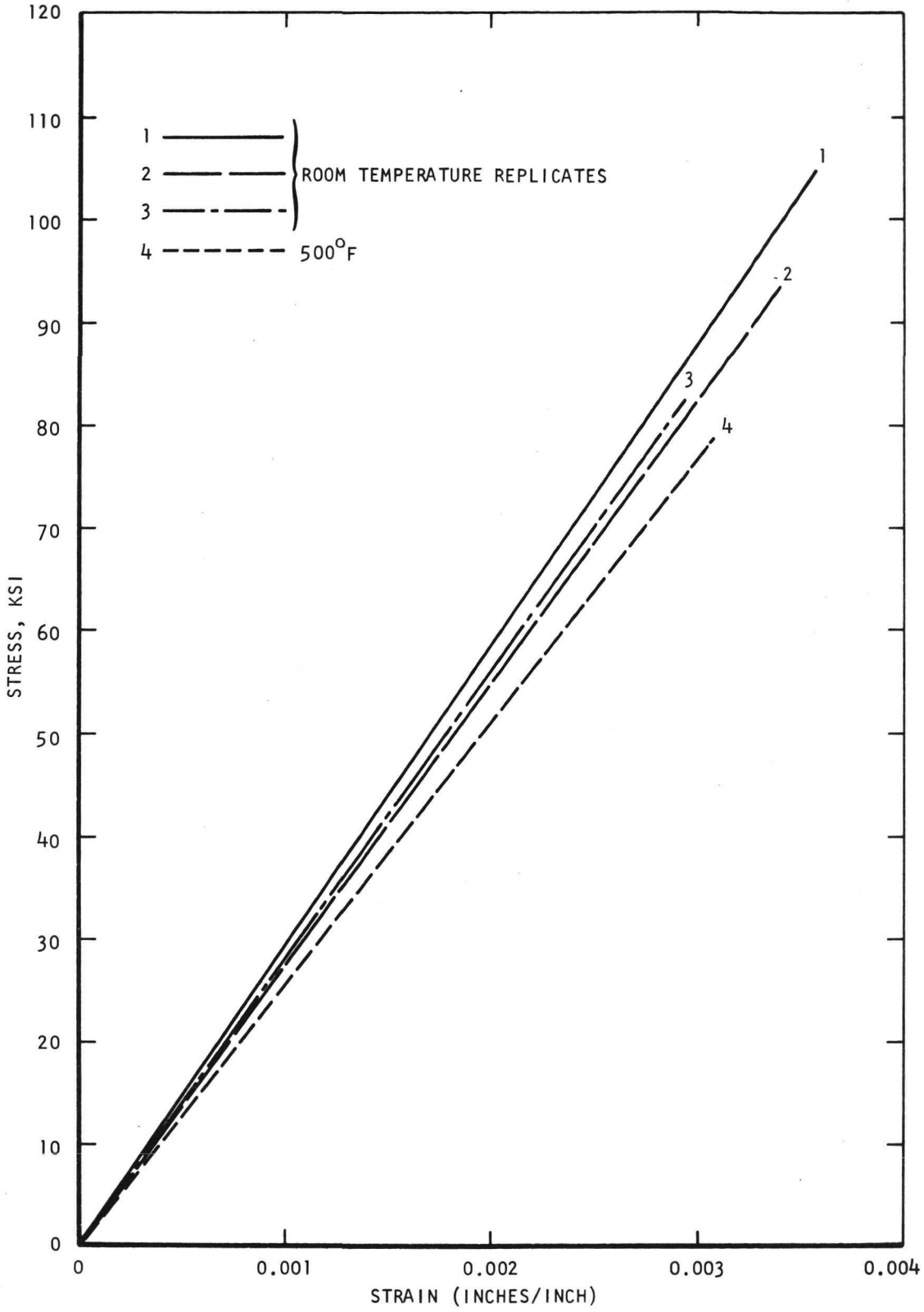


FIGURE 46 STRESS-STRAIN CURVES - LONGITUDINAL TENSILE

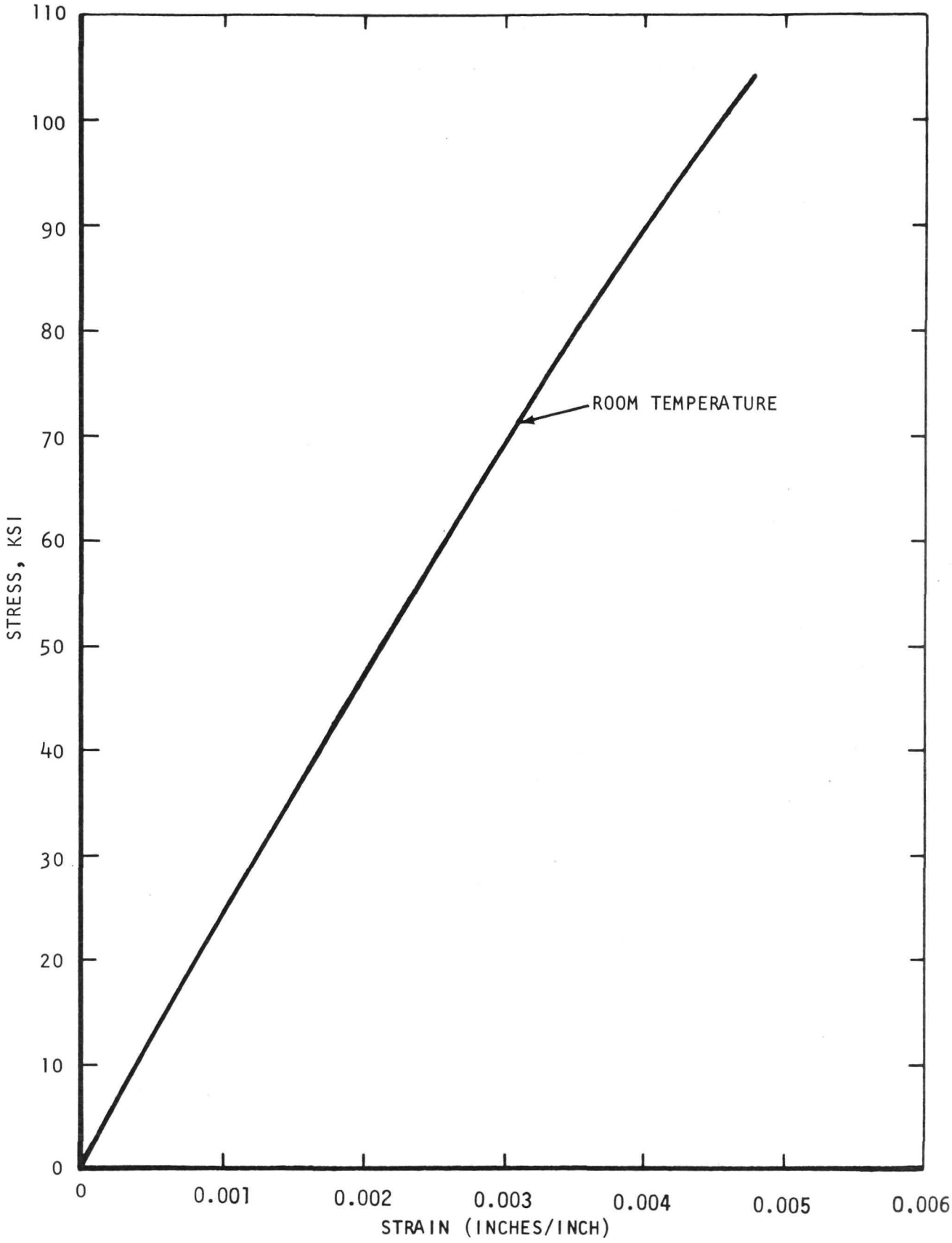


FIGURE 47 STRESS-STRAIN CURVE - LONGITUDINAL COMPRESSION

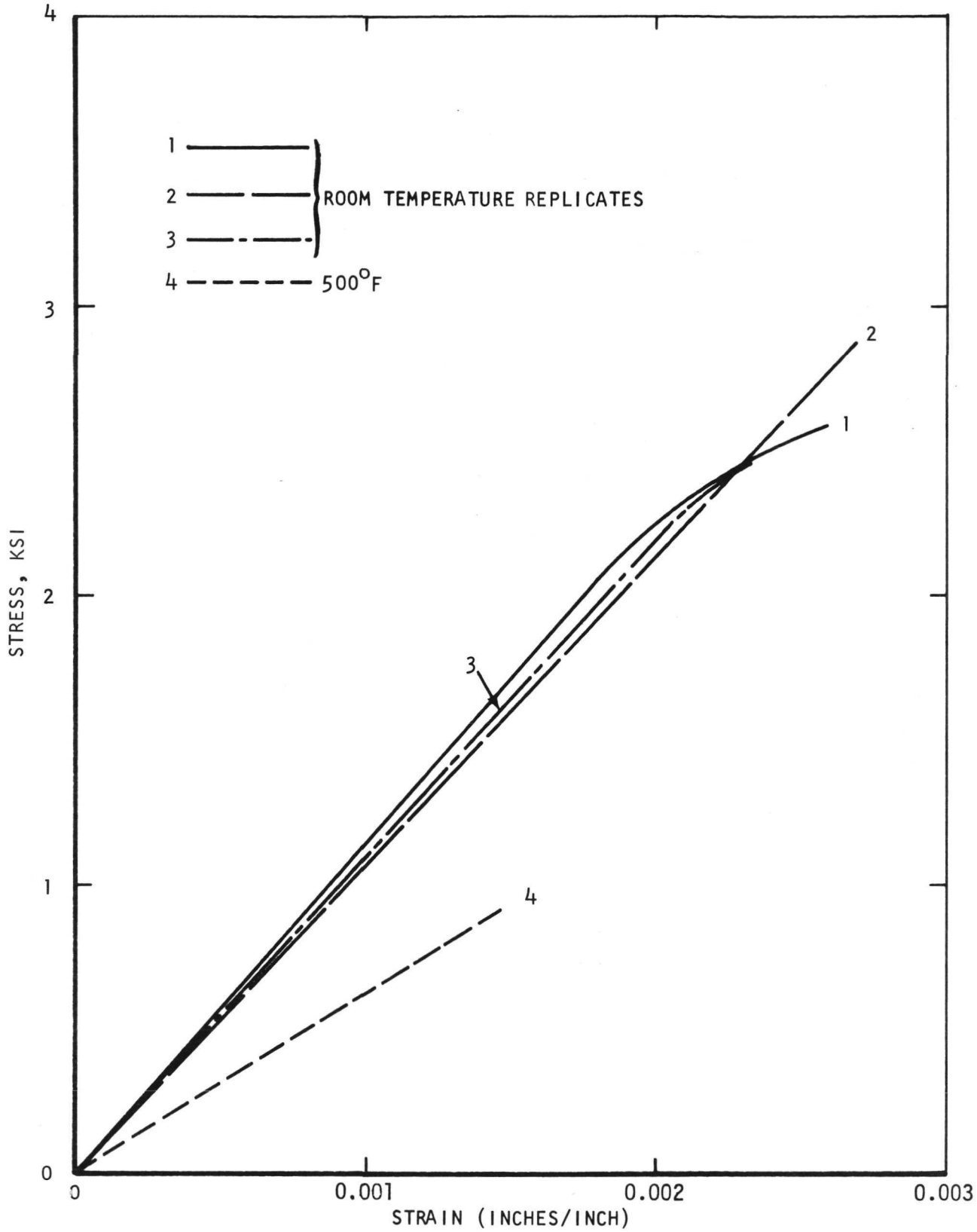


FIGURE 48 STRESS-STRAIN CURVES - TRANSVERSE TENSILE

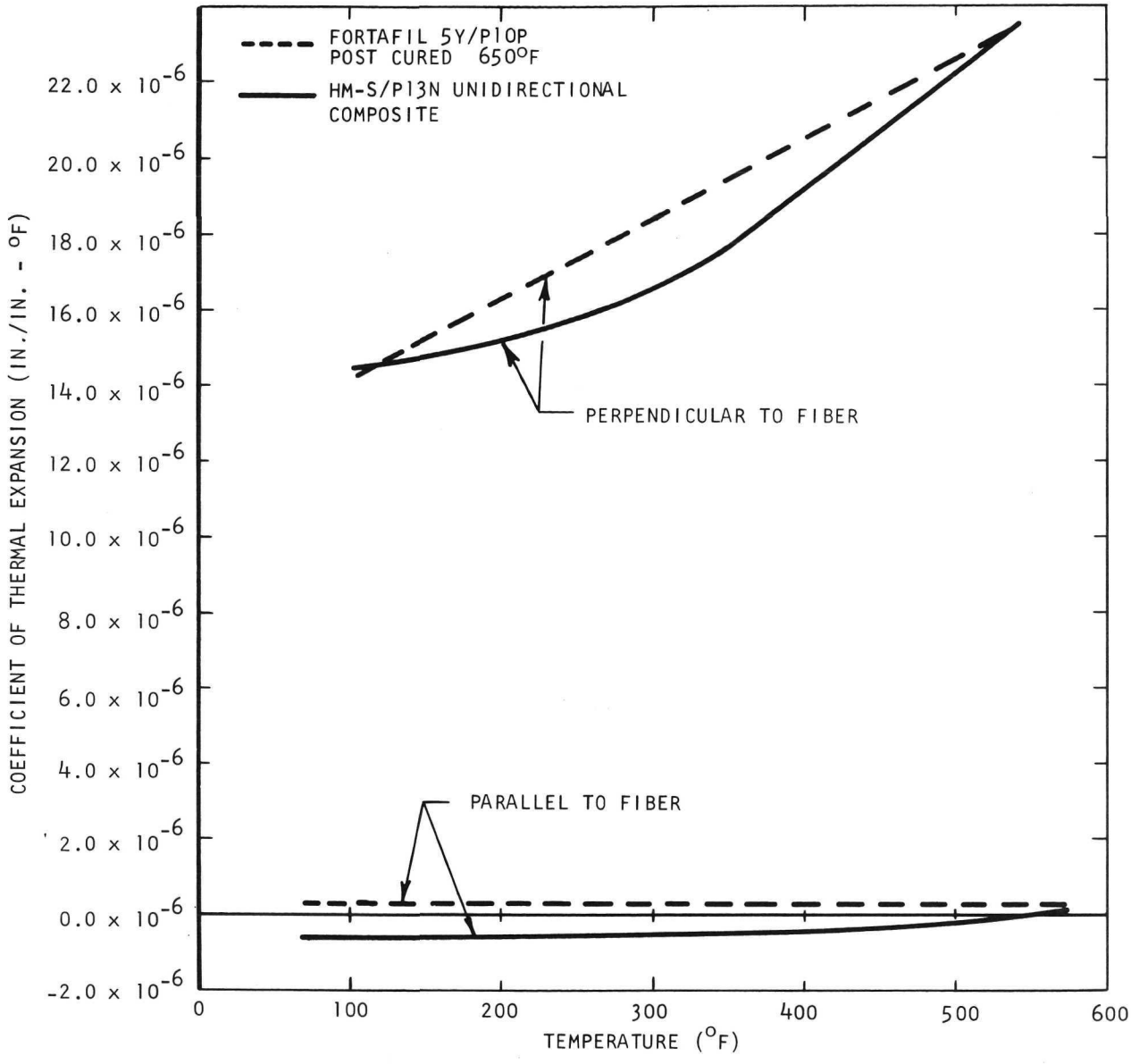


FIGURE 49 COEFFICIENT OF LINEAR THERMAL EXPANSION OF P10P/F5Y COMPOSITES

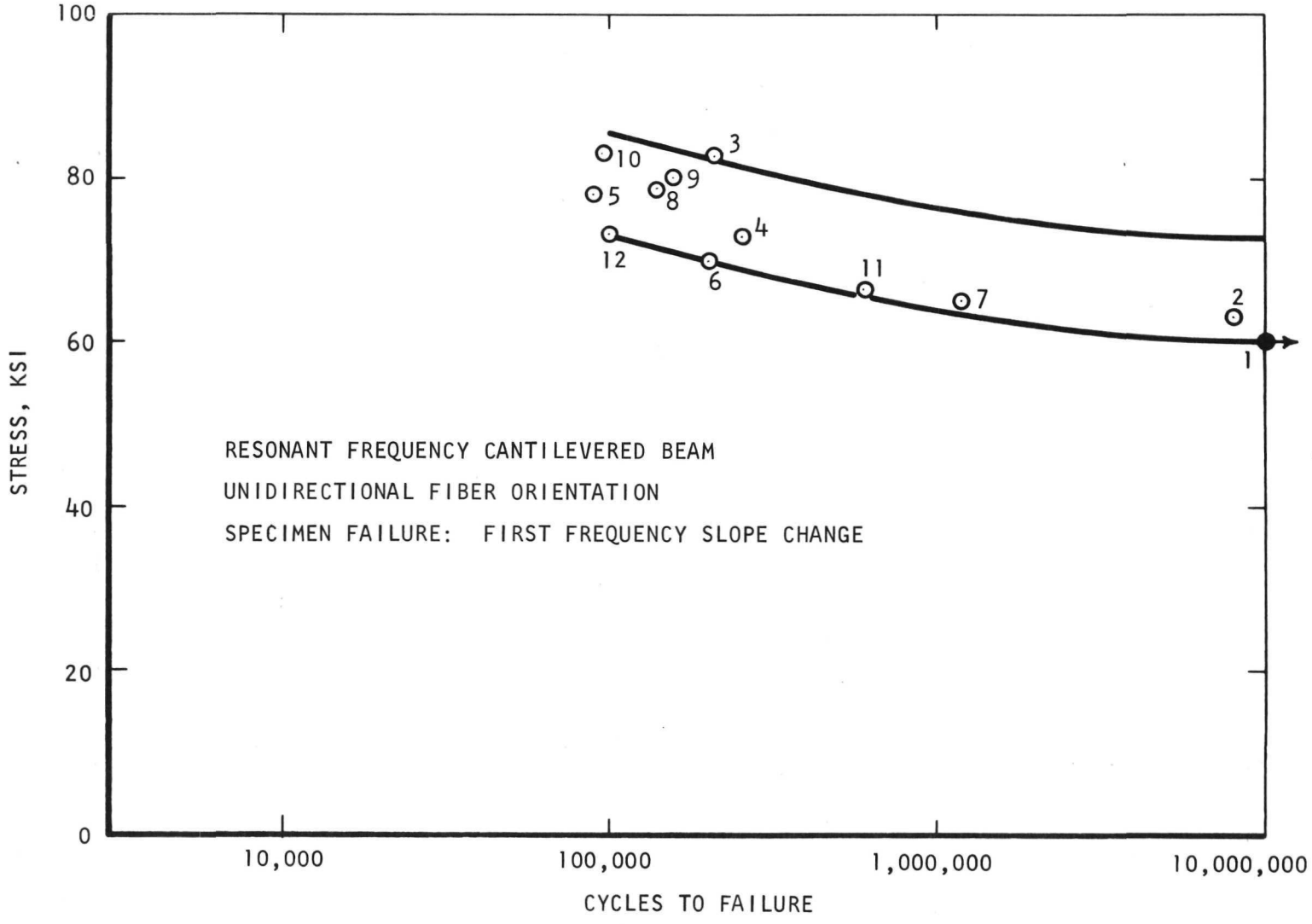


FIGURE 50 ROOM TEMPERATURE BENDING FATIGUE STRENGTH OF UNIDIRECTIONAL P10P/F 5-Y COMPOSITES

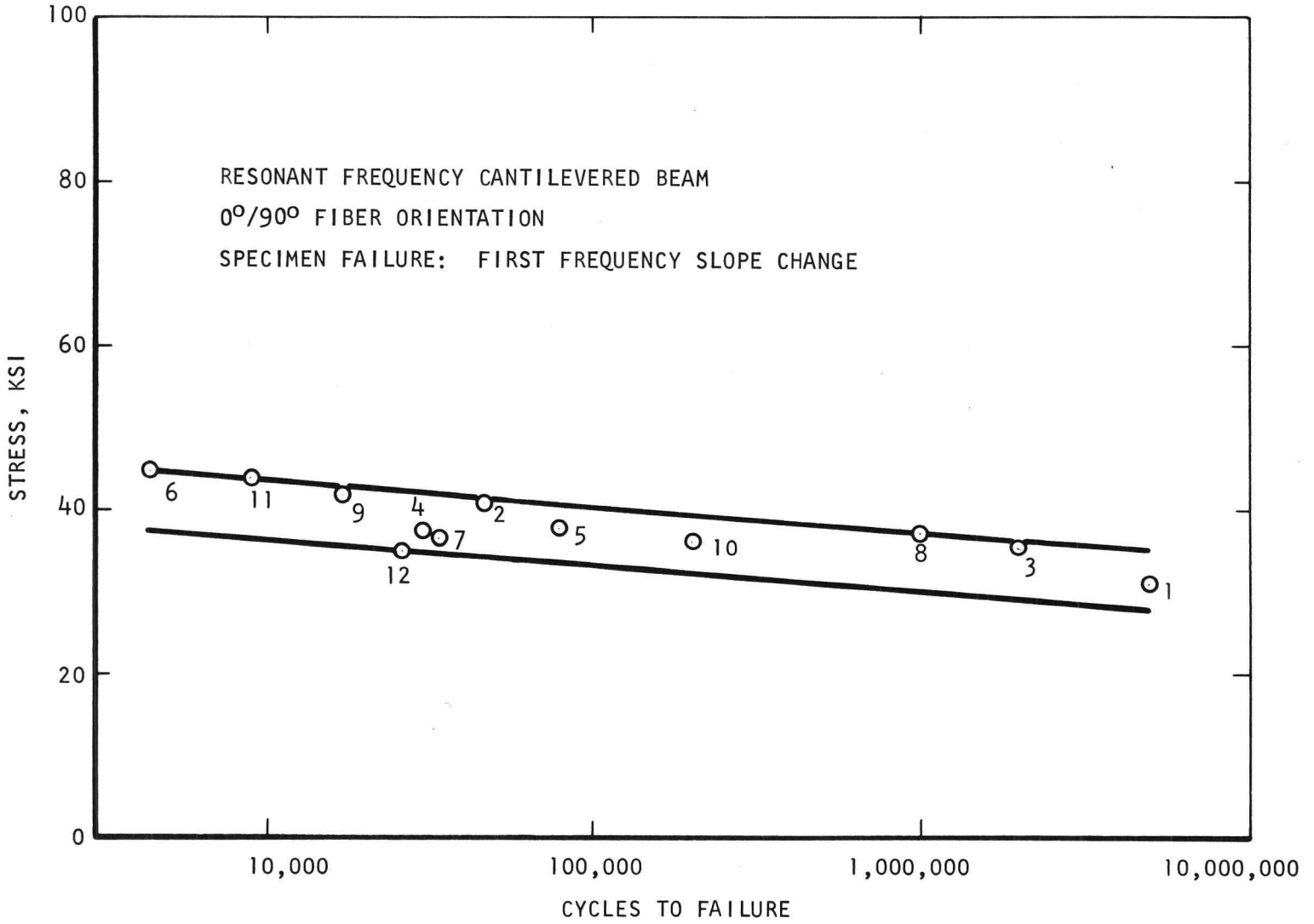


FIGURE 51 ROOM TEMPERATURE BENDING FATIGUE STRENGTH OF 0°/90° CROSS PLY P10P/F 5-Y COMPOSITES

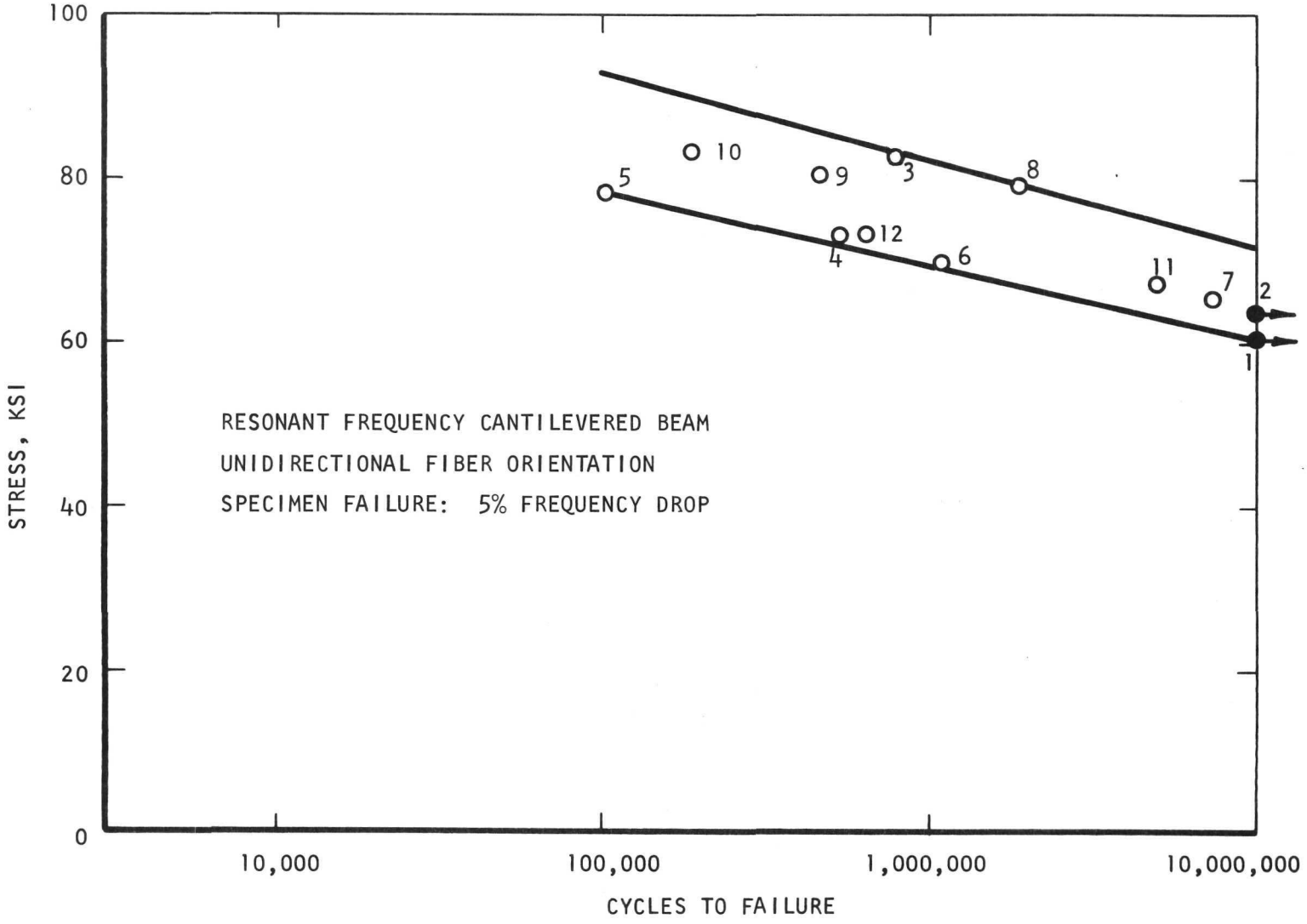


FIGURE 52 ROOM TEMPERATURE BENDING FATIGUE STRENGTH OF UNIDIRECTIONAL P10P/F 5-Y COMPOSITES

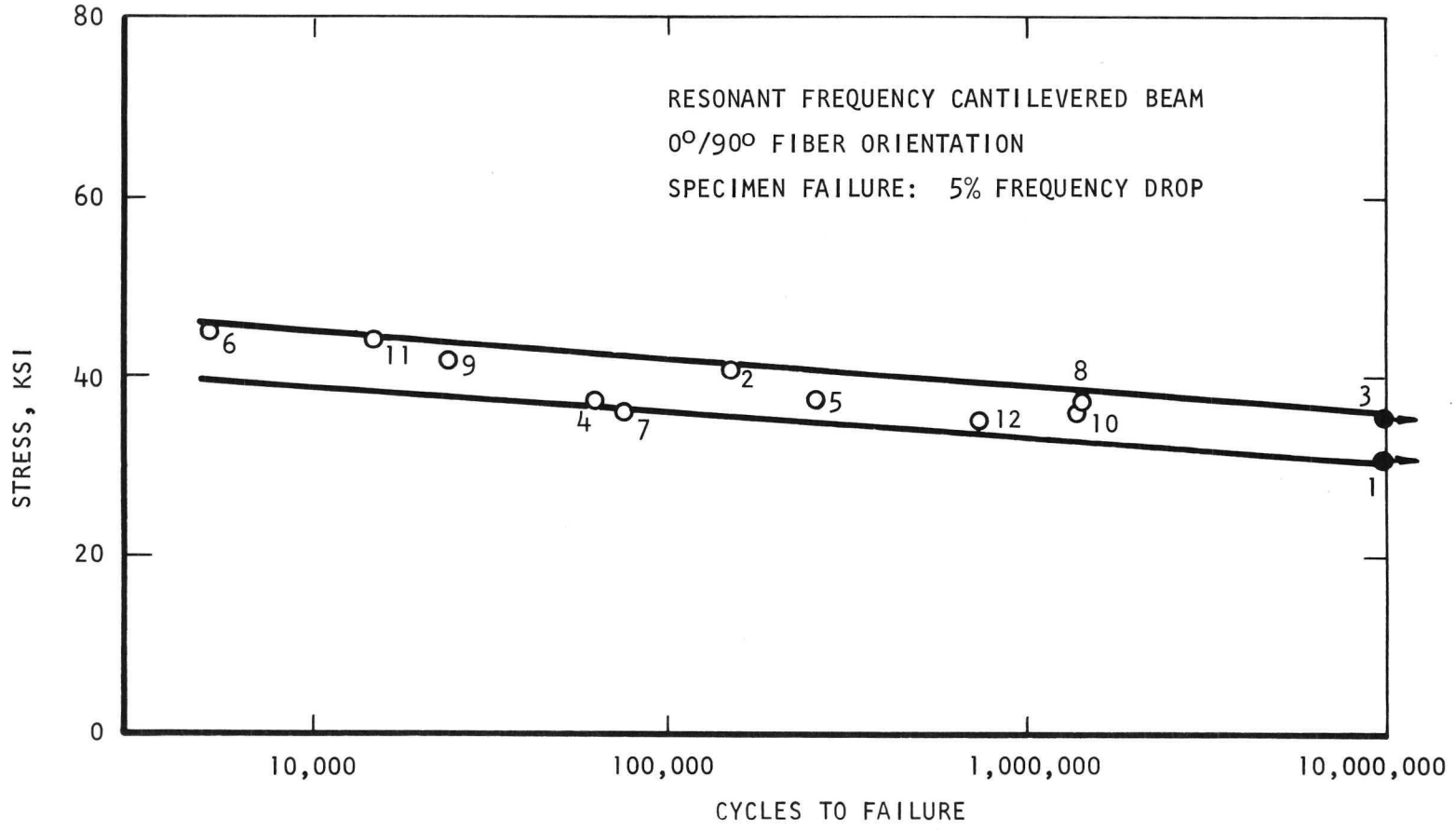


FIGURE 53 ROOM TEMPERATURE BENDING FATIGUE STRENGTH OF 0°/90° CROSS PLY P10P/F 5-Y COMPOSITES

APPENDIX A

STATISTICAL ANALYSIS AND INTERPRETATION OF DATA FROM SUB-TASK IIC

I INTRODUCTION

As was indicated in the main body of the text (Section 3.3), a statistically designed experiment was employed in Sub-Task IIC "Composite Processing Optimization and Final Resin Selection" to both choose between two resin systems and identify an optimal processing method. The specific type of experiment chosen was the one-quarter replication of eight factors in two blocks of 32 units each. The two resins were represented by the two blocks and the eight factors represent variables to be studied at two different levels. This type of experiment yields a significant cost savings and permits treatment of variable interactions.

The specific design was taken from the NBS Applied Mathematics Series #48 (ref. 2) and is shown in table A-1. The analysis of experimental data was performed on the computer and was based on Appendix 10C of The Design and Analysis of Industrial Experiments, (ref. 6).

A level of significance of 0.95 was chosen for the evaluation before the experiment was started. This indicates that effects flagged by the analysis as significant at this level were 95% certain to be real differences due to the variables in the experiment and not occurrences that could be effects due to experimental error. In the case of the 0.90 level of significance, the results were 90% certain to be real differences due to the variables in the experiment.

II TECHNIQUES USED IN THE INTERPRETATION OF STATISTICAL ANALYSIS

Tables A-2 through A-4 illustrate the output of the computer analysis of the data for one response or criterion, "ultimate flexure strength at room temperature." Similar sheets were produced for each of the other five responses.

The right hand column entitled "F-Ratio," of table A-2, indicates for each block, main effect, and possible first order interaction effect, the statistics used in the determination of the significance of the results of the analysis of the ultimate flexure strength at room temperature. If the tabulated F ratio exceeded 4.23, the effect measured was statistically significant at the 95% confidence level. If the F ratio exceeded 2.91, the effect measured was statistically significant at the 90% confidence level.

In the analysis of block effects, if the F ratio were deemed to be significant, the signs in the "Effect" column and the "Mean Effect" column (shown in table A-3) were compared. If they were of like sign then the second of the two blocks (P1OP in this experiment) was the one yielding higher results.

In interpreting the main effects of a factor, the signs of the same two columns, "Effect" and "Mean Effect", were similarly compared. If alike, then the higher of the two factor levels used in the experiment yielded a higher property value by the amount shown in the "Mean Effect" column. As example, in the analysis of variance (AOV) shown in table A-2, the factor "A" shows an F ratio of 7.06, well above the 4.23 level. In table A-3, a comparison of the

"Effect" and "Mean Effect" signs for the "A" effect are seen to be different; therefore, the lower level of the "A" factor (not compacted) was the level producing the higher flexure strength by 5,430 psi.

It should be noted that in cases where interactions were significant, the main effects corresponding to the factors involved were discounted. This is logical since it can be misleading to make statements about a main effect when it is clear that it is strongly interrelated with other factors which control its response.

Once an interaction was determined to have a significant F ratio, the analysis was somewhat different. Table A-5 and figure A-1 illustrate the process. The columns of data shown in table A-5 were taken from the schematic display and averaged as shown. These averages were plotted, as in figure A-1, to provide a graphic presentation of the interaction. The consequences of selecting any of the four combinations of the upper and lower levels of the two factors interacting can easily be seen.

In cases where no significant results occurred (as shown by F ratio), it was assumed that either level of the factor could be safely chosen.

The comparisons described above were made for each factor and criterion. Significant effects are shown, along with F ratio values, in tabular form in table A-6. Table A-7 is a compilation showing the interpretation of significant effects for blocks and factors in relation to each of the six experimental criteria.

The latter table is a summary of the results from the statistical analysis and shows responses for each of the eight factors for each of the six experimental criteria used; also shown, to the right, are the TRW recommendations based on both analysis and engineering judgement. Judgement was involved in forming the final conclusions since the influence of the factors were found to vary from criterion to criterion. This was not unexpected since it is well known that in designing a composite for a specific application, frequent compromises must be made among properties to enhance the single most important characteristic. In this case, the problem was to integrate the responses from each criteria to choose a single set of factor responses that produced the best over-all composite.

In examining table A-7, it should first be noted that three levels of statistical significance are shown. The boxed entries represent an F ratio above 4.23 (.95 level of significance), the entries in a grey background represent an F ratio between 2.91 (.90 level of significance) and 4.23, and the unmarked entries represent a few selected responses close to but below 2.91. Each entry is followed, in parentheses, by the main effect of interaction from which the statement came and the F ratio of the effect.

In making judgements, it became necessary to assign a resultant value to possible alternative choices when the recommended factor level for one criterion was in conflict with the same factor levels from other criteria. The pertinent alternative choices are given as footnotes with expected attendant property losses incurred in making the alternative choice.

An example of the use of the chart (table A-7) can be seen in the interpretation of factor "A" for flexural modulus at room temperature. It will be noted that the "AG" interaction is significant at the 0.95 level and recommends the use of "no compaction" with an "air postcure" (see factor G). Additionally, the "AC" interaction recommends the use of "compaction" (in an air imidizing environment) at a fairly high level of significance (F ratio 4.14). Engineering judgement would recommend that compaction (into handleable preforms) be used since this provides a preform with integrity for subsequent handling in other operations and also tends to limit the possibility of fiber wash encountered in molding of a loose stack of prepreg plies. The question is then, what would be the effect on flexural modulus at room temperature if a compacted preform were to be used. Footnote (1) to the "no compact" statement of the AF interaction shows that if compaction with an air postcure is substituted, a potential loss of 1.1×10^6 psi could be expected. This would be a loss of room temperature flexure modulus of approximately 4%. This was considered to be an insignificant decrease in comparison to the advantage of using a preform in processing. Therefore, TRW's recommendation was for the use of compaction. In the same way, each of the factors for the six criteria was examined and potential losses considered for the selection of obviously preferred processing procedures. Then, a concensus was taken for each factor against criteria. In this way, the conclusions shown to the right of the chart were reached.

III RESULTS OF INTERPRETATION OF THE STATISTICAL ANALYSIS

Employing the procedures described above, the blocks and factors were carefully considered. In the block comparison of table A-7, it can be seen that two strong statements (short beam shear and flexural modulus at room temperature) were made indicating PIOP as the superior choice. Additionally, two statements of lesser significance also endorsed the PIOP choice; there were no conflicting results for any of the criteria. Very clearly then, the PIOP resin system was the outstanding choice.

While some opposing results are shown in examining the compaction responses (factor A) for each of the criteria, it was felt that these could easily be resolved with only a minimal strength loss in flexure in choosing the preferred processing technique, i.e., compaction of the preform. No strong statements were made in the analysis about the imidizing temperature (factor B) option so that either choice could be made. However, one relatively weak statistical statement (F ratio 2.04) recommended the use of one hour at 400°F. Since there were no conflicting results, it was logical to choose the quicker of the two processing options and select the one hour at 400°F as the preferred method.

Three responses recommended the use of an air atmosphere in imidizing (factor C) and the one vacuum response was resolved easily in accepting the air environment in an interaction with the preferred compaction choice discussed above. In considering molding pressure (factor D), quite plainly, 1000 psi was the clear choice after examining mold pressure factor responses. This same straightforward situation was also seen in reviewing the responses for mold temperature (factor E) and mold dwell time (factor F), i.e., the higher temperature for the longer time was clearly preferred.

In the area of postcure atmosphere (factor G) and time (factor H), the

situation was not clearly defined. For example, to get statement on the use of postcure, lesser levels of significance had to be considered to get three positive statements endorsing the 16 hour postcure. As to the choice of gaseous environment in postcure, some minor conflict was shown in the chart, but again, these were resolved by compromises of the footnoted interactions. Additionally, it was clear that in engineering practice the preferred choice would be an air atmosphere. Since it is expected that the service of the polyimide systems will be at high temperature, good practice then recommends the use of the postcure with air as the most acceptable environment.

A summary of the conclusions and recommendations discussed above is given in Section 3.3.3 of the main text.

TABLE A-1
EXPERIMENTAL DESIGN DISPLAY

PLAN 4.8.32. (Ref. 2) 1/4 Replication of 8 Factors in 2 Blocks of 32 Units Each.

Factors: A, B, C, D, E, F, G, H

I = ABCEG = ABDFH = CDEFGH

Block Confounding: ACD

Blocks Only: All Two-Factor Interactions are Measurable.

Blocks								
1				2				
(1)	cdgh	abcg	abdh	bdefh	bcefg	acdefgh	aef
abcfgh	abdf	fh	cdfg	acdeg	aeh	bde	bcegh
bcdeg	beh	ade	acegh	cfgh	df	abfh	abcdfg
adefh	acefg	bcdefgh	bef	ab	abcdgh	cg	dh
efgh	cdef	abcefh	abdefg	bdg	bch	acd	agh
abce	abdegh	eg	cdeh	acdfh	afg	bdfgh	bcf
bcdfh	bfg	adfgh	acf	ce	degh	abeg	abcdeh
adg	ach	bcd	bgh	abefgh	abcdef	cefh	defg

TABLE A-2

YATES ANALYSIS OF 1/4 REPLICATE OF 2 TO THE 8TH FACTORIAL IN 2 BLOCKS.
FLEX STRESS IN 1000 PSI AT ROOM 08/25/70

ANALYSIS OF VARIANCE				
SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F RATIO
BLOCKS	1	30.24	30.24	0.45
A	1	473.06	473.06	7.06
B	1	50.05	50.05	0.74
C	1	81.90	81.90	1.22
D	1	119.90	119.90	1.79
E	1	191.13	191.13	2.85
F	1	133.40	133.40	1.99
G	1	66.01	66.01	0.98
H	1	160.02	160.02	2.38
AB	1	1.96	1.96	0.02
AC	1	478.51	478.51	7.14
AD	1	13.50	13.50	0.20
AE	1	33.64	33.64	0.50
AF	1	3.90	3.90	0.05
AG	1	357.21	357.21	5.33
AH	1	1.38	1.38	0.02
BC	1	15.20	15.20	0.22
BD	1	30.25	30.25	0.45
BE	1	111.83	111.83	1.66
BF	1	13.69	13.69	0.20
BG	1	7.42	7.42	0.11
BH	1	88.36	88.36	1.31
CD	1	73.53	73.53	1.09
CE	1	19.80	19.80	0.29
CF	1	41.92	41.92	0.62
CG	1	18.06	18.06	0.26
CH	1	141.01	141.01	2.10
DE	1	40.95	40.95	0.61
DF	1	45.22	45.22	0.67
DG	1	344.10	344.10	5.13
DH	1	4.95	4.95	0.07
EF	1	111.30	111.30	1.66
EG	1	399.00	399.00	5.95
EH	1	89.30	89.30	1.33
FG	1	4.84	4.84	0.07
FH	1	9.45	9.45	0.14
GH	1	119.90	119.90	1.79
ERROR	26	1741.24	66.97	
TOTAL	63	5667.24		

TABLE A-3

YATES ANALYSIS OF 1/4 REPLICATE OF 2 TO THE 8TH FACTORIAL IN 2 BLOCKS. FLEX STRESS IN 1000 PSI AT ROOM 08/25/70

LAB ID	TREATMENT	RESPONSE	(1)	(2)	(3)	(4)	(5)	(6)	MEAN EFFECT	SUM SQUARES	EFFECT
1	1	106.70	231.40	463.70	887.09	1797.40	3692.30	7476.99	0.00	0.00	-
S	A(GH)	124.70	232.30	423.40	910.30	1894.90	3784.69	-174.00	-5.43	473.06	A
4	B(GH)	112.00	199.90	451.10	923.70	1885.80	-79.09	-56.59	-1.76	50.05	B
R	AB	120.30	223.50	459.20	971.20	1898.90	-94.90	-11.20	-0.35	1.96	AB
A	C(G)	112.50	236.30	467.70	945.40	-19.80	-13.49	-72.39	-2.26	81.90	C
19	AC(H)	87.40	214.80	456.00	940.40	-59.29	-43.09	-175.00	-5.46	478.51	AC
D	BC(H)	119.20	218.90	494.70	938.50	-90.40	-14.50	31.19	0.97	15.20	BC
18	ABC(G)	104.30	240.30	476.50	960.40	-4.49	3.29	-159.80	-4.99	399.00	-EG
C	D(H)	127.60	236.70	468.50	-13.70	24.39	-62.10	87.60	2.73	119.90	D
17	AD(G)	108.70	231.00	476.90	-6.09	-37.89	-10.29	-29.39	-0.91	13.50	AD
B	BD(G)	102.80	245.10	467.50	-37.29	-10.40	-122.70	44.00	1.37	30.25	BD
20	ABD(H)	112.00	210.90	472.90	-21.99	-32.69	-52.30	-24.59	-0.76	9.45	-FH
3	CD(GH)	100.90	247.39	482.70	-11.79	-2.00	39.30	68.59	2.14	73.53	CD
Q	ACD	118.00	247.30	455.80	-78.60	-12.49	-8.10	43.99	1.37	30.24	ACD(BLOCK)
2	BCD	126.90	237.19	478.80	-9.50	13.39	-101.30	29.40	0.91	13.50	
T	ABCD(GH)	113.40	239.30	481.60	5.00	-10.10	-58.49	57.20	1.78	51.12	
9	E(G)	124.70	245.30	26.29	24.49	-32.20	70.70	110.59	3.45	191.13	E
AA	AE(H)	112.00	223.20	-40.00	-0.10	-29.90	16.90	46.40	1.45	33.64	AE
12	BE(H)	113.30	234.90	-9.69	-39.90	13.80	22.90	-84.59	-2.64	111.83	BE
Z	ABE(G)	117.70	242.00	3.60	2.00	-24.09	-52.30	-33.99	-1.06	18.06	-CG
I	CE	118.80	231.70	-8.29	-15.00	-53.00	17.30	-35.60	-1.11	19.80	CE
26	ACE(GH)	126.30	235.80	-29.00	4.59	-69.70	26.69	-21.79	-0.68	7.42	-BG
L	BCE(GH)	123.70	236.20	13.50	-19.89	-23.60	38.30	-151.20	-4.72	357.21	-AG
25	ABCE	87.20	236.70	-35.50	-12.79	-28.69	-62.89	-65.00	-2.03	66.01	-G
K	DE(GH)	122.30	240.69	3.10	0.49	65.59	41.89	51.19	1.59	40.95	DE
24	ADE	125.10	242.00	-14.89	-2.50	-26.29	26.69	89.00	2.78	123.76	
J	BDE	118.30	238.50	-36.50	-26.89	25.60	51.29	54.00	1.68	45.56	
27	ABDE(GH)	129.00	217.30	-42.10	14.40	-33.70	-7.30	12.99	0.40	2.64	
11	CDE(H)	129.10	239.80	-2.50	14.59	-38.80	50.90	-22.20	-0.69	7.70	
Y	ACDE(G)	108.10	239.00	-7.00	-1.19	-62.50	-21.49	-140.00	-4.37	306.24	
10	BCDE(G)	126.90	246.80	14.60	18.50	-8.59	-18.90	54.60	1.70	46.58	
BB	ABCDE(H)	112.40	234.80	-9.59	-28.60	-49.90	76.10	148.40	4.63	344.10	-DG

TABLE A-4

YATES ANALYSIS OF 1/4 REPLICATE OF 2 TO THE 8TH FACTORIAL IN 2 BLOCKS. FLEX STRESS IN 1000 PSI AT ROOM 08/25/70

LAB ID	TREATMENT	RESPONSE	(1)	(2)	(3)	(4)	(5)	(6)	MEAN EFFECT	SUM SQUARES	EFFECT
7	F(H)	126.30	18.00	0.89	-40.29	23.20	97.50	92.39	2.88	133.40	F
U	AF(G)	119.00	8.29	23.59	8.09	47.50	13.09	-15.80	-0.49	3.90	AF
6	BF(G)	106.40	-25.10	-21.50	-11.70	-5.00	-39.49	-29.60	-0.92	13.69	BF
X	ABF(H)	116.80	-14.90	21.39	-18.20	21.90	85.90	17.79	0.55	4.95	-DH
G	CF(GH)	120.40	-18.89	-5.70	8.40	7.60	-62.29	51.80	1.61	41.92	CF
21	ACF	114.50	9.20	-34.19	5.40	15.30	-22.29	70.40	2.20	77.44	
F	BCF	125.50	17.10	-0.09	-26.89	-66.80	-10.49	-47.40	-1.48	35.10	
30	ABCF(GH)	116.50	-13.50	2.10	2.79	14.50	-23.49	42.80	1.33	28.62	
E	DF	123.30	-12.69	-22.10	-66.30	-24.59	2.29	-53.80	-1.68	45.22	DF
23	ADF(GH)	108.40	4.40	7.10	13.29	41.90	-37.90	-75.20	-2.35	88.36	-BH
H	BDF(GH)	128.70	7.50	4.09	-20.70	19.59	-16.70	9.39	0.29	1.38	-AH
22	ABDF	107.10	-36.50	0.50	-49.00	7.09	-5.09	-101.20	-3.16	160.02	-H
5	CDF(G)	130.00	2.80	1.30	-18.00	-2.99	-91.89	-15.20	-0.47	3.61	
W	ACDF(H)	106.20	10.70	-21.20	-5.60	41.30	-59.30	-58.59	-1.83	53.65	
8	BCDF(H)	127.50	-21.00	-0.79	-4.50	-15.79	-23.70	-72.39	-2.26	81.90	
V	ABCDF(G)	109.20	-14.50	-12.00	-24.19	-47.10	-41.30	95.00	2.96	141.01	-CH
15	EF(GH)	129.10	-7.29	-9.70	22.69	48.39	24.29	-84.40	-2.63	111.30	EF
CC	AEF	111.60	10.39	10.19	42.90	-6.50	26.90	125.40	3.91	245.70	
14	BEF	113.50	-5.89	28.10	-28.49	-3.00	7.69	39.99	1.24	24.99	
FF	ABEF(GH)	128.50	-9.00	-30.60	2.20	29.69	81.30	-13.00	-0.40	2.64	
O	CEF(H)	117.50	-14.89	17.10	29.20	79.60	66.50	-40.20	-1.25	25.25	
28	ACEF(G)	121.00	-21.60	-44.00	-3.59	-28.30	-12.50	11.60	0.36	2.10	
N	BCEF(G)	113.90	-23.80	7.90	-22.50	12.39	44.29	32.59	1.01	16.60	
32	ABCEF(H)	103.40	-18.30	6.50	-11.20	-19.69	-31.30	-17.60	-0.55	4.84	-FG
M	DEF(G)	113.10	-17.50	17.69	19.90	20.20	-54.89	2.60	0.08	0.10	
31	ADEF(H)	126.70	15.00	-3.10	-58.70	30.69	32.69	73.60	2.30	84.64	
P	BDEF(H)	119.00	3.50	-6.70	-61.10	-32.79	-107.90	-79.00	-2.46	97.51	
29	ABDEF(G)	120.00	-10.50	5.50	-1.40	11.30	-32.09	-75.60	-2.36	89.30	-EH
13	CDEF	121.80	13.60	32.50	-20.79	-78.60	10.49	87.59	2.73	119.90	GH
EE	ACDEF(GH)	125.00	1.00	-14.00	12.20	59.70	44.10	75.80	2.36	89.77	
16	BCDEF(GH)	123.80	3.20	-12.60	-46.50	33.00	138.30	33.60	1.05	17.64	
DD	ABCDEF	111.00	-12.79	-16.00	-3.39	43.10	10.09	-128.20	-4.00	256.80	

TOTAL 7476.99 TOTAL 5667.24

CORRECTED SUM OF SQUARES 5667.25 AVERAGE 116.82

ESTIMATE OF ERROR VARIANCE 66.97 BASED ON 26 DEGREES OF FREEDOM

TABLE A-5

RT FLEX STRESS (AC INTERACTION)

	a_o c_o	a_o c_1	a_1 c_o	a_1 c_1		
	106.7	118.8	112.0	87.4		
	126.3	117.5	111.6	114.5		
	124.7	112.5	124.7	126.3		
	129.1	120.4	119.0	121.0		
	127.6	129.1	125.1	118.0		
	123.3	121.8	126.7	106.2		
	122.3	100.9	108.7	108.1		
	113.1	130.0	108.4	125.0		
	113.3	119.2	120.3	87.2		
	113.5	125.5	116.8	103.4		
	112.0	123.7	117.7	104.3		
	106.4	113.9	128.5	116.5		
	118.3	126.9	112.0	112.4		
	119.0	127.5	107.1	111.0		
	102.8	126.9	129.0	113.4		
	128.7	123.8	120.0	109.2		
Σ	1887.1	1938.4	1887.6	1763.9	$\Sigma\Sigma$	7477.0
AVG.	117.9	121.2	118.0	110.2	GRAND AVG.	116.8

	a_o	a_1	AVG.
c_o	117.9	118.0	118.0
c_1	121.2	110.2	115.7
AVG.	119.6	114.1	116.8

TABLE A-6

SIGNIFICANT EFFECTS (WITH F RATIOS) FROM AOV

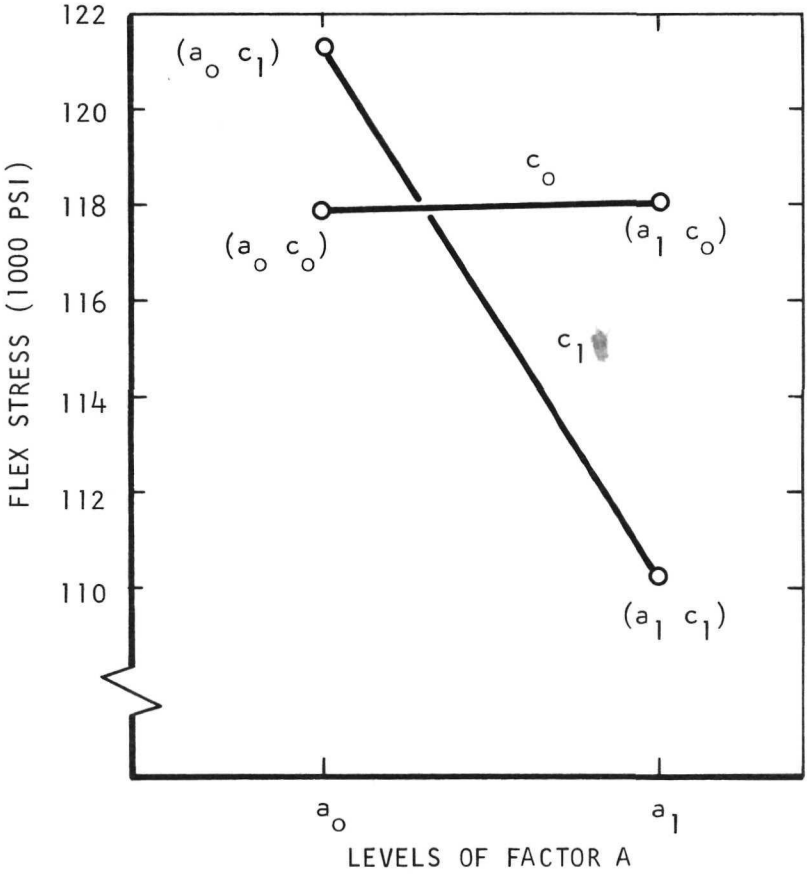
	SB SHEAR 600°F	FLEXURE STRENGTH 600°F	SB SHEAR RT	FLEXURE STRENGTH RT	FLEXURE MODULUS 600°F	FLEXURE MODULUS RT
All Effects with F Ratio above 4.23	E (5.03)	AD (5.15)	BLK. (6.76)	A (7.06) AC(7.14) AG(5.33) DG(5.13) EG(5.95)	C (5.18)	BLK. (45.17) C (6.50) D (6.00) F (6.70) AG (5.91)
All Effects with F Ratio Between 4.23 and 2.91	BLK(3.77) G (3.03)				BLK(3.59)	AC (4.14) EG (3.67) FH (3.45)
Selected Effects with F Ratio Below 2.91		FH (2.43) B (2.04)	FH (2.03)		FH (2.46)	

TABLE A-7
INTERPRETATION OF FRACTIONAL FACTORIAL EXPERIMENT RESULTS

FACTORS & LEVELS \ CRITERIA	SHORT BEAM SHEAR STRENGTH AT 600°F	ULTIMATE FLEXURE STRENGTH AT 600°F	SHORT BEAM SHEAR STRENGTH AT ROOM TEMPERATURE	ULTIMATE FLEXURE STRENGTH AT ROOM TEMPERATURE	FLEXURAL MODULUS AT 600°F	FLEXURAL MODULUS AT ROOM TEMPERATURE	TRW RECOMMENDATIONS
BLOCKS Block 1 = P13N Block 2 = P10P	**P10P (Block-3.77)**		P10P (Block-6.76)		**P10P (Block-3.59)**	P10P (Block-45.17)	P10P
COMPACTION (A) a_o a_1 No Yes		Compact (AD-5.15)		No Compact (AC-7.14)(1) No Compact (AG-5.33)(2)		No Compact (AG-5.91)(1) **Compact (AC-4.14)**	Compact
IMIDIZING TEMPERATURE (B) b_o b_1 300°F-40 HRS. 400°F-1 HR.		400°F (B-2.04)					400°F-1 Hour
IMIDIZING ENVIRONMENT (C) c_o c_1 Air Vacuum				Vacuum (AC-7.14)(1)	Air (C-5.18)	Air (C-6.50) **Air (AC-4.14)**	Air
MOLD PRESSURE (D) d_o d_1 500 Psi 1000 Psi		1000 Psi (AD-5.15)		1000 PSI (DG-5.13)		1000 Psi (D-6.00)	1000 Psi
MOLD TEMPERATURE (E) e_o e_1 P13N 550°F 600°F P10P 600°F 650°F	Higher Temp. (E-5.03)			Higher Temp. (EG-5.95)(3)		**Higher Temp.(EG-3.67)(2)**	Higher Temp.
MOLD TIME (F) f_o f_1 30 Minutes 60 Minutes		60 Minutes (FH-2.43)	60 Minutes (FH-2.03)(1)		60 Min. (FH-2.46)	60 Min. (F-6.70) **60 Min. (FH-3.45)**	60 Minutes
POST CURE ENVIRONMENT (G) g_o g_1 Air Nitrogen	**Air (G-3.03)**			Air (AG-5.33)(2) Air (DG-5.13) Nitrogen (EG-5.95)(3)		Air (AG-5.91)(1) **Nitrogen (EG-3.67)(2)**	Air
POST CURE TIME (H) h_o h_1 0 Hours 16 Hours (NB)		16 Hours (FH-2.43)	0 Hours (FH-2.03)(1)		16 Hours (FH-2.46)	**16 Hrs. (FH-3.45)**	16 Hours
NB Post Cure Temperature 50°F above mold temperature except for P10P molded at 650°F which were post cured at 650°F							
			(1) 60 Min./16 Hrs. -500 Psi	(1) Compact/Air -3200 Psi (2) Compact/Air -10,000 Psi Compact/Nitrogen -4000 Psi (3) Higher Temp./Air -7100 Psi		(1) Compact/Air -1.1×10^6 Psi Compact/Nitrogen -0.1×10^6 Psi (2) Higher Temp./Air -0.6×10^6 Psi	

FIGURE A-1

GRAPH OF AC INTERACTION-ULTIMATE FLEXURE STRESS AT ROOM TEMPERATURE



a_o	=	NOT COMPACTED	$a_o c_o$	=	117.9 PSI
a_1	=	COMPACTED	$a_o c_1$	=	121.2 PSI
c_o	=	AIR IMIDIZATION	$a_1 c_o$	=	118.0 PSI
c_1	=	VACUUM IMIDIZATION	$a_1 c_1$	=	110.2 PSI

APPENDIX B

FATIGUE TEST METHOD

The test setup for fatigue evaluation is shown in figure B-1. An electrodynamic shaker was used to excite first mode resonance of the specimen mounted as a cantilever beam. Figures B-2 and B-3 show the split steel block that was used to clamp the specimen. A 0.420 inch radius was provided on each half of the block to minimize the stress concentration at the clamped end of the specimen. Clamping was shim adjusted to 0.0015-0.0025 inch compression, which proved sufficient to retain the specimen without crushing deformation.

During vibration, the specimen tip double amplitude was measured by means of a telemicroscope with cross hairs mounted on a micrometer slide. Strain gages were used to measure tip amplitude versus stress. It was determined experimentally, with strain gages, that a gage mounted on the specimen centerline two inches from the base would measure one-half of the maximum stress. Figure B-4 is a curve of stress versus gage distance from the fixed end. This location was used on all specimens as a means of extending strain gage fatigue life. A balanced potentiometer circuit, AC voltmeter, and oscilloscope were used in conjunction with the strain gage for strain measurements. The specimen resonant frequency was determined by peak amplitude detection and readout of the shaker oscillator setting with an EPUT meter. An electronic totalizing counter was used to determine the total number of fatigue cycles.

All of the specimens were 6 inches long and 0.5 inches wide. Thickness varied from 0.076 to 0.080 inch for the 0-90° laminates, and 0.081 to 0.085 inch for the unidirectional laminates. The free length when clamped in the holding fixture was 5.5 inches.

Prior to fatigue testing, each specimen was vibrated to obtain a curve of stress versus tip double amplitude as shown in figure B-5. The measured strain was converted to stress using a modulus of elasticity calculated from the measured natural frequency. Figure B-6 is a calculated plot of natural frequency versus modulus of elasticity for several specimen thicknesses.

The 12 specimens from each group were vibrated at their first mode resonant frequency and constant amplitude until failure or completion of 10,000,000 cycles. The stress level of each specimen was selected to provide a data spread as needed to plot an S-N curve for each material. During testing each specimen was vibrated at its peak resonance as detected by peak amplitude, while adjusting the driving frequency. After each adjustment of frequency, the driving power was set to provide the tip amplitude required for that specimen. Also, during testing, a graph of frequency versus total cycles was maintained for each specimen. A typical curve is shown in figure B-7. The data for the graph was obtained from the EPUT meter and totalizing counter. As indicated in figure B-7, the first change in slope was defined as specimen failure. Testing was continued until at least two additional slope changes were detected. The data points were plotted on the S-N graph as each specimen was completed. A second S-N graph was also plotted for each material; this graph was based on failure defined as a 5% drop in frequency.

FIGURE B-1 EQUIPMENT SET-UP USED IN FATIGUE TESTING

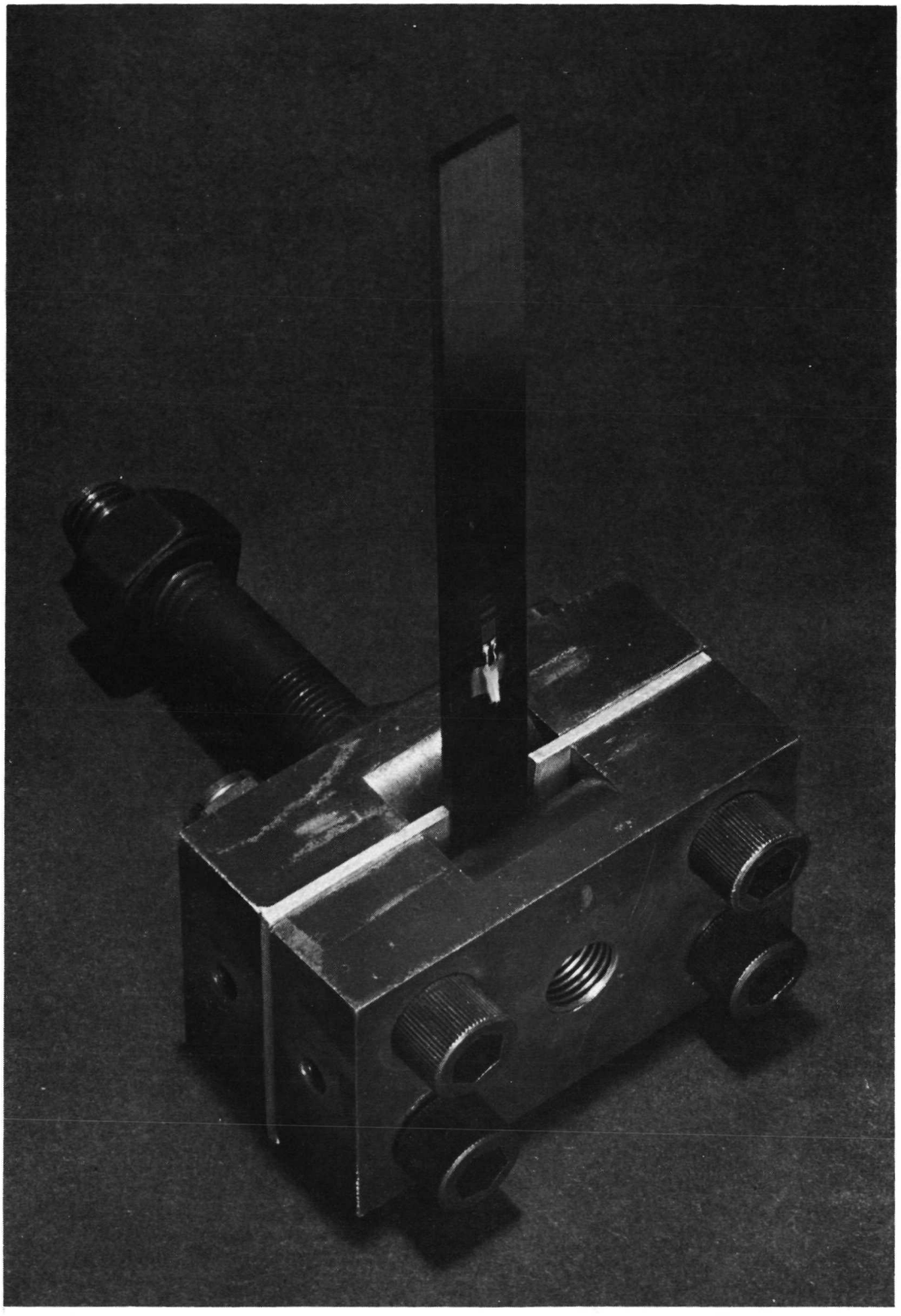


FIGURE B-2 SPECIMEN HOLDING FIXTURE

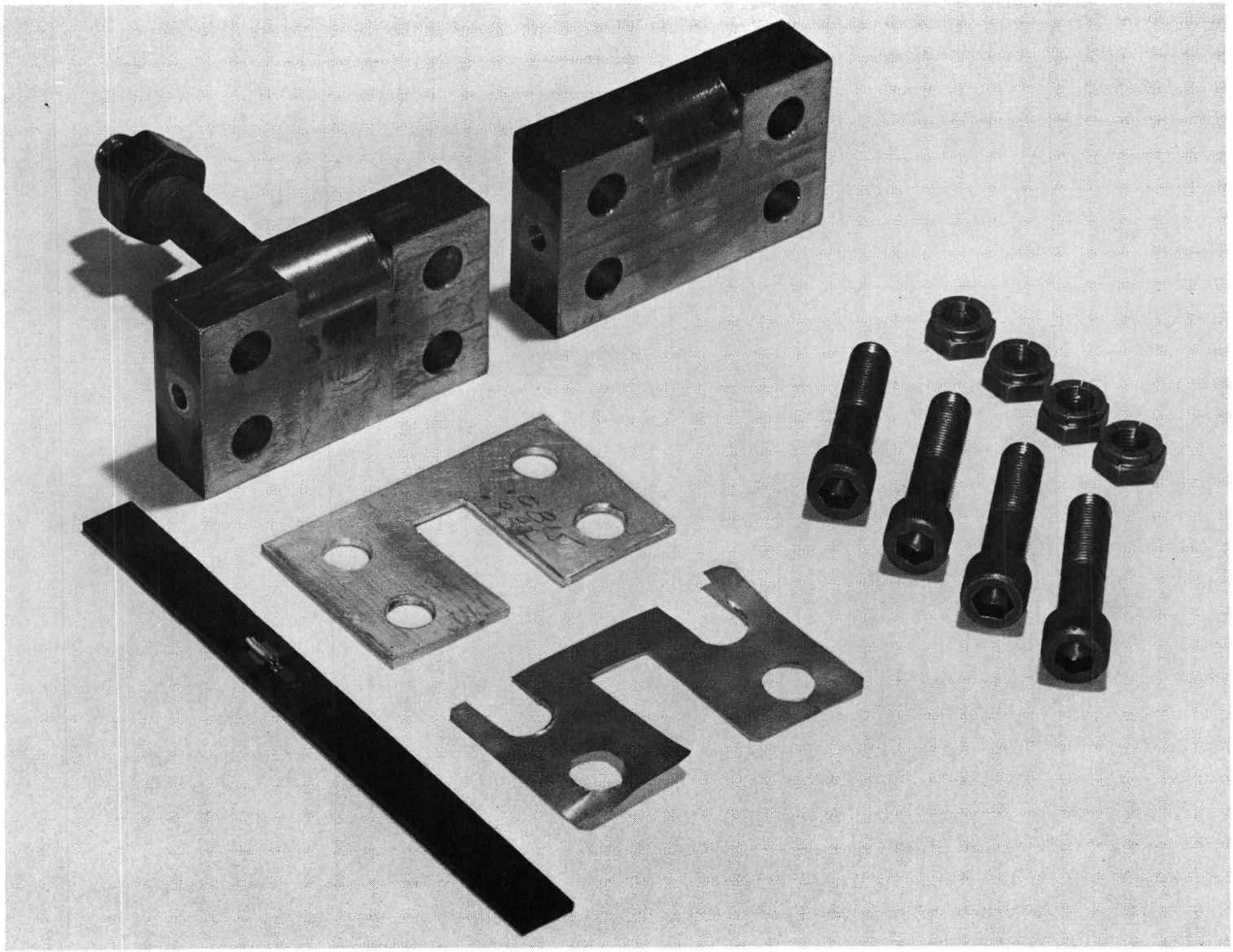


FIGURE B-3 HOLDING FIXTURE COMPONENTS

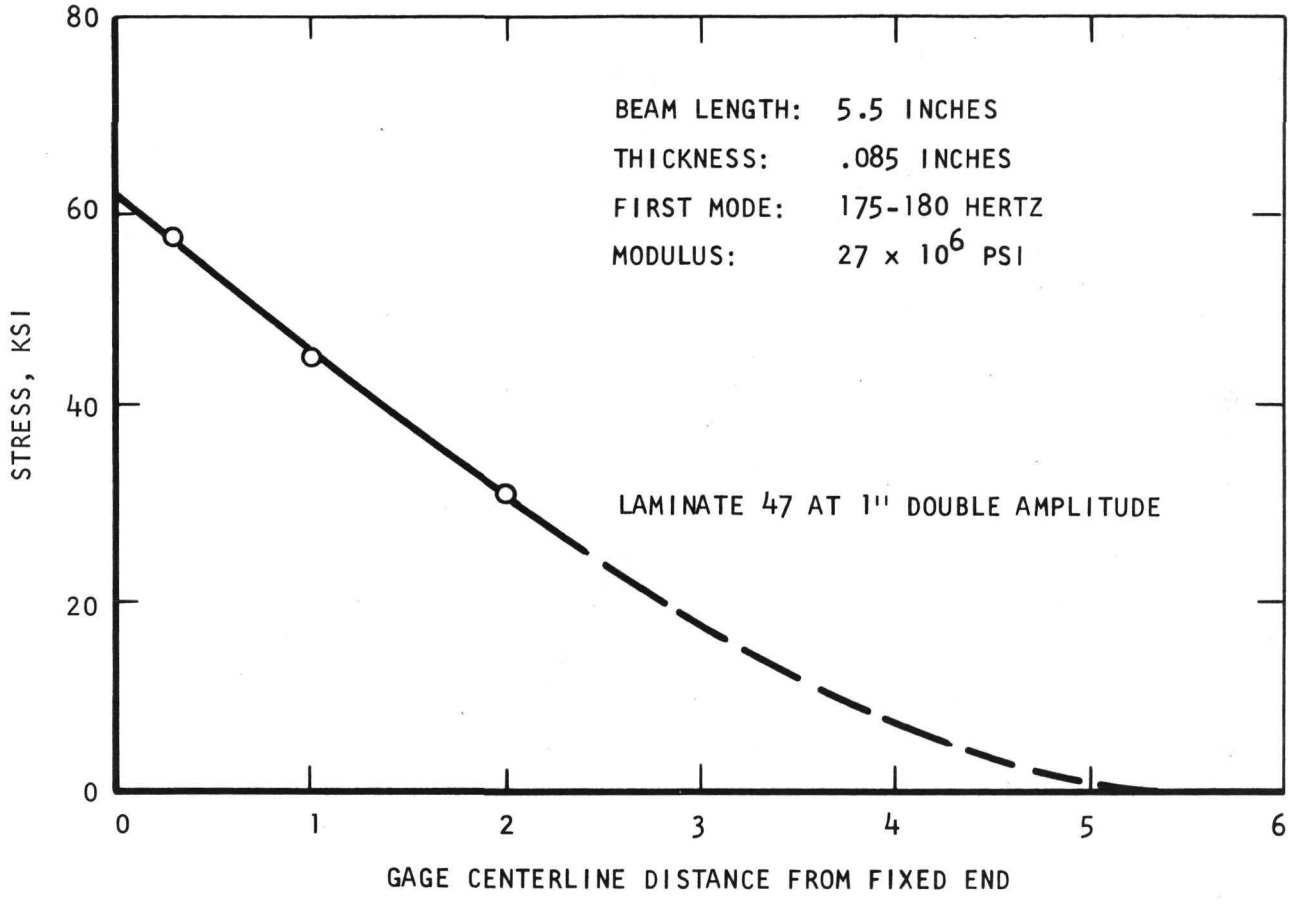


FIGURE B-4 STRESS VERSUS GAGE DISTANCE FROM FIXED END

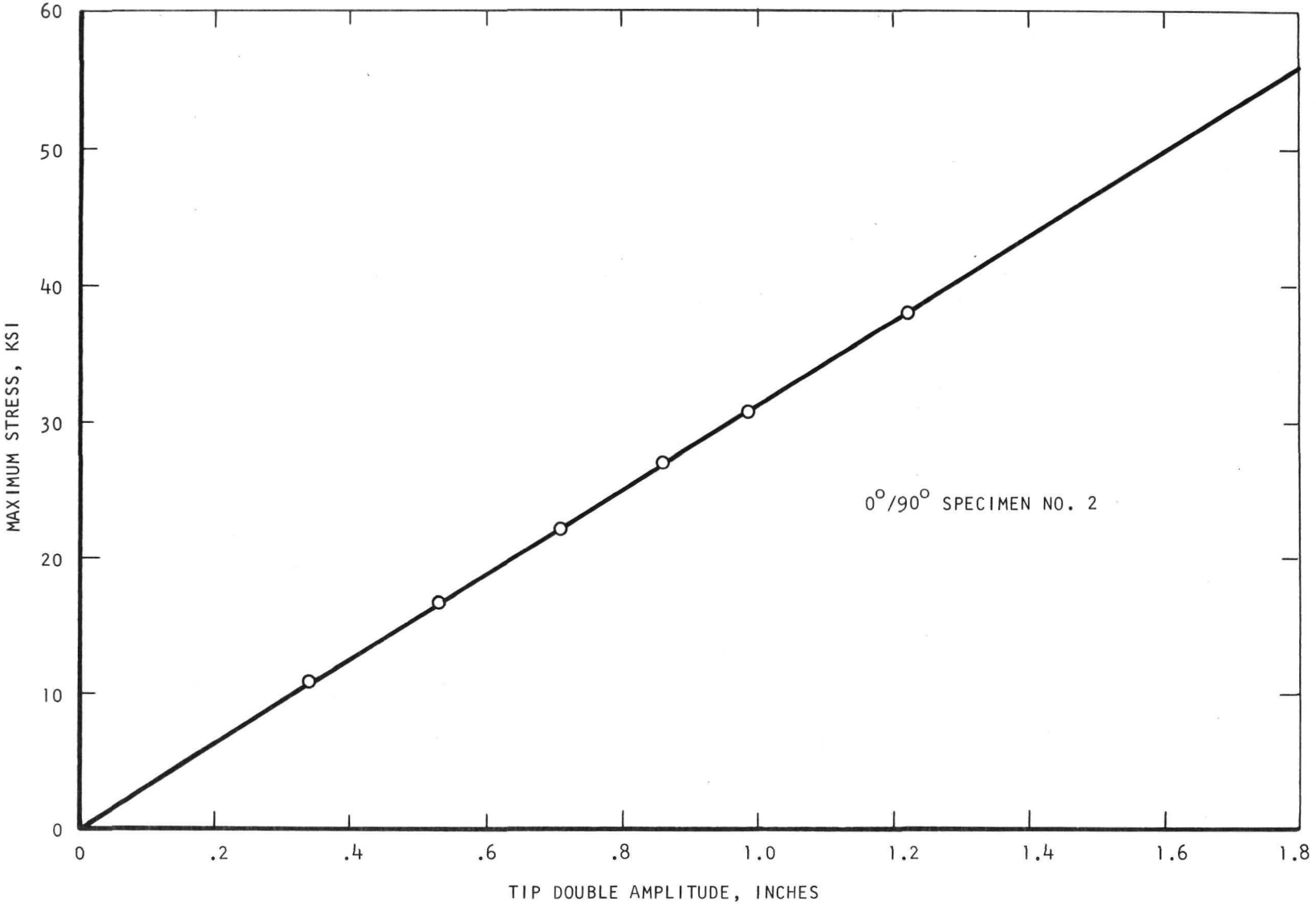


FIGURE B-5 MAXIMUM STRESS VERSUS TIP DOUBLE AMPLITUDE - TYPICAL CURVE

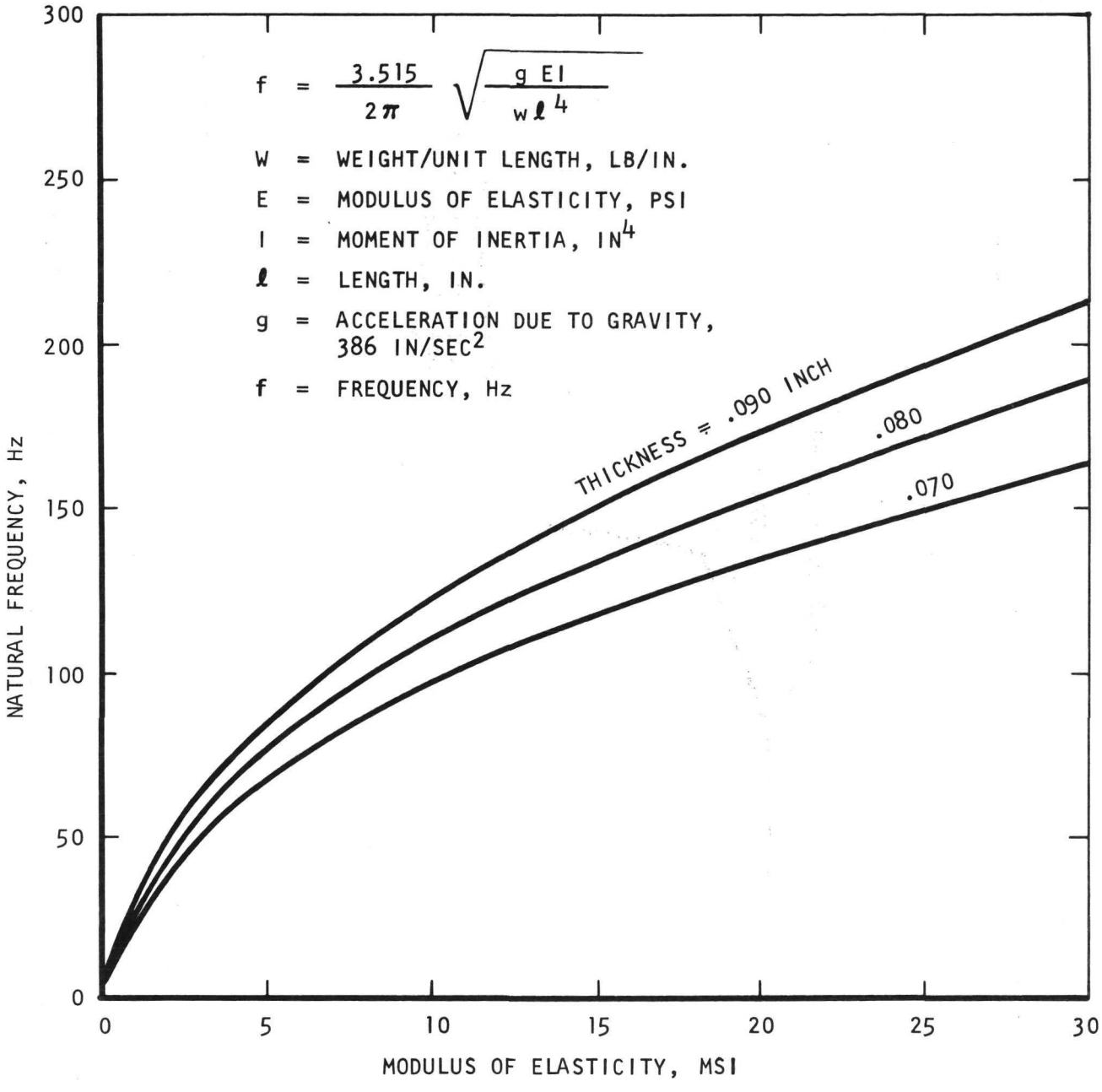


FIGURE B-6 VIBRATING CANTILEVER BEAM (FIRST MODE) FREQUENCY VERSUS MODULUS OF ELASTICITY.

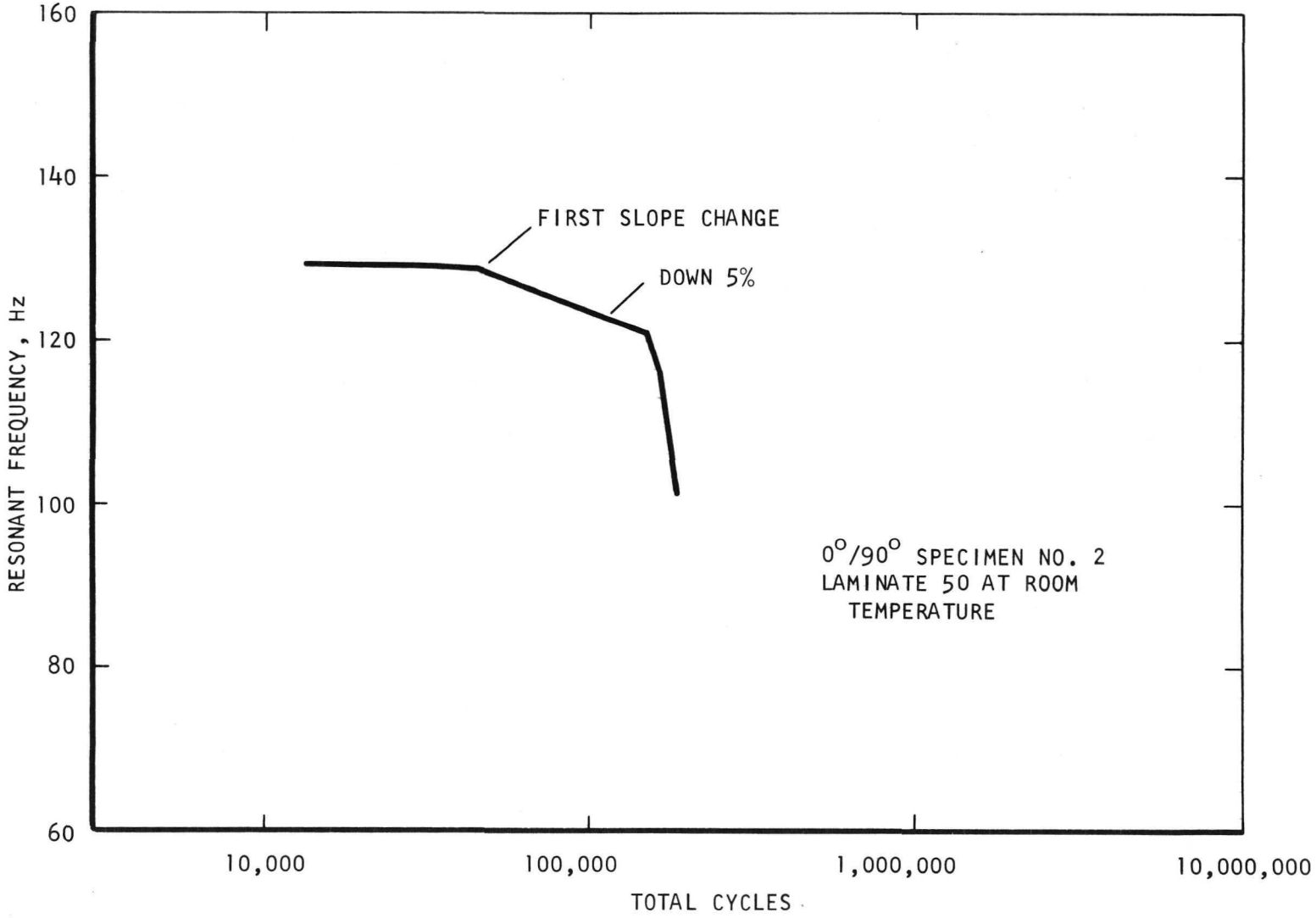


FIGURE B-7 RESONANT FREQUENCY VERSUS TOTAL CYCLES - TYPICAL CURVE

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