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AFML-TR-77-158

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EXTENDED FLOW LIFE LAMINATING RESIN SYSTEM

Acurex Corporation/Aerotherm Division
485 Clyde Avenue
Mountain View, California 94042

October 1977

Final Report for the Period 2 February 1976 — 31 May 1977

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limited solubility in the resins. Diaminodiphenyl sulfone, diaminonaphthalene and diaminobenzophenone showed promise for 350°F performance and extended flow life capability when blended with the resins as powders (<400 mesh). Diaminodiphenyl sulfone with tetraglycidylmethylenedianiline and diglycidyl aniline provided the following composite strengths with Thorne 300 graphite fibers: short beam shear, 19.1 ksi at room temperature and 10.7 ksi at 350°F; transverse tensile, 7.6 ksi at room temperature and 5.6 ksi at 350°F; flexural, 267 ksi at room temperature and 209 ksi at 350°F. Transverse tensile strain to failures were 5550 $\mu\text{in/in}$ at room temperature and 5180 $\mu\text{in/in}$ at 350°F. All tests conducted on this composite system have shown equivalence to state of the art 350°F epoxy graphite composites. The prepreg has a 10-week flow life.

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FOREWORD

This final report was prepared by Acurex Corporation/Aerotherm Division, Mountain View, California, 94042 under Air Force Contract No. F33615-76-C-5133, "Extended Flow Life Laminating Resins." The work was performed under the sponsorship of the Air Force Materials Laboratory (AFML/MBL), Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, under the direction of Mr. T. J. Aponyi as Project Monitor. The effort at Aerotherm was conducted within the Materials Department under the direction of Mr. R. M. Washburn. Mr. C. B. Delano was the Program Manager and Mr. R. J. Milligan was the Principal Investigator. Mr. J. D. Dodson was responsible for the graphite composites effort and Mrs. H. L. Atkins provided chemical support.

This report covers work performed during the period of 2 February 1976 through 31 May 1977.

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SECTION 1

INTRODUCTION

As the use of advanced composites is steadily increasing in aircraft and space-related structures so too is the comparative size of individual components increasing. Efforts to simplify and economize manufacturing techniques are not always successful due to the limited shelf life of high performance graphite fiber/epoxy prepreg materials currently available.

Those epoxy resin based prepreps presently enjoying by far the largest use in high performance applications are generally limited to a nominal 14-day flow life under ambient shop conditions. Projected layup schedules for very large (sub)assemblies far exceeds this 2-week limitation. Although the flow life may be extended by refrigeration techniques, the anticipated size of items in preliminary design phases prohibits the use of this means of circumventing this shortcoming in today's prepreps.

An extended flow life prepreg is needed for the fabrication of these large complex monolithic subassemblies (skins, support and stiffening structures, ancillary mounting, etc.) where prolonged layup schedules are encountered and co-curing procedures would prove effective.

In our efforts to provide the Air Force with a laminating resin which would have a minimum 75-day flow life, careful attention was paid to other requirements which placed restrictions on the allowable variations in resin modification and curing agent/cure schedule alternatives. These included:

1. Virtually equivalent handleability properties (i.e., drape, tack, flow, etc.) as state-of-the-art prepreg
2. Cure schedule (temperature/pressure profile) not to exceed 350°F/100 psi with a 400°F free-standing post-cure allowed
3. No volatiles be evolved during cure
4. Low (<1 percent) void content composites
5. Environmental stability (i.e., moisture resistance) at least as good as the best state-of-the-art epoxy

6. Thermomechanical performance profile at least equal that of state-of-the-art epoxy/graphite fiber composite (≈ 80 percent retention of room temperature flexural strength be retained at 350°F)
7. Prepregging procedures be readily adaptable to high volume production equipment

SECTION 2

TECHNICAL DISCUSSION

2.1 BACKGROUND

Epoxy/graphite prepregs are available which provide satisfactorily performing 350°F composites. However, the majority of these systems provide a nominal 2-week flow life. This is, of course, due to the cure chemistry of the system.

The approach generally used with epoxy resin systems to achieve extended flow lives/short cure times is to employ "latent" curing agents. Latency is achieved through several methods. One method, for example, is to employ a RT insoluble curing agent in the epoxy resin. The insolubility at room temperature provides the required latency while dissolution at elevated temperatures allows the cure reactions to occur.

Acceptable flow characteristics for state-of-the-art epoxies are by definition those which provide the desired tack, drape, etc., consistent with layup and cure procedures employed by the user. Thus, when a prepreg ceases to exhibit good handleability during storage and fails to provide high quality layups at room temperature due to insufficient drape and tack, its flow life is considered expired.

This effort is a continuation of the efforts described in AFML TR-76-49 dated June 1976 by E. S. Harrison and C. B. Delano. These prior efforts were principally epoxy resin formulation studies conducted to define both resin and curing agent compositions which would provide the properties cited in Section 1.

The basic approach was to employ curing agents which would exhibit virtual insolubility in the resin combinations at slightly elevated prepregging temperatures (<150°F) but become soluble at processing (≈250°F) temperatures.

The system developed in the first effort is equivalent to available state-of-the-art epoxy/graphite prepreg. It was derived from CIBA-Geigy MY 720 and 0510 resins and used carefully purified 4,4'-diaminodiphenylsulfone ground to -400 mesh particle size as a curing agent. Zinc linoleate proved to be an effective co-catalyst.

Evaluations (in T-300 reinforced composite form) included thermomechanical strengths, response to >1000 hours exposure to 95+ percent relative humidity at 120°F, 500-hour aging studies at 350°F and regain characteristics after drying the moisture laden composites.

The present effort expanded upon prior efforts with principal focus on optimization of the resin composition, expansion of the graphite composite data base and a search for alternate curing agents.

2.2 THE RESIN SYSTEM

At the end of the efforts described in AFML TR-76-49, the constituents of the extended flow life resin system were:

Ciba Geigy	Araldite MY 720	~94 pbw
Ciba Geigy	Araldite 0510	~ 6 pbw
E. V. Roberts & Assoc.,	Diaminodiphenylsulfone (DADS) -400 mesh	~26.7 pbw
Harshaw Chemical	Zinc linoresinate	~3 pbw

By the end of the current program the final constituents had become:

Ciba Geigy	Araldite MY 720	~94 pbw
Mobay Chemical	Lekutherm X-50 (distilled)	~ 6 pbw
E. V. Roberts & Assoc.,	Diaminodiphenylsulfone (DADS) -400 mesh	~29.9 pbw

The experiments that led to these changes in formulation are presented below. See Section 3 for parts by weight (pbw) to be used in the formulation.

2.2.1 The Major Resin

Ciba Geigy's Araldite MY 720* has remained the major resin. Araldite MY 720 is Ciba Geigy's trade name for the epoxy resin; N,N,N',N'-tetraglycidylmethylenedianiline (Figure 1). Two batches of this resin were used under the current program. The first batch, N-80194 had an epoxide equivalent weight (eew) of 135 and the second an eew of 130. The theoretical eew for MY 720 is 105.5. Epoxide equivalents were measured by the pyridinium chloride method using potentiometric end points. No chemical differences were noted between these two batches in the program.

2.2.2 The Minor Resin

Diglycidylaniline (DGA)

The change from Ciba Geigy's Araldite 0510 to diglycidylaniline was made near the beginning of the program. It was shown that diglycidylaniline, despite its known slight lowering effect on distortion temperature under

*The authors are indebted to Ciba Geigy, Ardsley, New York for samples of their Araldite MY 720 and 0510 resins.

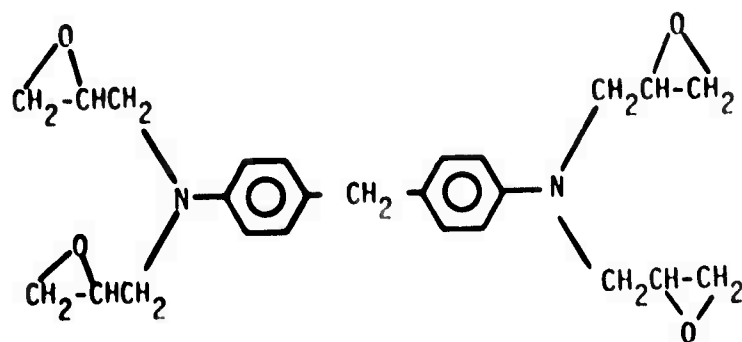


Figure 1. N,N,N',N',-Tetraglycidylmethylenedianiline.

load (DTUL)* increased both the flow life of the resin system and the prepreg. The expected slight 350°F property loss with the 6-percent DGA was easily balanced against the benefits to flow and tack life. Structures of both reactive diluents are given in Figure 2.

The first laminate prepared with the DGA formulation, No. 204, showed a possible decline in 350°F (177°C) flexural properties compared to laminates Nos. 201 and 203 prepared with the 0510 formulation.* These results are shown in Table 1. Subsequent composite test results indicated that the DGA formulation could provide acceptable 350°F composite properties with a slight increase in the DADS used in the formulation.

Lekutherm X-50

Initially, the diglycidylaniline used in this program was synthesized from aniline and epichlorohydrin. However, halfway through the program, a commercial source for this resin was located.† Mobay Chemical sells the resin under the trade name Lekutherm X-50.

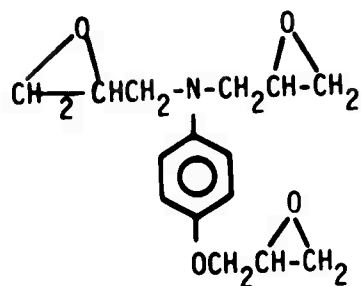
A sample of this diluent was obtained and incorporated without purification into the extended flow life formulation which at this time had been finalized. Properties of laminates prepared with the unpurified DGA formulated resin, as shown in Table 2, were quite poor. Although cure conditions were not finalized at the time these laminates were prepared, the properties were poor enough to suggest that the as-received Lekutherm was, at least, partially responsible.

This is supported by the observed 4°C loss in DTUL obtained on a cured casting prepared with unpurified Lekutherm X-50 when compared with one of the same formulation prepared with distilled diglycidylaniline and cured side by side. Thus, a sample with distilled diglycidylaniline had a DTUL of 241°C and with unpurified Lekutherm X-50 had a DTUL of 237°C (side by side cure).

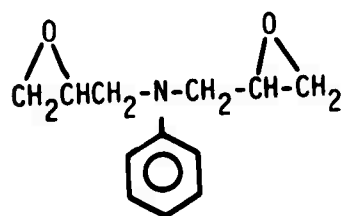
A high vacuum distillation of Lekutherm X-50 was then undertaken. The collected center cut had a 1° boiling point range (109°C to 110°C at 0.1 m Hg) and an eew of 102 exactly equal to the theoretical value. As received from Mobay, Lekutherm X-50 had an eew of 109. Distilled Lekutherm X-50 was used throughout the rest of the program.

* AFML TR-76-49

† The authors wish to express their gratitude to Mobay Chemical for samples of Lekutherm X-50.



N,N,O-Triglycidyl-4-aminophenol,
Ciba-Geigy's Araldite 0510



N,N-Diglycidylaniline, Mobay
Chemicals' Lekutherm X-50

Figure 2. Reactive diluents used to modify the
extended flow life resin formulations.

TABLE 1. INITIAL LAMINATE DATA

Laminate No.	Resin Formulation (pbw)	Cure Schedule	Resin Content (%)	Fiber Volume (%)	Void Content (%)	Flexural Strength/Modulus ksi/msi (avg) RT 350°	Short Beam Shear Strength ksi (avg) RT 350°
201	MY 720 (94) 0510 (6) DADS (267) Zn lineresonate (3)	a	26.8	67.1	0	260/18.8 190/18.6 (73) ^d	15.5 8.3
203	↓	b	27.9	65.8	0	275/18.8 178/18.5 (65) ^d	16.9 8.5
204	MY 720 (94) DGA (6) DADS (267) Sn octoate (0.87)	c	29.7	63.9	0	256/17.8 175/18.4 (68) ^d	17.8 8.5
Narmco 5208	—	—	—	—	—	247/- 196/-	15.2 8.6

^aLayup in cold press, increase temperature to 270°F in 60 minutes under contact pressure and 10 in. Hg. Hold 100 min. at temp., apply 75 psi, vent to air. Increase temperature to 350°F in 20 min. Hold 2.5 hrs. at 350°F. Cool under pressure. Post-cure 4 hrs. at 400°F, free standing.

^bSame as "a" except dwell 90 minutes at 270°F under 10 in. Hg.

^cSame as "a" except dwell 150 minutes at 270°F under 10 in. Hg and temperature increase to 350°F held to 25 minutes.

^dpercent of room temperature value.

TABLE 2. MECHANICAL PROPERTIES OF LAMINATES CONTAINING DISTILLED DIGLYCIDYLANILINE, LEKUTHERM X-50 AND DISTILLED LEKUTHERM X-50

Laminate No. ^a	Resin Formulation ^b	Processing and Cure Schedule	Resin Content (%)	Fiber Volume (%)	Void Content (%)	Interlaminar Shear Strength (ksi) ^f	
						RT	350°
225	MY 720 (94) DGA (6) DADS (29.9)	c	31.8	61.6	0	16.7	9.4
226A	↓	d	29.1	64.6	2.5	10.7	6.6
226B		d	28.5	65.8	2.5	9.0	-
227		e	30.5	63.1	0	14.9	8.9

^aAll laminates 4 in. x 4 in., 12 ply.

^bLaminate 225 contains distilled diglycidylaniline, laminates 226A and 226B contain as-received Lekutherm X-50 and laminate 227 contains distilled Lekutherm X-50.

^cPress autoclave layup. In cold (10°F) press held under maximum vacuum for 1 hour prior to heating. Decrease vacuum to 10 in. Hg and increase temperature to 275°F in 60 minutes. Hold 2 hours at 275°F, then apply 75 psi and vent vacuum; increase to 325°F and hold for 3 hours at 325°F. Post-cure free standing 4 hours at 375°F.

^dLike "c" above, except at 275°F hold for 2 hours 30 minutes prior to application of pressure.

^eLike "c" above, except temperature increase to 275°F was over a period of 70 minutes and the dwell at 275°F was 2 hours 20 minutes.

^fAll are the average of five specimens.

2.2.3 The Curing Agent, Diaminodiphenylsulfone

Purification

Diaminodiphenylsulfone (DADS) was purchased from E. V. Roberts in 4-pound lots. As received, it consists of the product, a chromophore and a second compound which appears to be much more reactive than diaminodiphenylsulfone. (The active compound and the chromophore may be the same compound.) Purification of the amine was accomplished by recrystallization from methanol/water. The second crop of crystals from this recrystallization gave a purer product than the first crop (DSC). A second recrystallization gave DADS in pure enough form to give a prepreg with the sought room temperature flow life.

Curing Agent Stoichiometry Studies

The effects of amine/epoxide stoichiometry on the performance of the resin was extensively investigated during the program. Three series of castings were made in which the amine/epoxide stoichiometric ratio was varied between 0.5 to 1 and 1 to 1. In all cases, -400 mesh doubly recrystallized DADS was mixed into a weighed amount of MY 720/DGA (94 to 6) at a temperature no greater than 150°F. The mixture was then transferred to a vial, deaerated at 250°F and subsequently cured through a predetermined time/temperature regimen. Each series was then post-cured to a final condition. The DTUL's of these specimens are plotted in Figure 3. The data shows the expected benefit to DTUL measurements with higher cure temperatures. Cure temperatures of 350°F (177°C) provided DTUL's of from 220°C to 230°C and cure temperatures of 400°F (204°C) provided DTUL's of from 240°C to 250°C.

Also apparent from the curves is an optimum DTUL which is achieved at 75 percent DADS stoichiometry. The downward slope of the curve seen after the optimum DTUL is not as pronounced as that reported by Illman* for the m-phenylenediamine/EPON 828 system.

The stoichiometry studies showed the expected variations in both room temperature flow life and in the DSC cure curves. Table 3 contains, besides an analysis of these DSC curves, the room temperature flow life data for DADS loadings of differing stoichiometries. As will be discussed again later, an excellent relationship between the room temperature flow life and the initial cure onset temperature was found to exist. This is also seen in Table 3.

Particle Size Studies

There are at least two reasons to use a fine particle size for an insoluble curing agent. If upon dissolution the curing agent reacts rapidly with the epoxy, a homogeneous solution should be achieved prior to gel. Furthermore, there is need to maintain a uniform suspension of the curing agent in the resin.

*J. C. Illman, J. Applied Poly. Science, 10, 1519 (1966).

- △ 4 hrs @ 350°F (177°C)
- 4 hrs @ 400°F (205°C)
- 2 hrs @ 400°F (205°C)
- ▽ 4 hrs @ 375°F (191°C)
- ◇ 5 hrs @ 400°F (205°C)

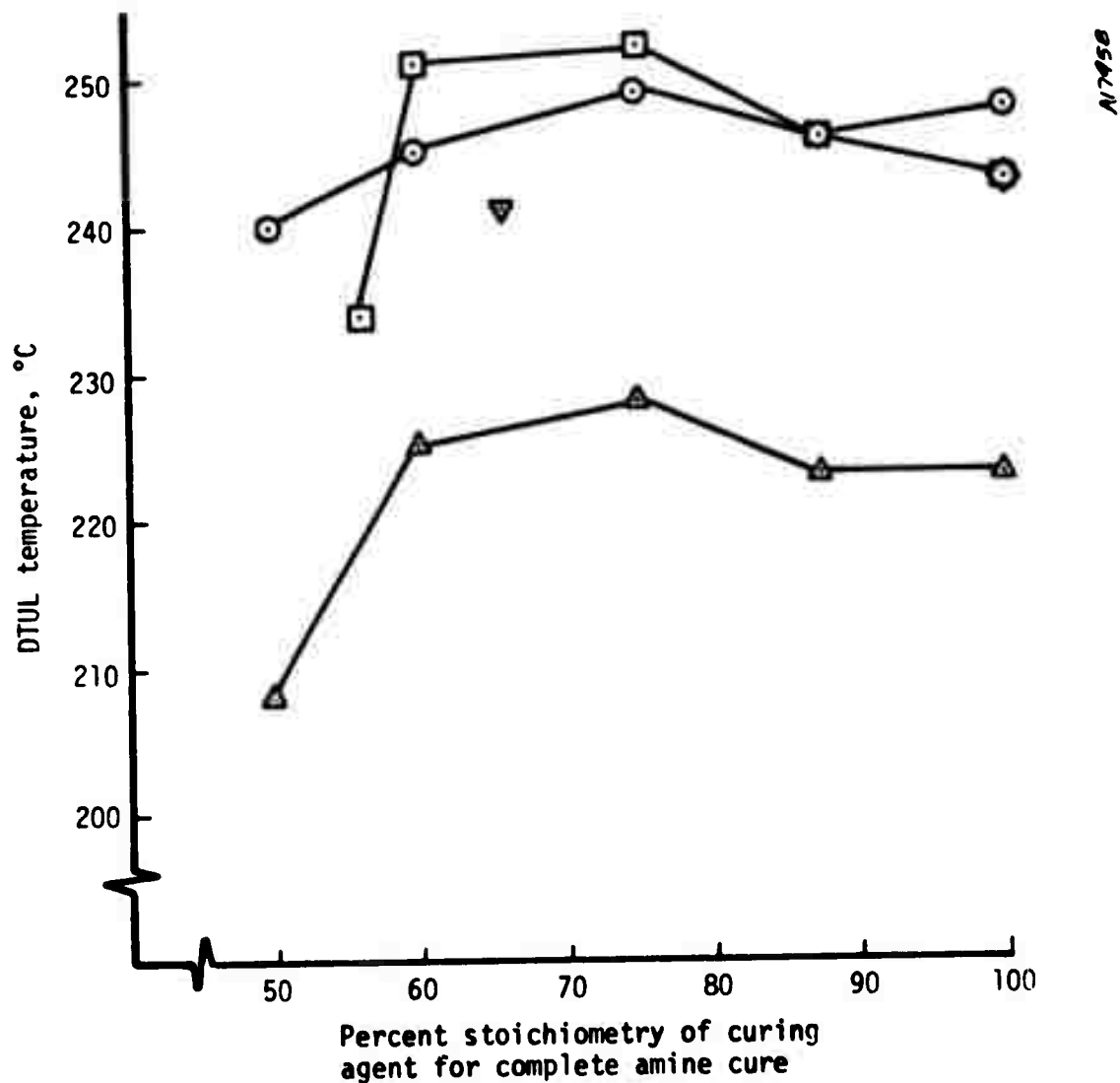


Figure 3. Distortion temperature under loads versus stoichiometry and cure temperature for DADS/MY 720/DGA.

TABLE 3. DIFFERENTIAL SCANNING CALORIMETRY (DSC) TRACES
OF THE CURE EXOTHERMS OF DIAMINODIPHENYLSULFONE
(DADS) AND 94 PARTS MY 720/6 PARTS DGA AT
VARIOUS AMINE/EPOXIDE STOICHIOMETRIES

Stoichiometric Ratio Amine : Epoxide	DSC Cure Exotherm			RT Flow Life (Days)
	Initial Temp. (°C)	Maximum Temp. (°C)	Width at Half Height (°C)	
0.56 : 1.00	175	268	35	75
0.60 : 1.00	170	266	41	73
0.75 : 1.00	155	253	40	69
0.875: 1.00	150	244	40	40
1.00 : 1.00	150	237	38	40

It was found, however, that DADS dissolves in the resin long before the gel onset at 300°F. In all but the two highest loadings, DADS completely dissolved during the 250°F deaeration step. The prolonged time between the dissolution of DADS into the resin and gel onset indicates that DADS is successful not only because it is insoluble but also because of its slow reactivity with epoxy resins.

Samples of DADS were collected after being passed through 200 and 325 mesh sieves. These were then blended with weighed portions of premixed MY 720/DGA (94:6) at 50- and 100-percent amine-epoxide stoichiometries. No catalyst was employed. The temperatures used for blending the curing agent with the resin and for preparing the castings were the same as described above. The results are listed in Table 4.

It was found for all samples that the DADS dissolved long before the resin gelled. Samples of all six resins placed in the laboratory showed no signs of separation prior to gel which for the 50-percent stoichiometry series was on the order of 13 weeks and for the 100-percent stoichiometry series, on the order of 7 weeks.

The final experiment was the preparation of two laminates from prepreg made with resin containing -200 mesh DADS. A sufficient number of plies were cut from the prepreg for two 4-inch x 4-inch x 12-ply laminates. The first laminates' plies were stacked top to top, bottom to bottom with respect to the prepreg while those of the second laminate were stacked top to bottom. It was felt that this difference in ply layup would enhance any filtering effects the fiber bundles might exert on the particulated DADS during the impregnation step.

Both laminates were laid up and cured in a similar manner as shown in Table 5. Short beam shear values were used to monitor the results. Laminate 218A (top to top, bottom to bottom) had an average interlaminar shear value of 12.6 ksi while laminate 218B (top to bottom, top to bottom) had an average interlaminar shear value of 14.7 ksi. These reduced values from the 16 to 17 ksi routinely obtained for 4-inch x 4-inch x 12-ply laminates prepared with -400 mesh DADS (same formulation) indicates that the particle size of the catalyst does have an effect on laminate performance. This is probably due to filtering of the insoluble particles by fibers during the impregnation process. Even when the DADS dissolved in the resin, there would probably be a stoichiometric upset due to incomplete diffusion throughout the fiber bundles.

TABLE 4. PARTICLE SIZE STUDIES OF DIAMINODIPHENYLSULFONE
AS CURING AGENT FOR MY 720/DGA

Particle Size ^a	DTUL 50% Stoichiometry (°C)	DTUL 100% Stoichiometry (°C)
-200	242	248
-325	229	246
-400	234	248

^aTwice recrystallized and sieved to pass the indicated mesh sizes.

TABLE 5. LAMINATE DATA FOR LAMINATES PREPARED FROM PREPREG MADE WITH RESIN CONTAINING -200 MESH DADS

Laminate No.	Resin Formulation (PBW)	Processing and Cure Schedule	Resin Content (%)	Fiber ^b Volume (%)	Void Content (%)	RT. Interlaminar Shear Strength, ksi (Average, Range, No. Samples)
218A	$\left. \begin{array}{l} \text{MY 720 (94)} \\ \text{DGA (6)} \\ \text{DADS (26.7)} \\ \text{Nuocure 28 (0.87)} \end{array} \right\}$	a	29.4	64.1	1	12.6 (10.9-13.9)6
218B		a	29.6	64.0	1	14.7 (13.9-15.8)5

^aPress autoclave layup. In cold (10°F) press held under maximum vacuum for 1 hour prior to heating. Decrease vacuum to 10 inches Hg and increase to 275°F in 70 minutes. Hold 3 hours 20 minutes at 275°F, then apply 75 psi and vent vacuum, increase to 325°F and hold for 4 hours at 325°F. Post-cure free standing 4 hours at 350°F.

^bThorne1 T-300

2.2.4 Catalyst Systems

Since prior formulation* for the extended flow life resin had only half the stoichiometric equivalent of amine N-H to epoxide, a metal salt catalyst was added to insure that the epoxide groups in excess of stoichiometry would react with each other to complete resin cure at a moderate (375°F to 400°F) temperature. At the end of the previous program, zinc linoresinate was used for the catalyst. It was found, however, that tin II octoate, sold under the trade name Nuocure 28 by Tenneco, produced resins having equivalent DTUL's after equivalent cures at lower catalyst concentrations. At the same time, N,N-diglycidylaniline was substituted for 0510 as the minor resin, tin II octoate was substituted for zinc linoresinate.

During the previously discussed stoichiometric experiments, one series post-cured 2 hours at 400°F, was conducted with resin containing no catalyst. Table 6 shows the DTUL results on both catalyzed and uncatalyzed formulations. No benefit to the resin system by the catalyst is seen if the DADS stoichiometry is between 60 and 87.5 percent. Benefit is seen for the 56-percent DADS stoichiometry.

The catalystless resin formulation was tested for its composite performance. Prepreg was prepared from Thornel 300 and a resin system with 94 parts MY 720, six parts DGA, and 29.9 parts DADS (66-percent stoichiometry). Details for the prepreg are given in Table 7. A 4-inch x 4-inch, 12-ply composite was fabricated from the prepreg. The elevated temperature (350°F, 177°C) short beam shear results were the highest obtained on the program, averaging 10.1 ksi even though the room temperature result was somewhat below expectation. This and data from succeeding laminates were sufficiently convincing to select this formulation as the best developed on both programs. This composition has been coded AF-R-800.[†] Table 8 lists the pertinent data for this laminate.

Unfortunately, a slight sacrifice was made to achieve this formulation and the sacrifice was in flow life. Up to a 91-day room temperature flow life had been demonstrated for prepreg and resin (although tack was lost some time before that) at 50-percent stoichiometry. The prepreg from the 29.9 parts DADS resin had a 70+ day flow life. Flow life on similarly formulated samples have varied from 68 days to 77 days.

2.3 PREPREG

2.3.1 Blending of the AF-R-800 Resin

The manner in which the extended flow life resin is prepared was not varied during the course of the program. Thus, 94 parts of MY 720 was

* AFML TR-76-49

[†] Air Force Resin 800

TABLE 6. DADS MY 720/DGA STOICHIOMETRY STUDIES

Stoichiometry DADS as percent of MY 720/DGA	Uncatalyzed DTUL ^a (°C)	With Tin Octoate Catalyst	
		400°F Cure ^b DTUL (°C)	350°C Cure ^c DTUL (°C)
56	234	240 ^d	208 ^d
60	251	245	225
75	252	249	228
87.5	246	246	223
100	243	248	223

^aSpecimens cured 4 hours at 300°F, 1 hour at 350°F, 2 hours at 400°F.

^bSpecimens cured 4 hours at 300°F, 1 hour at 350°F, 4 hours at 400°F.

^cSpecimens cured 4 hours at 300°F, 4 hours at 350°F.

^d50-percent stoichiometry

TABLE 7. PREPREG DATA

Prepreg No.	Formulation	Deaired	Impregnation Temperature (°F)	Tows per Inch	Prepreg Resin Content (%)
222	94 parts MY 720 6 parts DGA 30 parts DADS	Yes	150	24.4	53.9

TABLE 8. LAMINATE DATA

Prepreg No.	Laminate No.	No. Plies	Dimensions (Inches)	Processing and Cure Schedule	Resin Content (%)	Fiber Volume (%)	Void Content (%)	Average Interlaminar Shear Strength	
								RT ksi (#tested)	350°F, ksi (#tested)
222	222	12	4 x 4	a	30.2	62.8	1	14.5 (5)	10.1 (5)

^a Press autoclave layup. In cold (10°F) press held under maximum vacuum for 1 hour prior to heating. Decrease vacuum to 10" Hg and increase temperature to 275°F in 1 hour. Hold 3 hr 30 min at 275°F, then apply 75 psi and vent vacuum. Increase temperature to 325°F and hold for 4 hours at 325°F. Post-cure free standing 4 hours at 350°F.

weighed out and to it was added six parts of DGA. The two resins are warmed to 150°F and blended to a uniform consistency. A carefully weighed portion of 29.9 parts 4,4'-diaminodiphenylsulfone, doubly recrystallized, ground and passed through a 400 mesh sieve, is then added. Blending is continued until the curing agent is homogeneous. At this point, the catalyst, if required, is added and blended into the mixture.

No variations to the method of DADS addition were attempted as this was judged to be the best route to prepare the suspension of curing agent in the resin. As discussed in the previous sections, variations were run in the amount of curing agent, the type of minor resin and the catalyst.

2.3.2 The Reinforcement

The fiber reinforcement for all prepreg used on the current program was untwisted Thornel 300. The only change during the course of the program was to the sizing used on the fibers. During most of the program the sizing was UC-307. However, this finish was discontinued by Union Carbide. Thus, the concluding work of the program, including all of the test matrix, was accomplished using Thornel 300 with a UC-309 finish.

2.3.3 Preparation of AF-R-800 Graphite Prepreg

The prepregging procedure did not vary through the course of the program. Once the curing agent was thoroughly blended with the resin mixture, the system was degassed at 150°F. The degassed resin system was then hot melt coated onto a mylar sheet and this sheet attached to a drum with the resin side out. Thornel 300 fiber was then wrapped onto the turning drum over the resin. At the end of the wrapping sequence, the prepreg with the mylar backing is cut from the drum and placed on a vacuum hot table. Under vacuum and heat, never exceeding 150°F (66°C), the resin flows up through the fiber bundles until impregnation is complete. The prepreg, now with a sheet of mylar on top, is ready to store until needed. In this manner, prepreps 12 inches x 188 inches (0.30 m x 4.77 m) were prepared.

The flow life of the prepreg closely matched that of the resin from which it was made. Neither the protection from ambient conditions by the mylar nor introduction of fibers into the resin system seemed to affect the flow life.

2.4 AF-R-800 COMPOSITES

2.4.1 Introduction

This section describes the processing of AF-R-800 preregs, their fabrication into composites and mechanical testing of those composites. Prepreg shelf life and composite moisture studies are also included in this section. These mechanical test results are compared to state-of-the-art, 350°F resin systems. It is concluded from these comparisons that the AF-R-800 formulation meets the objective of providing equivalent performance to state-of-the-art, 350°F resin systems with extended flow life capabilities.

The cure cycle required for the preparation of AF-R-800 composites is somewhat longer than that for state-of-the-art systems. This was expected. Program efforts did not focus as heavily on this feature as they did on the successful attainment of mechanical properties equivalent to current state-of-the-art 350°F epoxy resin systems.

Processing development efforts were focused on short beam shear strengths. Once they were reproducible and equivalent to state of the art, the other mechanical properties were expected to be consistent with state-of-the-art performance. This was seen to be the case in essentially all instances.

2.4.2 State-of-the-Art, 350°F Systems

The establishment of final user acceptance criteria for a graphite prepreg system depend heavily upon standardized resin composition, prepreg processing, specimen preparation methods and composite test methods. The items listed below must be addressed prior to establishing final acceptance criteria for graphite preregs:

- Batch to batch fiber and resin reproducibility
- Prepreg processing reproducibility
- Prepreg fiber collimation-composite fiber collimation
- Composite properties-fiber volume, voids, other factors

It is difficult to establish a universal norm for existing 350°F performing graphite systems because of the above factors. One of the better efforts was carried out by Dr. Ken Hofer at IITRI.*

He characterized the Thornel-300/5208 system in some detail. These values, shown in Table 9, became the target for this development effort. Although individual test values for a specific system may exceed the values

* AFML TR-74-266, February 1975

TABLE 9. STATE-OF-THE-ART EVALUATION - DRY LAMINATE PROPERTIES

Test Type	Target State-of-the-Art Properties ^a	
	RT	350°F
Flexure ultimate, ksi	240 (295)	190 (235)
Flexure modulus, x 10 ⁶ psi	18 (22)	18 (20)
Short beam shear, ksi	15.2 (17.8)	8.6 (9.9)
0° Tensile ultimate, ksi	218 (215)	208 (200)
0° Tensile modulus, x 10 ⁶ psi	26 (20.5)	26
90° Tensile ultimate, ksi	5.8 (6.75)	2.89
90° Tensile modulus, x 10 ⁶ psi	2.89 (1.47)	1.50
90° Tensile strain to failure, μ in/in	3750 (4680)	1690
0° Compressive strength, ksi	218 (198)	206 (134)
0° Compressive modulus, x 10 ⁶ psi	23 (21.2)	23 (21.3)

^aAbstracted from AFML TR-74-266 (February 1975). Values in parenthesis were abstracted from Narmco's product bulletin for the 5208/Thorne 1 300 system.

shown by as much as 50 percent, weighted average values shown in the table should be obtained by newly developed resin systems to achieve state-of-the-art performance. The very high compressive strengths obtained by IITRI are discussed under the AF-R-800 composite testing results below.

With this exception, the IITRI values became our target mechanical strengths for development of the AF-R-800 system. As previously mentioned, our development efforts keyed on the development of equivalent short beam shear strengths.

2.4.3 Composite Fabrication Procedures

The fabrication of AF-R-800 composites is accomplished with standard shop materials and practices. As discussed below the cure cycle requires close attention to obtain sought fiber volumes.

Composite layup for the AF-R-800 prepreg is as commonly practiced in the industry and is diagrammed in Figure 4. Materials used include Style 116 fiberglass bleeder cloth, porous teflon coated fiberglass release fabric,* bleeder plies and other fabrication aids. The inclusion of a release ply to the bottom of layup was found useful for air removal between the part and the composite. This release ply was used in fabrication of all of the AF-R-800 composites for this test program.

Cure Cycle Development

Cure and post-cure schedules developed for the AF-R-800 graphite composites are consistent with state-of-the-art systems. Cure temperature of 325°F and post-cure temperature of 375°F at pressures of less than 100 psi are used. The developed cure cycle is given below.

1. Layup composite on unheated tool
2. Apply full vacuum and hold for 1 hour
3. Heat to 275°F in 60 ± 5 minutes under no less than 10 inches of mercury vacuum
4. Hold at 275°F for the time determined from the prepreg gel time determined at 275°F less 50 minutes
5. Apply 75 psi and vent vacuum
6. Heat to 325°F in 30 ± 5 minutes
7. Hold at 325°F for 4 hours
8. Cool under pressure to 120°F

*TX-1040 from Paciflex Corporation

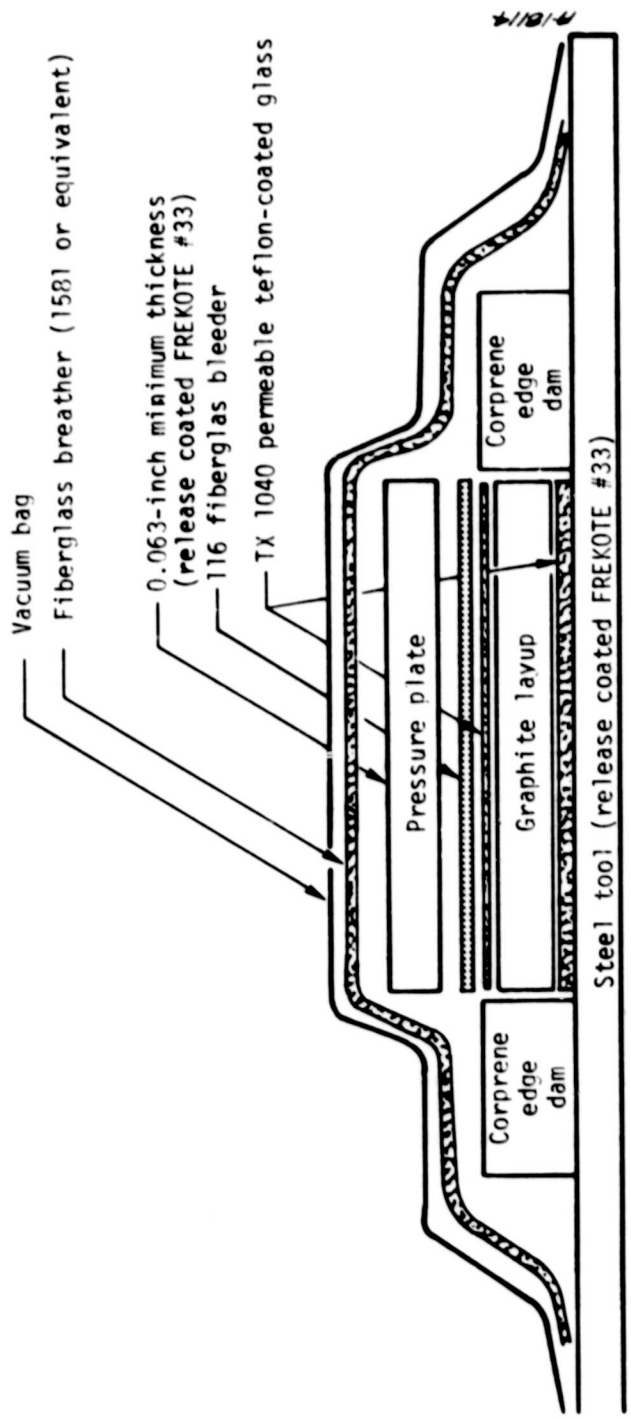


Figure 4. Layup system for AF-R-800 laminates.

9. Remove composite from tool
10. Post-cure unrestrained laminate in an air circulating oven for 4 hours at 375°F (60-minute heat up to 375°F)
11. The composite may be removed hot

All composite test results presented below were from composites cured as described above unless noted.

The 375°F post-cure schedule was selected based upon the study shown in Table 10. Several composites cured at 325°F were given post-cure schedules up through 400°F. The short beam shear strengths of these composites were measured and can be seen in the table. The 4-hour 400°F post-cure resulted in slightly reduced short beam shear strengths.

Test results on laminate 216 also showed that the 4 hours at 400°F were detrimental to both the short beam shear and the transverse tensile strengths of the system. These results are presented in Table 11. These studies were conducted with the tin catalyzed formulation. The final AF-R-800 formulation was determined from DTUL studies as described in Section 2.2 of this report.

As will be seen in the test results presented below, this post-cure schedule may not be optimum for the uncatalyzed AF-R-800 resin system. Even though short beam shear strengths are equivalent to the state-of-the-art 350°F performing resin systems, there may be a need to increase the temperature of the final post-cure to increase the modulus of the resin system in those tests that are more dependent on the compressive properties of the resin such as flexural and compressive strength testing.

2.4.4 Test Specimen Geometries

Specimens used to establish the composite performance of the AF-R-800 extended flow life prepreg were designed to conform to the Advanced Composites Design Guide.

Composite specimens configurations used throughout all phases of this program are identified in Table 12(a). Tab stock was used for all tension and compression specimens. A summary of tab stock materials and adhesives used in bonding tabs to composites are provided in Table 12(b). Tab stock were cured as per the manufacturers recommended cure cycles.

Strain gages were bonded to tension and compression specimens with M-Bond adhesive. All specimens were machined from their respective laminates with a diamond coated radial saw.

2.4.5 AF-R-800 Composite Test Results

All mechanical test results presented below were conducted on laminates using Thornel 300 with a UC309 finish as reinforcement and AF-R-800 as the matrix. All were post-cured to 375°F as described above. Testing was

TABLE 10. SHORT BEAM SHEAR FOR CURE SCHEDULE OPTIMIZATION

Prepreg No.	Laminate No.	No. Plies	Processing and Cure Schedule	Resin Content (%)	Fiber Volume (%)	Void Content (%)	Rt. Interlaminar Shear Strength, ksi (Average, range, no. samples)
DX 212	DX 212	12	a	32.3	60.9	<1	12.1 (10.5 - 13.8) 18 values
DX 212	DX 213a	12	b	25.9	68.2	<1	17.1 (16.7 - 17.8) 5 values
	213b	12	p.c. 4hr @ 375°F/75psi	—	—	—	17.4 (17.1 - 17.6) 5 values
	213c	12	p.c. 4hr @ 400°F/75psi	—	—	—	16.2 (15.5 - 16.8) 5 values
DX 206	DX 214a	12	c	34.2	58.8	<1	16.7 (16.1 - 16.9) 6 values
	DX 214b	12	p.c. 4hr @ 350°F	—	—	—	17.2 (16.6 - 17.5) 6 values
	DX 214c	12	p.c. 4hr @ 375°F	—	—	—	17.2 (16.7 - 17.8) 6 values
	DX 214d	12	p.c. 4hr @ 400°F	—	—	—	16.8 (15.9 - 17.4) 6 values
DX 206	DX 215	12	d	38.8	54.0	<1	16.9 (16.4 - 17.3) 6 values
DX 206	DX 216a	12 ^e	f	38.5	54.4	<1	15.2 (13.3 - 16.4) 6 values
	DX 216b	12	f+p.c. 4hr @ 350°F	—	—	—	15.4 (14.5 - 15.8) 6 values
	DX 216c	12	f+p.c. 4hr @ 375°F	—	—	—	15.6 (15.4 - 15.8) 6 values
	DX 216d	12	f+p.c. 4hr @ 400°F	—	—	—	14.5 (14.1 - 14.7) 4 values

^a Vacuum trap mold layup. In cold press, increase temperature to 280°F in 65 minutes under contact pressure and 10" Hg. Hold 145 minutes at temperature, apply 75 psi, vent to air. Hold 2-1/2 hours at 350°F, cool under pressure, post-cure free standing 4 hours at 400°F.

^b Press autoclave layup. In cold press, increase temperature to 275°F in 60 minutes under pressure, post-cure free standing 4 hours at 400°F. 285°F, apply 75 psi, vent vacuum. Hold 2-1/2 hours at 350°F, cool under pressure.

^c Press autoclave layup. In cold press, increase temperature to 270°F in 30 minutes under contact pressure and 10" Hg. Hold 8 hours at 325°F and 75 psi, remove vacuum, cool under pressure.

^d Press autoclave layup. In cold press, increase temperature to 280°F in 60 minutes under contact pressure and 10" Hg. Hold 55 minutes at 280°F, apply 75 psi, vent vacuum. Hold 8 hours at 325°F and 75 psi, cup. Post-cure 8 hours @ 375°F.

^e 8" x 8" laminate.

^f Press autoclave layup. In cold press, increase temperature to 275°F in 60 minutes under contact pressure and 10" Hg. Hold 60 minutes at 275°F, apply 75 psi, vent vacuum. Hold 8 hours at 325°F and 75 psi, cup.

TABLE 11. ELEVATED (350°F) INTERLAMINAR SHEAR AND
TRANSVERSE TENSILE RESULTS FOR CURE
SCHEDULE OPTIMIZATION

Cure Conditions	Transverse Tensile Ultimate (psi)	350°F Interlaminar Shear, ksi (No. of Specimens)
8 hours @ 325°F	4930	7.3 (3)
a + p.c. 4 hours @ 350°F	5240	8.2 (3)
a + p.c. 4 hours @ 375°F	4960	8.0 (5)
a + p.c. 4 hours @ 400°F	4800	7.8 (5)

TABLE 12(a). COMPOSITE SPECIMEN CONFIGURATION SUMMARY

Specimen Type	Length (inch)	Width (inch)	Thickness (plies)
0° flexure	4.00	0.50	12
Short Beam Shear	0.60	0.25	12
0° Tension	9.00	0.50 and 1.00 ^a	6
90° Tension	9.00	1.00	8
0° Compression	5.50	0.25	8

^aTensile specimens from oriented panel had 1.00-inch width.

TABLE 12(b). TAB STOCK DEFINITION

Test Temperature	Tab Material	Specimen Type	Tab Construction	Bonding Adhesive
(°F) 70 ↓	Scotch ply 1009-26 ↓	Tension	[0,90,0,90,0,90,0]	FM-1000
		Compression	[0,90,0,90,0,90,0,90,0]	FM-1000
350 ↓	Scotch ply 1009-36 ↓	Tension	[0,90,0,90,0,90,0]	Metlbond 328
		Compression	[0,90,0,90,0,90,0,90,0]	Metlbond 328

conducted as per standard test methods described in the Advanced Composites Design Guide unless otherwise indicated. Elevated temperature testing was conducted with thermocoupled specimens. The specimen was allowed to come to temperature, held 10 minutes at temperature, as indicated by the specimen thermocouple, and then tested.

The laminates fabricated for the test program are given in Table 13 with their physical properties.

Short Beam Shear

AF-R-800 composite short beam shear strengths routinely exceeded target state-of-the-art values. Typical short beam shear strengths for AF-R-800 composites are shown in Table 14. These four laminates were the result of processing schedule variations and resulted in final selection of the processing schedule described above as well as tested the reproducibility of the schedule to provide quality laminates.

The agreement between the four laminates was adequate and it was judged that the processing schedule did not require further optimization. The key processing parameter was found to be the point of pressure application at the 275°F hold temperature. If sufficient attention is given to the time at which the pressure is applied, high quality laminates are invariably the result.

Additional short beam shear strength values for the AF-R-800/Thornel 300 composites are provided in other tables in this section.

Flexure Testing

AF-R-800 composite flexure properties provided strengths in excess of our target state-of-the-art values. This data is provided in Table 15.

In all cases our target 240-ksi flexure strengths were obtained at room temperature. 350°F strengths fell slightly short of the 190-ksi target value. As previously mentioned, cure schedule adjustment may increase this value. Laminate 233B and 234B are both in excess of our target value and were the result of allowing the prepreg to age at room temperature prior to cure. Compare to Table 23. This value may be due to experience in fabricating the AF-R-800 prepreg or possibly due to slight differences in the chemistry due to the room temperature aging process.

Tensile Testing, Transverse (90°)

The values for AF-R-800 composites strength and strain to failure are in excess of the program target values. The target values obtained by IITRI, however, represent an average of several laminates. It is our opinion that additional testing of a number of AF-R-800/Thornel 300 laminates will continue to provide the high transverse tensile strengths and strain to failures seen in Table 16. Stress-strain curves are shown in Figures 5 and 6.

TABLE 13. AF-R-800 TEST COMPOSITES — PHYSICAL PROPERTY SUMMARY

Laminate Identity	Specific Gravity	V_F^a (percent)	W_R^b (percent)
222	1.56	62.80	30.16
227A	1.57	63.00	30.45
227B	1.59	64.96	28.02
227C	1.52	53.21	38.83
229	1.56	66.51	27.33
230B	1.63	70.43	23.88
231B	1.54	62.79	30.69
232B	1.57	65.46	28.29
233A	1.59	63.36	30.17
233B	1.59	64.34	28.49
234A	1.57	61.40	31.51
234B	1.59	65.06	27.93
235A	1.56	63.15	30.35
236A	1.59	69.04	24.45
237A	1.56	63.88	30.14
237C	1.56	63.38	29.42
238B	1.58	63.35	30.18
239A	1.58	62.85	29.01
239D	1.56	64.42	29.22
240A	1.55	61.03	32.30
240B	1.57	62.58	30.14
241A	1.56	59.26	33.94

^aFiber volume percent

^bResin weight percent

TABLE 14. CURE SCHEDULE REPLICATION TEST SERIES (SHORT BEAM SHEAR TESTING)

LAMINATE IDENTITY ^a	SHORT BEAM SHEAR STRENGTH, psi	
	70°F	350°F
STATE-OF-THE-ART VALUES	15,200	8,600
222	15,000	11,100
	15,200	10,300
	13,900	10,100
	14,400	9,800
	<u>14,100</u>	<u>9,470</u>
	14,500 Avg	10,150 Avg
229	14,900	9,200
	15,600	9,300
	15,800	9,600
	15,700	9,500
	<u>15,600</u>	<u>9,000</u>
	15,500 Avg	9,300 Avg
232	16,900	8,850
	16,200	8,740
	14,700	8,590
	15,800	9,410
	<u>15,300</u>	<u>9,190</u>
	15,780 Avg	8,956 Avg
230	16,700	9,330
	17,600	9,790
	18,300	9,790
	19,000	9,630
	<u>18,100</u>	<u>9,710</u>
	17,940 Avg	9,650 Avg

^aListed in sequence tested.

TABLE 15. AF-R-800 FLEXURAL PERFORMANCE ASSESSMENT

Panel Identity	Specimen Identity	Test Temperature (°F)	Flexure Strength (10 ³ psi)	Flexure Modulus (10 ⁶ psi)	T-481
State of the art	—	70	240	18.0	
State of the art	—	350	190	18.0	
230B	1	70	260	20.5	
231B	1	350	153	16.3	
232	2	70	248	19.4	
↓	4	70	244	20.2	
			Avg 246	19.8	
	1	350	170	19.4	
	3	350	155	18.3	
↓			Avg 162.5	18.8	
233B ^a	—	70	Avg 251 ^a	17.8 ^a	
233B ^a		350	Avg 209 ^a	19.5 ^a	
234B ^a	—	70	Avg 260 ^a	—	
234B ^a		350	Avg 195 ^a	20.2 ^a	
237A ^b	1	70	236	17.7	
↓	3	70	265	18.1	
			Avg 251	17.9	
	2	350	189	18.0	
239A ^b	1	70	242	17.4	
↓	7	↓	250	19.3	
	13	↓	244	18.0	
			Avg 244	18.2	
	3	350	182	19.7	
	11	↓	180	17.4	
↓	18	↓	182	19.4	
			Avg 181	18.8	

^aIndividual specimen results are provided in Section 2.4.^bFabricated and tested prior to panels 233B and 234B.

TABLE 16. TRANSVERSE TENSILE PERFORMANCE

Panel Identity	Specimen Identity	Thickness (Inch)	Test Temperature (°F)	Tensile Strength (10 ³ psi)	Modulus (10 ⁶ psi)	Strain to Failure (μin/in)
238B ↓	A1	0.055	70	6.64	1.25	4850
	A2	0.055	↓	8.09	1.29	5900
	A3	0.055		8.18	1.30	5900
				Avg 7.64	<u>1.28</u>	<u>5500</u>
238B ↓	B1	0.056	350	5.18	0.992	4900
	B2	0.056	↓	5.45	1.050	4950
	B3	0.056		6.07	1.050	5700
				Avg 5.57	<u>1.03</u>	<u>5180</u>

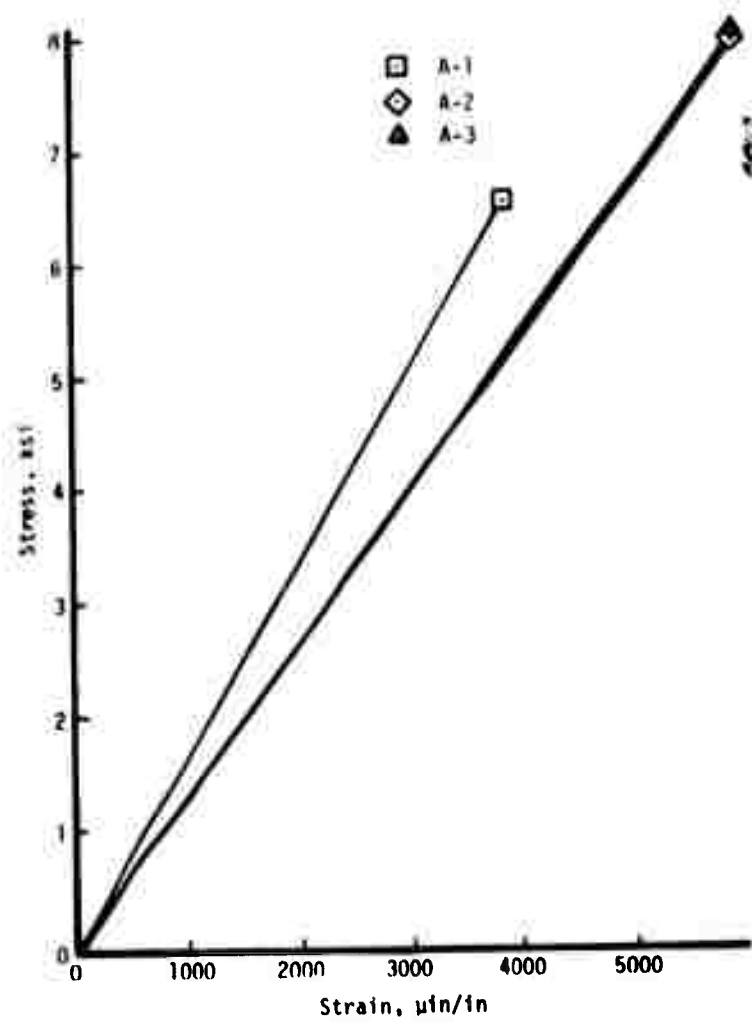


Figure 5. 90° tension stress-strain curves, room temperature.

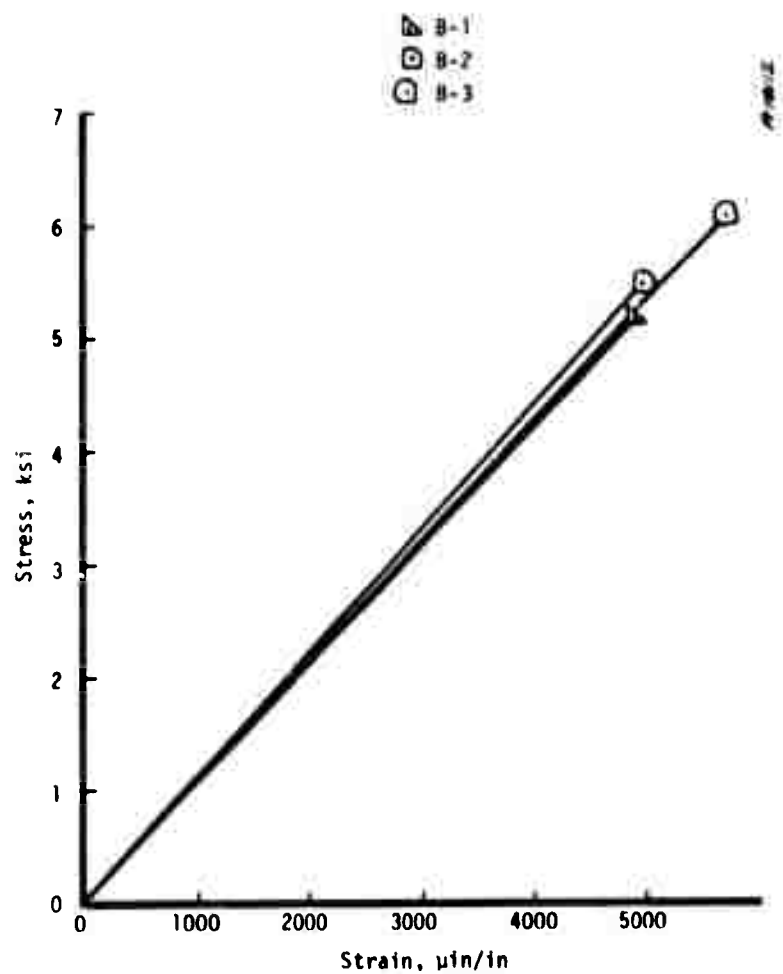


Figure 6. 90° tension stress-strain curves at 350°F.

Tensile Testing Longitudinal (0°)

Table 17 provides the results of 0° tensile testing of AF-R-800/T300 undirectional composites. Figures 7 and 8 give the stress-strain curves. Values for the ultimate tensile strength are slightly lower than the program target. This fiber controlled property is, however, consistent with tensile testing of graphite composites. These values are probably the result of machining errors resulting in a slight misalignment of the specimen to the 0° direction.

Compression Testing

Compressive test results on the AF-R-800 composites are shown in Table 18 and the stress-strain curves are provided in Figures 9(a) and 9(b). Compressive strength was determined using the Celanese specimen and Celanese test fixture.

The scatter is larger than expected, however, it is not unusual for this test method.

Test methods to obtain compressive strength from graphite composites vary. For example, the Advanced Composite Design Guide* describes edge loaded sandwich beam and end loaded test methods.

The room temperature test results seen in Table 18 are typical of those reported for graphite composites. AS/3501 provided a compressive strength of 125,500 psi and T300/5209 a strength of 129,000 psi.[†] The test methods used to achieve these composite strengths were not noted. Compressive strengths of 132,000 psi and 162,000 psi were obtained for AS/3501 using a modified cure cycle.[‡] A 218,000-psi compressive strength reported by IITRI (see Table 5) was obtained by using a Celanese compression specimen with IITRI's test fixture[§] different than the Celanese test fixture used in AF-R-800 composites tests.

Crossplied Panel Composite Properties

Oriented panels were fabricated to verify that the AF-R-800 Thornel 300 Composite System provided state-of-the-art properties with laminae in a quasi-isotropic design orientation. The verification was achieved.

*"Advanced Composites Design Guide," Volume IV, 3rd Edition, Contract F37615-71-0-1362.

[†]"Development, Manufacture and Test of Graphite-Epoxy, Composite Spoilers for Flight Service on 747 Transport Aircraft, NAS 1-11668," Final Report, 1976, p. 5.

[‡]"Structural Criteria for Advanced Composites," Quarterly Progress Report 7, 1976, Contract F33615-74-C-5182.

[§]"Development of Engineering Data on the Mechanical and Physical Properties of Advanced Composite Materials," 1975, Contract AFML-TR-266.

TABLE 17. 0° TENSILE PERFORMANCE

Laminate Identity	Specimen Number	Temp. Test	Thickness (inch)	Tensile Ultimate (10 ³ psi)	Modulus of Elasticity (10 ⁶ psi)	Strain to Failure (μin/in)
235A	A3	70	0.041	179	18.8	8900
	A1	70	0.042	145 ^b	18.5 ^a	7400
	A2	70	0.042	195	18.1	10000
				Avg 187	18.4	8767
	B1	350	0.041	214	19.6	10300
	B2	350	0.043	203	18.7	10200
241A	B3	350	0.043	193	18.5	10300
				Avg 203	18.9	10300
	A1	RT	0.044	203	17.1	11200
	A2	RT	0.044	187	17.5	9900
	A3	RT	0.044	206	17.8	10600
				Avg 199	17.5	10566

^aStrain gage and function not included in average^bNot included in average

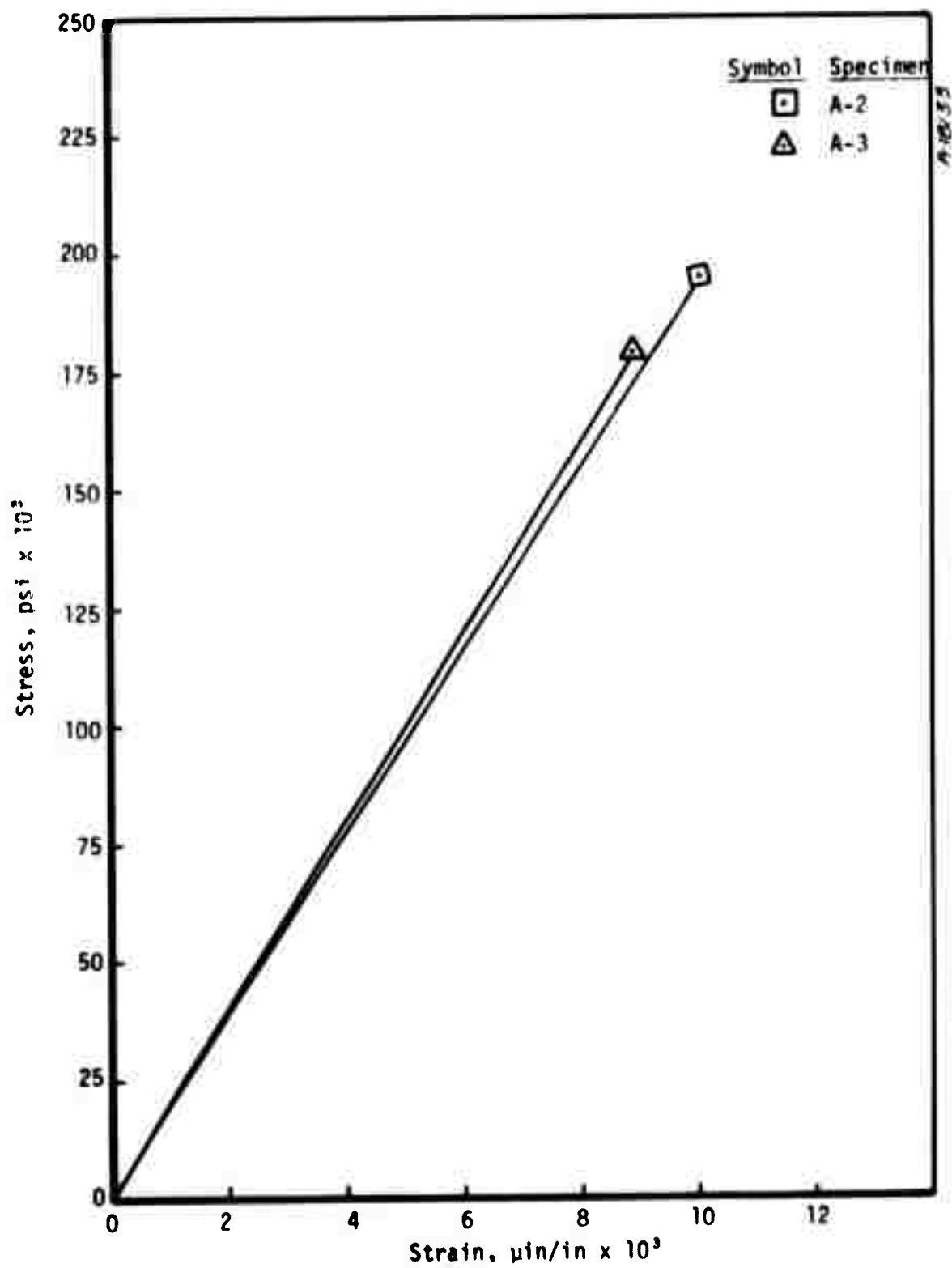


Figure 7. AF-R-800 0° tensile stress-strain curves.

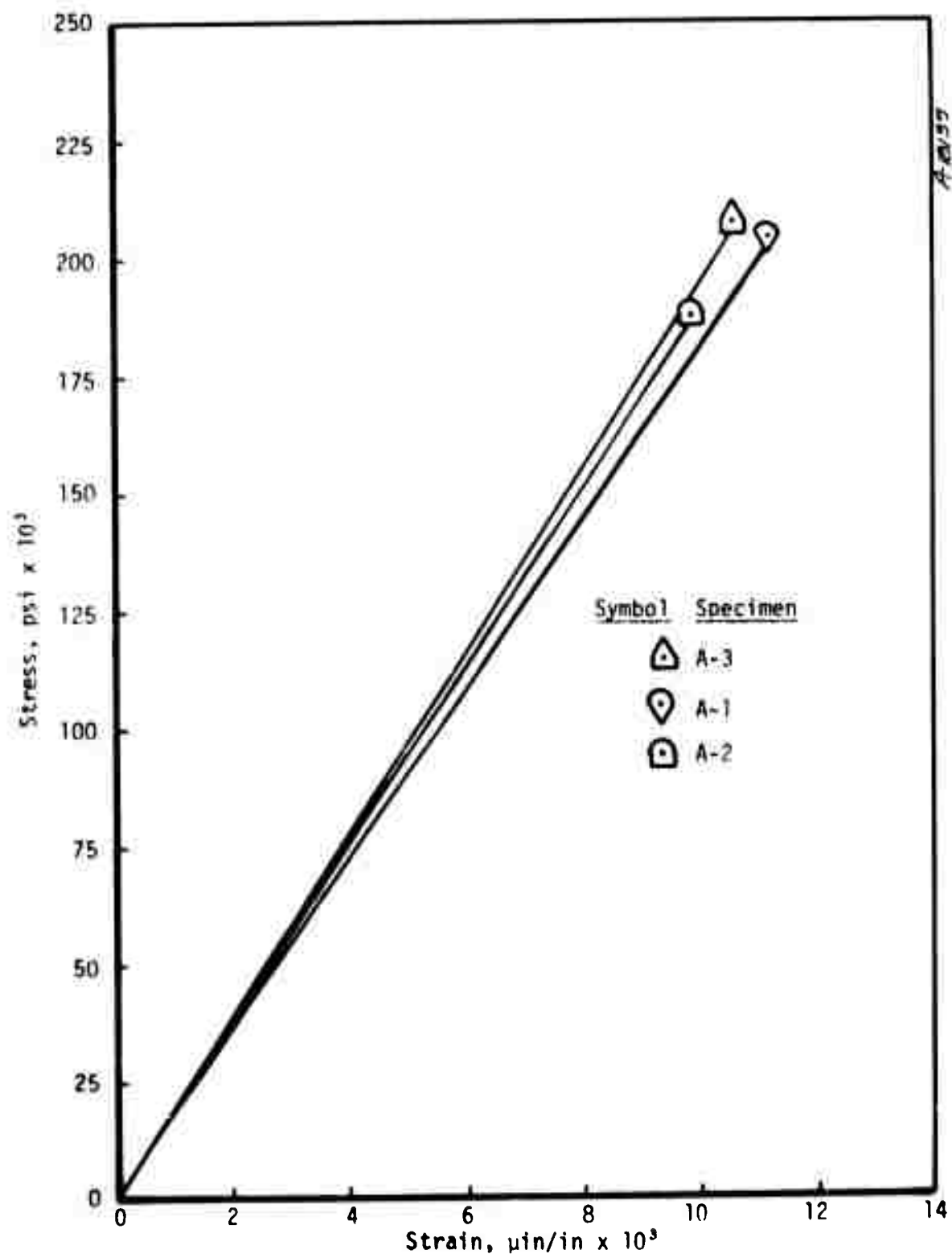


Figure 8. AF-R-800 0° tensile stress-strain curves.

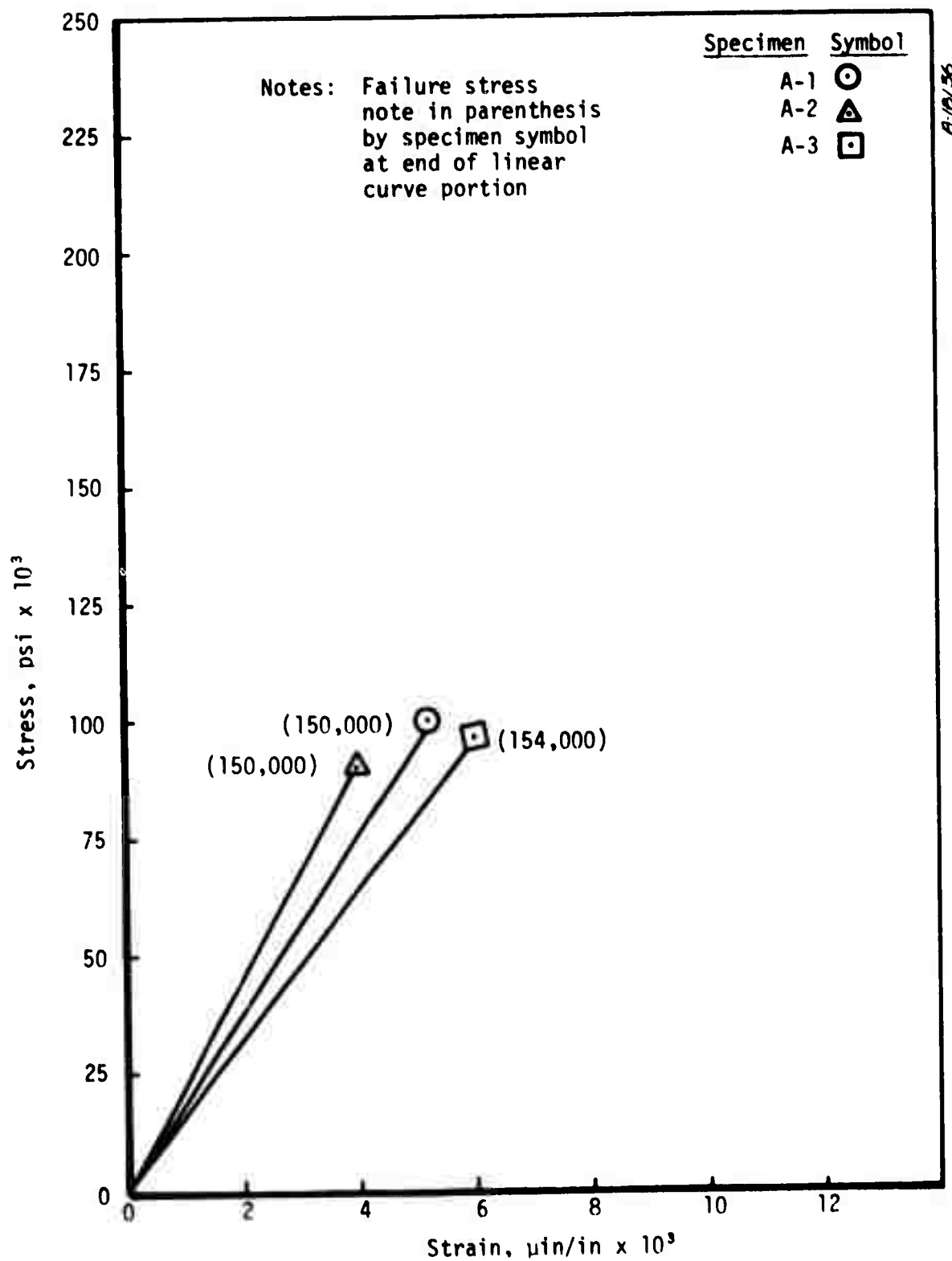


Figure 9(a). AF-R-800 0° compression stress-strain curves at room temperature.

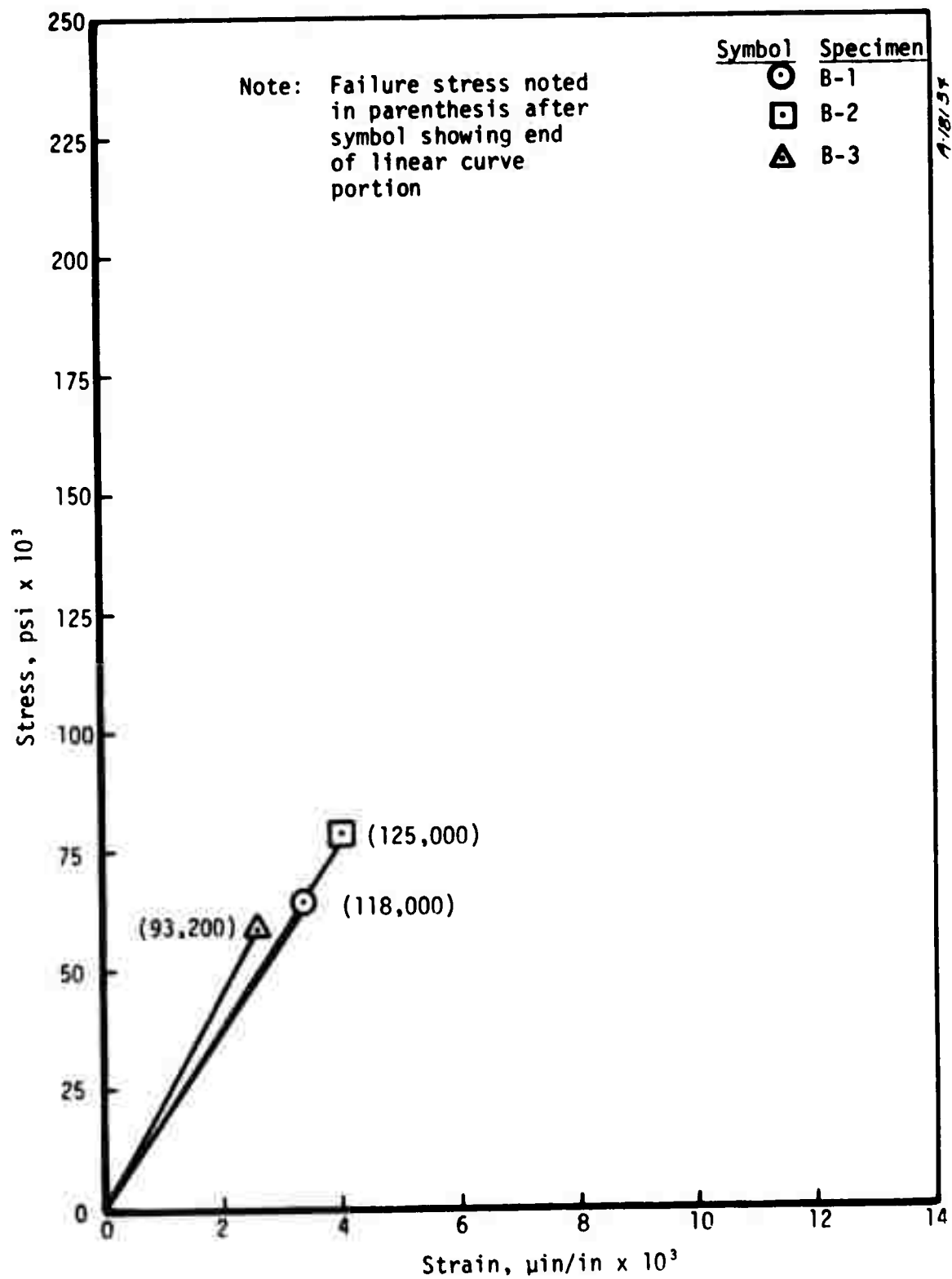


Figure 9(b). AF-R-800 0° compression stress-strain curves at 350°F.

TABLE 18. COMPRESSION PERFORMANCE

Laminate Identity	Specimen Number	Test Temperature (°F)	Thickness (inch)	Compression Ultimate (10 ³ psi)	Modulus of Elasticity (10 ⁶ psi)	Notes
239D	A-1	70	0.056	150	19.2	
	A-2		0.055	150	21.4	
	A-3		0.056	<u>154</u> Avg 151	<u>16.2</u> 18.9	
	B-1	350	0.056	118	17.8	a
	B-2		0.056	125	17.8	a
	B-3		0.056	<u>93.2</u> Avg 112	<u>21.4</u> 19.0	a

^aSpecimen bending suspected

Prepreg batch DX 240 was used in the determination. Two laminates were fabricated. Each laminate contained eight plies with [0,+45,-45,90,90,-45,+45,0] and was tested in the 0° direction. The results are shown in Table 19. Compare favorably with IITRI results obtained on 5208/Thornel 300 laminates. These laminates contained two additional 0° plies. (IITRI test results of 104,000 psi tensile strength and 13.9×10^6 psi modulus were obtained with 10 ply [0,+45,0,90]s laminates.)

As a further comparison, for the same laminate construction as used for the AF-R-800/Thornel 300 results shown above, the room temperature tensile strength reported in the Advanced Composites Design Guide for Hercules 3002/AS was 52,000 psi.

2.4.6 Shelf Life Studies

Room Temperature Prepreg Aging

Determination of shelf life by composite property assessment confirmed the ability of the AF-R-800 prepreg to provide state-of-the-art epoxy composite properties after a 14-week exposure to ambient shop conditions.

Three prepreg batches were prepared for the shelf life verification effort. These batches were DX-227, DX-236 and DX-237. Prepreg batches DX236 and DX237 used the same resin batch.

As shown in Table 20, no degradation in shear strength properties was observed over a 9-week exposure period. Laminate 237C (5-week exposure) had reduced shear strengths. This was caused by poor composite quality resulting from late pressure application in the standard processing schedules.

The low 350°F flexure strengths observed for laminates 237B and 237C may be due to the aging process. However, low flexural strengths were not observed for the composites obtained from the stepwise layup described below. The need for further definition of the cure cycle or post-cure cycle for prepregs which have been aged is indicated.

Table 21 provides short beam shear results of AF-R-800 composites fabricated from prepreg aged for 14 weeks at room temperature and from prepreg aged an additional week at 100°F and 93-percent relative humidity. The room temperature and 350°F short beam shear strengths show that high quality composites result from prepreg aged for 14 weeks under simulated shop conditions. After exposure of the 14-week prepreg to the 93-percent relative humidity condition seen in the table, a composite was obtained with adequate room temperature short beam shear strengths but reduced 350°F short beam shear strengths.

TABLE 19. ORIENTED PANEL COMPOSITE PROPERTY SUMMARY

Laminate Identity	Site Temperature (°F)	Specimen Identity	Tensile Strength (psi x 10 ³)	Tensile Modulus (psi x 10 ⁶)	Strain at Failure (μin/in)
240B ↓	RT	1A	53.7	6.9	8200
	RT	3A	<u>54.2</u>	<u>7.0</u>	<u>8300</u>
			Avg 53.9	6.9	8250
	350	1B	61.0	4.0 ^a	7300
	350	3B	<u>68.2</u>	<u>4.4^a</u>	—
			Avg 64.5	4.2 ^a	—
240A ↓	RT	A-1	53.6	6.75	8800
	RT	A-2	<u>51.4</u>	<u>6.73</u>	<u>8200</u>
			Avg 52.5	6.74	8600
	350	B-1	56.9	6.51	9400
	350	B-2	<u>61.3</u>	<u>6.68</u>	(b) —
			Avg 59.1	6.60	—

^aSuspect values^bStrain gage failed at 8900 μin/in

TABLE 20. SHELF LIFE VERIFICATION RESULTS

Panel Identity	Shear Strength (10^3 psi)		Flexure Strength (10^3 psi)		Flexure Modulus (10^6 psi)	
	RT	350°F	RT	350°F	RT	350°F
Initial Data						
237A	19.3	9.3	236	189	17.7	18.0
	17.9	8.9	265	—	18.1	—
	17.8	9.3	—	—	—	—
	Avg 18.3	9.2	251	189	17.9	18.0
4-Week Prepreg Exposure						
237B	19.2	9.3	256	135	17.6	16.7
	19.1	9.3	262	—	17.8	—
	19.1	9.4	—	—	—	—
	Avg 19.1	9.3	259	135	17.7	16.7
5-Week Exposure						
237C	9.8	6.2	295	159	18.7	18.9
	—	6.5	250	143	18.7	18.7
	10.1	6.5	237	151	18.7	18.7
	Avg 9.9	6.4	244	149	18.7	18.8
9-Week Exposure						
236A	18.2	10.5	—	—	—	—
	19.8	10.9	—	—	—	—
	19.4	10.8	—	—	—	—
	Avg 19.1	10.7	—	—	—	—

TABLE 21. SHELF LIFE VERIFICATION — MULTIPLE EXPOSURE CONDITION

Prepreg Batch	Resin Formulation Date	Prepreg Date	Test Date	Laminate Identity	Specimen Number	Test Temp. (°F)	Short Beam Shear Strength (10 ³ psi)	Exposure Conditions
DX-227	1/17/77	2/1/77	2/14/77	DX-227A	3	70	14.8	Initial test data (5 weeks from resin formulation) →
					5		16.3	
					9		15.6	
					11		15.3	
			4/30/77	DX-227B	13		14.3	→
							Avg 14.8	
					4	350	9.7	
					6		8.9	
					8		7.7	14 weeks at ambient →
					10		9.4	
					12		8.6	
							Avg 8.9	
			5/21/77	DX-227C	1	70	14.5	14 weeks at room temperature +1 week at 100°F and 93-percent relative humidity
					3		16.8	
					5		17.1	
							Avg 16.1	
					2	350	8.0	
					4		8.3	
					6		8.0	
							Avg 8.1	
					1	70	17.1	
					3		15.7	
					5		15.3	
							Avg 16.0	
					2	350	5.4	
					4		6.1	
					6		6.2	
							Avg 5.9	

Stepwise Layup

The ability of the AF-R-800 extended flow life preregs by a stepwise layup to produce high quality composites was also evaluated. In this procedure, plies were added to the layup at predetermined intervals extending over a 12-week period. The ambient aged preregs were applied to the layup as shown in Table 22. The protective sheet of mylar was left on the added ply until a new ply was added.

The flexure property data for this test series are summarized in Table 23. Table 24 presents the respective short beam shear data summary. These results are among the highest obtained in the program and show the ability of prepreg to provide high quality composites after extended storage under ambient conditions (in excess of the system's flow life of ~10 weeks).

2.4.7 Moisture Studies

24-Hour Water Boil

Data developed on the moisture resistance of AF-R-800/Thornel 300 composites after 24-hour water boil test indicate that shear strength retention, dimensional stability and weight change are equivalent to state-of-the-art composites.

Data was developed on composites produced from three prepreg batches. Moisture resistance data for panels 230B, 233A, and 234A include short beam shear strength retention, dimensional stability and weight change. Dimensional stability and weight change data were developed on flexure specimens for 230B and shear specimens from 233A and 234A. Composite property retention was evaluated on the shear specimens from panels 233A and 233B.

Data for these specimens are provided in Tables 25 and 26.

The 25.2- and 21.7-percent reduction in 350°F short beam shear strengths after 24-hour water boil represents better water performance than any of those reported by Hertz.* The highest shear strength reported by Hertz after such exposure was 4.7 ksi. The two AF-R-800/Thornel 300 composites provided short beam shear strengths of 6.8 and 7.2 ksi after such treatment.

Exposure to 120°F/95+ Percent Relative Humidity

Hygroscopic moisture absorption data indicates that the extent of water absorption and its effect on AF-R-800 composite properties is equivalent to

*Hertz, "Investigation into the High Temperature Strength Degradation of Fiber Reinforced Resin Composite During Ambient Aging," NASA 8-27435, June 1973.

TABLE 22. STEPWISE LAYUP PROCEDURE

Date of Ply Addition	Number of Plies Added to Layups DX-233B and DX-234B
3/14/77	2
3/18/77	1
3/25/77	1
4/1/77	1
4/15/77	1
4/22/77	2
4/27/77	1
5/6/77	1
5/13/77	1
5/18/77	1

TABLE 23. STEPWISE LAYUP — FLEXURAL PERFORMANCE

Laminate Identity	Specimen Number	Test Temp.	Flexure ^a Ultimate (ksi)	Flexure ^a Modulus (10 ⁶ psi)
DX-233B ↓	2	RT	256	18.3
	4	↓	250	17.8
	6	↓	<u>251</u>	<u>17.4</u>
			Avg 251	17.8
	1	350	199	17.9
	3	↓	217	20.3
	5	↓	<u>210</u>	<u>20.3</u>
			Avg 209	19.5
DX-234B ↓	2	RT	277	20.0
	4	↓	266	20.3
	6	↓	<u>257</u>	<u>18.8</u>
			Avg 267	19.7
	1	350	192	19.6
	3	↓	197	20.9
	5	↓	<u>195</u>	<u>20.1</u>
			Avg 195	20.2

^aAfter 12-week stepwise layup.

TABLE 24. STEPWISE LAYUP — SHORT BEAM SHEAR PERFORMANCE

Panel Identity	Specimen Number	Test Temp. (°F)	Short Beam Shear Strength (10 ³ psi)
Initial Data			
DX-233A	(a)	70	Avg 17.1
DX-234A	(a)		Avg 17.2
DX-233A	(a)	350	Avg 9.1
DX-234A	(a)		Avg 9.2
After 12-Week Stepwise Layup			
DX-233B ↓	2	70	18.9
	4		19.5
	6		<u>18.4</u>
			Avg 18.9
	1	350	9.9
	3		9.8
DX-234B ↓	5		<u>9.4</u>
			Avg 9.8
	2	70	18.3
	4		17.1
	6		<u>18.0</u>
			Avg 17.8
	1	350	10.0
	3		9.5
	5		<u>9.4</u>
			Avg 9.6

TABLE 25. MOISTURE RESISTANCE ASSESSMENT - DIMENSIONAL AND WEIGHT CHANGES (24-HOUR WATER BOIL)

Panel Identity	Specimen ^a Identity	Thickness		Water Pickup			
		Unexposed (inch)	Exposed (inch)	Change (percent)	Initial Weight (gm)	Final Weight (gm)	Change (percent)
233A ^a	1A	0.0764	0.0766	0.3	0.2409	0.2428	0.79
	2A	0.0763	0.0768	0.6	0.2425	0.2442	0.70
	3A	0.0756	0.0762	0.8	0.2416	0.2431	0.62
	4A	0.0759	0.0762	0.4	0.2428	0.2444	0.66
	5A	0.0759	0.0763	0.5	0.2446	0.2461	0.61
	6A	0.0757	0.0758	0.1	0.2440	0.2456	0.66
	Average	0.0759	0.0763	0.45	0.2427	0.2443	0.67
234A ^a	1A	0.0832	0.0834	0.2	0.2366	0.2386	0.85
	2A	0.0842	0.0845	0.4	0.2394	0.2414	0.84
	3A	0.0849	0.0853	0.5	0.2422	0.2444	0.91
	4A	0.0847	0.0851	0.5	0.2422	0.2443	0.87
	5A	0.0847	0.0849	0.2	0.2416	0.2438	0.91
	6A	0.0848	0.0853	0.6	0.2426	0.2450	0.82
	Average	0.0844	0.0847	0.4	0.2407	0.2429	0.86
2308 ^b	2	0.0742	0.0742	0.0	3.7485	3.7656	0.46
	3	0.0740	0.0740	0.0	3.7660	3.7773	0.46
	4	0.0738	0.0739	0.1	3.7392	3.7561	0.45
	5	0.0739	0.0739	0.0	3.7284	3.7447	0.44
	Average	0.0739	0.0740	0.02	3.7455	3.7609	0.45

^aShort beam shear specimens

^bFlexure specimens

TABLE 26. MOISTURE RESISTANCE ASSESSMENT — SHORT BEAM
SHEAR STRENGTH (24-HOUR WATER BOIL)

Panel Identity	Specimen Number	Exposure	Test Temperature (°F)	Shear Strength (10 ³ psi)	Percent Change
233A ↓	2	a	RT ↓	18.4	+2.3
	4	a		18.2	
	6	a		14.6	
				Avg 17.1	
	2A	b		17.9	
	4A	b		16.3	
	6A	b		18.2	
				Avg 17.5	
234A ↓	2	a	RT ↓	16.8	0
	4	a		17.8	
	6	a		17.0	
				Avg 17.2	
	2A	b		17.5	
	4A	b		16.9	
	6A	b		17.2	
				Avg 17.2	
233A ↓	1	a	350 ↓	9.2	-25.2
	3	a		9.0	
	5	a		9.1	
				Avg 9.1	
	1A	b		6.9	
	3A	b		6.7	
	5A	b		6.8	
				Avg 6.8	
234A ↓	1	a	350 ↓	9.1	-21.7
	3	a		8.7	
	5	a		9.7	
				Avg 9.2	
	1A	b		7.2	
	3A	b		7.3	
	5A	b		7.1	
				Avg 7.2	

^aUnexposed

^b24-hour water boil

that found in state-of-the-art composites. Data presented on 5208/Thorne1 300 in AFML TR-75-51, Volume 1* and AFML TR-74-266 (IITRI)[†] was used as a basis for comparison.

IITRI found 5.7- and 4.3-ksi short beam shear strengths for 21- and 42-day aged 5208/Thorne1 300 composite specimen. The AF-R-800/Thorne1 300 composite specimens provided a 4.3-ksi short beam shear strength after 31 days under the same conditions.

A comparison of AF-R-800 performance to the data presented in AFML TR-75-51 shows the following:

1. Shear specimen moisture absorption values are less than state of the art under equivalent aging conditions
2. Flexure specimen moisture absorption values are approximately equal to state of the art
3. Higher retention of room temperature flexure strength was obtained compared to state of the art at equal moisture values using original dry room temperature strength as the basis
4. Equal retention of 350°F short beam shear strength to state of the art (same basis as 3 above)
5. State-of-the-art data were slightly in excess of the AF-R-800 data for room temperature short beam shear and 350°F flexure strength (same basis as 3 above)

These comparisons are made with the following factors:

1. 12-ply AF-R-800 composites were used while the 5208/Thorne1 300 composites were 16 ply. The higher surface to volume ratio of the AF-R-800 12-ply laminates would tend to permit higher moisture absorption.
2. AF-R-800 data was developed in unidirectional panels while the AFML TR-75-51 data used $[0 \pm 45]$ panels

*"Life Assurance of Composite Structures," Volume 1, Moisture Effects, AFML TR-75-51, Contract F33615-73-C-5104.

[†]"Development of Engineering Data on the Mechanical and Physical Properties of Advanced Composite Materials," AFML TR-74-266, Contract F33615-73-C-5125.

All AF-R-800 composite hygroscopic absorption tests were conducted on Laminate 239A. One laminate was used to minimize potential variables which could arise due to use of multiple prepreg batches and processing in more than one laminate. Flexure and short beam shear specimens were machined from designated areas of the unidirectional, 12-ply laminate.

Hygroscopic absorption assessment was conducted by the following sequence:

1. Test unexposed specimens to verify composite quality
2. Expose remaining specimens to 120°F, 98-percent reactive humidity
3. Remove designated specimens after 20 days; test for dimensional at weight and composite mechanical property change
4. Remove designated specimens after 31 days and repeat tests noted in 3 above

During testing to verify unexposed composite quality, the flexure and shear data indicated Laminate 239A was not of optimum quality. However, the decision was made to use Laminate 239A since AF-R-800 hygroscopic absorption effects would be monitored as a percent change from the original dry values for the AFML TR-75-51 comparison.

Data obtained are presented in Tables 27, 28, and 29.

2.4.8 Cocure Capability

AF-R-800 prepregs can be cocured with standard 350°F capability adhesives. Cocuring required demonstration that AF-R-800 prepregs could be cured in direct contact with structural adhesives. The demonstration also required that the adhesive to composite bond strengths was not degraded.

A tensile specimen was selected for this demonstration. AF-R-800 prepreg was layed up by the standard fabrication methods. The ends of the specimen layup were then covered by Metlbond 329 adhesive. The adhesive was then in turn covered by precured tabstock. The completed layup (235) was then cured and post-cured by the standard AF-R-800 processing cycle.

An inability to be cocured would have been indicated by cohesive failure within the adhesive or adhesive failure within the bond to the AF-R-800 composite. When tested, no failures occurred in the adhesive or failure at a lower tensile failure or the adhesive to composite-tabstock bond. All failures were within the tensile specimen gage length (see Table 30).

TABLE 27. MOISTURE ABSORPTION — DIMENSIONAL AND WEIGHT STABILITY
(95+ PERCENT RELATIVE HUMIDITY)

Specimen Type	Specimen Number	Thickness			Width			Weight		
		Initial (inch)	Final (inch)	Change (percent)	Initial (inch)	Final (inch)	Change (percent)	Initial (gm)	Final (gm)	Change (percent)
20-Day Exposure ^a										
Flexure	4	0.0819	0.0819	0	0.5095	0.5052	+0.1	3.1904	3.2132	+0.7
	9	0.0814	0.0816	+0.2				3.2043	3.2250	+0.6
	10	0.0829	0.0832	+0.4				3.2161	3.2410	+0.8
	16	0.0804	0.0806	+0.2				3.1950	3.2169	+0.7
	Average	0.0816	0.0818	+0.2				3.202	3.224	+0.7
31-Day Exposure ^a										
↓	5	0.0825	0.0823	-0.2	0.5039	0.5053	+0.3	3.2237	3.2499	+0.8
	6	0.0821	0.0821	0				3.2046	3.2304	+0.8
	8	0.0812	0.0816	+0.5				3.2112	3.2370	+0.8
	12	0.0809	0.0810	+0.1				3.1786	3.2060	+0.9
	15	0.0805	0.0808	+0.4				3.1616	3.1885	+0.9
	17	0.0808	0.0809	+0.1				3.2028	3.2289	+0.8
	Average	0.0813	0.0815	+0.2				3.1971	3.2235	+0.8
	20-Day Exposure ^a									
Shear	8	0.833	0.838	+0.6	0.2505	0.2513	+0.3	0.2546	0.2575	+1.1
	9	0.838	0.838	0				0.2549	0.2579	+1.2
	13	0.829	0.832	+0.4				0.2512	0.2538	+1.0
	15	0.818	0.820	+0.2				0.2534	0.2561	+1.1
	Average	0.830	0.832	+0.3				0.2535	0.2563	+1.1
31-Day Exposure ^a										
↓	2	0.0830	0.0831	+0.1	0.2539	0.2551	+0.5	0.2518	0.2544	+1.0
	4	0.0833	0.0837	+0.5				0.2538	0.2567	+1.1
	10	0.0838	0.0840	+0.2				0.2561	0.2590	+1.1
	12	0.0837	0.0841	+0.5				0.2543	0.2572	+1.1
	17	0.0816	0.0819	+0.4				0.2519	0.2598	+1.2
	18	0.0811	0.0812	+0.1				0.2522	0.2551	+1.1
	Average	0.0828	0.0830	+0.3	—	—	—	0.2534	0.2562	+1.1

^aTime of exposure at 95+ percent relative humidity and 120°F.

TABLE 28. MOISTURE EXPOSURE — SHORT BEAM SHEAR STRENGTH
(95+ PERCENT RELATIVE HUMIDITY)

Panel Identity	Specimen Identity	Exposure Period (days) ^a	Test Temp (°F)	Short Beam Shear Strength (10 ³ psi)	Percent ^c	d
239A	1	—	70	15.4		
	5		↓	14.6		
	16	↓	↓	<u>14.1</u>		
				Avg 14.7		
	3		350	8.21		58
	7		↓	8.39		
	14		↓	<u>8.93</u>		
				Avg 8.51		
	8	20	70	13.2	96	96
	15	↓	70	<u>14.8</u>		
				Avg 14.0		
	9	↓	350	5.36	61	35
			350	<u>4.96</u>		
				Avg 5.16		
	2	31	70	12.8	84	84
	10	↓	↓	13.0		
	17			<u>11.5</u>		
				Avg 12.4		
	4	↓	350	4.3	51	30
	12		↓	4.3		
	18		↓	<u>4.4</u>		
				Avg 4.3		

^aTime at 120°F, 98-percent relative humidity.

^bAll specimens were 12-ply unidirectional.

^cExpressed as a percent of comparable unexposed results for the same temperature.

^dExpressed as a percent of unexposed room temperature result.

TABLE 29. MOISTURE EXPOSURE — FLEXURAL STRENGTH
(95+ PERCENT RELATIVE HUMIDITY)

Panel Identity	Specimen Identity ^b	Exposure Period (Days) ^a	Test Temperature (°F)	Flexure Ultimate (10 ³ psi)	Flexure Modulus (10 ³ psi)	Residual Strength (Percent)	
						(c)	(d)
239A	1	0	70	242	17.4		
	7			250	19.3		
	13			<u>242</u>	<u>18.0</u>		
				Avg 244	18.2		
		↓	350	182	19.7		
				180	17.4		
				<u>182</u>	<u>19.4</u>		
				Avg 181	18.8	25.8	25.8
	10	20	70	244	18.4		
	16			<u>265</u>	<u>18.9</u>		
				Avg 250	18.7	102.5	102.5
	4	↓	350	115	15.6		
	9			<u>111</u>	<u>15.6</u>		
				Avg 113	15.6	63	53.6
	5	31	70	245	18.6		
	8			255	18.2		
	15			<u>248</u>	<u>18.3</u>		
				Avg 235	18.4	96	96
	6	↓	350	98.2	15.4		
	12			109	14.3		
	17			<u>102</u>	<u>14.7</u>		
				Avg 103	14.8	57	44

T-48A

^aTemperature at 120°F, 98-percent relative humidity.

^bAll specimens were 12 ply, unidirectional.

^cExpressed as a percent of comparable unexposed results for the same test temperature.

^dExpressed as a percent of unexposed room temperature result.

TABLE 30. AF-R-800 COCURE ASSESSMENT

Laminate Number	Specimen Number ^a	Failure Location		
		Adhesive Bond		Composite Gage Length
		Cohesive	Adhesive	
235B	1			X
	2			X
	3			X

^aScotchply 1009-36 tabs bonded to AF-R-800 composite with Metlbond 328.

2.4.9 Summary

Composite data developed on AF-R-800 prepreg indicates that it is at least equivalent and in many instances superior to user-reported results for state-of-the-art epoxy systems. The program objectives of extended flow life were fully met. Specifically, the AF-R-800 composites provided:

- Short beam shear strengths higher than state of the art at room temperature and 350°F
- Flexure strengths equal to state of the art at room temperature and 350°F
- Transverse tensile strength and strain-to-failure higher than state of the art at room temperature and 350°F
- Oriented panel tensile strengths equal to state of the art
- Moisture resistance equal to state-of-the-art systems in mechanical property retention and weight gain
- Compression properties at room temperature and 350°F equal to reported results for other prepregs

Further, the AF-R-800 prepreg demonstrated:

- Retention of composite properties from prepreg exposed to ambient conditions for 14 weeks prior to layup and cure
- Retention of composite properties with layup performed over a 12-week interval in a stepwise sequence prior to cure
- An ability to be cocured with conveniently available 350°F adhesives
- An ability to be cured at less than 350°F using state-of-the-art layup procedures and to be post-cured in a free standing state

As previously noted, these test results obtained to date should not be considered final representation of the capability of the AF-R-800 resin system. It is possible that efforts directed toward optimizing all properties of the AF-R-800 system would find a slightly different post-cure schedule useful. Specifically, the present efforts focused on optimum short beam shear values, whereas higher flexural strength retention or compressive strengths might be obtained with a slightly higher temperature post-cure at only minimal sacrifice to short beam shear or transverse tensile strength properties.

2.5 ALTERNATE LATENT CURING AGENTS

2.5.1 Selection Criteria and Experimental Conditions

Selection

A total of 12 primary aromatic diamines were selected to determine whether they possessed latency as curing agents for the MY 720/DGA resin blend. They were selected for the reasons listed below:

- Basicity, as deduced by inductive effects
- Steric hinderance of amine by groups ortho to the amine
- Commercial availability

Solubility of the selected amines in the resins was not predictable, however, solubility plays an important role in latency. Three amines, m-phenylenediamine (MPDA), p-phenylenediamine (PPDA), and diaminodiphenylsulfone (DADS) were employed as standards. The 15 amines, their sources, reason for being selected, and their melting points are listed in Table 31.

Experimental Conditions

The experiments were conducted in the following manner. The as-received aromatic diamines were ground to pass 325 mesh. The ground amines were then checked for purity (mp by DSC) and blended with a mixture of 94 parts MY 720 and 6 parts DGA so that the stoichiometric ratio of amine to epoxide was one to one. During the blending sequence, the mixture was heated to no more than 150°F (66°C) to reduce the viscosity of the resin and speed the blending process. The blended mixture was then portioned; one portion was set aside for room temperature aging, a second was submitted for aging at 212°F (100°C), a third was submitted for differential scanning calorimetry (DSC) and the fourth was placed in a vial and degassed at 250°F (121°C). After this sample was degassed, it was aged at 300°F (149°C), until the gel time was recorded and finally cured at 400°F (204°C). The resultant casting was cut to size and DTUL and moisture gain data determined. The process described above, is diagrammed in Figure 10.

2.5.2 Analysis of the Data

Gel Time, Solubility and DSC Cure Exotherm Data

The data obtained from the gel time studies and DSC's showing cure exotherms are presented in Table 32. The data is arranged in the order of increasing initial cure onset temperatures. This is measured as the point the DSC curve begins to leave its baseline as shown in Figure 11. Figure 11, which presents a typical DSC cure curve, also shows how the maximum and the width at half height were determined.

TABLE 31. ALTERNATE CURING AGENTS

Name ^a	Abbreviation	Reason for Selection	Company	Mp. ^f °C
m-phenylenediamine	MPDA	Baseline	MCB ^b	63-64
p-phenylenediamine	PPDA	Baseline	MCB	139-142
2,4-diaminotoluene	2,4-DAT	Steric	Aldrich	92-94.5
2,6-diaminotoluene	2,6-DAT	Steric	Aldrich	103.5-105
4-chloro-m-phenylenediamine	4-CIMPDA	Steric	MCB	90-92
2,6-diaminopyridine	2,6-DAP	Inductive	MCB	119-121
2,4-diamino-6-phenyltriazine	DAPT	Inductive	Eastman	226-228
1,5-diaminonaphthalene	DAN	c	Aldrich	190.5-192
4,4'-diaminodiphenylsulfone	DADS	Baseline	EVRA ^d	180-182
4,4'-diaminoazobenzene	DAAB	Inductive	Polysciences	150-153
methylene-bis-o-chloroaniline	MOCA	Steric	ICN ^e	108-111
3,6-diaminoacridine	3,6-DAA	Inductive	Aldrich	280-284
4,4'-diaminobenzophenone	DABP	Inductive	Ash Stevens	243-245
1,5-diaminoanthraquinone	1,5-DAAQ	Inductive	Aldrich	322-325d
2,6-diaminoanthraquinone	2,6-DAAQ	Inductive	Aldrich	395-430d

^aMany aromatic diamines, most notably benzidine and dichlorobenzidine are known carcinogens. Although among the listed, only MOCA has been identified as a carcinogen, all of the rest should be treated with respect.

^bMatheson, Coleman & Bell

^cCombination of solubility and potential for high distortion temperature under load (DTUL)

^dE. V. Roberts and Associates

^eICN Pharmaceuticals

^fBy differential scanning calorimetry

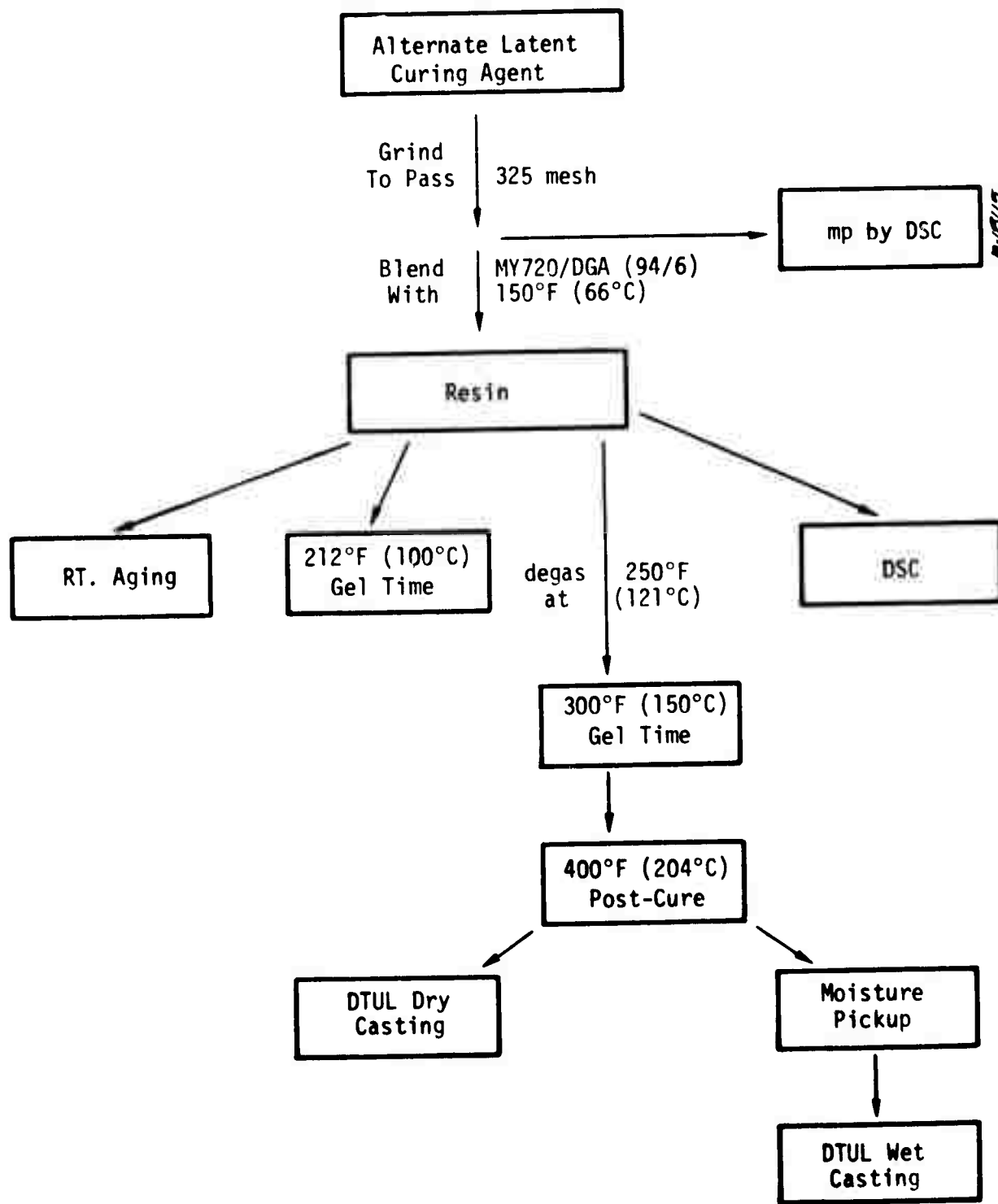


Figure 10. Scheme for screening alternate latent curing agents.

TABLE 32. GEL TIMES AND ANALYSIS OF DSC TRACES OF THE CURE EXOTHERM CONSISTING OF 94 PTS MY 720/6 PTS DGA AND A STOICHIOMETRIC EQUIVALENT OF THE LISTED CURING AGENTS

Curing Agent ^a	DSC Cure Exotherm		Width At Half-Height (°C)	Flow Life RT, Days	Dissolution/Gel Time	
	Initial Temperature (°C)	Maximum Temperature (°C)			101°C (212°F) (Hour)	149°C (300°F) (Hour)
p-phenylenediamine	65	115	15	d/<1	--	d/<1
m-phenylenediamine	70	128	42	d/<1	--	f
2,4-diaminotoluene	85	143	31	d/<1	--	d/<1
2,6-diaminotoluene	100	157	29	d/3	--	d/<1
3,6-diaminoacridine	102	139	19	e/7	--	g
4-chloro-metaphenylenediamine	110	197	34	c/3	d/1.67	d/<1
1,5-diaminonaphthalene	120	190	42	e/12	e/2.5	<1/<2
2,6-diaminopyridine	145	201	35	d/17	d/3	d/<1
4,4'-diaminoazobenzene	150	200	22	e/17	e/4.5	f
4,4'-diaminodiphenylsulfone ^b	150	240	40	e/45 ¹	1/6-7	h/<4
4,4'-diaminobenzophenone	165	201	22	e/74	--	h/<4
methylene-bis-o-chloroaniline	170	238	31	e/43	<0.33/6-7	h/<4
2,4-diamino-6-phenyltriazine	190	233	40	e/6mos	--	e/~∞
2,6-diaminoanthraquinone	195	287	15	e/8mos	e/9days	e/<97
1,5-diaminoanthraquinone	205	276,288 ^c	29	e/8mos	e/12days	e/<97

^aAll except DADS were as-received.

^bStandard, recrystallized from methanol.

^cTwo maxima.

^dSolubilized during mixing at 150°F, the preferred prepregging temperature.

^eHardened/gelled prior to complete dissolution.

^fExothermed during cure.

^gExothermed during deaeration at 250°F.

^hSolubilized during deaeration step.

ⁱNote: The 45 days is at 100-percent stoichiometry.

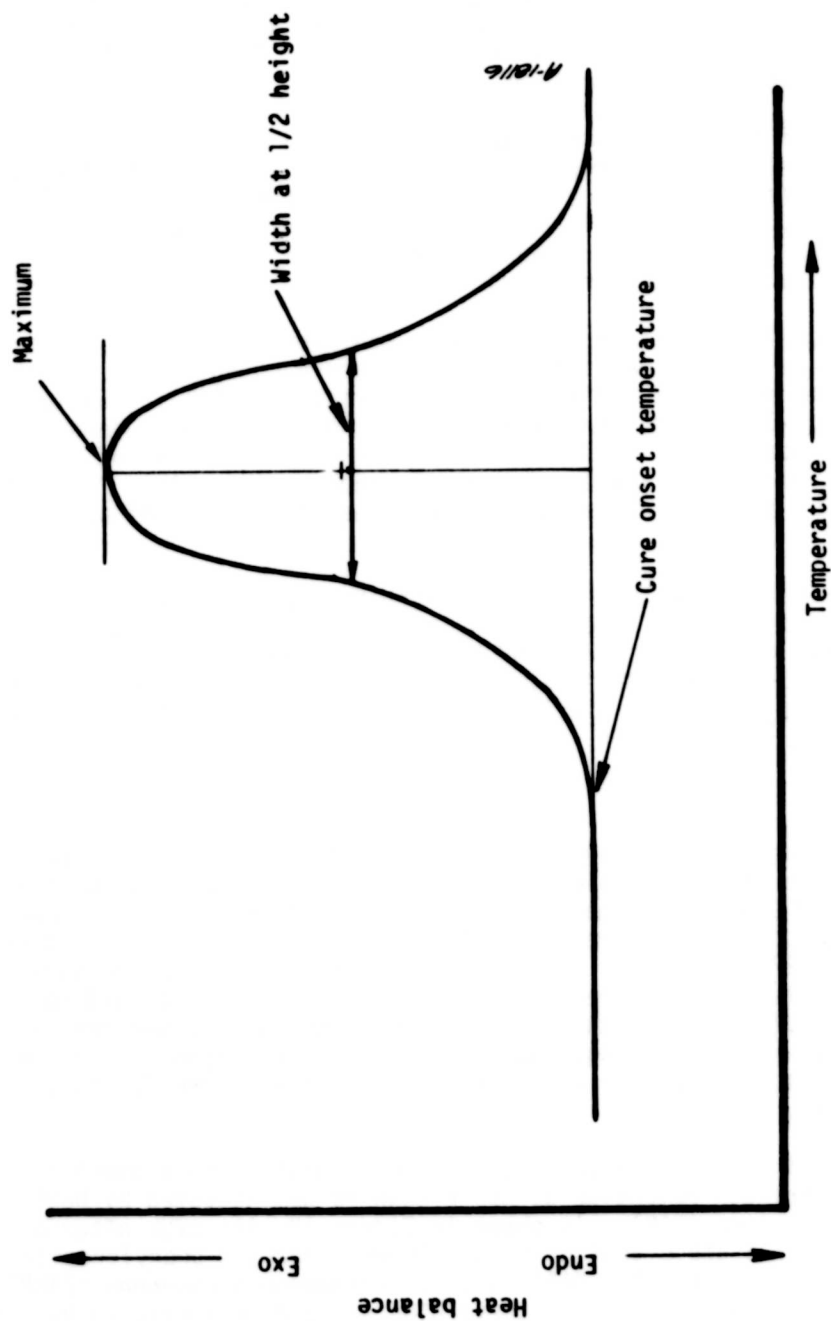


Figure 11. Typical cure DSC of an epoxy resin system and its method of analysis.

An excellent correlation exists between cure onset temperature and the room temperature flow life. Only two discrepancies were observed. The first is 3,6-diaminoacridine (3,6-DAA) which is definitely due to insolubility and the second, methylene bis-o-chloroaniline (MOCA). The reason MOCA does not fit this relationship is not clear.

The width of the cure exotherm peak is an excellent indicator of the rate at which the reaction progresses once it is initiated. Thus, although the room temperature flow life for 4,4'-diaminobenzophenone (DABP) is longer than that for DADS, the relatively narrow DSC cure exotherm peak indicates that the cure will be much faster once initiated. This could prove to be detrimental when curing large parts with a high volume to surface area ratio.

Only two curing agents, MOCA and DABP, achieved homogeneity in the cured state and had room temperature flow lives approaching or exceeding that of DADS. The amines, 2,4-diamino-6-phenyltriazine (DAPT), 1,5-diaminoanthraquinone (1,5-DAAQ) and 2,6-diaminoanthraquinone (2,6-DAAQ) demonstrated excellent room temperature flow lives, however, the samples did not achieve homogeneity upon cure. The amines, 1,5-diaminonaphthalene (DAN), 2,6-diaminopyridine (2,6-DAP) and diaminoazobenzene (DAAB) had flow lives of approximately 2 weeks.

The results indicate that inductive effects are more important than steric effects in developing latent curing agents. However, solubility plays the most important role. Thus, 2,6-DAP had a far longer flow life than 2,6-diaminotoluene (2,6-DAT) and MPDA (all soluble at room temperature) but DAN which should have a reactivity similar to MPDA, had a 2-week flow life due to its insolubility in the resin.

DTUL Data

Ten curing agents were investigated for their ability to provide useful DTUL's with the MY 720/DGA blend. Useful DTUL was defined as one that occurs at least 50°C above the maximum composite use temperature. In our case, the maximum use temperature is 350°F (177°C). Thus, the useful DTUL would be at least 227°C. Figure 12 presents the results of DTUL measurements on the curing agents with this resin blend. Three curing agents did not achieve complete solubility in the resin system. They were 1,5-diaminoanthraquinone, 2,6-diaminoanthraquinone, and 2,4-diamino-6-phenyltriazine. Their low DTUL's can probably be attributed to incomplete cure due to curing agent insolubility.

Of the remaining seven diamines, one shows outstanding promise to provide greater strength retention at 350°F than is demonstrated by DADS. It is 1,5-diaminonaphthalene (DAN). As shown in Figure 12, its DTUL after a 5-hour cure at 400°F exceeds that of DADS. Three others, m-phenylenediamine (MPDA), 2,6-diaminopyridine (2,6-DAP), and 4,4'-diaminobenzophenone (DABP) have DTUL's that approach 227°C. If their DTUL's could be increased by using reduced stoichiometry such as was found useful for DADS, then these curing agents may be useful in 350°F performing resin systems.

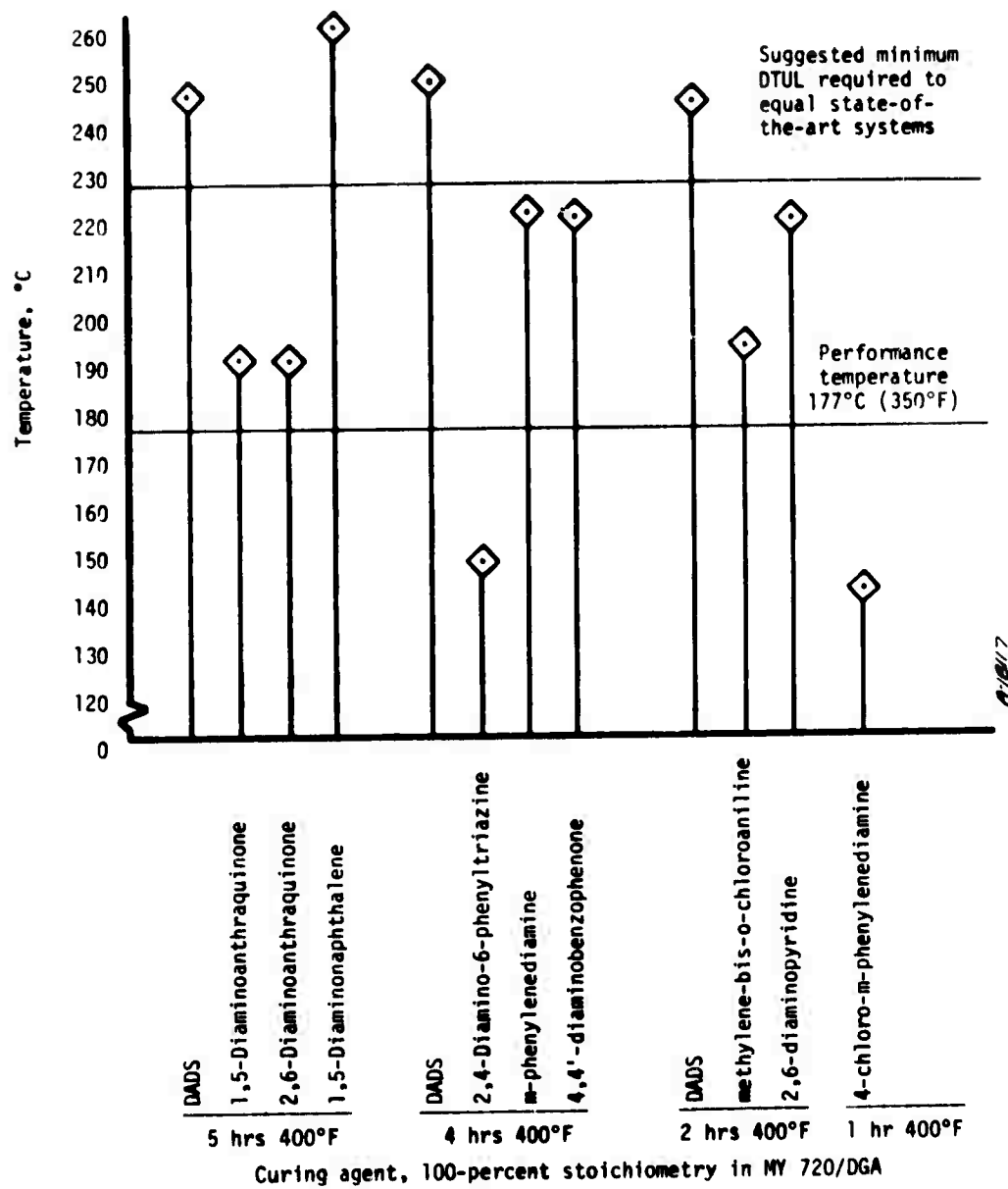


Figure 12. DTUL for various curing agents with MY 720/DGA (94/6).

Methylene-bis-o-chloroaniline (MOCA) had such a surprisingly low DTUL with the MY 720/DGA that it was repeated twice. All three determinations were within 10 degrees of one another.

In a brief investigation of what properties a curing agent mixture might provide with the MY 720/DGA blend, a 50-mole percent MOCA/50-mole percent DADS mixture was prepared and blended into the MY 720/DGA (100-percent stoichiometry). The DTUL recorded was 237°C, much better than MOCA alone and promising for use in a 350°F (177°C) performing resin. Figure 13 shows the DTUL curve of this sample. It is probable that blends of DADS with other curing agents may impart sought for characteristics in the MY 720/DGA not achieved with the individual curing agents.

Water Boil Data

Table 33 presents the percent weight pickup of samples exposed to 24- and 48-hour water boil. This data, as plotted in Figure 14, shows that even after 48 hours, equilibrium has not been reached for any of the systems except possibly DABP.

DTULs were conducted on wet specimens. The DTUL for the wet DADS system showed a break at 172°C (60 percent stoichiometry) and 122°C (75-percent stoichiometry) while the DTUL for the DAN system shows a break at 204°C. These are shown in Figures 15, 16, and 17 respectively. These breaks in the DTUL curves are known to be caused by water and are attributed to plasticization of the resin by water. Actual resin softening related to Tg or HDT occurs at the peak. Sample weights after DTUL measurement near the peak temperature showed that the DAN cured resin was completely dry while the DADS cured MY 720/DGA resin still contained 1.2-percent moisture (60-percent stoichiometry).

2.5.3 Conclusions

Two alternate curing agents emerged which warrant further study; DAN and DABP. DAN merits further study for its exceptional DTUL and its moisture resistance and DABP for its flow life properties. Mixtures of these curing agents with DADS may also provide promising curing agent systems. Composites were not prepared from the alternate curing agents.

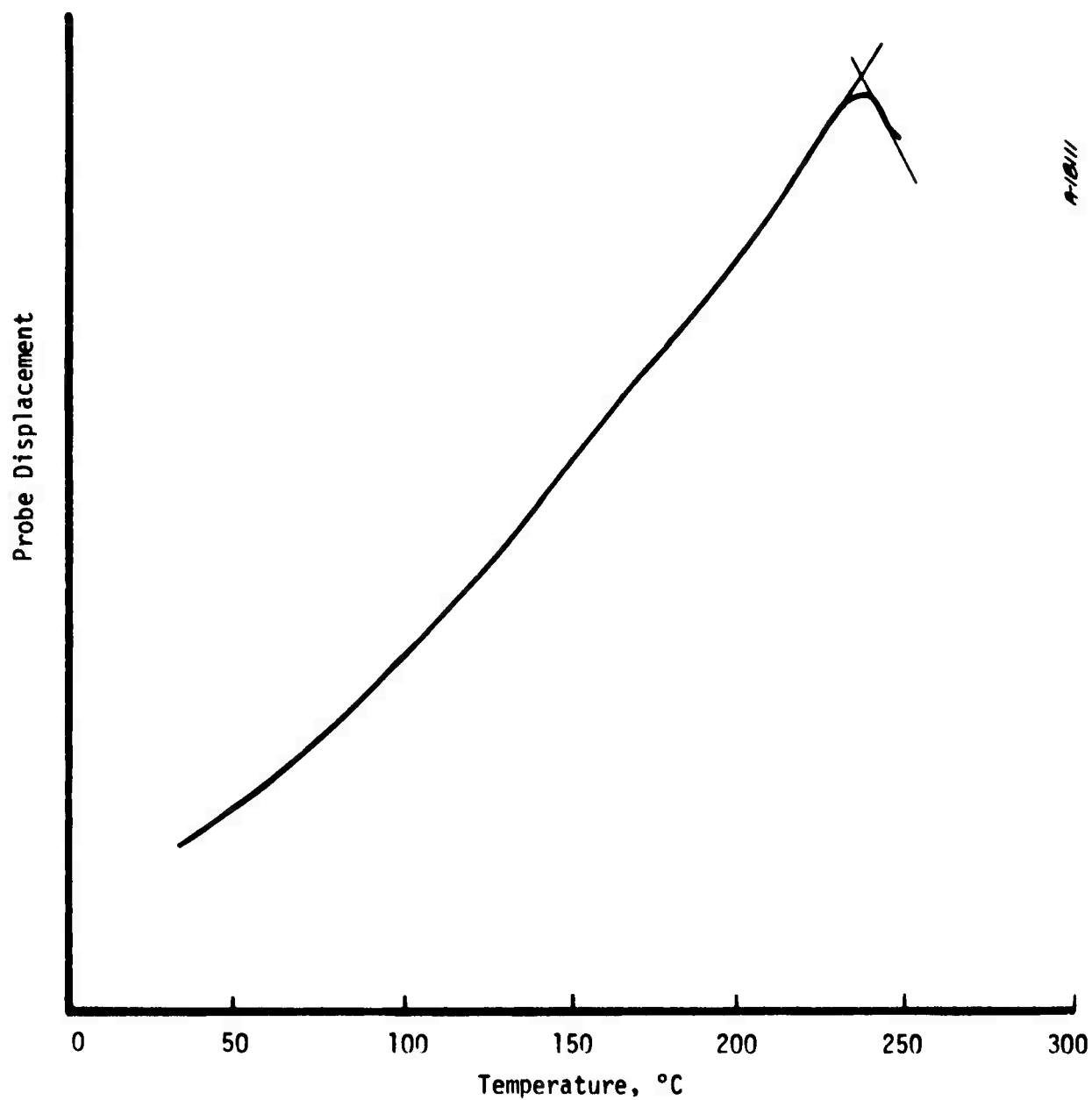


Figure 13. DTUL curve for MY 720/DGA resin cured with 50-percent MOCA, 50-percent DADS (100-percent stoichiometry).

TABLE 33. PERCENT MOISTURE PICKUP OF MY 720/DGA RESIN
CASTINGS CURED WITH A STOICHIOMETRIC AMOUNT
OF THE LISTED DIAMINE

Curing Agent	Cure Conditions (hr @ °C)	% Weight Increase	
		24-Hour Water Boil	48-Hour Water Boil
1,5-Diaminonaphthalene	5 @ 204	2.54	3.61
4,4'-Diaminobenzophenone	4 @ 204	4.43	5.25
4,4'-Diaminodiphenylsulfone	5 @ 204	4.17	6.40
m-Phenylenediamine	4 @ 204	3.51	4.76

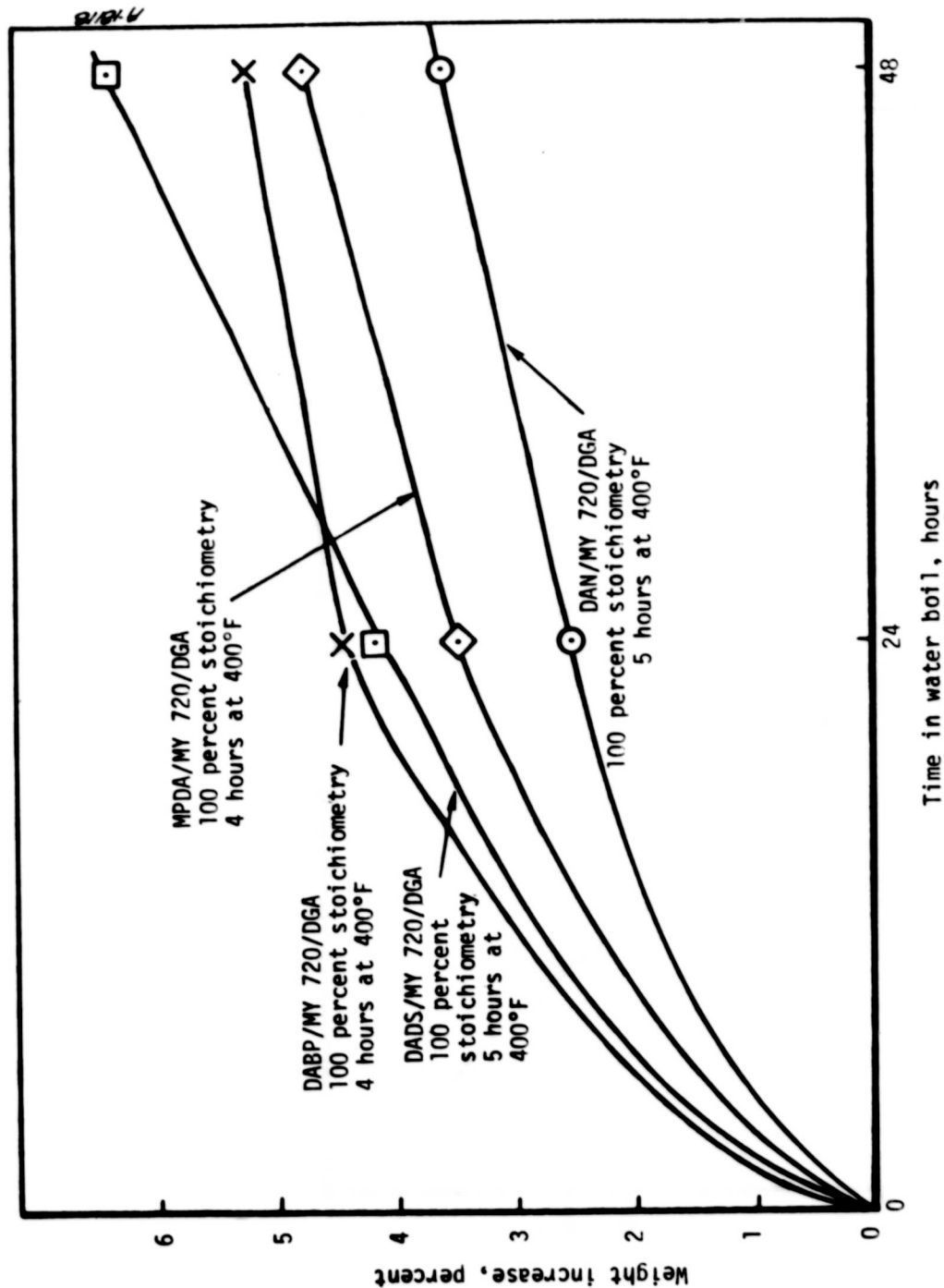


Figure 14. Percent moisture uptake of MY 720/DGA resin castings cured with a stoichiometric amount of the listed diamine.

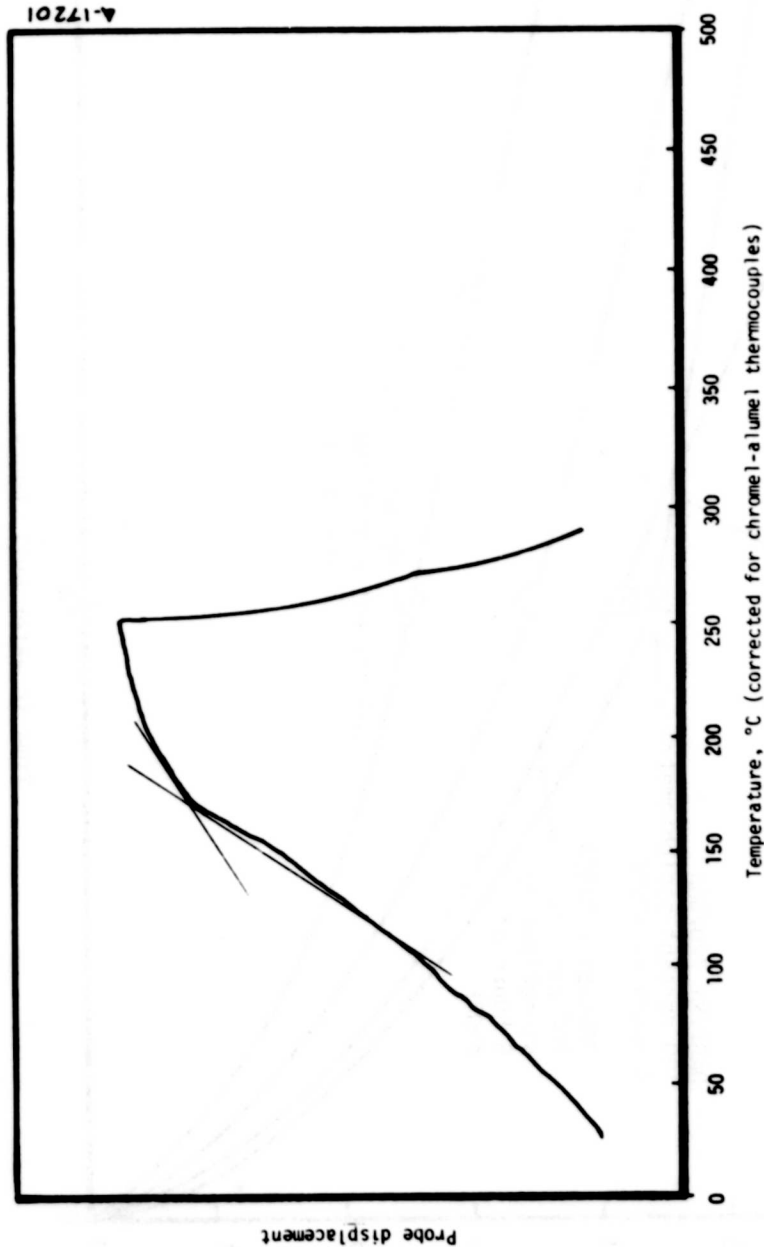


Figure 15. Distortion temperature under load (DTUL) of diaminodiphenylsulfone (DADS) cured MY 720/DGA resin, 60-percent stiochiometry, after 48-hour water boil.

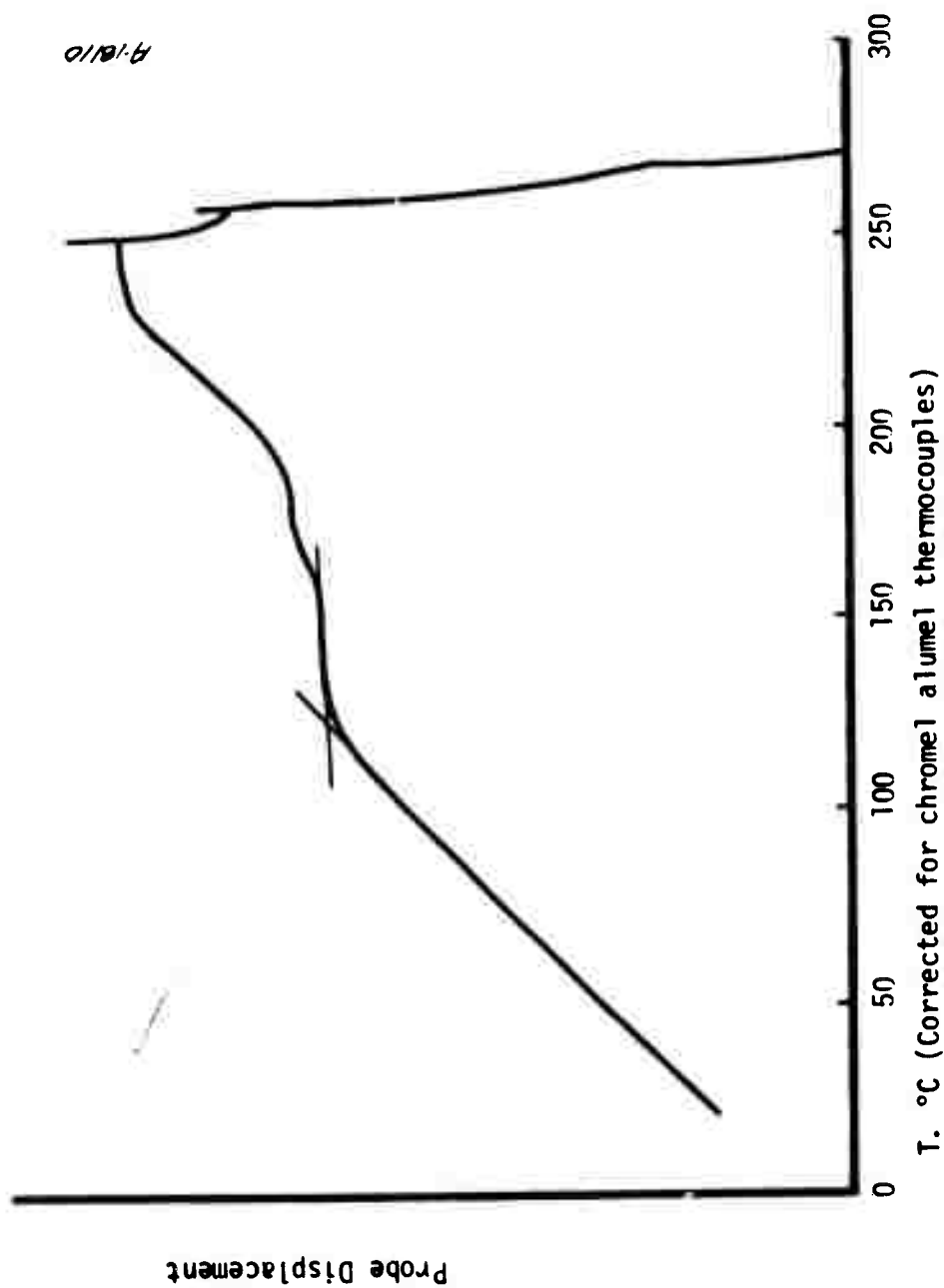


Figure 16. DTUL of DADS cured MY 720/DGA (75-percent stoichiometry) after 48-hour water boil.

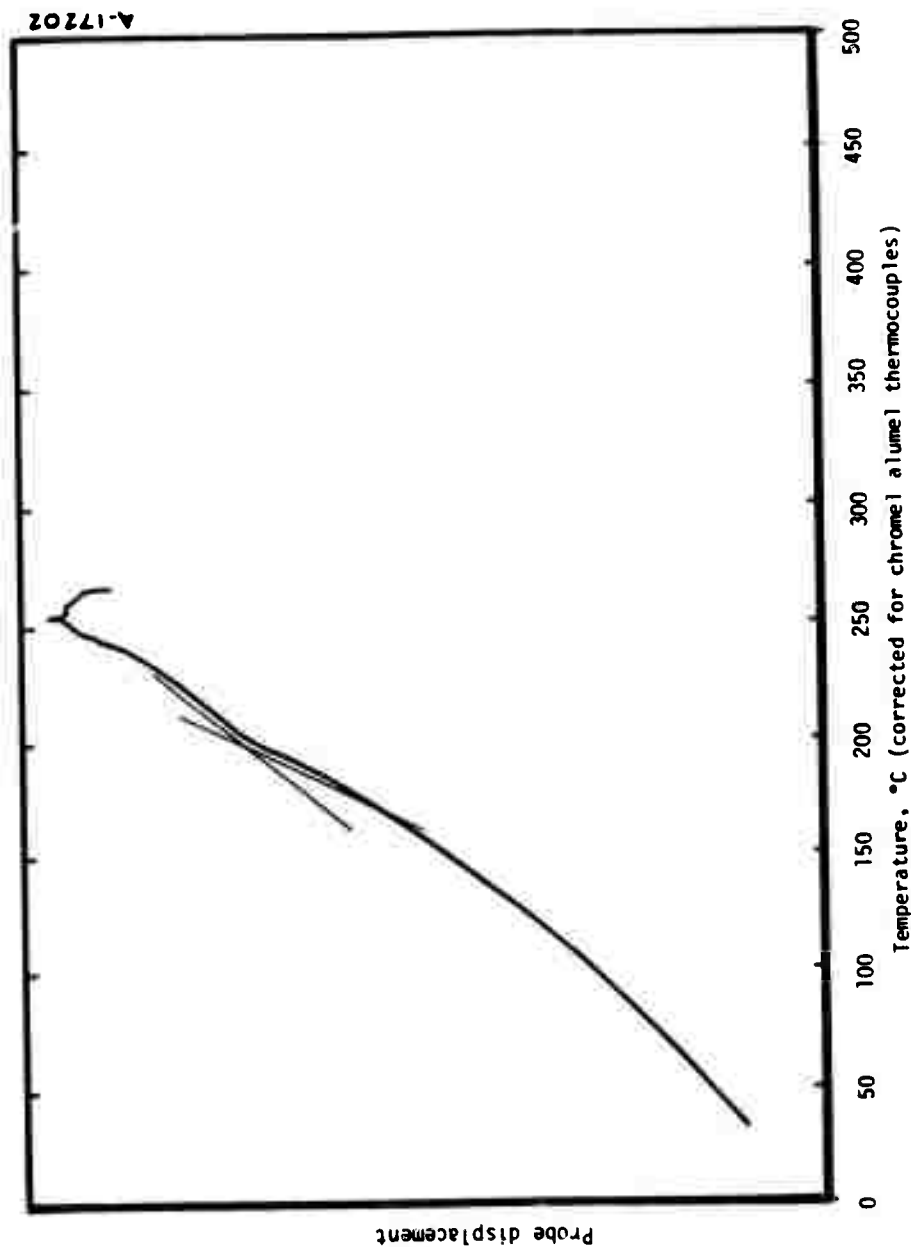


Figure 17. DTUL of 1,5-diaminonaphthalene (DAN) cured MY 720/DGA, 100-percent stoichiometry, after 48-hour water boil.

2.6 ALTERNATE RESINS SYSTEMS

2.6.1 Selection Criteria and Experimental Conditions

Resin Selection

Consideration of alternate resins for investigation on this program were based on several criteria. Among the most important were:

- Known 350°F performance capability
- Commercial availability of the resin
- Blendability of the resin with other resins
- Viscosity low enough to allow facile addition of particulated curing agents

In addition, as the majority of commercially available epoxy resins contain glycidyl ether groups, answers to the following questions were sought.

- Do glycidyl ethers have a shorter flow life with particulated diamine curing agents than diglycidyl amines?
- Can glycidyl ether resins provide cured systems with the same or higher DTULs than diglycidyl amine resins with the same diamine curing agents?

Preliminary blending experiments addressed the problems of formulating a resin system that (1) would provide a viscosity equivalent to that of the baseline MY 720/DGA system, (2) could be blended without the use of a solvent, and (3) would consist, for the most part, of glycidyl ether containing resins. Structures and properties of all resins used in these efforts are shown in Figure 18.

Initial attempts to blend SU-8 with 0510 were not successful. The 0510 is only sparingly soluble in SU-8 below its melting point. At the melting point of SU-8, solubility is achieved but the 0510 appears to have advanced. After brief experimenting with a SU-8/DEN 438/0510 blend, efforts with SU-8 were set aside. Work then concentrated on a DEN 438/0510 blend. A mixture, comprising 90-percent DEN 438 and 10-percent 0510 was prepared with the proper viscosity, however, subsequent prepregging studies showed that this blend had slightly high flow. Accordingly, the unmodified DEN 438* which was found to have nearly the proper flow for prepregging was used in the studies described below.

* Subsequent to these efforts, a second sample of DEN 438 (Lot TBO 3096101) was obtained from Dow Chemical. This material was much more viscous than the first batch and would require the addition of a viscosity diluent such as 0510.

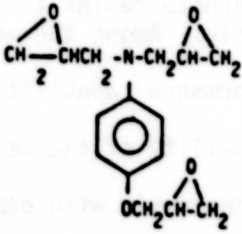
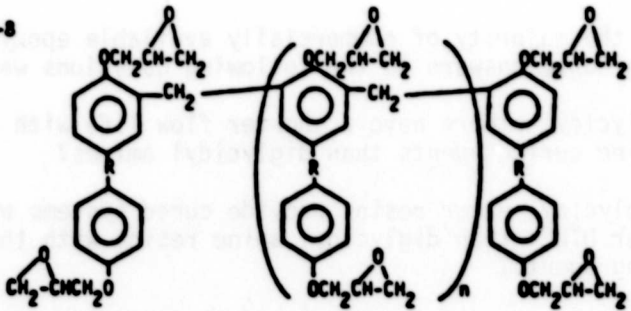
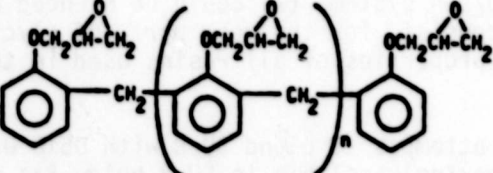
Manufacturer	Resin	Idealized Structure	Comments
CIBA-Geigy	0510 (N,N,O-triglycidyl-4-aminophenol)		Low viscosity, previously marketed by Union Carbide
Celanese	SU-8		Solid resin (mp 85°C-90°C)
Dow Chemical	DEN 438 poly[methylene-2,6-[1-(2,3-epoxy-1-propoxy)]phenylene]		Viscous semi-solid

Figure 18. Multifunctional epoxy resins screened for alternate resin systems.

Experimental Conditions

The setup for the experiments used to define the flow life and the DTUL of the unmodified DEN 438 was basically the same as that described previously for the MY 720/DGA resin system. Seven curing agents were screened. Instead of the 100-percent amine stoichiometry used for the MY 720/DGA studies, 70-percent stoichiometry was used to more closely simulate the AF-R-800 formulation. At this amine loading one should see an increase in the DTUL and a lengthening of the room temperature flow life properties over the 100-percent stoichiometry.

Two sets of castings were prepared. The first set was post-cured at 375°F (191°C) and, to assure cure completion, the second set was post-cured at 425°F (218°F).

2.6.2 Analysis of the Data

Gel Time, Solubility, and DSC Cure Exotherm Data

Table 34 lists the aromatic diamines used, their melting points and data obtained from the gel time studies. Also included for comparison are the room temperature flow life results for resins prepared from these same amines and the MY 720/DGA blend.

Even though the flow lives of the curing agents in the DEN 438 resin paralleled the results for the MY 720/DGA blend, the flow lives were only about 50 percent of those for the MY 720/DGA systems. Thus, DADS only had a flow life of 23 days with DEN 438 compared to the AF-R-800's flow life of ~70 days, despite the reduction in the amine hydrogen to epoxide stoichiometry for the DEN 438 resin systems (compare to Table 32).

Analysis of the cure exotherm peaks of DEN 438 with the aromatic diamine curing agents is shown in Table 35. With the MY 720/DGA blend previously described, excellent correlation exists between the room temperature flow life of these resin systems and the initial temperature of the DSC peak. Comparison to the MY 720/DGA system (Table 32) shows that for equivalent room temperature flow lives, the DSC initial cure temperature is much lower for the DEN 438 systems.

DTUL Data

DTUL data were obtained on castings of DEN 438 with seven amines post-cured 4 hours at 375°F (191°C) and 4 hours at 425°F (218°C). The DTUL measurements of these specimens are given in Table 36 and in Figure 19. Table 36 also includes a comparison to the MY 720/DGA DTUL data. The 2,4-diamino-6-phenyltriazine (DAPT) was insoluble in both cured specimens which accounts for their low DTUL's. The remainder of the curing agents seen in the figure provided homogeneous samples.

TABLE 34. ALTERNATE RESIN SYSTEM (DEN 438)/CURING AGENT SCREENING STUDY, GEL TIMES^a

Curing Agent ^c	Mp by DSC (°C)	Flow Life		Dissolution/Gel Time		RT Flow Life ^b MY 720/DGA Resin (days)
		RT (days)	100°C (212°F) (hours)	149°C (300°F) (hours)		
m-phenylenediamine	63-64	e/<1	e/0.5	3/0.33	e/<1	
1,5-diaminonaphthalene	190.5-192	f/4	f/1	f/0.17	f/12	
methylene-o-chloroaniline (MOCA)	108-111	e/11	e/3.75	e/0.83	f/43	
4,4'-diaminoazobenzene	150-153	f/23	f/4.5	f/2.0	f/17	
4,4'-diaminodiphenyl- sulfone (DADS) ^d	180-182	f/23	3/7	0.17/1.17	f/459	
4,4'-diaminobenzophenone (DABP)	243-245	f/85	f/2.5	f/0.83	f/74	
2,4-diamino-6-phenyl- s-triazine (DAPT)	226-228	f/>150	f/96	f/2.75	f/6 months	

^aSamples run at 70-percent amine hydrogen-epoxide stoichiometry^bValues obtained from indicated curing agent with 94 points MY 720, 6 points DGA at 100-percent stoichiometry^cAll except DADS were used as received, ground to pass 325 mesh^dStandard, twice recrystallized from methanol, ground to pass 400 mesh^eSolubilized upon mixing^fGelled prior to complete dissolution^gNote: 45-day flow life at 100-percent stoichiometry

TABLE 35. DIFFERENTIAL SCANNING OF CALORIMETRY (DSC) TRACES OF CURE EXOTHERM OF DEN 438 WITH THE FOLLOWING CURING AGENTS (70-PERCENT STOICHIOMETRY)

Curing Agent	DCS Cure Exotherm			RT Flow Life (days)
	Initial Temp. (°C)	Max Temp. (°C)	Width at Half Height (°C)	
m-phenylenediamine	65	133	24	<1
1,5-diaminonaphthalene	95	160	40	4
methylene-bis-o-chloroaniline	100	195	45	11
4,4'-diaminodiphenylsulfone	125	200	40	23
4,4'-diaminoazobenzene	130	175	35	23
4,4'-diaminobenzophenone	145	191	25	85
2,4-diamino-6-phenyl-s-triazine	175	230	45	>150

TABLE 36. DISTORTION TEMPERATURE UNDER LOAD RESULTS OF DEN 438 AND MY 720/DGA CURED WITH DADS AND SIX OTHER AROMATIC DIAMINE CURING AGENTS

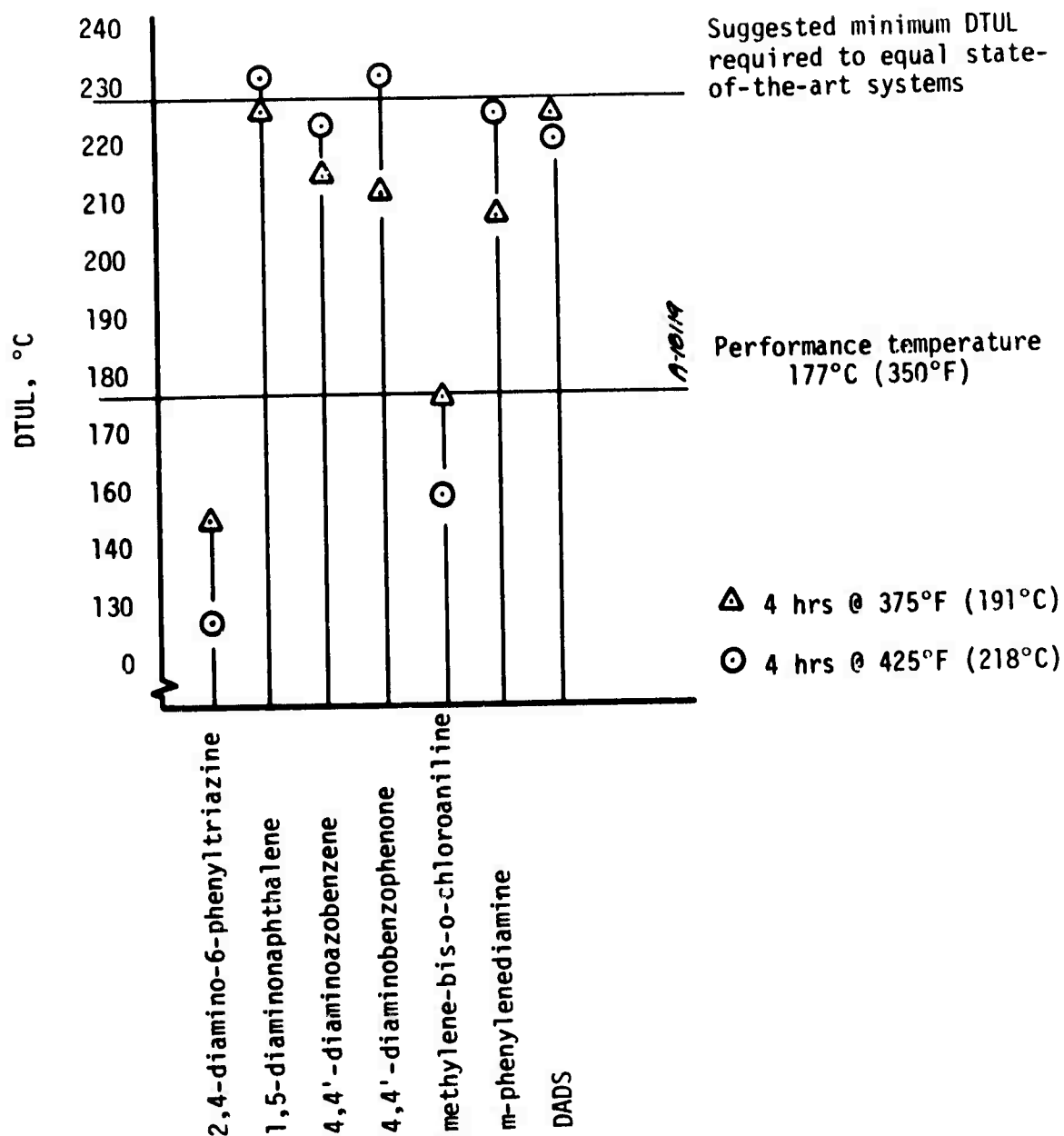
Curing Agent ^a	DTUL by TMA, °C ^b		
	70 Percent in DEN 438/ 375°F	70 Percent in DEN 438/ 425°F	100 Percent in MY 720/DGA 400°F
m-phenylenediamine	208	225	224
4,4'-diaminobenzophenone	210	234	219
1,5-diaminonaphthalene	227	229	258
methylene-o-chloroaniline (MOCA)	176	158	197
diaminoazobenzene	213	223	d
4,4'-diaminodiphenyl sulfone (DADS) ^c	227	220	234
2,4-diamino-6-phenyl-s- triazine (DAPT)	155	153	152

^aAll except DADS were used as received; ground to pass 325 mesh

^bDTUL, distortion temperature under load; TMA, thermomechanical analysis

^cStandard, twice recrystallized from methanol, ground to pass 40C mesh

^dCasting lost when resin exothermed



Curing agent, 70 percent stoichiometry in DEN 438

Figure 19. Distortion temperature under loads for various curing agents with DEN 438, at two final cure temperatures.

Approximate DTUL equivalence to the DADS curing agent after the 425°F cure is seen for 1,5-diaminonaphthalene (DAN), 4,4'-diaminoazobenzene (DAAB), 4,4'-diaminobenzophenone (DABP), and phenylenediamine (MPDA). Inspection of Figure 19 provides some information as to the benefit to DTUL one might expect by employing higher cure temperatures for each amine. In some instances, the 375°F post-cured resin provided a higher DTUL than the 425°F post-cured samples. This is suspected to be due to decomposition of the resin due to the higher cure temperature.

The highest DTULs seen for the diamine DEN 438 systems are on the order of 230°C suggesting only marginal performance in 350°F performing resins. The MY 720/DGA resin system cured with the DADS shows a 15°C to 20°C DTUL benefit over all of these systems and it is easily understood why this composition became the basis for the AF-R-800 resin.

Moisture Data

Moisture data for the DEN 438 diamine systems were carried out on samples which were post-cured for 4 hours at 425°F (218°C). Table 37 presents the percent weight pickup of samples exposed to 24- and 48-hour water boil. As seen with the MY 720/DGA systems, most of the DEN 438 systems do not appear to be equilibrated even after 48 hours. Even though the specimens were not taken to an equilibrium moisture content, comparison of the DEN 438 data to the MY 720/DGA data suggests that the DEN 438 resins may have lower equilibrium moisture contents.

2.6.3 Conclusions

Comparison of DEN 438 to MY 720/DGA cured with the same aromatic diamines leads to the following conclusions:

- Substitution of DEN 438 for MY 720/DCA shortens the flow life of the resulting resin systems
- Only subtle differences in solubility of the diamine curing agents were noted between the DEN 438 and MY 720/DGA blends
- Despite higher cure temperatures, observed DTULs for the DEN 438 diamine systems would suggest only marginal 350°F (177°C) performance

TABLE 37. PERCENT MOISTURE PICKUP OF DEN 438 RESIN
CASTINGS CURED WITH 70-PERCENT STOICHIOMETRIC
AMOUNT OF THE LISTED DIAMINES

Curing Agent	Final Cure Conditions (hr @ °C)	Water Boil % Weight Increase	
		24 hr	48 hr
1,5-diaminonaphthalene	4 @ 218	2.49	3.27
4,4'-diaminobenzophenone	↓	2.44	3.53
m-phenylenediamine	↓	2.34	3.37

SECTION 3

FINDINGS AND RECOMMENDATIONS*

Successful attainment of project goals has been demonstrated by achieving thermomechanical, humid and elevated temperature aging properties which are virtually equivalent to present state-of-the-art 350°F graphite reinforced epoxy systems. This has been achieved with an increase in prepreg effective flow life from the previously allowable 2 weeks at ambient temperature to ~10 weeks.

The resin formulation has been finalized and assigned the designation Air Force Resin 800 (AF-R-800). Its composition is:

- Resin
 - 100 parts of a mixture of tetraglycidylmethylenedianiline and distilled diglycidylaniline blended to a useable viscosity. A typical ratio of the two resins is 94 to 6 parts, respectively.
- Curing Agent
 - Diaminodiphenylsulfone (DADS), 66 percent of the stoichiometry quantity calculated from the measured ~~ew~~ of the blended resins. The DADS is doubly recrystallized and ground to pass 400 mesh. A typical DADS quantity used is 30 parts of DADS to 100 parts of the blended resins.
- Catalyst
 - None. Of those investigated (proton and Lewis acids) all were found to reduce the flow life and/or provide no benefit to obtainable HDT for the AF-R-800.

Tetraglycidylmethylenedianiline (Ciba Geigy MY 720) is the basis of the AF-R-300 formulation. Glycidylether epoxy resins were found to be not as effective as the glycidylamine epoxy, MY 720 in providing strength retention to elevated temperatures.

*Includes prior program (AFML TR-76-49) as well as present program.

The purpose for the addition of the distilled diglycidylaniline (available unpurified from Mobay as Lekutherm X-50) is to provide the formulator with a reactive viscosity diluent. Minor adjustments in the quantity of X-50 used may be required to offset viscosity variations of the as-received MY 720 or better address user requirements. Glycidylether epoxy viscosity diluents were found to shorten the flow life of the MY 720, whereas the low viscosity glycidylamine epoxy, diglycidylaniline did not effect the flow life.

Screening the commercially available curing agents resulted in the selection of DADS to be the curing agent of choice. The selection and final quantity to be used in the AF-R-800 composition were based upon heat distortion temperature (HDT) development, flow life characteristics and the ability to achieve homogeneity with the MY 720/DGA blend. Two alternate diamines showed promise for high HDT development equivalent to the DADS. They were 1,5-diaminonaphthalene and 4,4'-diaminobenzophenone. Ground to pass a 325 mesh screen and formulated at a 100-percent stoichiometry flow lives of 12 and 74 days were determined for these diamines, respectively. (Same conditions DADS - only 45 days.) Even though both diamines showed less (compared to DADS) susceptibility to plasticization by moisture, both required elevated temperatures to achieve homogeneity. These diamines or similar structures should be the subject of future investigations.

The preparation of the AF-R-800 formulation and its graphite prepregs is within the state-of-the-art procedures. To maximize the flow life properties of the resin prepregging temperatures of no more than 150°F were utilized in the program for blending and prepregging operations. The constituents of the formulation are blended together in a straightforward manner and is easily accomplished. Impregnation times at 150°F are on the order of 5 minutes. Reduction of this impregnation time would be most beneficial and the investigation of thermal spikes to reduce impregnation times is recommended.

Processing of AF-R-800 graphite prepregs into composites is essentially state of the art with the single exception being a longer cure schedule due to the reduced reactivity of the AF-R-800. Even though precise adherence to the cure schedule virtually assures the attainment of a high quality composite, the high flow characteristics at temperature should be addressed. Useful in this regard may be the addition of insoluble catalysts which would not reduce the flow life of the system but would dissolve and become active upon heating.

Graphite composites prepared with the AF-R-800 (94 parts MY 720, 6 parts DGA, 30 parts DADS) and Thorne 300 provided the program high strengths given below:

	<u>RT</u>	<u>350°F</u>
Short beam shear strength, ksi*	19.1	10.7
Transverse tensile strength, ksi	7.64	5.57
Transverse tensile strain, $\mu\text{in/in}$	5550	5180
Flexural strength, ksi [†]	267	209

Virtual equivalence to state-of-the-art 350°F composites has been exhibited by the AF-R-800 composites in all tests conducted to date. Development of acceptance criteria for AF-R-800 graphite composites was not addressed on this program, however, upon completion of limits of variability investigations for the items listed below, such acceptance standards should be greater than or equal to existing standards for 350°F epoxy systems.

Material Specifications

AF-R-800 raw materials
 AF-R-800 (resin)
 AF-R-800 prepregs
 AF-R-800 composites

Processing Specifications

AF-R-800 formulation
 AF-R-800 prepregging
 AF-R-800 laminate fabrication

* Composite prepared from prepreg aged 9 weeks at room temperature.

[†] As above, 14 weeks at room temperature.

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