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EXTENDED FLOW LIFE LAMINATING RESIN SYSTEM

ACUREX CORPORATION/AEROTHERM DIVISION
485 CLYDE AVENUE
MOUNTAIN VIEW, CALIFORNIA 94042

JUNE 1976

FINAL REPORT FOR THE PERIOD 1 OCTOBER 1974 - 31 JANUARY 1976

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AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

NOTICE

This technical report has been reviewed and is approved for publication.

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FOR THE COMMANDER

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Epoxy resin/curing agent/catalyst combinations were investigated in efforts to obtain state-of-the-art performance (350°F) from graphite fiber reinforced composites coupled with prolonged prepreg out-times (>75 days) under ambient shop conditions. Resins evaluated included multifunctional commercially available glycidyl ethers and glycidyl amines. Curing agent studies were limited to potentially latent, high functionality systems and included hydrazides, amino-hydrazides and aromatic diamines with attenuated reactivity. The basic approach was to employ curing agents which would exhibit virtual

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insolubility in the resin combinations at slightly elevated prepregging temperatures (<150°F) but become soluble at processing (≅250°F) temperatures. The most successful system, which is virtually equivalent to presently available state-of-the-art epoxy/graphite prepreg was derived from CIBA-Geigy MY-720 and 0510 resins and uses carefully purified 4,4'-diaminodiphenylsulfone ground to -400 mesh particle size as a curing agent. Zinc linoresinate proved to be an effective co-catalyst. Evaluations (in T-300 reinforced composite form) included thermomechanical strengths, response to >1000 hours exposure to 95+% relative humidity at 120°F, 500 hour aging studies at 350°F and regain characteristics after drying the moisture laden composites. The effective flow-life of the prepreg was in excess of twelve weeks under ambient conditions.

FOREWORD

This final report was prepared by Aerotherm Division, Acurex Corporation, Mountain View, California and WRD, a Division of Whittaker Corporation, San Diego, California. Aerotherm assumed responsibility for the contract performance on September 12, 1975. This report was prepared for Air Force Contract No. F33615-74-C-5181, "Extended Flow Life Laminating Resin System".

The work was performed under the sponsorship of the Air Force Materials Laboratory (AFML/MBC), Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, under the direction of Mr. T. J. Aponyi. The manuscript of this report was released by the author in February 1976 for publication.

Efforts at WRD were conducted within the Polymer Chemistry Department under the technical direction of Mr. C. B. Delano. Mr. E. S. Harrison served as principal investigator.

This report covers laboratory efforts from 1 October 1974 to 31 January 1976.

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SUMMARY

Epoxy resin/curing agent/catalyst combinations were investigated in efforts to obtain state-of-the-art performance (350°F) from graphite fiber reinforced composites coupled with prolonged prepreg out-times (>75 days) under ambient shop conditions. Resins evaluated included multifunctional commercially available glycidyl ethers and glycidyl amines. Curing agent studies were limited to potentially latent, high functionality systems and included hydrazides, amino-hydrazides and aromatic diamines with attenuated reactivity.

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 most successful system, which is virtually equivalent to presently available state-of-the-art epoxy/graphite prepreg was derived from CIBA-Geigy MY-720 and 0510 resins and uses carefully purified 4,4'-diaminodiphenylsulfone ground to -400 mesh particle size as a curing agent. Zinc linoresinate proved to be an effective co-catalyst.

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

The effective flow-life of the prepreg was in excess of twelve weeks under ambient conditions (i.e. 25°, 40-50% RH).

SECTION I

INTRODUCTION

As the use of advanced composites is steadily increasing in aircraft and space-related structures so to is the comparative size of inidividual 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 prepregs presently enjoying by far the largest use in high performance applications are generally limited to a nominal fourteen day flow-life under ambient shop conditions. Projected layup schedules for very large (sub)assemblies far exceeds this two-week limitation. Although the flow-life may be dramatically 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 prepregs.

A 75 day 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 resins which would have the 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) that the developed system have 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 postcure allowed

3) no volatiles be evolved during cure

4) low (<1%) void content composites

5) environmental stability (i.e., moisture resistance) at least as good as the best state-of-the-art epoxy

6) the thermomechanical performance profile at least equal that of state-of-the-art epoxy/graphite fiber composite (≅80% retention of room temperature flexural strength be retained at 350°F).

7) prepregging procedures be readily adaptable to high volume production equipment

SECTION II

TECHNICAL DISCUSSION

A. BACKGROUND

Epoxy resins provide the most fruitful area for attaining the objective of this developmental effort. Epoxy/graphite prepregs are available which provide satisfactorily performing 350°F composites. However, the majority of these systems provide a nominal two 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 the long flow life/short cure time 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. Prior to the thermally activated cure, the insoluble curing agent must not dissolve. 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.

High temperature (350°F) performing epoxy resins are almost invariably derived from blends of multifunctional resins. The requisite viscosity/flow parameters for drape and tack are most readily obtained by blending low and high viscosity epoxy resin systems and adjusting blend viscosities, if required, for appropriate hardener/curing agent additions. Alternatively, resin/curing agent combinations are partially pre-reacted under carefully controlled conditions to rather precisely defined end points. These various combinations are then "finely tuned" to achieve the best overall characteristics for the various end use requirements.

Those commercially available products which come closest to achieving the required out-times are generally based on epoxy-resin blends which are cured with either BF_3·MEA or dicyandiamide. The resulting laminates are unfortunately deficient in critical areas which are required for high quality graphite reinforced composite structures. Most notable is lower interlaminar shear strengths; consequently premature shear failures in flexural tests are translated to lower ultimate flexural strengths. Moisture resistance, while acceptable for most applications, may be inadequate for high temperature service.

B. DISCUSSION

1. Candidate Epoxy Resins

A number of high volume epoxy resins with a functionality in excess of 2 are available at reasonable cost. At the onset of this program those manufacturers were contacted regarding both current and future availability of the resins under consideration. The recent petroleum shortage with its allocation requirements caused temporary shortages of almost all of these systems and temporary discontinuation of one of the more widely used resins (Epon 1031). We naturally considered only those resins where current and projected availabilities do not present a problem. Table I lists the manufacturers contacted and the various candidate resin systems considered for use in this program.

2. Curing Agent Considerations

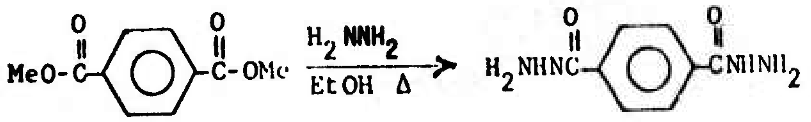
Latent curing agents generally operate on one of four principles as causative factors for their latency characteristics:

1. Very sluggish reaction rates which require protracted cures at incrementally higher temperatures
2. Thermally induced shifts in salt-like equilibria to provide higher concentrations of curing agents at elevated temperatures
3. Thermally induced rearrangements
4. Insolubility of the curing agent at ambient temperatures which becomes soluble upon application of heat

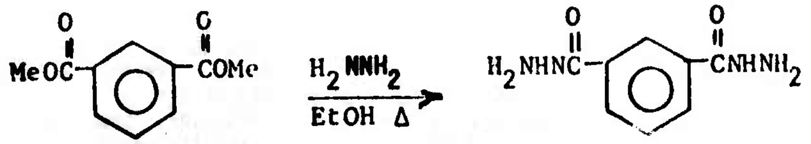
The fourth area is where many commercially available systems operate.

3. Hydrazides as Curing Agents for Epoxy Resins

Aromatic dihydrazides(1) are useful hardeners; particularly iso- and terephthalhydrazide. Both of these were prepared in high yields by the following routes.



Tere-phthalhydrazide
TPH (mp >325°C)



Iso-phthalhydrazide
IPH (mp 224°-225°C)

The lower melting isomer is more useful as an epoxy curing agent as evidenced by differential scanning calorimetry (DSC) data. DSC data were acquired for both TPH and IPH with the unblended resins mentioned above. Epon 828 was similarly evaluated for use as a reference.

It is instructive at this point to consider the DSC scan of the cure exotherm of Epon 828 cured with 4,4'-diaminodiphenylsulfone (DADS) and IPH. Figure 1 is Epon 828/DADS while Figure 2 is Epon 828/IPH.

---

(1) R. L. Wear, US Patent 2,847,395 (1958), Minnesota Mining & Manufacturing Co.

TABLE I

MULTIFUNCTIONAL EPOXY RESINS FOR INITIAL SCREENING PURPOSES

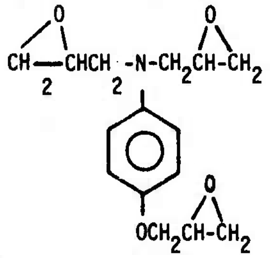
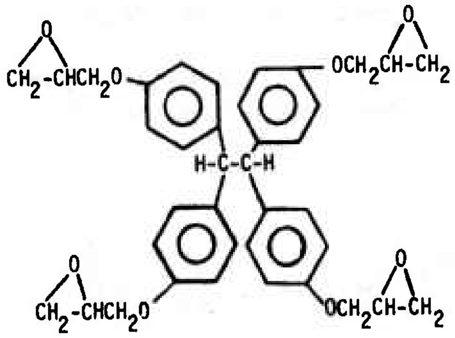
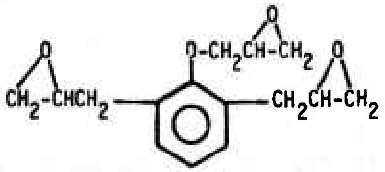
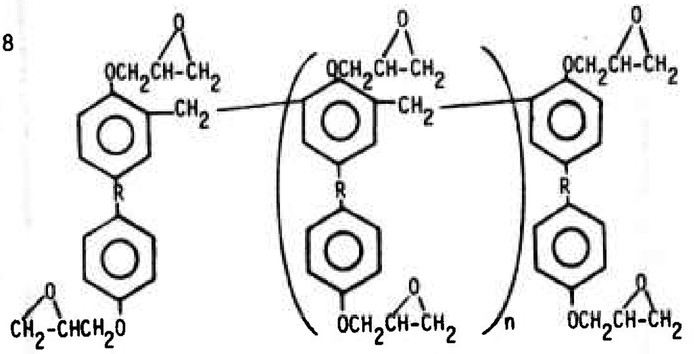
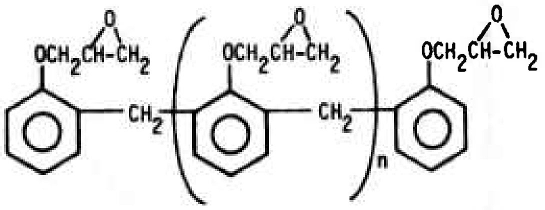
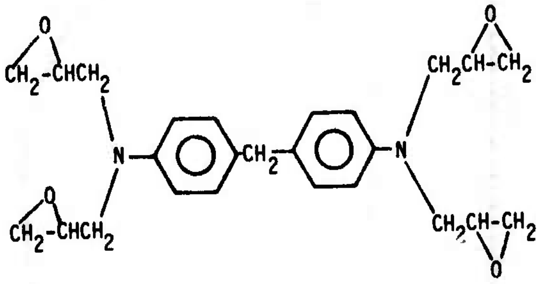
Manufacturer	Resin	Idealized Structure	Comments
CIBA-Geigy	0510 (N,N,O-triglycidyl-4-aminophenol)		Low viscosity, previously marketed by Union Carbide
Shell Chemical and Resins	1031 1,1,2,2-tetra-[4-(2,3-epoxy-1-propoxy)phenyl] ethane		Not available for 2-1/2 to 3 years
Shell Chemical and Resins	X801 1,3-di-(2,3-epoxy-1-propyl)-2-(2,3-epoxy-1-propoxy) benzene		~10,000 lbs. on hand. Current production curtailed. Low viscosity resin

TABLE I

(Concluded)

Manufacturer	Resin	Idealized Structure	Comments
Celanese	SU-8		Solid resin (mp 85°C-90°C)
Dow Chemical	DEN 438 DEN 439 poly{methylene-2,6-[1-(2,3-epoxy-1-propoxy)]phenylene}		Viscous semi-solid
CIBA-Geigy	MY-720 N,N,N'N'-Tetraglycidyl-4,4'-methylenedianiline		Viscous semi-solid

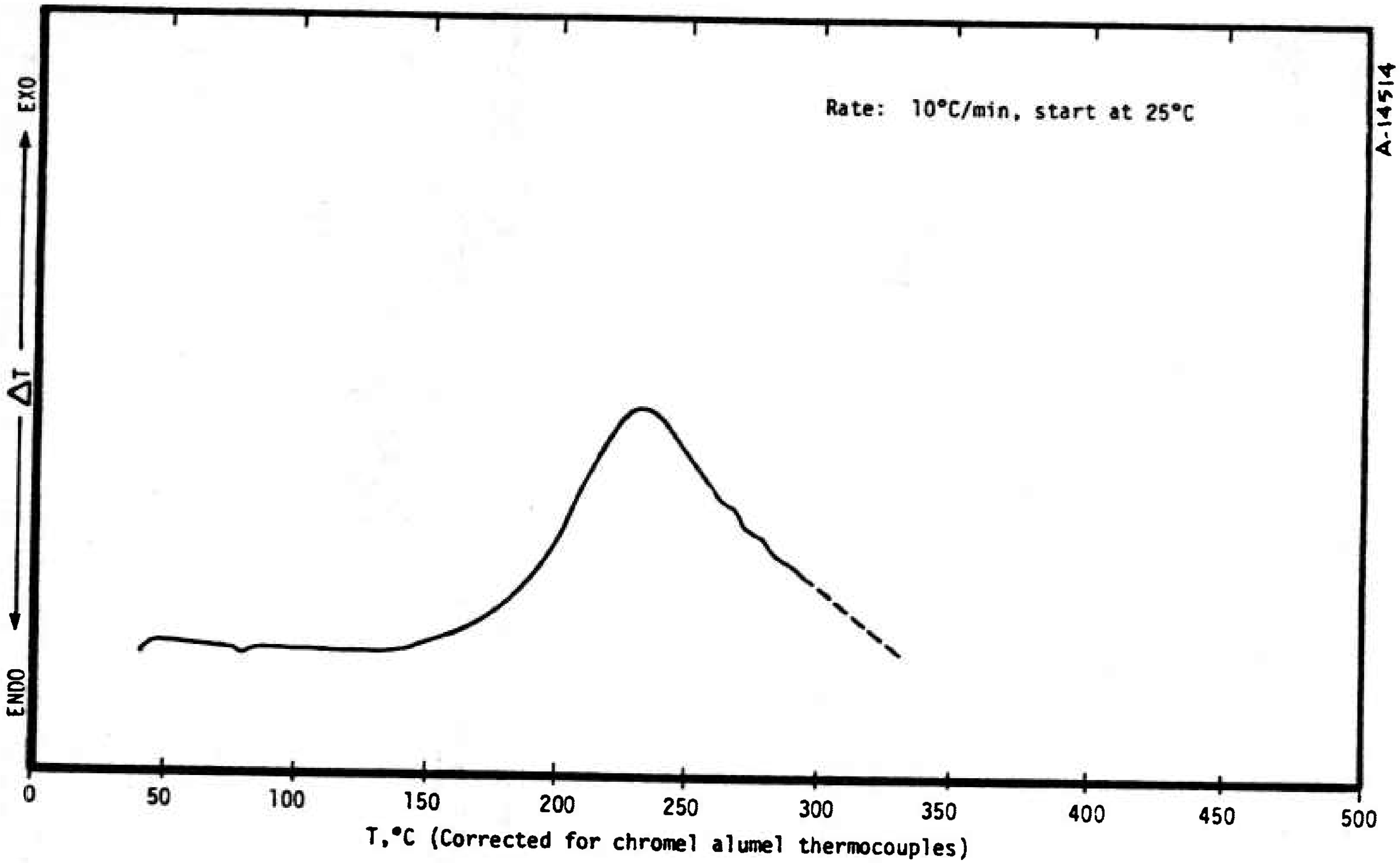


Figure 1. Cure exotherm of Epon 828/DADS.

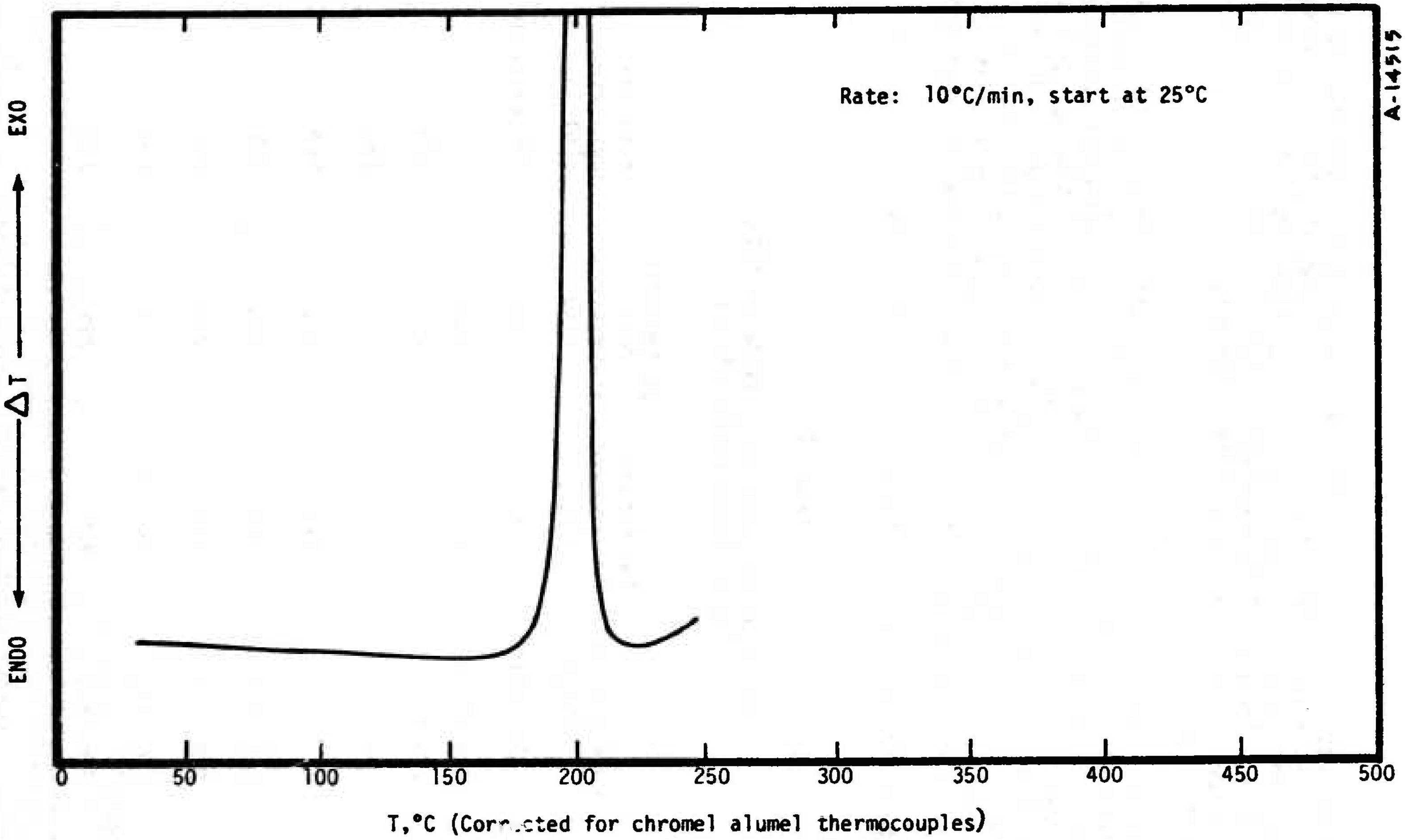


Figure 2. Cure exotherm of Epon 828/IPH.

The DSC of ≅30 day flow life of the 828/DADS system shows a broad curve with an initiation temperature of 136°C and an exothermic peak at 232°C. In comparison the "latent" 828/IPH cured system shows an initiation temperature at 165°C and a peak at 200°C. The end of the exotherm is found at 330°C (extrapolated) for the 828/DADS and at 220°C for the 828/IPH. These two curves may be interpreted in the following manner.

The initiation temperature is a rough measure of the attainable latency where lower temperatures correspond to a shorter flow life. Thus, the initiation temperature is a measure of that temperature at which sufficient curing agent is solubilized to initiate the exothermic cure reaction. A broad curve is indicative of a system which would require a stepped and somewhat protracted cure schedule since it requires very high temperatures to complete the cure. A narrow curve is indicative of a rapid efficient cure mechanism with potentially shorter cure schedules (assuming that the cure exotherm does not char the resin).

Table II describes the resin/curing agent combinations evaluated by DSC.

TABLE II

DIFFERENTIAL SCANNING CALORIMETRY DATA
(10°C/Minute Heating Rate)

		Cure Exotherm		
Resin (Mfg)	Curing Agent (phr)*	Initiation Temperature (°C)	Peak Temperature (°C)	Termination Temperature (°C)
Epon 828 (Shell)	DADS (32)	136	232	330 (extrapolated)
"	IPH (25)	165	200	220
"	TPH (25)	190	255	270
DEN 438 (Dow)	IPH (27)	172	200	220
"	TPH (27)	210	245	260
Epon X801 (Shell)	IPH (51)	160	186	205
"	TPH (51)	190	224	245
0510 (CIBA-Geigy)	IPH (49)	145	185	200
"	TPH (49)	200	225	240

---

* phr = parts of curing agent per hundred parts of resin.

a. Flow-Life Results

Isophthalhydrazide (IPH) catalyzed resin systems were mixed during the first month of the program. The curing agent, which was first ground to -400 mesh, was added to the resins listed in Table 1 in stoichiometric amounts and milled into the resin on a small 3-roll mill. Those resins which are semi-solid at room temperature were warmed as required to give adequate flow. A heat gun was passed over the mill rolls to insure adequate flow and mixing during this operation. The thus-catalyzed systems showed essentially no advancement after 6 months under ambient conditions. Some settling of the particulate curing agent is apparent in the low viscosity epoxy resins (viz. Epon X-801 and CIBA-Geigy 0510). However, even in the over-catalyzed portion (bottom of the dish) no significant advancement occurred.

b. Effect of Particle Size

Dry Grinding and Classification - The settling of the curing agent can be overcome by fine-grinding to reduce particle size. Our first efforts along these lines used dry-grinding techniques and separation of the fines. These dry powders were classified into the following particle size ranges using an American Instrument Company Roller Particle Size Counter - Model 5-445.

0-10 μ; 10-20 μ; 20-30 μ; and >30 μ

This separation is not absolute, but simply represents a distribution of particles with mean diameters approximating the mid-point of the range. This particular separation technique is time-consuming and yields small amounts of material (≅0.25 g/day). However, even these small quantities have proved very useful in the preliminary screening studies.

It appears that particle sizes of less than 20 μ diameter are quite effective in overcoming the settling problem. Two observations are pertinent to our effort:

1. Admixture into the low viscosity 0510 resin system is not only stable (to settling) but also stable at cure temperatures (see subsequent sections).

2. The catalyzed mixture exhibits thixotropic behavior in that very little flow occurs with no applied pressure during cure conditions. The system is readily spreadable and no separation is apparent during the cure of either thin films or reasonably thick (>1/4 in.) sections. When pressure is applied the material readily flows and wets the newly covered substrate. Again no striations or separation are observed. Only slight changes in cure exotherms are apparent when DSC scans are run on 0510 cured with various particle sizes of IPH. Table III lists the salient temperatures in the same manner as previously reported.

TABLE III

DIFFERENTIAL SCANNING CALORIMETRY DATA
(10°C/Minute Heating Rate)

Resin/Catalyst (phr)			Particle Size Range (μ)	Initiation Temperature (°C)	Peak Temperature (°C)	Termination Temperature (°C)
0510	IPH	(49)	0-10	125	180	194
0510	IPH	(49)	10-20	137	182	195
0510	IPH	(49)	20-40	145	185	200

These data indicate a significant lowering of the initiation temperature with no significant change in the general shape of the curve. Figure 3 is a typical curve using 10-20 μ size IPH.

Wet Grind Techniques - The laborious nature of dry-grinding with the concurrent low yields of very fine particles prompted us to investigate an alternate method of reducing the particle size. A wet grinding procedure which proved to be adequate was developed and is described below.

A one quart Waring blender was clamped at about 30° off vertical. The top was fitted with a sealed cover which had a water cooled condenser attached. The isophthalhydrazide (50 g) was loaded into the blender with about three times its weight of hexane(s) added. The blender was run for 8 hours at the highest speed with periodic addition of hexane to compensate for that lost through the condenser. At the end of this time a non-settling suspension was obtained with total solids content of 30.6±0.1%.

The distribution of particle sizes could not be accurately determined since agglomeration occurred during solvent removal (either under vacuum or attempting to spray the material onto a hot metal surface). It was felt at that time that the non-settling behavior in very low viscosity non-polar hexane was adequate demonstration of very fine particle size.

Using hexane as a grinding/suspension medium causes an interesting effect when the mixture is mixed with epoxy resins. The hexane is virtually insoluble in the resins, consequently when the materials are mixed the hexane separates as a clear layer on top of the catalyzed resin mixture. This allows ready removal of, by far the bulk of the unwanted solvent, by simple decantation. Vacuum stripping easily removes the remaining traces.

c. Cure/Stoichiometry Studies

Using the hexane suspended, finely ground IPH system, we prepared castings of the various resins listed below. The catalyzed resins were thoroughly de-aired at ≅90°C in a vacuum oven prior to cure initiation. Samples were set aside for flow-life determinations. In all the systems tested, a destructive exotherm

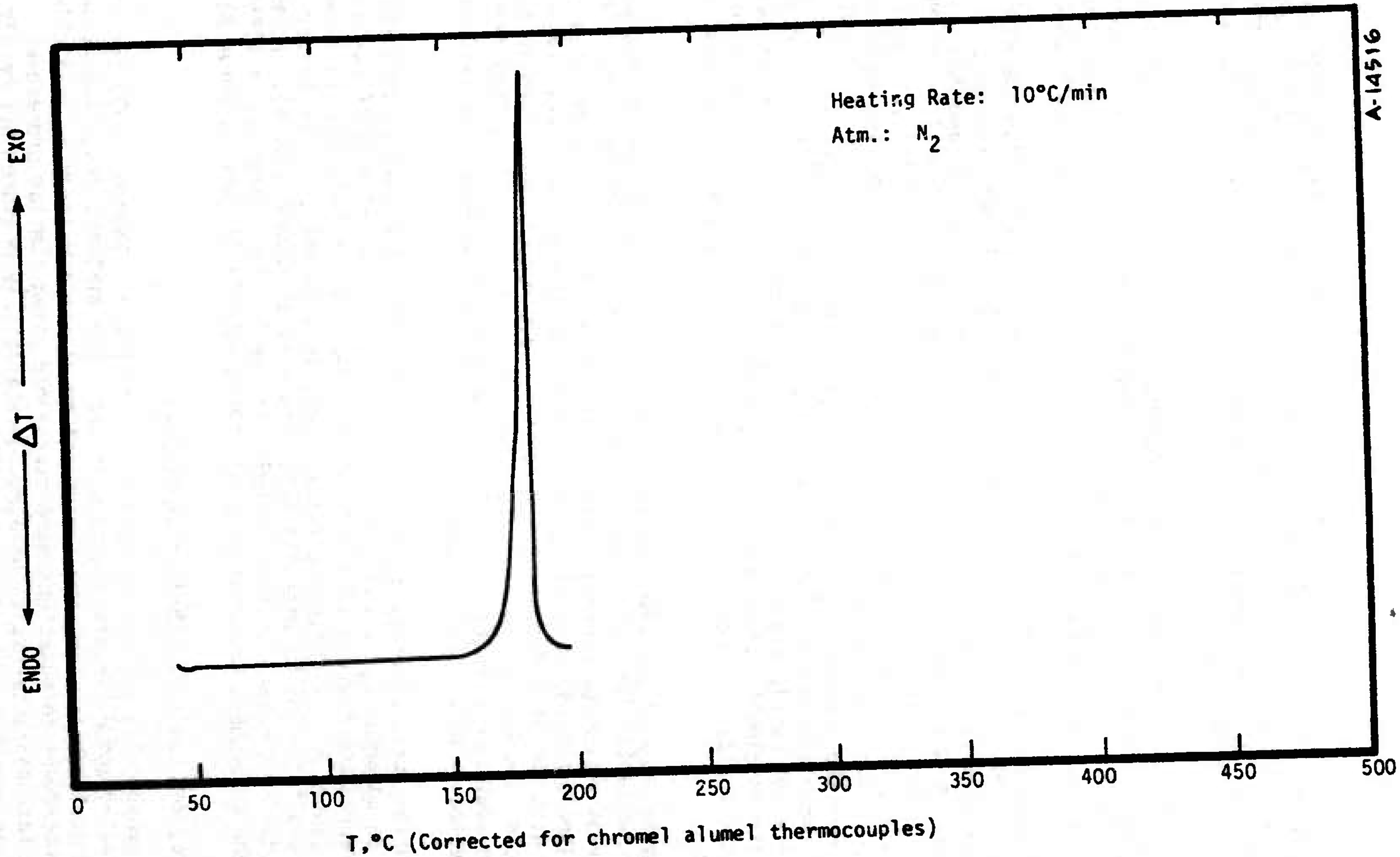


Figure 3. DSC of isophthalhydrazide (IPH) (10-20 μ) and 0510.

occurred if the resins were placed directly in a 350°F oven, regardless of stoichiometry. In the highly reactive systems as indicated by DSC (notably 0510 and X-801) initial gelation was carried out at 250°F. Others investigated were gelledat 300°F and cured for 1.5 hours at 350°F. Second samples were then postcured one hour at 400°F.

Following the cure, the samples were machined into ≅1/4 in. cubes and tested under ≅450 psi compression load in the Dupont 990 TMA apparatus at a heating rate of 10°C/min. This setup was chosen to provide a screening technique similar to HDT determination defined as Distortion Temperature Under Load (DTUL).

The resin/curing agent stoichiometry was also upset to establish the effect of inadequate curing agent on the resin as measured by TMA performance. Three stoichiometries were investigated for each system (100%, 95%, and 90%). A significant result from these data is in the apparent unsuitability of IPH as an efficient curing agent with high functionality, essentially monomeric, resins (e.g., Epoxy X801, CIBA-Geigy 0510 and XB-2793). The high functionality resins cured with the IPH were expected to provide apparent T_g's in excess of 350°F. When the apparent T_g is much less than ≅350°F, the system was assumed to be incompletely cured. The reason(s) for incomplete cure with heterogeneous systems are not easily traced to the chemistry of the system since the surface area of the insoluble curing agent, its degree of dispersion in the resin, and other factors play an important role in how efficiently the curing agent is utilized.

This inefficiency of the IPH with the high functionality resins was not anticipated. These particular resins were to be used in relatively low concentration, primarily as viscosity control devices. The dilution by the major resin components should provide more efficient systems and reduce the effects seen in Table IV with the high functionality resins. Such reduction is seen in the two mixed resin formulations in Table IV. By reducing the amount of 0510 from 35% to 25% in admixture with the solid SU-8, the approximate upper use temperature was increased by 85°F (385° to 470°F).

The expansion curve of entry #5 in Table IV (25% 0510/75% SU-8 at 100% IPH) provided an apparent T_g of 244°C (470°F). The TMA curve of a 350°F cured resin from a prepregging mixture (10% 0510/45% SU-8/45% 438 at 100% IPH) is shown in Figure 4 (Curve A). A softening (under load) is apparent over the temperature range of ≅150° to ≅195°C, with the DTUL occurring at ≅200°C (390°F). Further cure of another specimen at 400°F results in the initial softening at ≅195°C (390°F) and subsequent apparent DTUL at ≅225°C (430°F) (Figure 4, Curve B).

d. Prepreg and Laminate Fabrication Studies

Hot melt prepregging procedures were straightforward. Thornel T-300 fiber was pre-collimated and hot-knife coated with the resin mixtures described above at 190°F. Consolidation using the vacuum hot table was similarly quite facile at 180°F. Subsequent formulations were prepregged using similar procedures. The drape and tack characteristics were not quantitatively measured but merely given simple qualitative evaluation. All were acceptable.

TABLE IV

EFFECT OF CURE SCHEDULE AND STOICHIOMETRY ON EPOXY RESINS CURED WITH WET GROUND ISOPHTHALHYDRAZIDE

No.	Resin	Stoichiometry (% Theory)	Cure Temp and Time, hr (gel time in minutes)				Distortion Temperature Under Load (450 psi) (°F) (from TMA)
			250°F	300°F	350°F	400°F	
1.	X-801	100		*			N/A
		100	**				N/A
2.	0510	95	1.5(50)	+1	+1		340
3.	XB-2818	100	2(25)	+1	+1		240
		100	2(25)	+1	+2		230
		100	2(25)	+1	+1	+1	320
		100	2(25)	+1	+2	+2	310
4.	XB-2793	100	2(75)	+1	+1		**
5.	25% 0510/75% SU-8	100	1(35)	+1	+1		470
			1(35)	+1	+1	+1	455
6.	35% 0510/65% SU-8	100	1(35)	+1	+1		385
		95	1(35)	+1	+1	+1	390
		95	1(35)	+1	+1		365
		90	1(35)	+1	+1	+1	400
		90	1(35)	+1	+1		300
7.	10% 0510/45% SU-8/ 45% 438	100	2(65)	+1	+1		310 (390)***
		100	2(65)	+1	+1	+1	375 (430)***

---

*Destructive exotherm

**Sample decomposes, blisters and darkens

***Subsequent transition occurs at this temperature

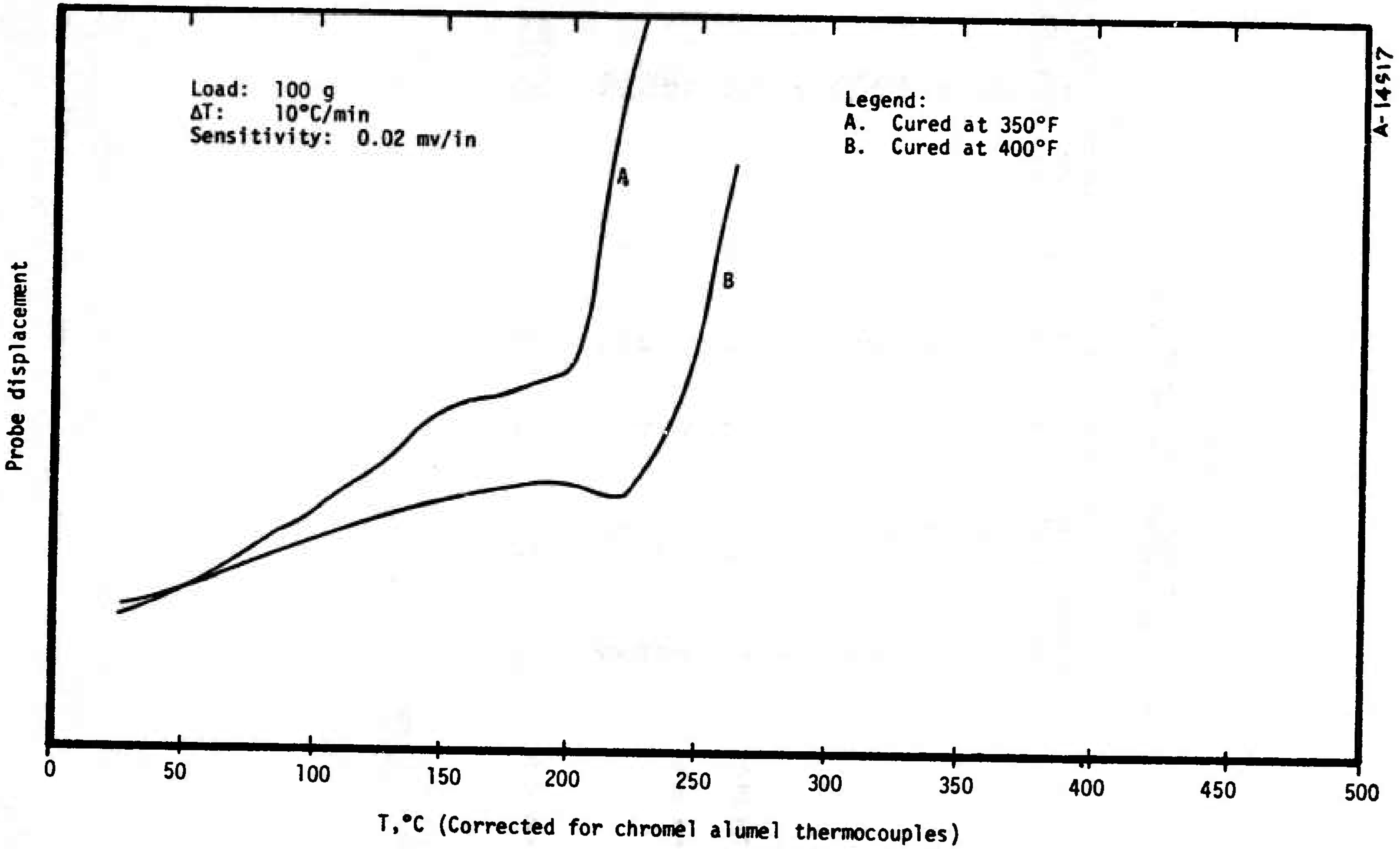


Figure 4. Thermomechanical analysis of 100% IPH cured epoxy blend (45% SU-8, 45% 438, and 10% 0510).

Cure of the laminates were generally the same with slight adjustments for different resin characteristics (e.g., flow and gel time). Table V outlines the various formulations evaluated with pertinent data included. The first entry (Table V) was not successful due to insufficient flow and premature gellation at the preliminary gel temperature (250°F).

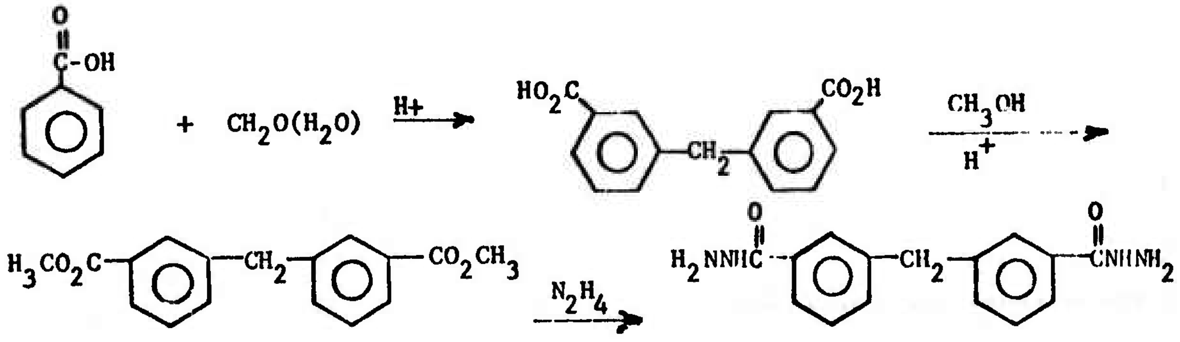
Cures were carried out in a trap mold under a vacuum bag in the press. The stacked prepreg was in a bagged mold and inserted in a preheated 250°F press under full vacuum as shown in Appendix A. The vacuum was released after the 275°F gel period and the system vented to the atmosphere. Pressure was applied after ≅20 minutes at 250°F.

As shown in Table V, excellent RT properties were obtained but the 350°F performance was disappointing. The following explanation is offered. The bleeder ply (external to the mold) was partially saturated with resin during the gelling procedure. After the preliminary cure (350°F), this material was still not gelled. In fact, the resin between the side-walls of the mold and the laminate itself was only partially cured. The most obvious explanation lies in the particulate nature of the finely-ground curing agent which in effect is filtered (left behind) by the fiber reinforcement during the initial consolidation in the press. This results in a serious upset in stoichiometry with a calculated 52.8% <u>excess</u> curing agent in the laminate based on net resin loss due to flow and assuming no loss of curing agent.

LX-185 represents an attempt to alleviate this problem where the resin/curing agent stoichiometry was upset to allow for the calculated resin loss. Unfortunately a greater resin flow was experienced due to the lower curing agent loading level. Similar calculations to those above indicate 22.5% excess curing agent in the cured composite.

e. 3,3'-Methylenebis(benzhydrazide) (MBBH)

This bishydrazide, which was expected to have much better solubility characteristics than the IPH and TPH systems previously evaluated, was prepared by the following reaction sequence.



MBBH

TABLE V

LAMINATE DATA FOR THORNEL 300/EPOXY RESIN SYSTEMS CURED WITH ISOPHTHALHYDRAZIDE

Prepreg Data											
								Flexural Strength/ Modulus (ksi/psi x 10^6)		Interlaminar Shear Strength (ksi)	
Laminate Number	Resin Formulation (% by Wt.)	IPH Stoichiometry	Prepreg Resin Content	Cure Schedule	Cured Resin Density	Fiber Volume	Void Content	RT	350°F	RT	350°F
LX 182	45% SU-8 45% 438 10% 0510	100%	44.3	A	1.23	--	--	--	--	--	--
LX 183	22.5% SU-8	100%	40.8	A	1.24	58.7	Nil	197/19.0	34/13.5	8.8	2.0
	67.5% 438			B					59/15		3.4
	10% 0510			C							3.8
				D							3.7
				E							3.8
LX 185	20% SU-8	65%	40	A	1.24	63.8	Nil	246/20.5	24/8.3	7.9	1.0
	68% DEN 438			F					61.5/11.9		3.7
	12% 0510			G					50/8.5		2.9

A - One hour at 250°F + one hour at 275°F (vacuum removed) + one hour at 300° + one hour at 350°F under 100 psi
B - A + one hour at 400°F
C - A + 3 hours at 375°F
D - A + 6 hours at 350°F
E - A + 6 hours at 375°F
F - A + 15 min at 400°F + one hour at 420°F
G - A + 15 min at 400°F + 3-1/2 hours at 420°F

The white crystalline product (mp 204°C) was mixed, in stoichiometric amounts, with Epon 828 and placed in a 250°F oven. After one hour the curing agent had settled to the bottom with no evidence of reaction having taken place.

The settling of the curing agent at temperatures where the resin viscosity becomes very low has been overcome previously by wet grinding (hexane) to a nonsettling suspension. The small amount of material (5 g) synthesized required the use of a micro-blender which was found less efficient than the larger counterpart (larger particle size). Twelve hours in the micro-blender failed to reduce the particle size sufficiently to prevent the settling at 250°F.

A rerun of the 250°F exposure resulted in some improvement in the settling characteristics but not adequate for production of a high quality laminate. Increasing the temperature to 300°F resulted in marked solubility improvement. After only a few minutes at 300°F the curing agent was completely dissolved. The resulting clear solution was stirred to insure adequate mixing and allowed to remain at 300°F for 2 hours. It had not gelled but had thickened somewhat. The temperature was increased to 350°F and held for 2 hours and still the system had not cured.

Figure 5 is the DSC curve for the MBBH/828 resin mix. An initial scan was interrupted at 200°C and the specimen examined for curing agent solubility. Even though there had been an obvious cure exotherm, although relatively small, the material (while clear) was not gelled. The extremely sluggish nature of this particular bishydrazide is in sharp contrast to the IPH system evaluated previously.

4. Amino-benzhydrazides as Curing Agents

The obvious difficulties encountered in the processing of IPH cured epoxy graphite composites could probably be overcome with at least two approaches.

The first is simply an extreme reduction in particle size to avoid the "filtration" effect of the fibers. The requirements for particle size and distribution, which are unknown, must be determined by a trial and error method. Fine grinding can be done on as small as five pound batches by the Trost Company in Boston. Separation into selected size ranges can be done at the Majac Corporation facility in Oklahoma. Since this approach has a very large degree of uncertainity, a chemical modification proved more expedient.

The second approach consisted of using a hydrazide which would be more soluble in epoxy resins at elevated temperature. Thus, at those temperatures where maximum flow might occur, the curing agent would be in solution and not filtered by the fibers. Synthesis and evaluation of MBBH yielded the unexpected results above.
The three compounds below have a higher functionality than the IPH (lower equivalent weight) and the amine portion of the molecules, expected to be more efficient in curing epoxy resins than hydrazides. They were expected to be virtually insoluble in epoxy resin blends at ambient temperatures.

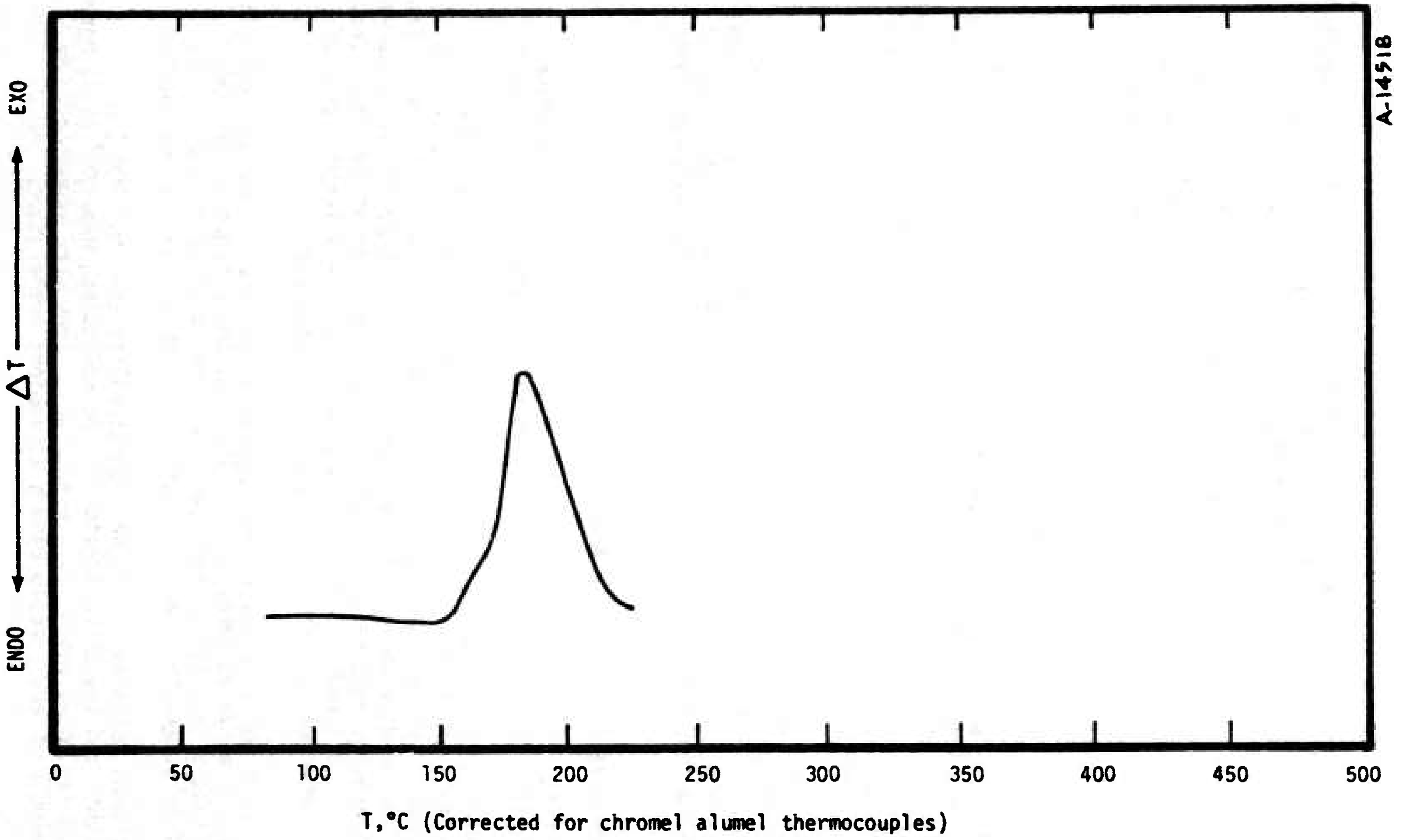
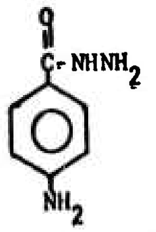
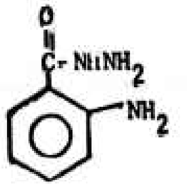


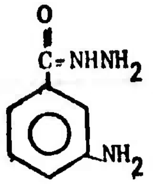
Figure 5. DSC scan for 100% MBBH/828.



p-aminobenzhydrazide
(PABH)



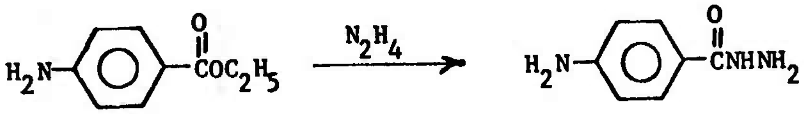
o-aminobenzhydrazide
(OABH)



m-aminobenzhydrazide
(MABH)

a. p-Aminobenzhydrazide (PABH)

This curing agent,(mp 220°C) prepared by the following reaction,was wet ground



PABH

in hexane and preliminary evaluation was carried out using Epon 828. Stoichiometric amounts of curing agent became soluble at 140°C and a clear homogeneous casting was obtained. Figure 6 is a DSC scan of the 828/PABH system.

When the resin mix described above was catalyzed with PABH and cured under similar conditions, it gelled in 5 minutes at 140°C although the curing agent was not completely dissolved. The solubility characteristics and gel times of PABH in stoichiometric amounts were then determined on the various resin components with the following results.

	Gel Time at 140°C	Clear Casting Achieved
Celanese SU-8	5	No
Dow DEN 438	12	No
CIBA-Geigy 0510	5	Yes
75% 438/25% 0510	11	Yes
50% SU-8/50% 0510	6	Marginal
50% 438/25% SU-8/25% 0510	9	Marginal

The room temperature viscosity characteristics of the above resin mixes were not sufficient for quality prepreg so an additional high viscosity resin, DEN 439, was added as a viscosity modifier. This was not expected to substantially detract from the resin performance.

The final formulation which was derived from a series of trial mixes exhibited a good combination of properties which included room temperature viscosity, solvent characteristics (for PABH) at 140°C and anticipated elevated temperature strengths. The formulation was:

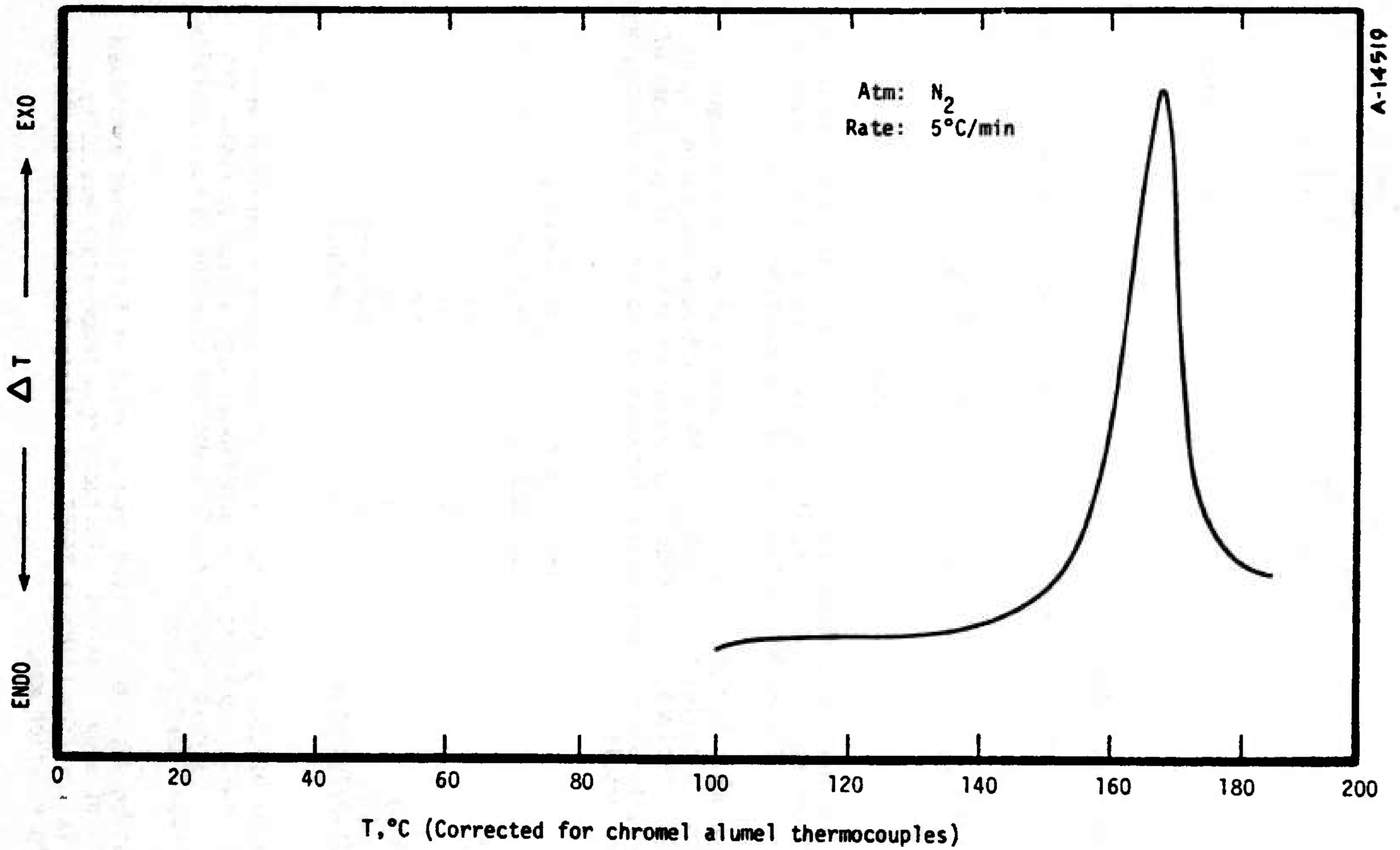


Figure 6. DSC scan of wet ground 100% PABH/828.

40% DEN 438
30% DEN 439
10% SU-8
20% 0510

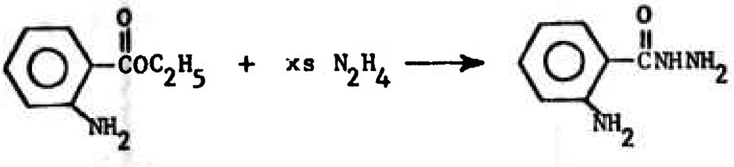
Gel time at 140°C was 7 minutes with a clear casting obtained. Figure 7 is the DSC scan of the above.

A small quantity of Thornel prepreg was prepared by hot melt coating the above formulation with PABH at 100% stoichiometry. A laminate was prepared in a press autoclave as shown in Appendix B. The layup was inserted into a 225°F press, 6 inches of vacuum was applied and held there for 15 minutes. This was followed by raising the temperature to 285°F and applying full vacuum. After 2 minutes at 285°F, 100 psi pressure was applied and the vacuum bag vented. Cure was 1.5 hr at 285°F plus 1.5 hr at 350°F under 100 psi.

Particles of curing agent were visible in the cured laminate. This unexpected result was traced to the difference in thermal history between the casting and the laminate. When an attempt was made to gel a 5 g mass at 285°F, an almost destructive exotherm occurred to 550°F. The higher temperatures obtained in bulk casting undoubtedly caused better solubilization of the curing agent. The maximum temperature reached in the laminate was probably not more than 25°F above the gel temperature due to the heat sink effect of the fiber and mold mass. Interlaminar shear strength at 350°F was disappointing with the following results obtained:

RT	11.6 ±0.8 ksi
350°F	2.9 ±0.2 ksi

b. o-Aminobenzhydrazide (OABH)



OABH

The purified material (mp 124°C) was cured with Epon 828 in stoichiometric ratio. Figure 8 is the DSC scan of the system. The onset of cure is at 100°C where the curing agent is solubilized. A clear almost water-white casting was obtained. Figure 9 is the DSC scan developed with the OABH and a laminating resin composed of 68% DEN 438, 20% SU-8 and 12% 0510. A clear cured resin is obtained in this instance also.

A Thornel 300 laminate was fabricated using the standard laminating formulation cured with OABH in stoichiometric amounts.

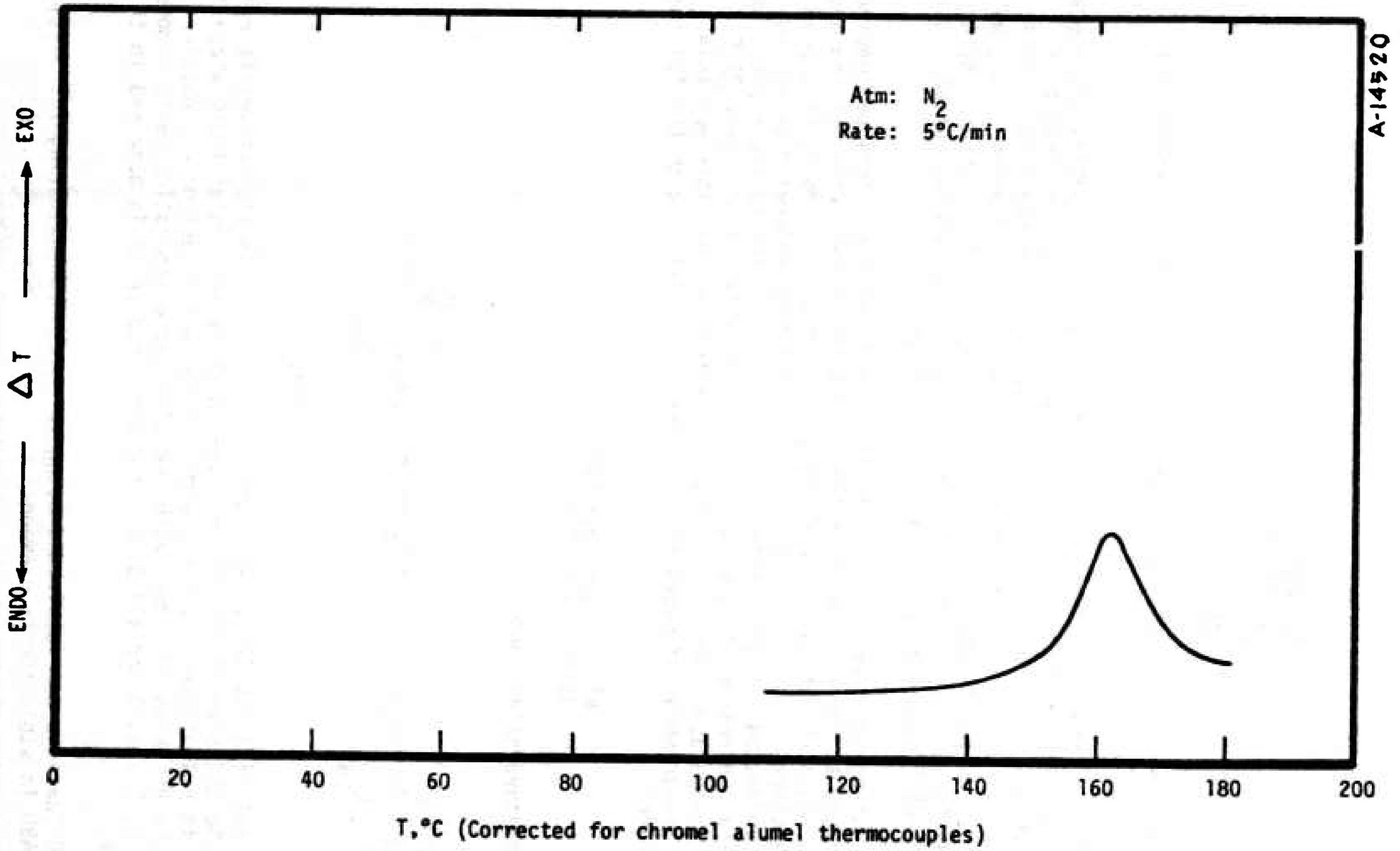


Figure 7. DSC scan of wet ground 100% PABH/40% DEN 438, 30% DEN 439, 10% SU-8, 20% 0510.

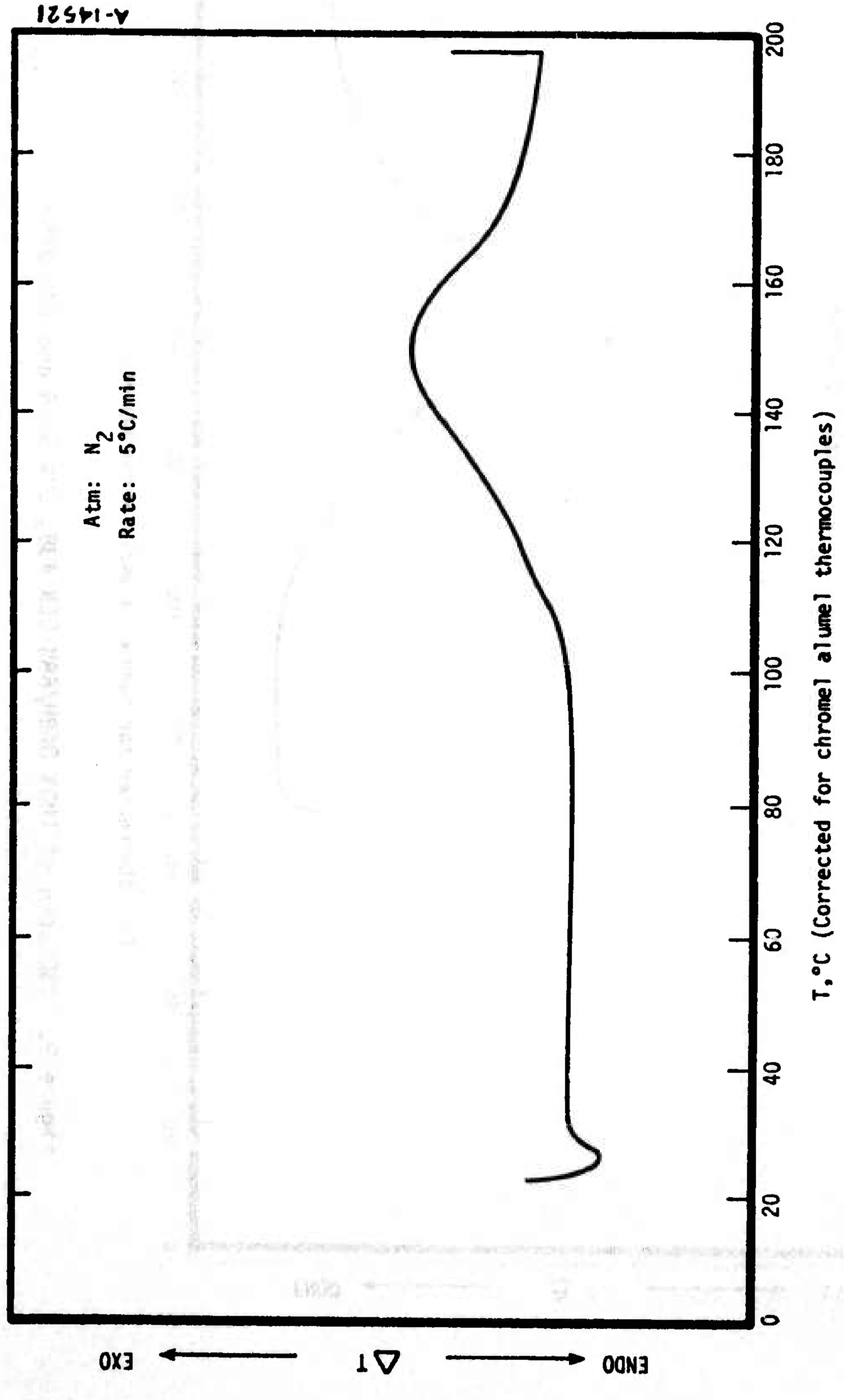


Figure 8. DSC scan of 100% OABH/828.

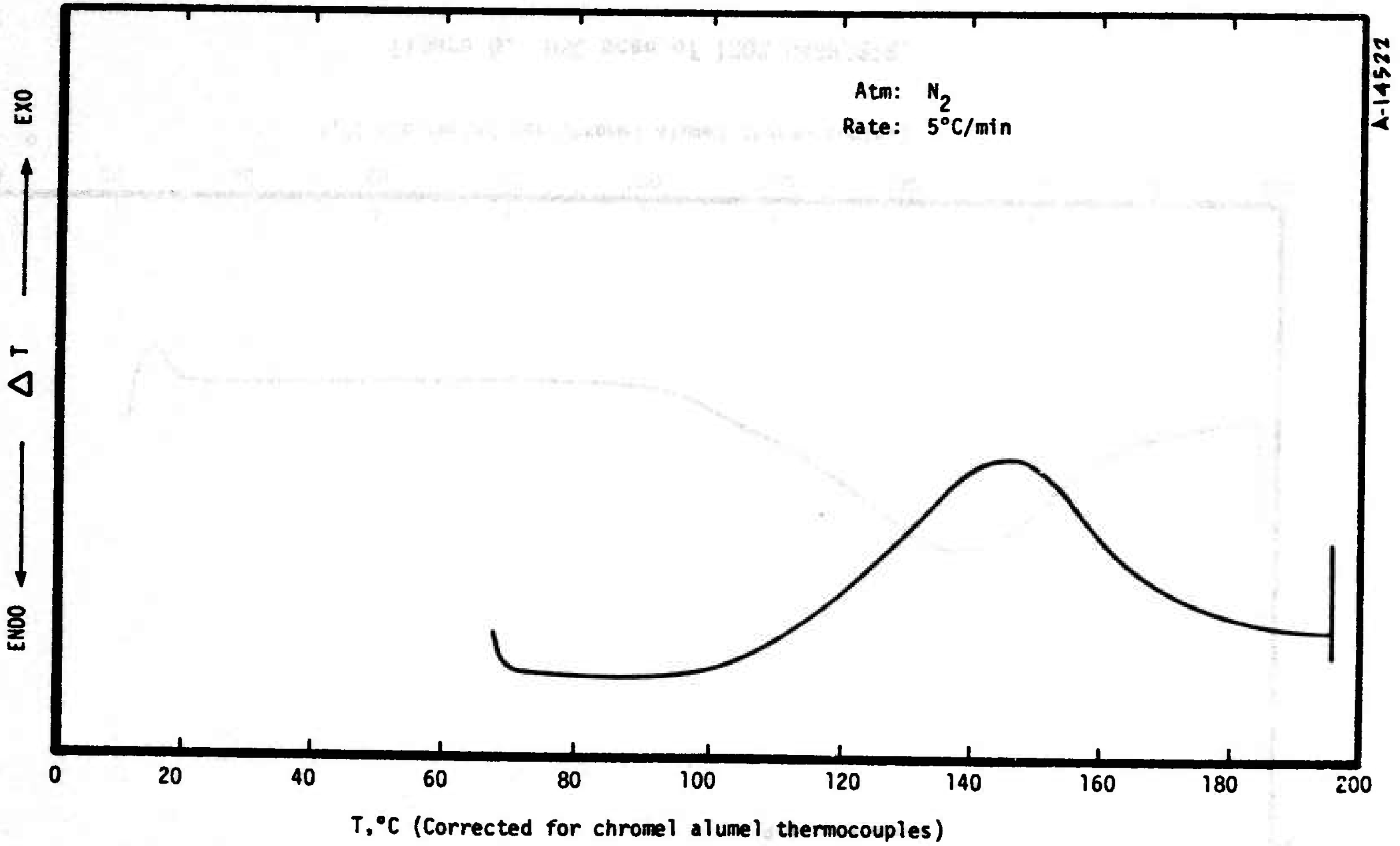


Figure 9. DSC scan of 100% OABH/68% DEN 438, 20% SU-8 and 12% 0510.

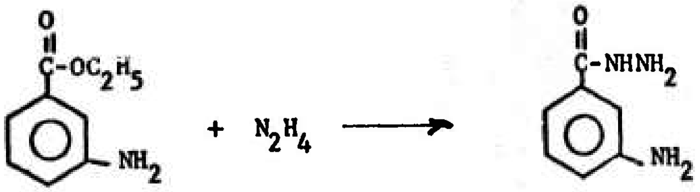
The solubility of this material in the devised formulation is such that hot melt coating is not practicable. Premature gellation at 150°F occurred when the catalyzed resin system was degassed. Solution (MEK) prepregging was accomplished quite readily. Surprisingly a prolonged gel time is required for laminating purposes. The simple mixed resin/curing agent combination required only seven minutes at 250°F to give a clear casting (thin film) while the solution coated prepreg required a longer time/temperature schedule for gellation:

30 min at 165°F
plus 15 min at 200°F
plus 15 min at 250°F
plus 15 min at 300°F
plus 5 min at 350°F

The necessity for prolonged times at high temperatures for the MEK treated system is not understood at the present time. Since we could recrystallize OABH at least three times from MEK with over 90% recovery each time (15 minute boil in solution) we may assume negligible reaction between the prepregging solvent and the curing agent.

The laminate properties are reported in Table VI (LX-188). Excellent room temperature properties were obtained but inadequate strength retention at 350°F was again apparent. This laminate did not demonstrate the hoped for effectiveness of the hydrazide cure in 350°F performance.

c. m-Aminobenzhydrazide (MABH)



MABH

The crystalline monomer melts at 94°C and is quite soluble in and active with either warm (120°F) 828 or the standard resin mix. Figure 10 is the DSC scan of the MABH/828 system at 100% stoichiometry. Flow life, as expected, suffered from the ready solubility. A flow life of <4 weeks was obtained with 828.

5. 4,4'-Diaminodiphenylsulfone (DADS)

The previous sections have described the investigations centered around bis-hydrazides and amino-hydrazides as latent curing agents for epoxy resins. The resin flow-life characteristics developed by the low temperature insolubility of the various candidate hardeners range from essentially indefinite to relatively short (≅4 weeks). Unfortunately, the outstanding shelf life made available by use of these curing agents was more than off-set by the inadequacies in composite performance at 350°F.

TABLE VI

PREPREG AND COMPOSITE DATA FOR STANDARD RESIN MIXTURE

Laminate No.	Resin Formulation (% by Wt.)	Curing Agent (% Stoichiometry)	Prepreg Resin Content (%)	Cure Schedule	Cured Resin Density (g/cc)	Fiber Volume (%)	Void Content (%)	Flexural Strength/Modulus (ksi/psi x 10^6)		Interlaminar Shear Strength (psi)	
								RT	350°F	RT	350°F
LX-188	438 (68) SU-8 (20) 0510 (12)	OABH (100)	44.3	*	1.25	68	<1	292/23.4	39.1/11.4 (TP)	15.4	1.3 (TP)

* 30 minutes at 165°F plus 15 minutes each at 200°F and 250°F, under contact pressure, 300°F applied 4 in. vacuum and held 15 minutes. The temperature was increased to 350°F and 60 psi was applied, the vacuum removed and the system vented; after one hour at 350°F the temperature was raised to 400°F and held two hours.

(TP) Thermoplastic, i.e., resin above its glass transition temperature

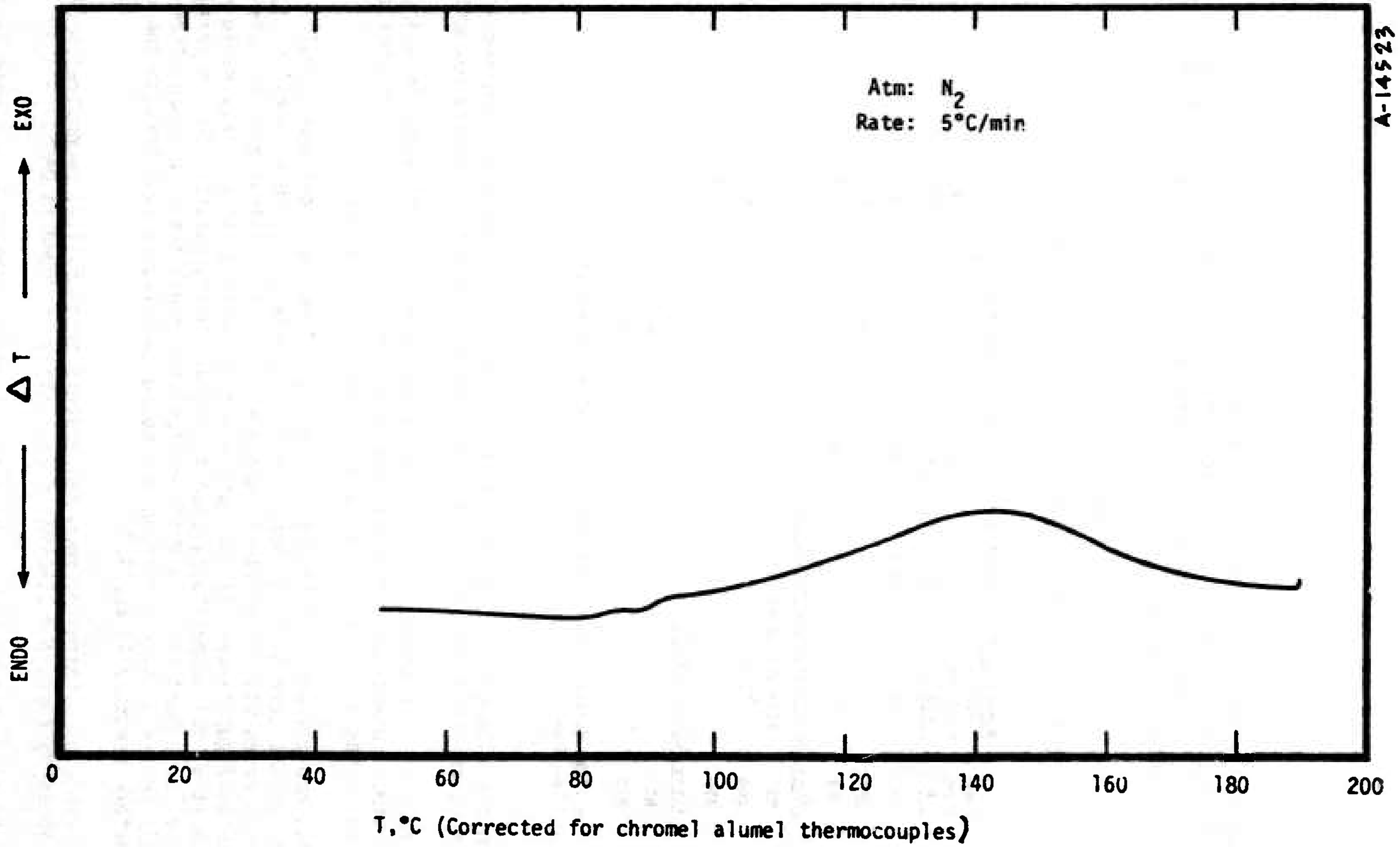


Figure 10. DSC scan of 100% MABH/828.

As stated in the objectives, our charter was to provide the desired 75 day flow life coupled with state-of-the-art composite properties and prepreg characteristics. State-of-the-art is represented by Narmco's 5208/T300 system, presented in Table VII.

TABLE VII

"STATE-OF-THE-ART" 5208/T300 COMPOSITE PROPERTIES

	Narmco Product Bulletin		IITRI* (Batch 53)		
Test Temp, °F	Flex Strength, ksi	Interlaminar Shear, psi	Flex Strength, ksi	Interlaminar Shear ksi	In Plane Shear
RT	304	17.8	247	15.9	9.7
260	--	--	227	12.5	7.2
350	242	9.9	196	8.9	5.5
After 1000 hr Exposure to 98% RH					
RT	Flex strengths not measured			11.3	9.7
260				7.9	6.8
350				4.3	6.6
After 500 hr @ 350°F					
RT				13.7	--
350				7.9	--

* IITRI Contract No. F33(615)-73-C-5125; private communication with Ken Hofer

Concurrently with the work on hydrazides, studies were proceeding on aromatic diamines which would possess the required solubility and reactivity parameters.

It was felt that an attenuated reactivity would prove advantageous in alleviating the sometimes runaway cure reaction exotherm which invariably occurs when the suspended curing agent is solubilized at higher temperatures.

A second, and perhaps more important reason, becomes apparent when consideration is given to the cure of large parts in an autoclave. Severe non-uniformity of the heatup rates will be a natural consequence of the various part geometries and oven configurations. If the cure reaction proceeds at a fairly rapid rate at the initial gel temperature, then it becomes quite possible that a particular area on a large part (e.g., a thin section) may reach the cure temperature considerably before a thicker section and could conceivably pass through the gel point before pressure is applied.

The desirable combination of room temperature insolubility, demonstrated efficiency in epoxy cure, and attenuated reactivity is found in DADS.

The "standard" resin mixture used in the hydrazide work above was used in the subsequent evaluations of DADS as a latent curing agent. The composition of this "standard" resin is shown below.

	Resin Component	pbw
Dow	DEN 438	68
Celanese	SU-8	20
CIBA-Geigy	0510	12

The effect of substituting the trifunctional CIBA-Geigy 0510 (N,N,O-triglycidyl-p-aminophenol) at the 12% level with difunctional resins is described in Table VIII. Two laminates from the "standard" resin formulation (hot melt prepreg) are also described. The resin formulations which used DER 332 (molecularly distilled diglycidyl Bisphenol A) (LX-189 and 191) or DER 331 (LX-192) in place of 0510 resulted in generally lower strengths at 350°F.

Table VIII describes the various blends, cure schedules and prepreg preparations. The solution coated prepregs (LX-189, 191 and 192) lose their useful flow life in about 3.5 weeks. The retained samples of LX-190 prepreg had an approximate 6 week flow-life, while the prepreg used to prepare LX-193 showed an approximate 8 week flow life (LX-193 was hot melt coated at a lower temperature, 160°F vs. 180°F).

The laminate data also includes elevated temperature strength retention properties after 1000+ hours at 120°F and 95+% relative humidity. A significant difference between IITRI data and the current aging procedure lies in the temperature of humid aging exposure. Our accelerated aging is carried out at 120°F, while IITRI data was acquired after room temperature exposure. Correlation of data is not directly applicable until studies are run to establish the expected differences in pickup rate and property loss at elevated temperature. At this juncture, it may be stated that the humid aging schedule at elevated temperatures results in a significantly greater property loss.

Table VIII lists the initial properties and those values obtained after the humid aging period. Elevated temperature values were obtained with no dwell period at the test temperature. This "no soak" condition was chosen to preclude any property regain as might be experienced by partial drying of the composite. The reported values show good retention percentages. There was some evidence of softening (induced thermoplasticity) which is particularly evident in the lowered modulus of the flex tests.

Moisture weight gains in the humidity cabinet, with time, show greater than 90% of the final equilibrium value is reached after ~500 hours exposure. Table IX lists the 500 hour and final 1000 hour weight gain percentages for the various laminates and specimen geometries.

TABLE IX

MOISTURE PICKUP (%) OF LAMINATE SPECIMENS

	Flexural Strength Specimens		Interlaminar Shear Specimens	
Laminate No.	500 hr	1000 hr	500 hr	1000 hr
LX-189	--	--	1.02	1.03
LX-190	--	--	1.08	1.15
LX-191	0.87	0.96	1.09	1.12
LX-192	1.09	1.10	0.97	1.02

TABLE VIII

LAMINATE PROPERTIES FROM DADS CURED FORMULATIONS/THORNEL 300

Laminate No.	Resin Formulation (pbw)	Prepreg Method	Prepreg Resin Content (%)	Cure Schedule	Fiber Volume	Void Content	Flexural Strength/Modulus (ksi/psi x 10^6)		Interlaminar Shear Strength (ksi)	
							RT	350°F	RT	350°F
LX-189	DEN 438 (68) SU-8 (20) DER 332 (12)	MEK solution	47	A	64.7	0.7	236/19.9	130/20.6	14.2	6.2
				B			232/20.4	119/20.0	11.0	5.6
				A					10.4*	4.3*
LX-190	DEN 438 (68) SU-8 (20) 0510 (12)	Hot melt (180°F)	46	A	65.6	2.0	216/19.5	143/19.4	15.5	7.6
				B			205/20.4	165/20.0	14.9	6.9
				A					12.4*	4.2*
LX-191	DEN 438 (68) SU-8 DER 332 (12)	MEK solution	46	A	61.9	<0.1	241/20.2	138/19.5	14.9	6.5
				A				84/14.8*	10.9*	3.8*
LX-192	DEN 438 (68) SU-8 (20) DER 331 (12)	MEK solution	49.5	A	60.6	<0.1	213/19.5	109/17.7	11.6	5.5
				A				75/13.0*	13.0*	3.8*
LX-193	DEN 438 (68) SU-8 (20) 0510 (12)	Hot melt (160°F)	60.4	A	66.8	0.3	254/20.5	138/19.2	16.3	8.2

A - Press/vacuum cure schedule was 250°F for 45 minutes under full vacuum. The temperature was raised to 300°F and 75 psi applied after 20 minutes at 300°F. The vacuum was removed and the laminate vented. After an additional 25 minutes at 300°F the temperature was raised to 350°F and held for 90 minutes, then 400°F for 120 minutes all under 75 psi.

B - A plus 16 hours at 400°F (unrestrained).

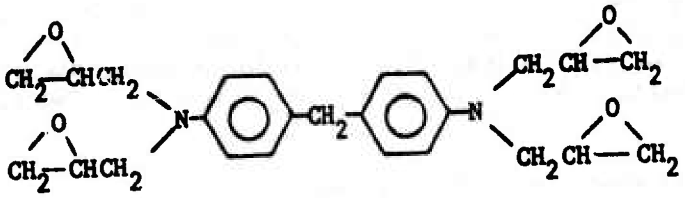
* - After 1050 hours at 120°F and 95+% RH.

6. Alternate Resin Systems

The base resin formulations above were derived from considerations of four basic requirements:

a) demonstrated thermomechanical performance
b) viscosity and flow properties to provide suitable prepreg drape and tack when mixed with an "insoluble" curing agent
c) solvent characteristics to provide long room temperature out-times coupled with moderate temperature solution of curing agent
d) cost and availability

CIBA-Geigy MY-720 (formerly CIBA 8183/137) is a 350°F performance resin system which according to the manufacturer is now stable at RT for prolonged periods. The idealized resin structure shown below (tetraglycidyl-4,4-methylenedianiline) would be expected to yield high modulus, high heat deflection temperature resins with improved moisture resistance when cured with suitable hardeners.



**N,N,N',N'-Tetraglycidyl-
4,4'-methylenedianiline**

Busso, Newey and Holler (Shell Development Co., AFML-TR-69-328) have shown that the mole percent oxygen content of crosslinked epoxy resins cured with m-phenylenediamine has a linear relationship with the % water pickup in a 28 day water soak cycle.

The considerations for base resin formulations listed above favorably apply in this instance with two exceptions:

1) the viscosity of commercially available MY-720 is too high for "insoluble" curing agent admixture

2) the solvent characteristics for insoluble diamines, etc., of this particular resin required demonstration.

7. MY-720/DADS System

a. MY-720/DADS Composite Data

A Thornel 300 reinforced laminate using CIBA-Geigy MY-720 cured with DADS at 95% stoichiometry (MEK solution coated prepreg) was fabricated and tested to provide baseline data (Table X). At this curing agent loading level (47.1 phr) the MY-720 resin system is not suitable for hot melt prepreg preparation without viscosity modifiers.

TABLE X

MY-720 CURED WITH 95% DADS/THORNEL 300 COMPOSITE
(Laminate No. LX-194)

Prepreg Resin Content (%)	Cure Schedule	Void Content (%)	Fiber Volume (%)	Flexural Strength/Modulus ksi/psi x 10^6		Interlaminar Shear Strength (ksi)				
							350°F			
				RT	350°F	RT Initial	Initial	150 hr Humid ① Aging	500 hr Humid ① Aging	1000 hr Humid ① Aging
47.5	A	<0.1	69.5	304/22.8	183/23.4	14.5	7.2	5.7*	4.6**	3.5***

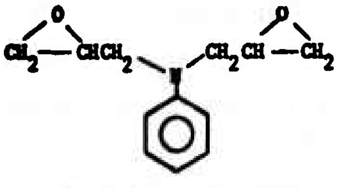
---

* 0.29% weight increase
** 0.61% weight increase
*** 0.82% weight increase
① 120°F exposure at 98+% RH

The relatively high fiber volume in this laminate is reflected in the exceptionally high flexural strength/modulus values which, of course, are direct functions of fiber volume and fiber tensile properties. The interlaminar shear strength values, including the elevated temperature humidity conditioned specimens, were very encouraging.

b. Viscosity Requirements and 350°F Performance

This particular combination of resin/curing agent is not suitable for hot melt prepreg preparations. Alternate lower viscosity multifunctional resins which would suitably lower the apparent viscosity of resin/curing agent include CIBA-Geigy 0510, Shell X-801 and diglycidyl aniline which was synthesized in our laboratories.



N,N'-diglycidylaniline
(DGA)

Thermomechanical tests most economically reflect the elevated temperature characteristics of these reactive diluents in the MY-720. As seen later in the report, the 0510 provides the least loss of mechanical strength and appeared the most promising.

The approximate upper use temperatures of the lower viscosity resins cured with DADS in 100% stoichiometric ratios and as blends with MY-720 are shown in Table XI. As expected, the reactive viscosity modifiers lower the upper use temperature, by reduction in crosslink density, as their concentration in the MY-720 is increased. The MY-720 alone with its measured 240°C upper use temperature is approximately 25°C higher than that obtained on the resin systems used to prepare the composites presented in Table VIII (cure Schedule B).

TABLE XI

DISTORTION TEMPERATURE UNDER LOAD (DTUL-450 PSI COMPRESSIVE LOAD) OF VARIOUS RESIN COMBINATIONS CURED WITH DADS

DTUL (°C)	Resin (pbw) MY 720	0510	X-801	DGA
240	100	--	--	--
230	--	100	--	--
237	90	10	--	--
234	80	20	--	--
231	70	30	--	--
223	--	--	100	--
217	90	--	10	--
212	80	--	20	--
210	70	--	30	--
120	--	--	--	100
207	90	--	--	10
192	80	--	--	20
181	70	--	--	30

All samples degassed and gelled at 250°F followed by 1 hour at 350°F and 4 hr at 400°F

c. Flow Life and Latency

Differential scanning calorimetry curves of the four basic resins catalyzed with DADS (-400 mesh) at 100% stoichiometry show the following cure characteristics:

Resin System	Onset of Cure °C*	Peak Temp °C	Termination Temperature °C
DGA/DADS	155	225	250
0510/DADS	125	215	275
X-801/DADS	125	215	275
MY 720/DADS	130	240	270

* Scan rate 10°C/min

Onset of cure corresponds to essentially complete solubilization of the suspended curing agent although there is some nondetectable cure occurring at lower temperatures. These results (and DSC curves obtained on the resin blends) indicated latency would not be sacrificed.

d. Purification of Commercially Available DADS

The DSC scans in Figure 11 show the melting endotherms of commercially available DADS and those obtained after recrystallizations (from methanol). The upper two scans are from two separate sources. The lower two are from one and two recrystallizations from methanol. The literature melting point is 176.5°C.

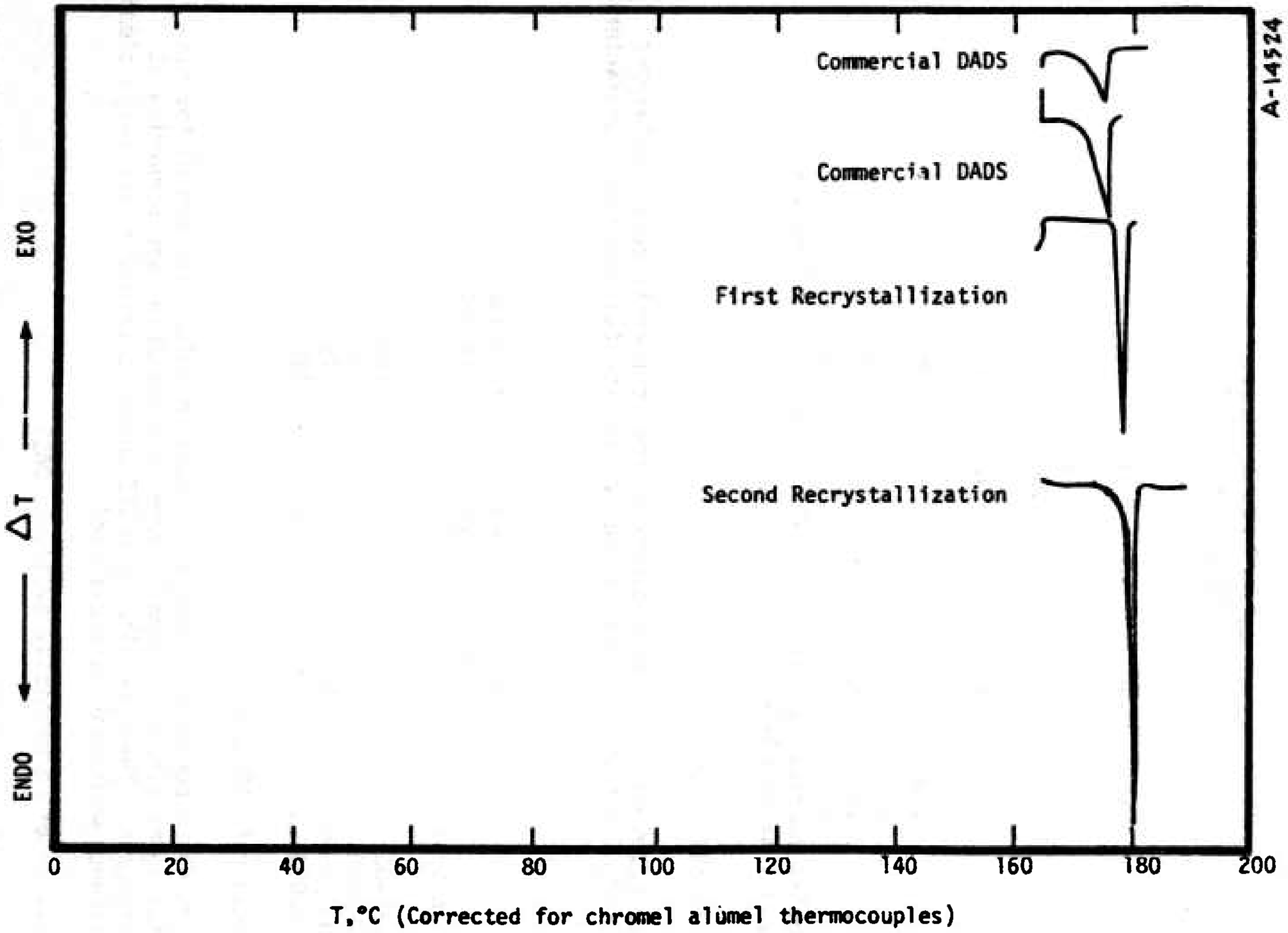


Figure 11. DSC of DADS (ΔT = 2°C/min).

These four samples were ground (dry) to pass 400-mesh sieves and were mixed with MY-720 resin at 100% stoichiometry to determine the effect of diamine purity on flow life.

The useful out-time is a direct function of apparent purity (mp by DSC). The as-received material is limited to ≅8 weeks, with the doubly crystallized mixture still showing flow after 13 weeks elapsed time.

e. Stoichiometry Variation of MY-720/DADS System

A brief study of stoichiometric variation in the MY-720/DADS system yielded interesting results. The ultimate DTUL of cured resin is only moderately affected by as much as a 50% upset in the NH/epoxy ratio.

Table XII lists the measured deflection temperatures with various stoichiometries using doubly recrystallized DADS.

TABLE XII

DEFLECTION TEMPERATURE UNDER LOAD
(450 psi COMPRESSIVE)
OF MY-720 CURED WITH DADS
IN VARYING STOICHIOMETRIC RATIOS

DTUL (°C)	Stoichiometry (%)
240	100
232	90
230	80
230	70
228	60
220	50

The amount of curing agent added naturally affects the effective viscosity of the matrix mixture; i.e., the less curing agent added, the lower the effective viscosity. Similarly, the effective out-time is lengthened for two reasons: (1) lower temperatures are required for hot melt impregnation, and (2) less curing agent is dissolved (concentration effect) during the impregnation procedure.

f. Laminate Fabrication

Using the above data as guidelines, four Thornel 300 reinforced laminates were prepared using MY-720 (+ 0510) and DADS at 100% and 75% stoichiometry levels. Table XIII presents the initial laminate data. The lower fiber volumes in the last two entries, of course, strongly influence the flexural strength and modulus values. Of particular interest are the retention values of 72% and 68% of room temperature properties at 350°F.

TABLE XIII

PRELIMINARY COMPOSITE DATA

Laminate No.	Resin Formulation MY-720 (pbw) + 0510 (pbw)DADS (% Stoich)	Prepreg Method	Prepreg Resin Content (%)	Cure Schedule	Fiber Volume (%)	Void Content (%)	Flexural Strength/ Modulus (ksi/psi x 10^6)		Interlaminar Shear Strength (ksi)	
							RT	350°F[*]	RT	350°F[*]
LX-195	100 + 0/(100)	MEK Solution	49	A	69	<0.1	300/21.9	150/21.6 [50]	15.3	6.0 [39]
LX-196	90 + 10/(100)	MEK Solution	51	A	71	<0.1	292/20.3	73/14.7 [39]	15.1	4.4 [39]
LX-199	100 + 0/(75)	Hot Melt (150°F)	44	A	57	<0.1	211/15.7	144/16.4 [68]	14.2	6.8 [48)
LX-198	90 + 10/(75)	Hot Melt (180°F)	51	A	64	<0.1	228/16.8	164/16.5 [72]	14.3	7.1 [50]

---

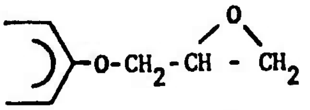
[*] % of RT value

A - Lay-up, in cold press, increase temperature to 270°F in 60 min under contact pressure and 10 in. Hg. Hold 100 min, apply 75 psi, vent to air. Increase temperature to 350°F in 20 min. Hold 2 1/2 hrs. at 350°F. Cool under pressure. Postcure 4 hrs. at 400°F, free-standing.

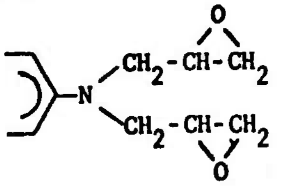
g. BF_3MEA Catalyzed

A most obvious means of obtaining improved elevated temperature performance and yet maintain equivalent processability and mechanical performance is in co-curing with an "acid" system.

Boron trifluoride-monoethylamine complex ($BF_3 \cdot MEA$) has long been used as a latent catalyst for moderately high temperature performance epoxy systems. We did not expect an appreciable difference in latency to occur when commonly used glycidyl ether based epoxy resins were replaced with glycidyl amines as are found in MY-720.



Glycidyl ether



Diglycidyl amine

Instead of the expected latent characteristics we found an acceleration of cure rate at room temperature. For example, all the MY-720/DADS systems have consistently shown >8 weeks flow life when doubly crystallized -400 mesh DADS is used. The flow life generally lengthens with a reduction in loading level so at 50-60% stoichiometry, flow life in excess of 13 weeks is obtained.

When $BF_3 \cdot MEA$ is admixed with the DADS cured (50% stoichiometry) MY-720/0510 (94/6) system, a reduction in flow life occurs. The reduction in flow life is approximately proportional to the concentration of catalyst where the effective viscosity of the heterogeneous mixture increases very slowly over a prolonged period. Mixtures showed steady buildup in viscosity over the elapsed test period. The samples with 1% catalyst (based on resin) effectively lost the usable flow life in ≅4-5 weeks while others at lower concentration (e.g., 0.4-0.6%) were still usable after a ten week period, with marginal usage after about 13 weeks.

The surface of the exposed resin/curing agent/catalyst (1%) mixtures should be mentioned since there is an obvious difference with the bulk of the underlying material. Advancement apparently proceeded much more rapidly at the surface; most probably due to an acceleration by absorbed moisture. The moderately hygroscopic nature of $BF_3 \cdot MEA$ undoubtedly contributed to this difference.

The surface material (<1 mm thick) is readily converted to a fluid state upon application of only moderate heat. 120°F is sufficient to bring about very acceptable viscosity for drape and tack requirements. Only a very slight difference in gel time is detectable between this surface material and that underlying the surface.

The reduction in out-time may probably be attributed to two factors: (1) the epoxy ring has a higher electron density due to the replacement of the more electronegative oxygen atom in the ether moiety with nitrogen, thus making it more susceptible to electrophilic attack; and (2) there is undoubtedly a significant increase in overall basicity due to the incorporation of nitrogen as a replacement for oxygen in the linkage to the aromatic substrate. This increased basicity may be reflected in a lowered energy of dissociation for the $BF_3 \cdot MEA$ complex (solvent effect) thereby reducing the out-time.

h. Alternate Lewis Acid Curing Agents

We screened a number of alternate catalyst systems with the ultimate goal described previously; to increase epoxy-epoxy reaction to yield a more tightly crosslinked system with improved elevated temperature performance at no sacrifice in effective flow life.

Differential scanning calorimetry provided useful data in comparison/screening tests by establishing the various cure initiation, peak and termination temperatures.

Table XIV below lists these temperatures for some representative formulations evaluated in this study.

TABLE XIV

DIFFERENTIAL SCANNING CALORIMETRY CURVES FOR
VARIOUS RESIN/CATALYST COMBINATIONS
SCAN RATE 10°C/MIN

Resin Type	pbw/pbw	Curing Agent Type/pbw	Catalyst Type/pbw	Initiation Temp °C	Peak Temp °C	Termination Temp °C
MY 720	100/--	None	None	250	319	345
MY 720/0510	94/6	DADS/26.7	None	160	274	290
MY 720/0510	94/6	None	BF_3.MEA/1	95	140	225
MY 720/0510	94/6	DADS/26.7	BF_3.MEA/1	95	140	--
				* --	210	240
MY 720	100/--	None	Zinc linoresinate/2	170	280	305
MY 720	100/--	None	Zinc linoresinate/3	160	275	300
MY 720	100/--	None	Manganese " /4	170	270	310
MY 720	100/--	None	Copper " /3	225	304	310

* Double peaked exotherm

A casting was prepared from the following formulation:

MY-720 - 94 pbw
0510 - 6 pbw
DADS - 26.7 pbw (50% stoichiometry)
Zn linoresinate - 3 pbw

TMA results are shown below with the DTUL determined under a 450 psi compression load.

Cure Schedule	DTUL
2-1/2 hrs at 270°F	--
plus 2 hours at 350°F	370°F (180°C)
plus 4 hours at 400°F	465°F (240°C)

The anticipated improvement in DTUL to equal that obtained with 100% stoichiometry DADS loading was gratifying and efforts were promptly redirected toward composite performance evaluations for this system.

8. Laminate Performance

Two T-300 reinforced laminates were prepared to establish initial thermomechanical properties and begin accelerated humidity and heat aging studies.

The first laminate (DX-203) was designed to serve as a baseline measure of the resin performance. Prepreg preparation was as follows: The various components of the resin mixture were mixed at 270°F and held at that temperature for ≅30 minutes to completely dissolve the -400 mesh doubly recrystallized DADS. After deaeration, the clear solution was then hot melt (150°F) coated (10 mil resin film) on Mylar film. After transferring the coated Mylar to a 12-1/2 in. dia. drum, the T-300 fiber was wound into the cold resin at 24.6 tows/inch, the overwrapped film was slit and removed from the winder, covered with another piece of Mylar film and squeeged on the heated vacuum table at 150°-200°F.

The second prepreg (DX-201) was processed at <140°F throughout to minimize solubility of the suspended curing agent. No deaeration was attempted and the heterogenous film pulled to a 13 mil thickness. This procedure will serve as a benchmark for any further processing studies.

Six by six inch laminates (12 ply) were prepared using customary practices as previously described. The following tables (Table XV and XVI) list the pertinent data along with target properties (NARMCO 5208).

Our primary objectives were achieved in this composite where virtual equivalence to the reference 5208/T-300 performance was attained. Humid aging studies show even slight improvement in moisture response while prepreg out-time was found to be on the order of 13 weeks duration for the heterogeneous system.

TABLE XV

PREPREG DATA

Laminate No.	Formulation (pbw)	Mixing Temp (°F)	Deaired	Pulled Film Thickness (mil)	Impregnation Temperature (°F)	Tows per Inch	Prepreg Resin Content (%)	Quality
DX-201	MY-720 (94) 0510 (6) DADS (27.6) Zn linoresinate (3)	130	No	13	130-140	24.4	48.3	Very good
DX-203	MY-720 (94) 0510 (6) DADS (27.6) Zn linoresinate (3)	270	yes	10	140-150	24.6	41.1	Excellent

TABLE XVI

LAMINATE DATA

	Initial Laminate Data				Flexural Strength/Modulus ksi/psi x 10^6 (avg)			Interlaminar Shear Strength ksi (Avg)		
Laminate No.	Cure Schedule	Resin Content (%)	Fiber Volume (%)	Void Content (%)	RT	300°F	350°F	RT	300°F	350°F
DX-201	(1)	26.8	67.1	0	260/18.8	211/18.8 (81)	190/18.6 (73)	15.5	9.4 (61)	8.3 (53)
DX-203	(2)	27.9	65.8	0	257/18.8	205/18.1 (80)	178/18.5 (70)	16.9	9.4 (56)	8.5 (50)
Narmco 5208	--	--	--	--	247/--	--	196/-- (79)	15.9	--	8.9 (56)

(1) Lay-up, in cold press, increase temperature to 270°F in 60 Minutes under contact pressure and 10 in. Hg. Hold 100 minutes, apply 75 psi, vent to air. Increase temperature to 350°F in 20 minutes. Hold 2 1/2 hours at 350°F. Cool under pressure. Postcure 4 hours at 400°F, free-standing.

(2) Same as (1) except dwell 90 minutes at 270°F under 10 in. Hg.

( ) % of RT value

a. Heat Aging Studies

Flexural specimens were aged (air) and tested at 350°F. During the 500 hour exposure an almost negligible weight loss in both laminates was found. Strength retentions at 350°F were exceptionally good. Over 100% retention was found in both laminates. These results, coupled with the very low experienced weight losses, is sufficient for prediction of long term performance at 350°F. Higher temperature use (e.g., 400°F) for shorter periods is certainly feasible. Table XVII shows the pertinent data.

TABLE XVII

LAMINATE DATA AFTER 500 HOURS AT 350°F (IN AIR)

Laminate Number	Average Weight Loss After Aging (%)	Flexural Strength/Modulus at 350°F (ksi/psi x 10^6 psi)		% Retention
		Initial	Aged	
DX-201	0.32	190/18.6	206/18.6	108
DX-203	0.37	178/18.5	190/18.4	106

b. Flow Life Characteristics

The stored prepreg from DX-201 (undissolved DADS) shows only negligible changes in drape and tack characteristics after ≅13 weeks at ambient conditions. The ultimate flow life depends on the particular end use application and is very difficult to establish precisely. After 13 weeks the prepreg was not boardy but had lost significant tack properties. Very slight warming (just the heat of the hand) readily restores desirable tack properties. Prepreg from DX-203, where the DADS was dissolved prior to impregnation (at 270°F) was beyond its useful out-time after approximately six weeks.

Prepreg samples (DX-201) which still had the cover sheets in place showed slightly less advancement when compared with samples exposed to the atmosphere. This slight acceleration in cure, due to sorbed moisture, was expected from the known catalytic activity of small amounts of hydroxyl containing species on the epoxy cure reactions. The degree of acceleration, which was unknown for the system under study, was slight and did not impose significant restrictions on attaining the desired 10 week flow-life.

c. Moisture Sorption Studies

Flex and short beam shear specimens were exposed to 120°F at 98+% R.H. for moisture pickup determination. Short beam shear samples were removed and tested at 350°F periodically throughout the 1000 hour aging studies.

Figure 12 shows the weight gain (as a % of the total specimen weight) of the shear specimens for the two laminates. Specimens from Laminate 203 (dissolved DADS) showed a slightly higher rate and ultimate value for total moisture pick-up. These greater values, of course, are directly attributable to the slightly higher resin volume fraction in DX203 vis-a-vis DX 201 (.342 vs. .329).

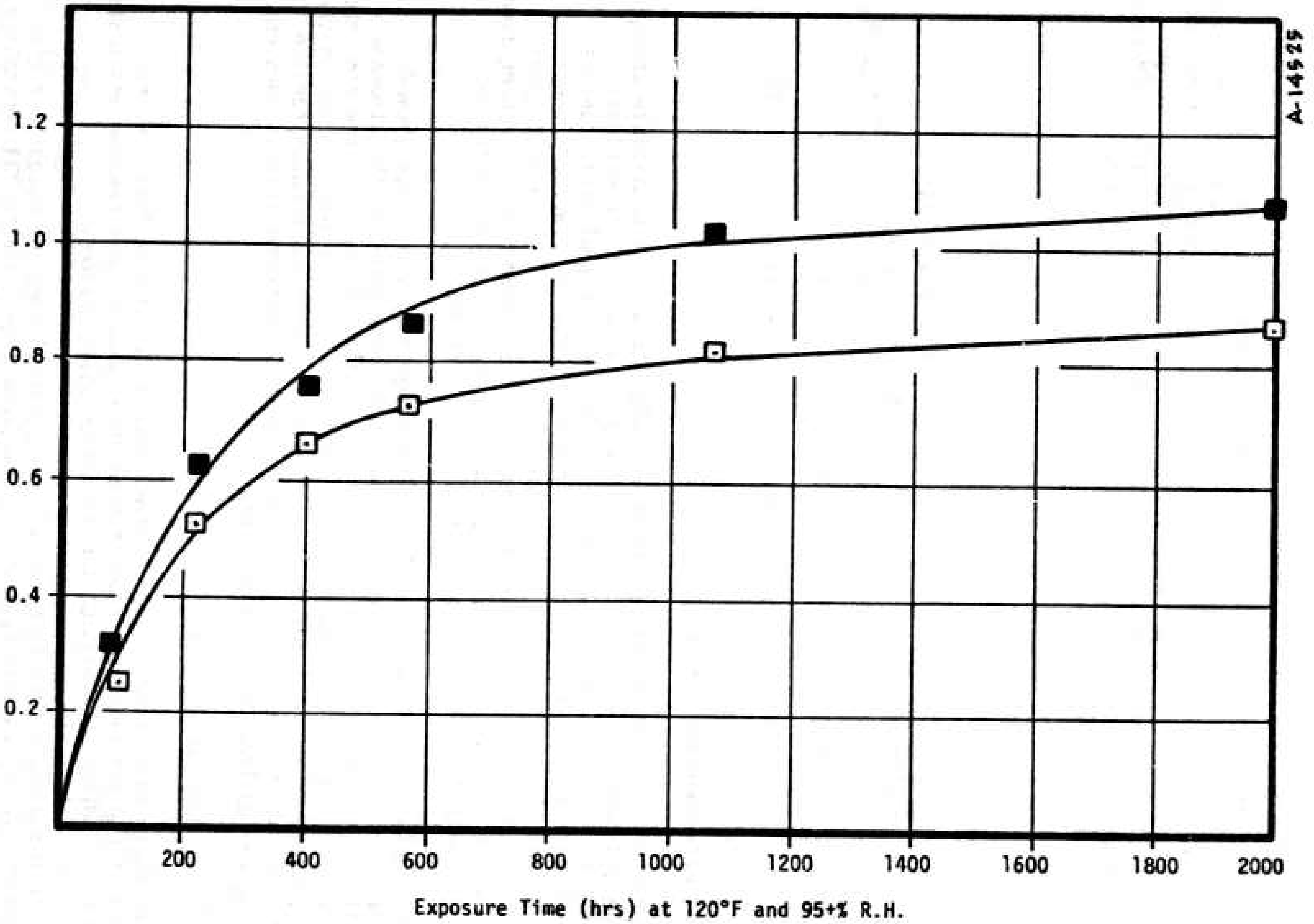


Figure 12. Sorption characteristics of DX-201 (□) and DX-203 (■) short beam shear specimens.

Fall-off in interlaminar shear strength (at 300°F and 350°F) with time and moisture content is described in Figures 13 and 14. These values were measured under a "zero time soak" at test temperature which is a more realistic and severe test than the normal 10-30 minute hold at test temperature, as shown subsequently.

Similar moisture sorbtion data for flexural specimens is presented in Figures 15 and 16, where the moisture sorbtion rate is shown to follow Fick's Diffusion Law (proportional to the square root of exposure time) to ≅80% of the ultimate saturation level (1.0-1.2 % of composite weight after 2000 hours at 120°F and 95+% R.H.).

d. Desorption Measurements

Measurements of desorption characteristics of moisture laden (1000 hour exposure) short beam shear specimens under three different conditions yields interesting results. Figure 17 shows the percent of original weight of sorbed moisture as a function of $t^{1/2}$ (Fick's Law). The three drying conditions were 150°F at $<5\%$ R.H. (over P_2O_5), 250°F and 350°F. All three conditions resulted in discontinuous straight line plots. This result may possibly be due to water being included in the polymer matrix in two distinct "modes", e.g., sorbed directly on and associated with the polymer and clusters in occluded "microvoids". The latter segments (lesser slope) were followed to the completion of the drying cylces (shown for 350°F). Extrapolation during the prolonged period at 150°F allowed prediction of the time to original dry weight to within 40 hours. The 1120 hour period required for desorption at 150°F was almost equal to the 1000 hours required for absorption at a lesser temperature, 120°F at 95+% R.H. as expected. Figures 18-20 present the same data as a function of time.

e. Test Procedure and Strength Regain Study

Flexural test specimens were aged for 2280 hours at 120°F and 95+% R.H. The aging was terminated when no change in moisture pickup was apparent during the final 100 hours. The saturated specimens were tested at 77°F, 250°F, 300°F and 350°F under two initiation conditions; immediately after reaching test temperature and after a 30 minute soak at temperature. Specimen weights were recorded immediately before and after test. Table XVIII outlines the results. Each data point reported is the average of three tests as before.

Short beam shear specimens were given a somewhat different evaluation. After 1080 hours exposure to 120°F and 95+% R.H, the specimens were weighed, given various soak times at the test temperature, tested at 350°F and immediately re-weighed. One set was also tested at 300°F. The data is presented in Table XIX.

The data indicates more significant strength regains in short beam shear strength using standard soak times at various test temperatures. The difference in surface to volume ratio between short beam shear and flexural test coupons resulting in correspondingly high sorbed moisture loss during test, accounts for the above observation. It should be recognized that these test results were obtained for standard test specimens and that residual sorbed moisture

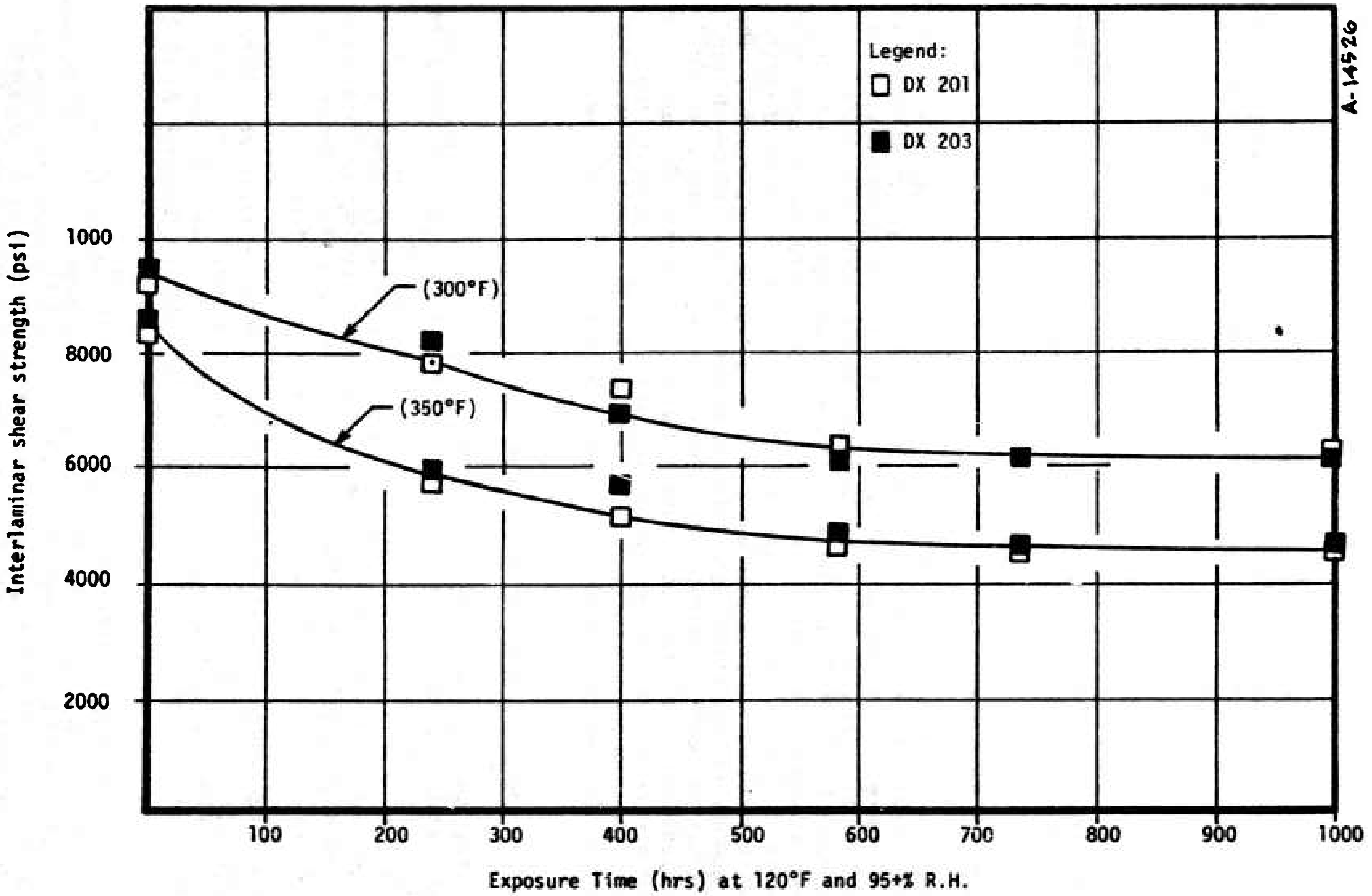


Figure 13. Interlaminar shear strength (at 300°F and 350°F) upon prolonged humid aging.

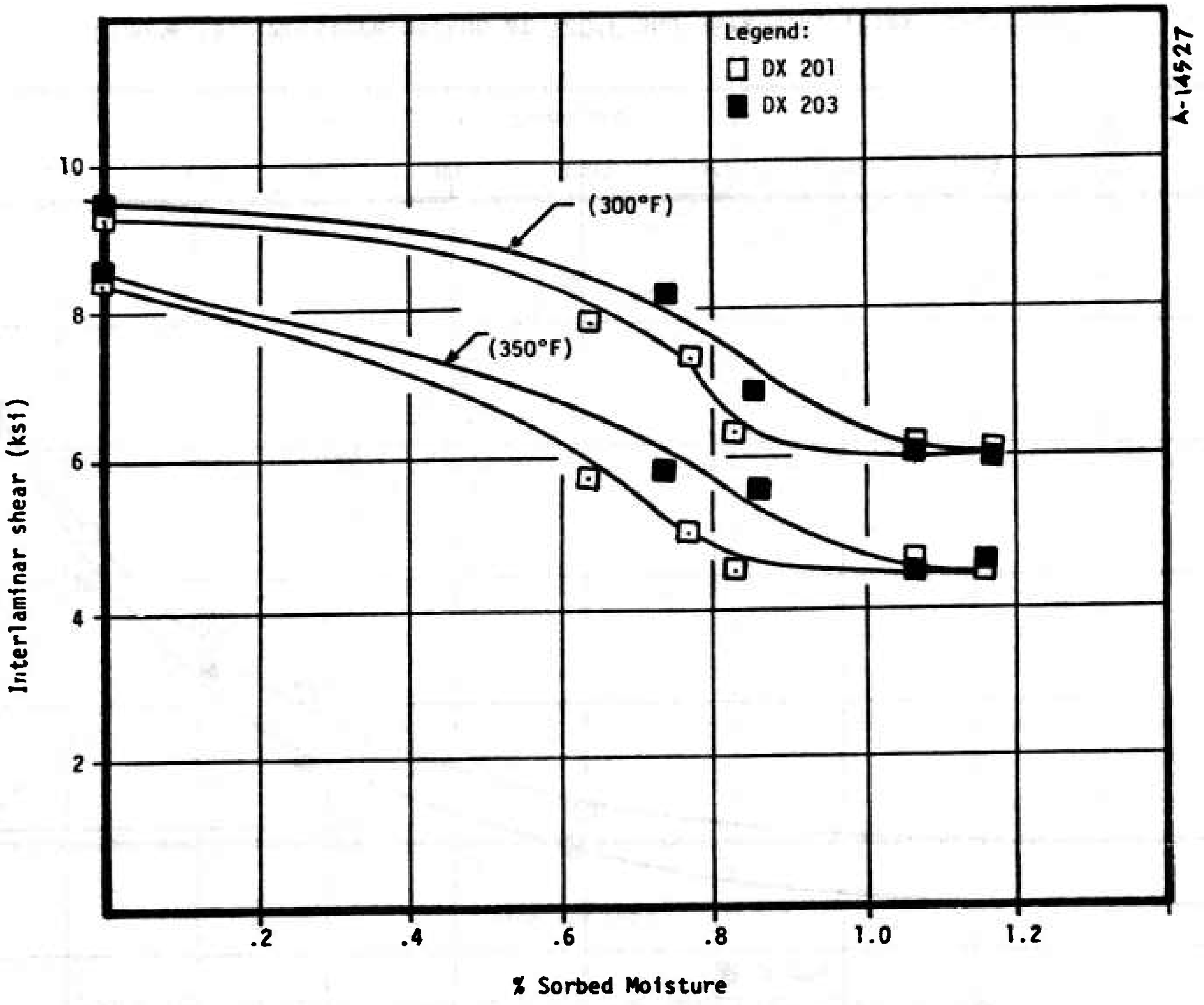


Figure 14. Interlaminar shear strength (300°F and 350°F) as a function of sorbed moisture.

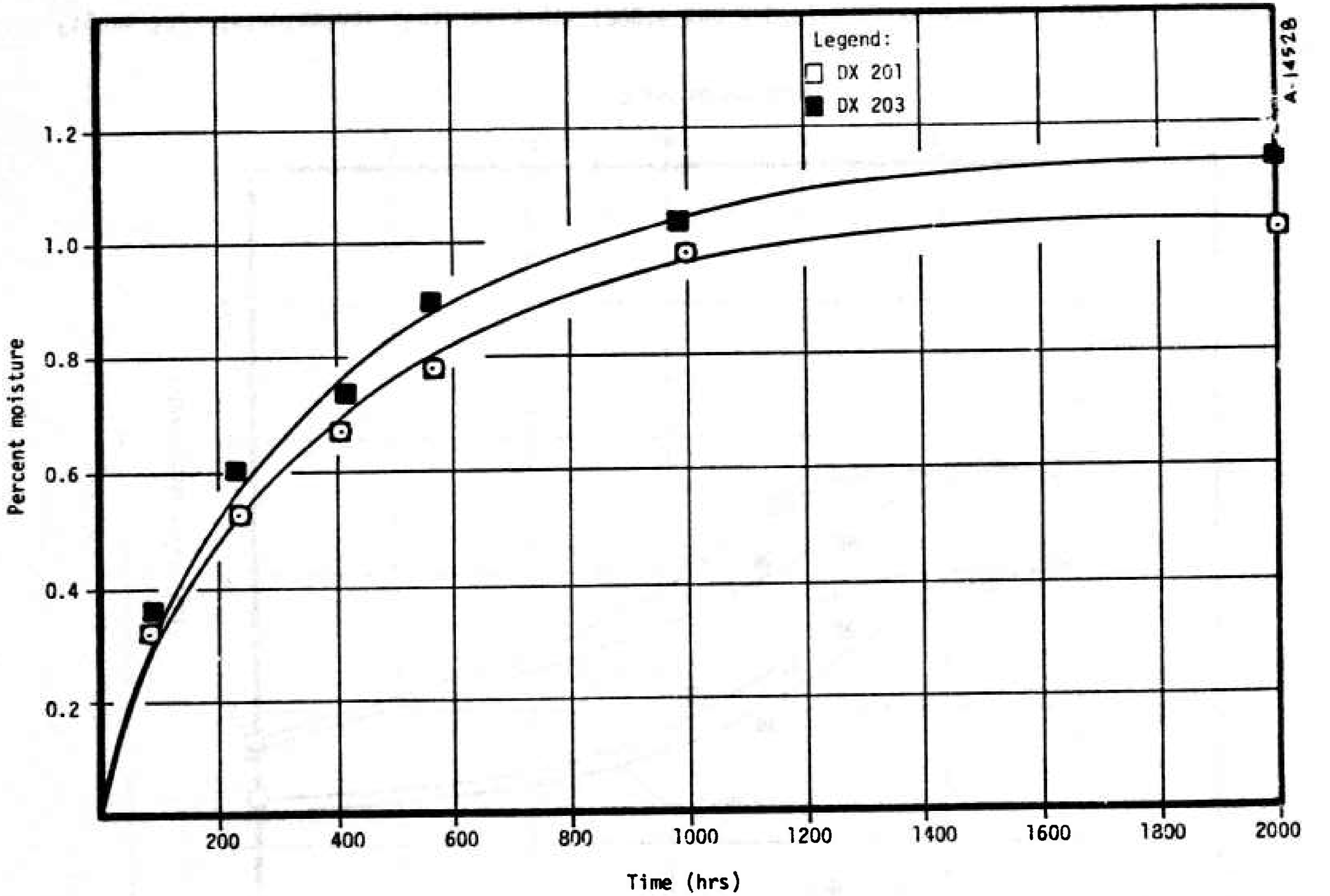


Figure 15. Moisture pickup at 120°F and 95+% R.H. (Flex specimens).

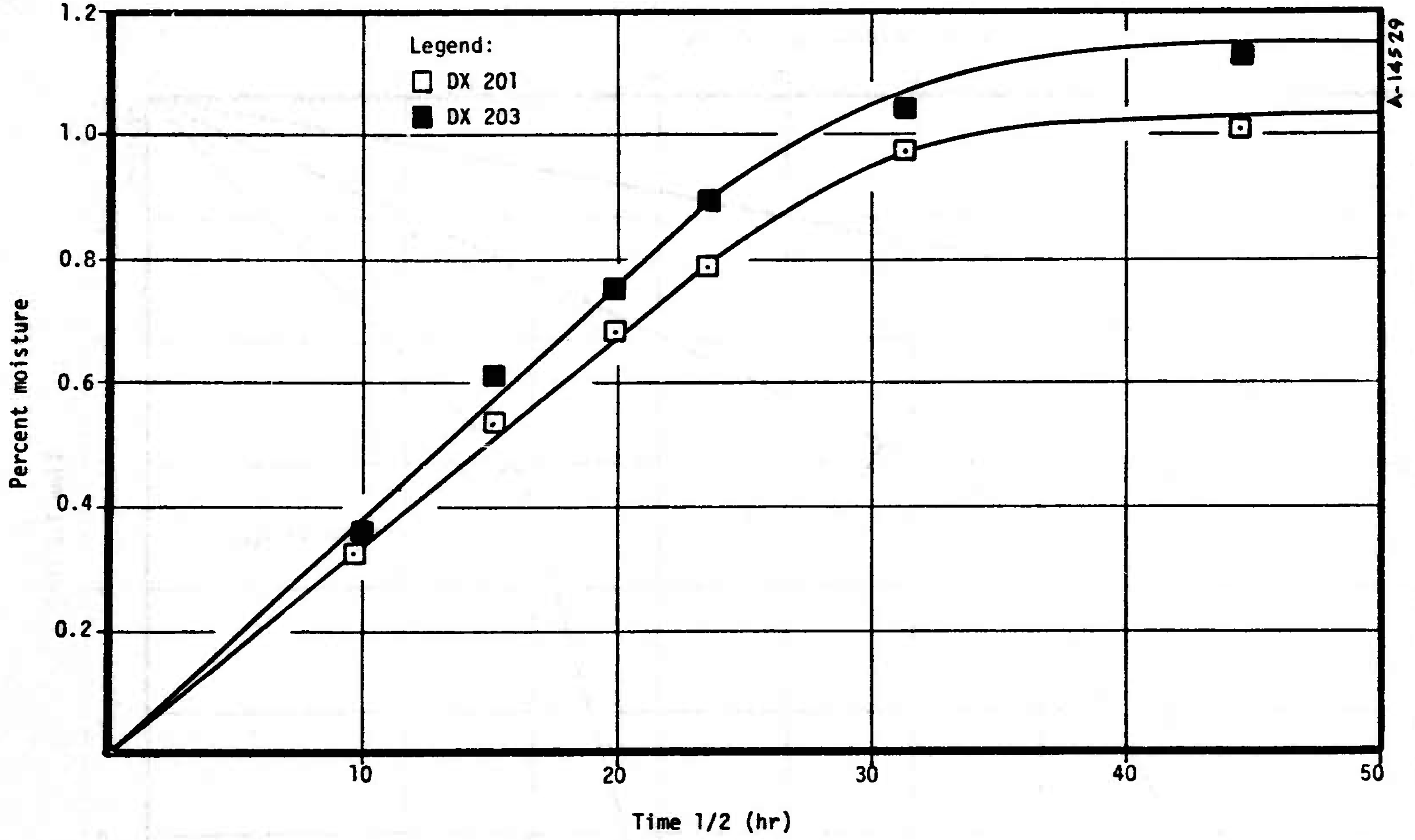


Figure 16. Moisture pickup at 120°F and 95+% R.H. (flex specimens).

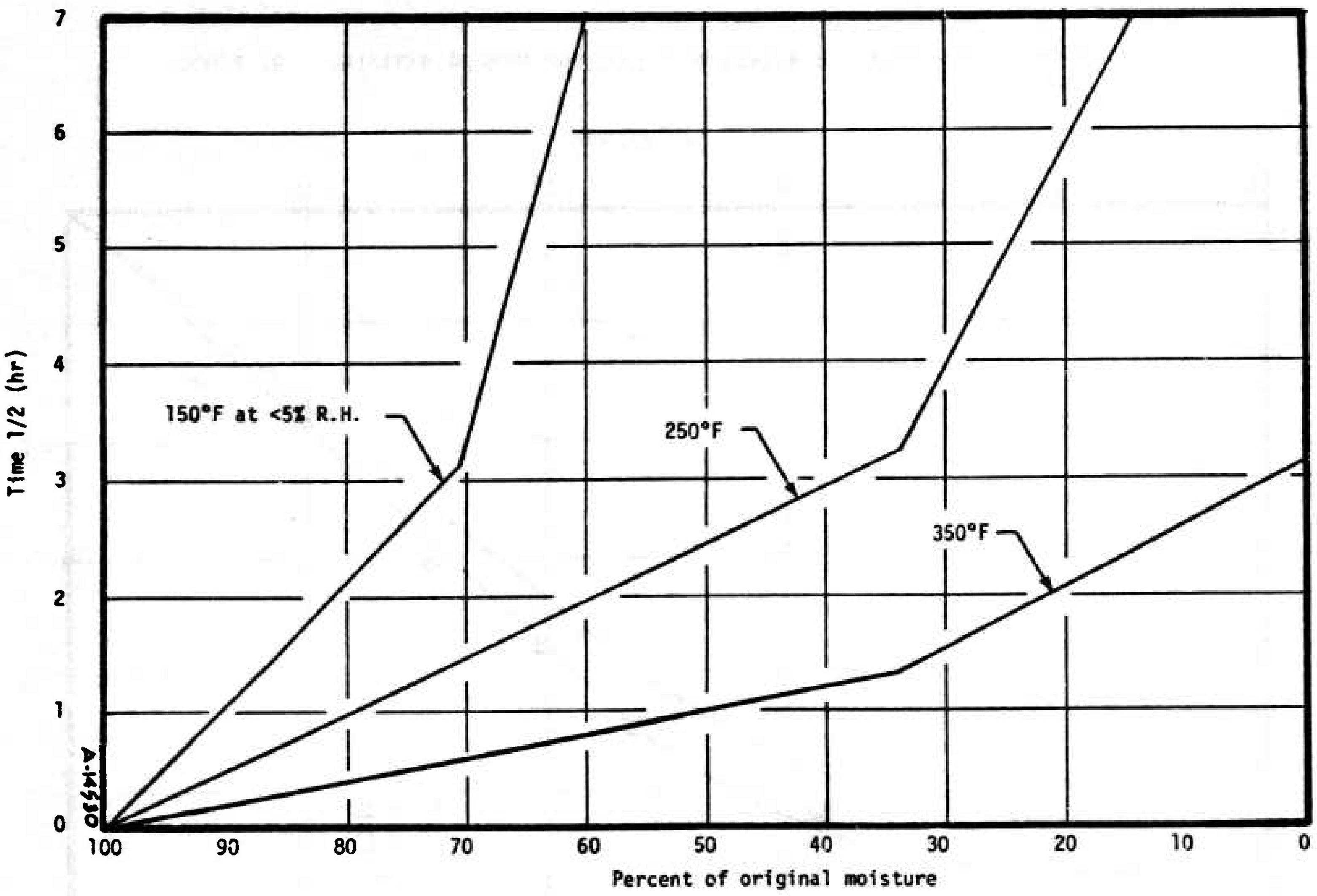


Figure 17. Desorption of short beam shear specimens.

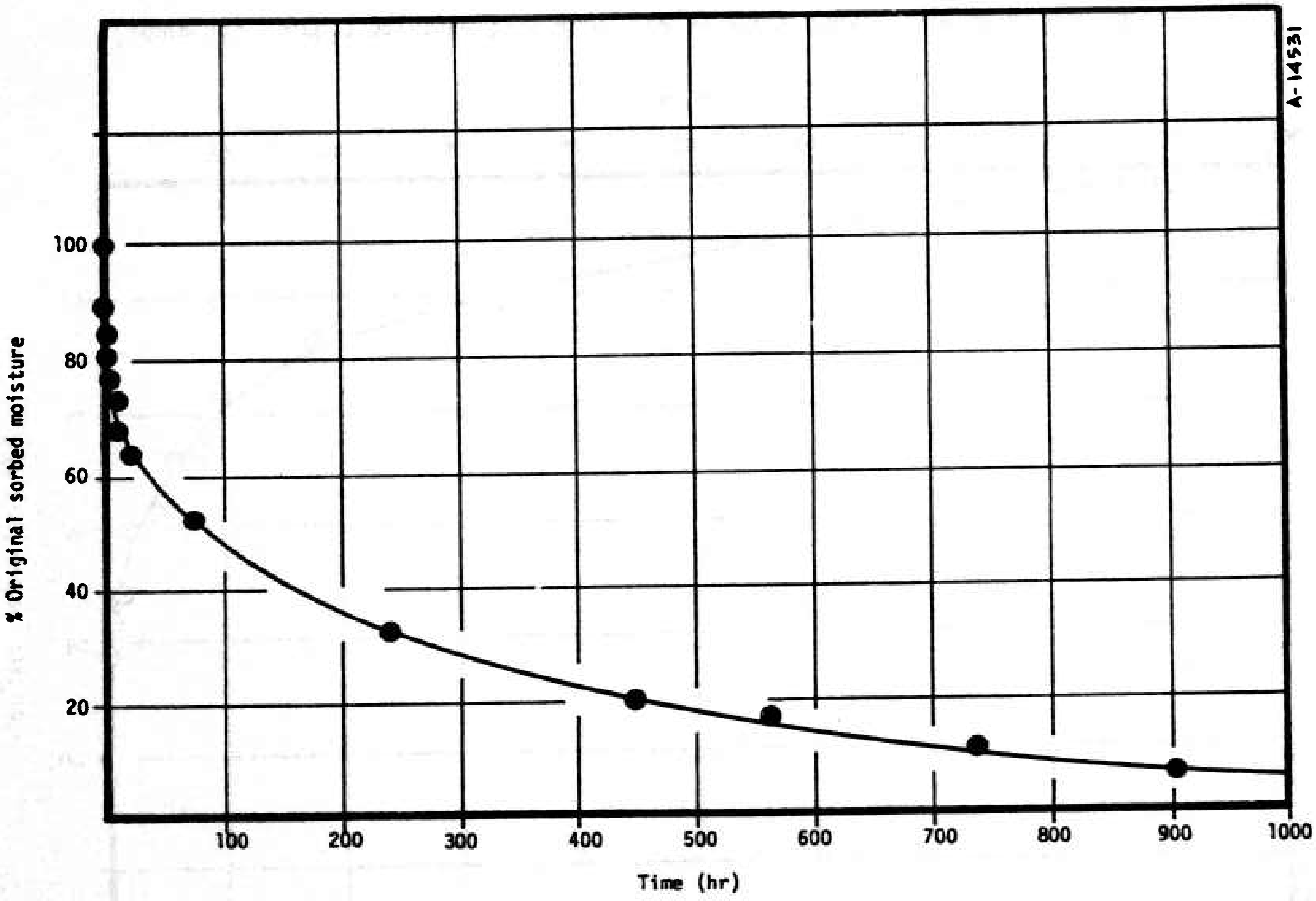


Figure 18. Sorbed moisture loss with time at 150°F (over P_2O_5) (short beam shear specimens).

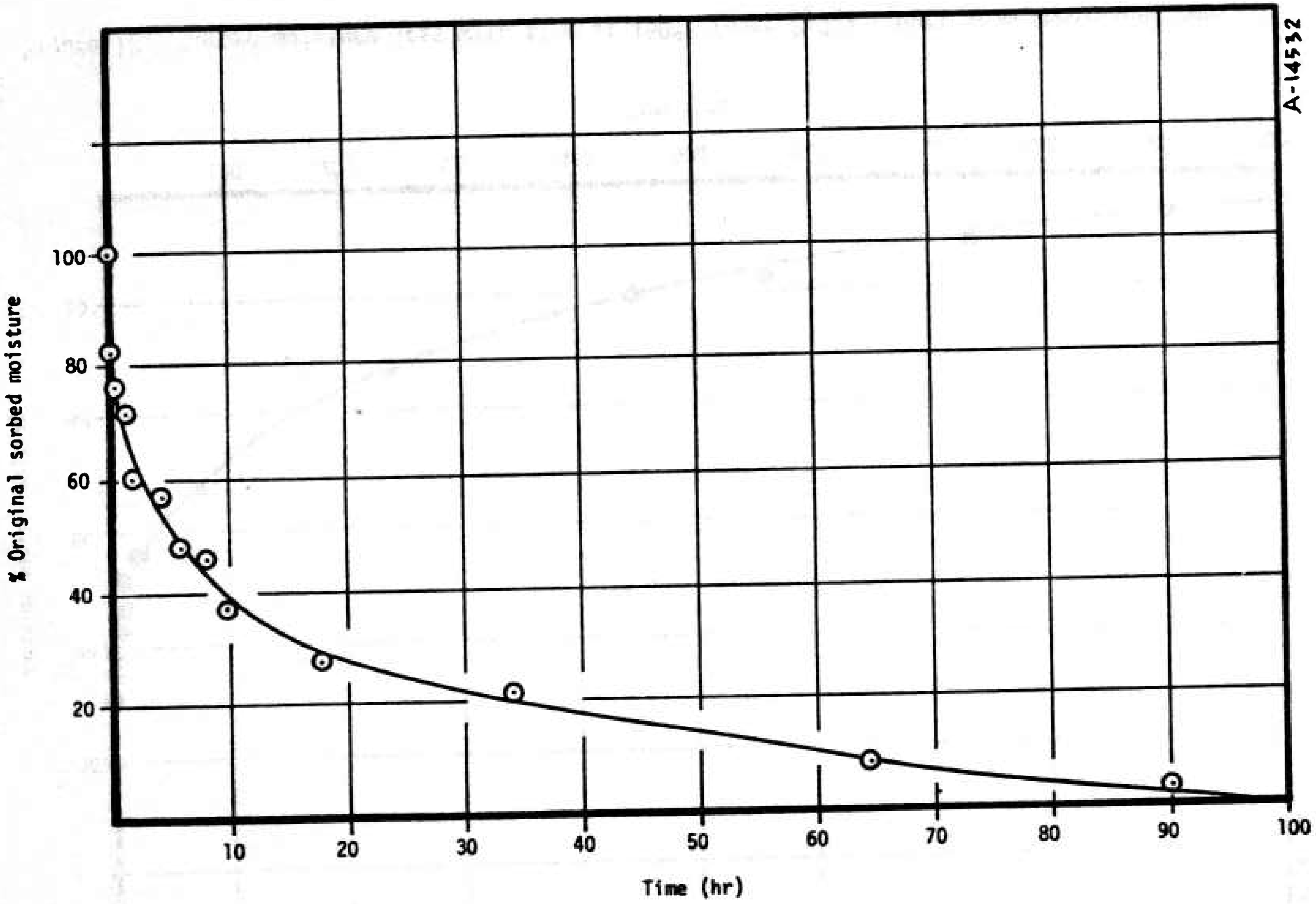


Figure 19. Sorbed moisture loss with time at 250°F (short beam shear specimens).

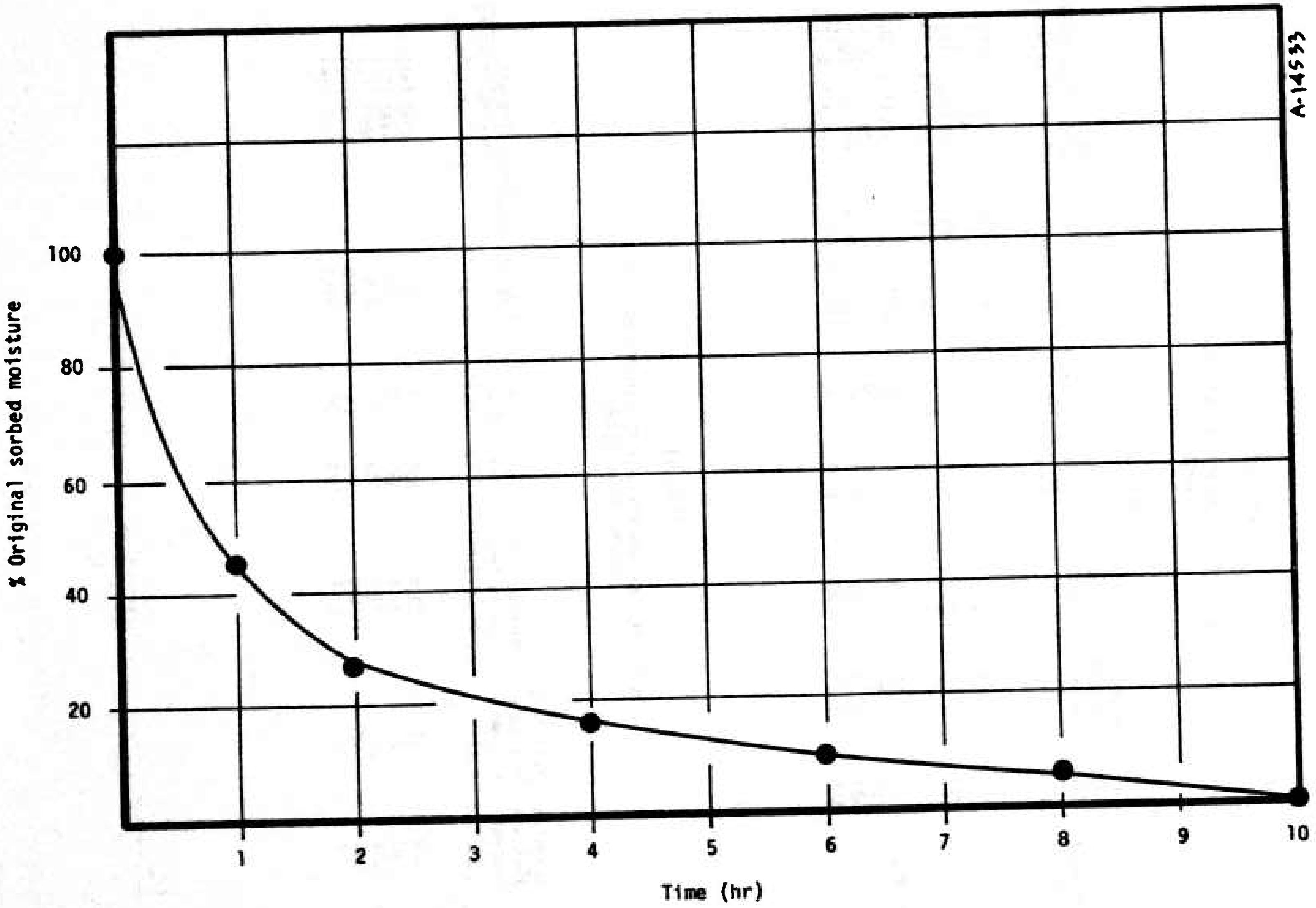


Figure 20. Sorbed moisture loss with time at 350°F (short beam shear specimens).

TABLE XVIII

MOISTURE LOSS AND STRENGTH REGAIN DURING TEST (FLEXURAL)

Laminate No.	Test Temp (°F)	Original Moisture Content (%)	Post-Test Moisture Content (%)	Moisture Lost During Test (%)	Soak Time (min)	Flexural Strength/Modulus ksi/psi x 10^6 Original	Flexural Strength/Modulus ksi/psi x 10^6 After Humid Aging (% of RT value)
DX 201	75	1.18	1.18	0	0	260/18.8 (100)	278/19.9 (100)
	250	1.12	1.04	7.1	0	--	164/18.2 (59)
	300	1.11	0.92	17.1	0	211/18.7 (81)	131/16.7 (47)
	350	1.15	0.78	32.2	0	190/18.6 (73)	83.9/13.6 (30)
DX 203	75	1.23	1.28	0	30	258/19.6 (100)	252/19.4 (100)
	250	1.25	0.97	22.4	30	--	170/18.7 (67)
	300	1.38	0.88	36.2	30	206/18.1 (80)	136/14.7 (54)
	350	1.27	0.68	40.9	30	178/18.5 (69)	92.3/12.6 (37)

TABLE XIX

MOISTURE LOSS AND STRENGTH REGAIN DURING TEST (SHORT BEAM SHEAR)

Laminate No.	Original Moisture Content (%)	Post-Test Moisture Content (%)	Moisture Lost During Test (% of Original)	Test Temp (°F)	Soak Time (min)	Interlaminar Shear Strength Original	Interlaminar Shear Strength After Humid Aging (% of Original)
DX 203	1.08	.94	13.0	300	0	9490	6050 (64)
	1.07	.84	21.5	350	0	8560	4390 (51)
	1.16	.71	38.8	350	10	8560	4680 (55)
	1.19	.58	51.3	350	20	8560	5170 (60)
	1.15	.42	63.5	350	30	8560	5510 (64)

content and distribution would certainly be different for other test specimen dimensions under the same test conditions. Hence, direct correlation of these test results with other data should not be necessarily expected.

Our testing methodology includes the routine use of thermocoupled specimens in all elevated temperature mechanical testing. Accordingly, an indicated soak time for a specific test, is time at the test temperature from the thermocouple response. No soak time is initiation of the test as soon as the thermocouple indicates that the desired temperature has been reached.

To complete the strength regain characteristics, short beam shear specimens previously used for desorption rate determinations were completely dried and were tested at 350°F under no soak time conditions. The results are presented below in Table XX.

TABLE XX

INTERLAMINAR SHEAR STRENGTH REGAIN OF HUMIDITY AGED SPECIMENS AFTER DRYING (LAMINATE DX-201)

Soak-dry conditions	Test temperature,°F*	Interlaminar shear strength, ksi (avg)
dry (initial)	RT	15.5
dry (initial)	350°	8.3
930 hrs @ 120°F/95% RH	350°	4.8
above followed by:		
1120 hrs @ 150°F	350°	7.9 (95%)
110 hrs @ 250°F	350°	7.7 (93%)
11 hrs @ 350°F	350°	8.1 (98%)
1240 hrs @ 120° and 95% RH		
followed by:		
1744 hrs @ 150°F	350°	7.9 (95%)
34 hrs @ 350°F	350°	8.1 (98%)

*Testing initiated when sample thermocouple reached the desired test temperature

( ) Percent initial 350°F number

In summary, efforts to date to develop a long flow life prepreg system capable of providing composites for 350°F use have been successful. Through this program effort a prepreg system was developed which had a flow life in excess of the target 75 days. Section III of this report further summarizes the progress on the program and suggests key directions for further research. The extensive moisture characterization efforts conducted in the program can be summed to provide basically the equivalence of our system to state-of-the-art performance of 350°F performing systems. The strength regain/composite drying activities conducted in this program show that the moisture/strength degradation process is reversable.

SECTION III

CONCLUSIONS 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 graphite reinforced epoxy systems. This has been achieved with a concurrent increase in prepreg effective flow-life from the previously allowable two weeks at ambient temperature to >12 weeks.

Demonstration of the effectiveness of utilizing "insoluble" curing agents which effect cure upon dissolution at laminate processing temperatures required both high purity and fine particle size of the dispersed curing agent. Settling of the dispersed phase was overcome by this technique as was the "micro inhomogeneity" problem associated with diffusion controlled mixing processes.

This technique may be similarly extended to include other curing agent/resin combinations which would perhaps allow even further extension of flow-life and improvement in moisture resistance.

Alternate co-catalysts should be more extensively evaluated for effectiveness and concentration allowance.

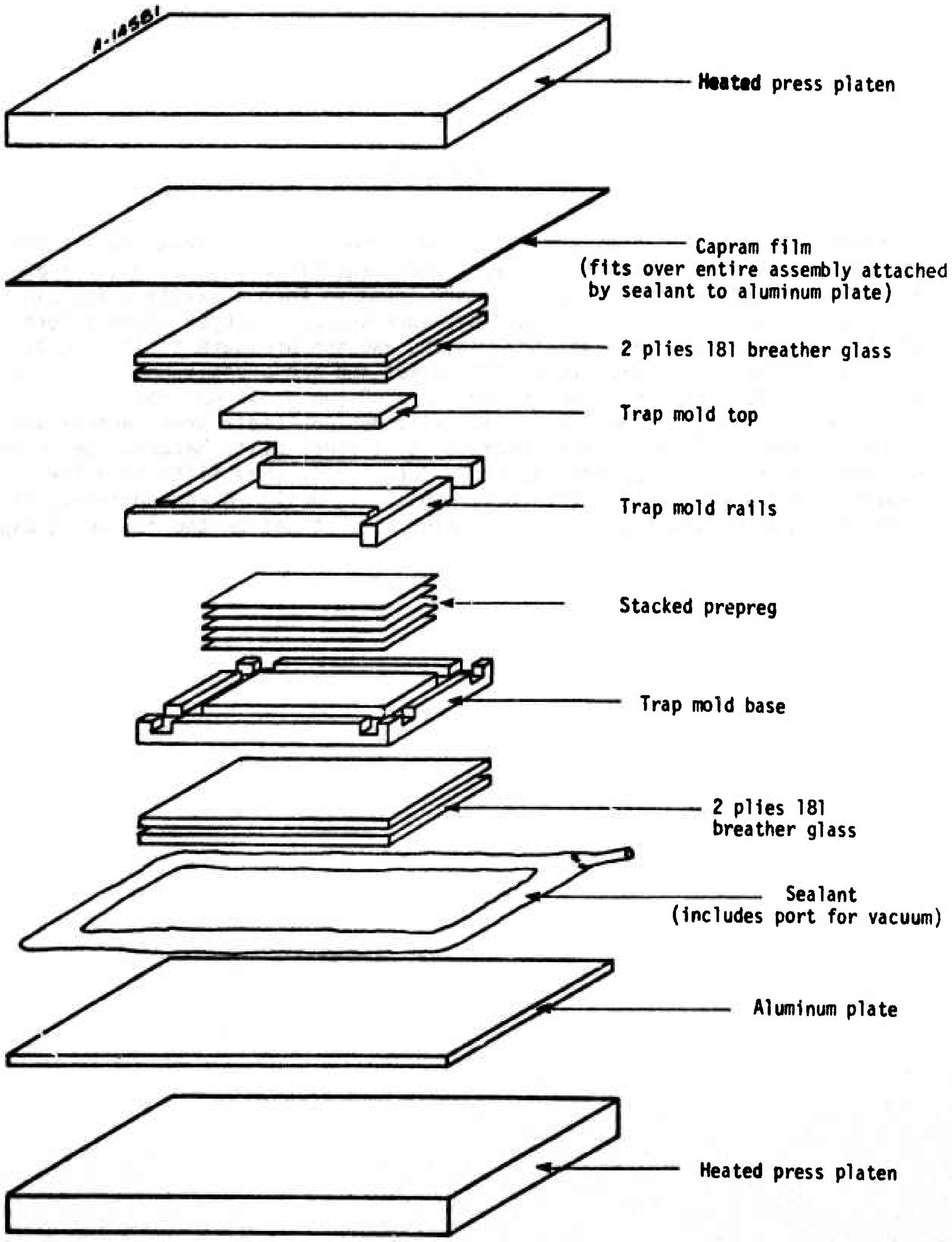
More extensive evaluation of prepregging techniques, cure schedules and composite performance with the already established formulation as well as future developments should allow a fine tuning of the various systems to a fully optimized end-product.

APPENDIX A

VACUUM TRAP MOLD LAYUP

The apparatus for vacuum trap mold processing as conducted on the program is sketched on the following page. This apparatus provides a method to achieve trap mold processing for resin flow control and at the same time achieve the advantages of vacuum bag processing.

SCHEMATIC OF A VACUUM TRAP MOLD LAYUP

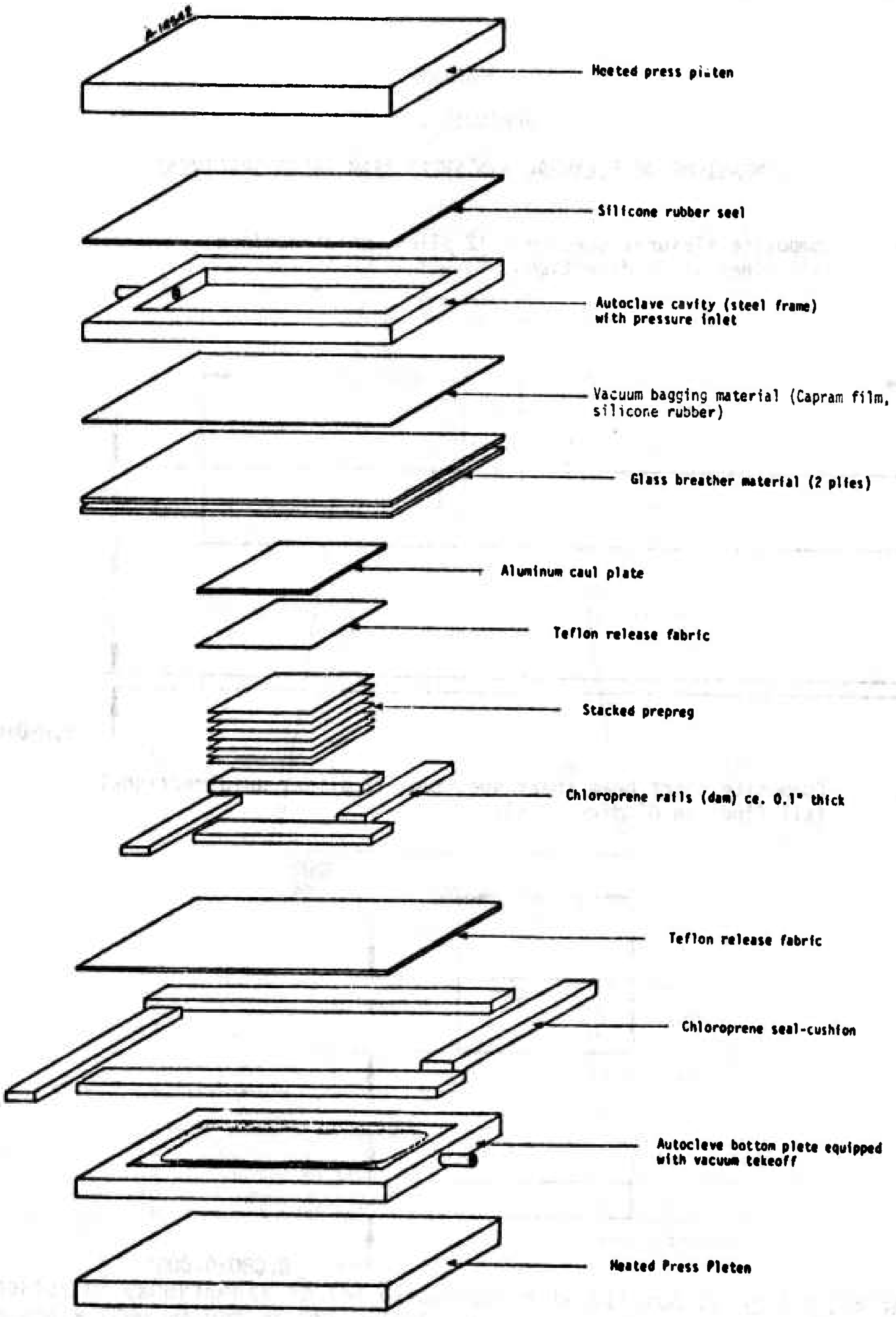


APPENDIX B

PRESS AUTOCLAVE LAYUP

A convenient method to simulate autoclave processing on a laboratory scale is with a device Aerotherm has named a press autoclave. Press platens are used in combination with a steel picture frame to form a cavity which can be pressurized by an internal fluid pressure source. Rubber gaskets form the seal between the frame and the platens and the pressure is limited by the frame design, the strength of the gasket and the press tonnage. Thus, if a one (1) foot square frame is used in a 60 ton press one could achieve a pressure of 694 psi. Aerotherm typically designs their press autoclaves to be capable of 200 psi. The insertion of a steel plate between the frame and the bottom platen expands the press autoclave's capability to allow vacuum processing as well. This bottom plate is designed appropriately to provide vacuum capability. This apparatus is sketched on the following page.

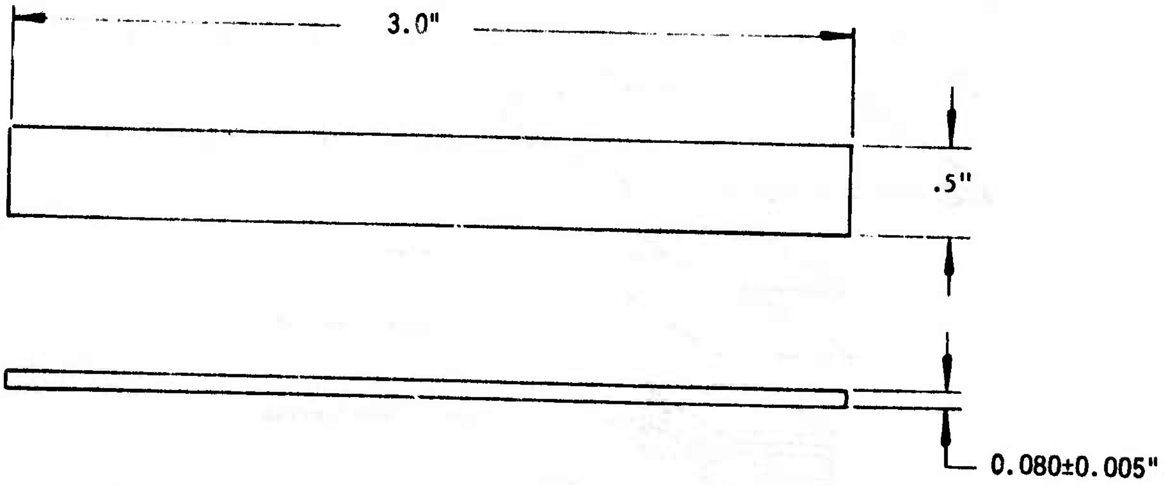
SCHEMATIC OF A PRESS AUTOCLAVE LAYUP



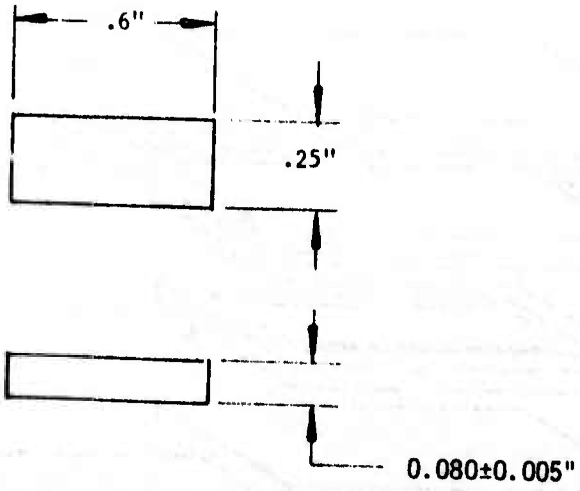
APPENDIX C

DIMENSIONS OF FLEXURAL AND SHORT BEAM SHEAR SPECIMENS

A. Composite flexural specimen, 12 plies, unidirectional (all fiber in 0° direction).

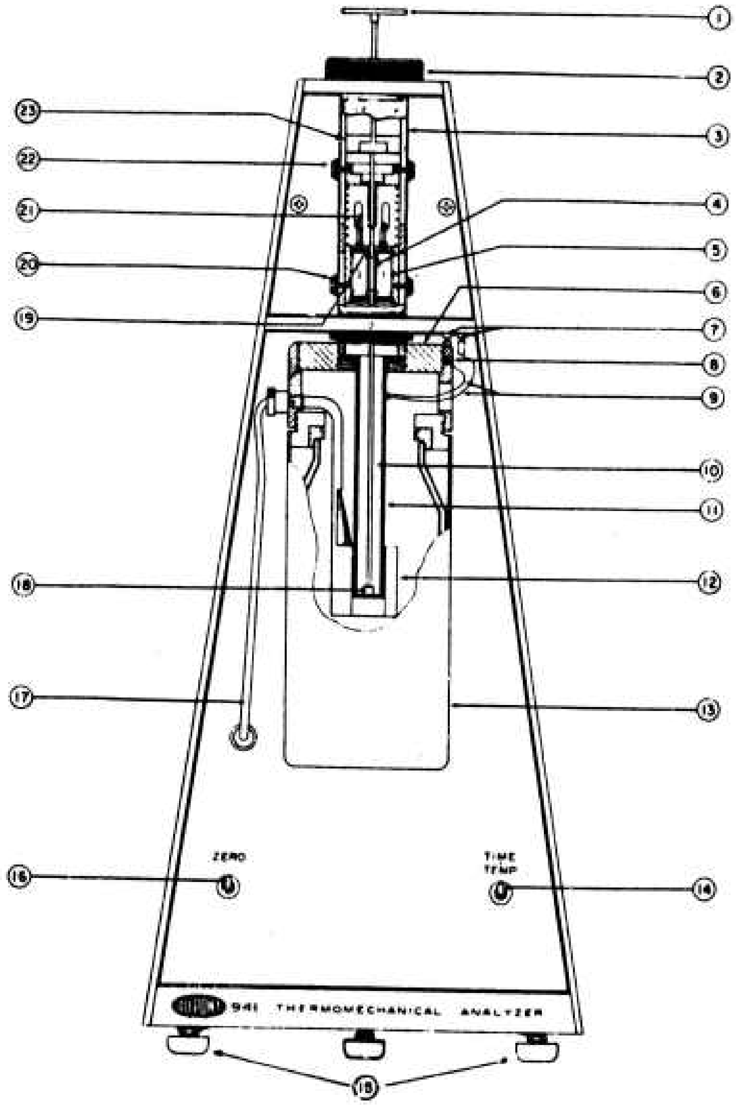


B. Composite short beam shear specimen, 12 plies, unidirectional (all fiber in 0° direction).



APPENDIX D

SKETCH OF SET-UP TO DETERMINE DISTORTION TEMPERATURE UNDER LOAD (DTUL)



Item	Description
1	Weight tray
2	Retainer nut
3	Head assembly
4	LVDT core
5	LVDT
6	Dewar cap
7	Thermocouple connectors
8	Set screws
9	Thermocouple wires
10	Shaft assembly (lower)
11	Sample holder tube

Item	Description
12	Heater assembly
13	Dewar
14	Time-Temp. switch
15	Adjustable legs
16	Zero switch
17	Heater lead wire
18	Sample
19	Shaft assembly (upper)
20	Transducer Position control
21	Zero spring
22	Probe Position control
23	Upper Bearing guide

The series of experiments in the discussion were all run using a $0.025\ \text{in}^2$ probe and a 100g weight on the weight tray.

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