

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

(NASA-CR-161426) DEVELOPMENT OF ULTRAVIOLET
RIGIDIZABLE MATERIALS Final Report (Hughes
Aircraft Co.) 42 p HC A03/MF A01 CSCL 11G

NEO-22491

G3/27 Unclas
17762

FINAL REPORT

DEVELOPMENT OF ULTRAVIOLET RIGIDIZABLE MATERIALS

OCTOBER 1979

AEROSPACE GROUPS

HUGHES

HUGHES AIRCRAFT COMPANY
CULVER CITY, CALIFORNIA

HUGHES

HUGHES AIRCRAFT COMPANY

AEROSPACE GROUPS
CULVER CITY, CA 90230

DEVELOPMENT OF ULTRAVIOLET
RIGIDIZABLE MATERIALS

FINAL REPORT

OCTOBER 1979


Contract NAS 8-32895

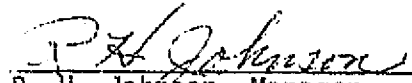
D. P. Salisbury

Advanced Technology Laboratory
Technology Support Division
Electro-Optical and Data Systems Group
Hughes Aircraft Company
Culver City, California 90230

Prepared for:

George C. Marshall Space Flight Center,
Marshall Space Flight Center, Alabama 35812


S. H. Goodman
Program Manager


R. H. Johnson, Manager
Materials Technology Department

ABSTRACT

A series of tests were performed to determine an optimum resin to be used as a UV rigidizable matrix in expandable - rigidizable space structures. The major portion of the tests were on commercially available resins including several types of polyesters, epoxies, epoxy-acrylics, an acrylic and a urethane. A polyester, produced by 3M Company's Solar Laboratory facility in Costa Mesa, California, was found the best from the standpoint of physical properties and ability to be "B" staged. Two Hughes Aircraft Company synthesized materials were also tested, but were not found to be superior to the Solar resin.

An optimum fabric for use with the preferred resin was not found in this program. However, the 15 ounce fabric from Solar Laboratories has the best combination of physical properties with respect to handling and processing characteristics.

Expansion techniques for tubular structures, "B" staging of the solar resin, and stowage techniques for up to 5 months were developed.

A one meter high tetrahedron preprototype structure was prepared to evaluate and demonstrate stowage, deployment, and rigidization techniques.

FOREWORD

This project was performed for the NASA Marshall Space Flight Center at Huntsville, Alabama. The Project Monitor was Dr. W. J. Patterson. The effort covered the period from May 1978 through September 1979.

The author would like to acknowledge the help of Mr. Joseph Biro and Mr. Don Gloor, at Hughes Aircraft Company, for their technical assistance in sample preparation and testing, and the help of Dr. Don Garwood of 3M-Company's Solar Laboratory facility for his invaluable help and sample procurement.

A special acknowledgement is due Mr. Seymour Schwartz, who, as program manager, guided this program throughout most of its term.

TABLE OF CONTENTS

1. ABSTRACT	1
2. FORWARD	2
3. TABLE OF CONTENTS	3
4. LIST OF TABLES	4
5. LIST OF FIGURES	5
6. INTRODUCTION	6
7. EXPERIMENTAL PROCEDURE	f
8. COMMERCIAL POLYMERS	11
9. CURING AGENTS	15
10. HUGHES' SYNTHESIZED MATERIALS	20
11. FABRIC INVESTIGATIONS	22
12. CHARACTERIZATION TESTS	26
13. STOWAGE INVESTIGATION	34
14. DEPLOYMENT TECHNIQUES	35
15. PREPROTOTYPE DEVELOPMENT	36
16. CONCLUSIONS	40
17. RECOMMENDATIONS	40

LIST OF TABLES

1. Ferro Ultraviolet Lamp Data	7
2. UV Rigidizable Materials Testing	12
3. Results of Initial Laminate Tests	13
4. Results of Aluminum Cup Tests	14
5. Vacuum Weight Loss Tests	16
6. Analytical Tests - Uncured Resin	17
7. Mechanical Properties Determinations	18
8. Curing Agents	19
9. Physical Properties of the Various Reinforcements Impregnated With Solar Resin	31
10. Physical Properties of Solar Resin Reinforced with 15 oz Solar Fabric	32
11. Compressive Strength Properties of Solar Resin	33
12. Comparison of Impregnated #15 and Solar Fabric Physical Properties ..	33
13. U.V. Exposure of 15 oz Solar Fabric System	33

LIST OF FIGURES

1. Spectral Energy Distribution-Mercury T-3 Lamp	8
2. Ferro UVFR-101 Lamp Output at 50 cms	9
3. Intensity vs. Distance of Ferro UVFR-101 Lamp	10
4. 10X Magnification of Solar Resin Fabric	24
5. 19X Magnification of Solar Resin Fabric	25
6. Sketch of Leno Fabric	26
7. Compression Testing	28
8. Tensile Testing	29
9. Torsion Testing	30
10. Tetrahedron Joints of Three Inches Height	37
11. Stowed Preprototype Configuration	38
12. Expanded and Rigidized Preprototype	39

INTRODUCTION

This project was concerned with the determination of an optimum ultraviolet catalyzed resin which could be used as the rigidizing matrix in stowable-expandable, composite structures for space applications. The desired polymer was to be one which could be easily impregnated into a fabric reinforcement, then "B" staged, so as to inhibit resin migration while the composite was in a stowed configuration. It was required that the final composite structure be capable of being stowed in a folded, rolled or compressed condition, and later be easily deployed by compressed gas, or mechanical means. Rigidization of the structure would then take place as a result of exposure to solar ultraviolet radiation in an earth orbit environment. Since deployment and rigidization in space would take a finite time, it was necessary that the resin used not incorporate any highly volatile reactive constituents, in order to preclude premature loss before rigidization was initiated or was complete.

The project was to concentrate on the investigation of commercially available resin systems. However, a small portion of the time was also to be spent on new resin synthesis, using, as a basis, work previously done at Hughes. While the principal objective of the project was the determination of the optimum UV curing system for use with a deployable structure, it was known that some effort would have to be expended to obtain an optimum fabric construction. This special fabric would have to be one which would combine minimum "shadowing" effect for tubular structures, and at the same time result in a high degree of orthotropism in the axial direction of the tube.

The last phase of the program involved the construction of a preprototype model. The purpose of the model was to demonstrate and study the stowage, deployment and joining techniques developed within this contract.

Experimental Procedure

U.V. Source

The UV source used for all the radiation tests was a Ferro Corporation ultraviolet lamp UVFR-101. This lamp, it should be noted, was specially produced by Ferro for cure of UV catalyzed resins. The lamp characteristics are shown in Table 1.

The spectral energy distribution of the lamp is shown in Figure 1. Figure 2 shows the lamp output per sq. cm. over the range from 250 to 380 nm. As shown, the output may be considered to be a fair average of solar radiation at air mass zero. Figure 3 shows the lamp intensity vs. distance. Curve #1 (in Figure 3) shows that at a distance of 60 in. the short wavelength intensity was approximately that of one sun. Accordingly the great majority of all the UV exposures were made using a lamp distance of 60 in.

Table 1. Ferro Ultraviolet Lamp Data - UVFR-101

Lamp Watts	1440	Arc Length, inches	24
Rated Life, Hours	750	Lamp Operating Volts	1200
Bulb Glass Type (Ozone Free)	Quartz	Ballast O.C. Volts	1450
Burning Position	Horiz.	Lamp Starting Current, Amps	2.20
Max. Length, inches	26-3/16	Lamp Operating Current, Amps	1.35
Leading - Watts per inch	60	Lumens	58,000

<u>Wavelength Band</u> <u>Nanometers</u>	<u>Principal Line</u>	<u>Radiant Energy - Watts</u>
Far U.V.		9.9
250-260	254	23.8
260-270	265	15.1
270-280	...	
Middle U.V.		14.5
280-290	280	27.3
290-300	296	33.6
300-310	302	41.2
310-320	313	
Near U.V.		4.1
320-330	...	7.5
330-340	...	1.7
340-350	...	1.7
350-360	...	69.6
360-370	365	1.7
370-380	...	3.4
380-390	...	
Visible		26.8
400-430	405	40.6
430-440	436	10.4
440-540	...	40.6
540-550	546	5.8
550-570	...	39.5
570-580	578	19.1
580-760		
Far U.V.		48.8
Middle U.V.		116.6
Near U.V.		89.7
Visible		182.8
<hr/>		
Total Radiated		437.9
<hr/>		

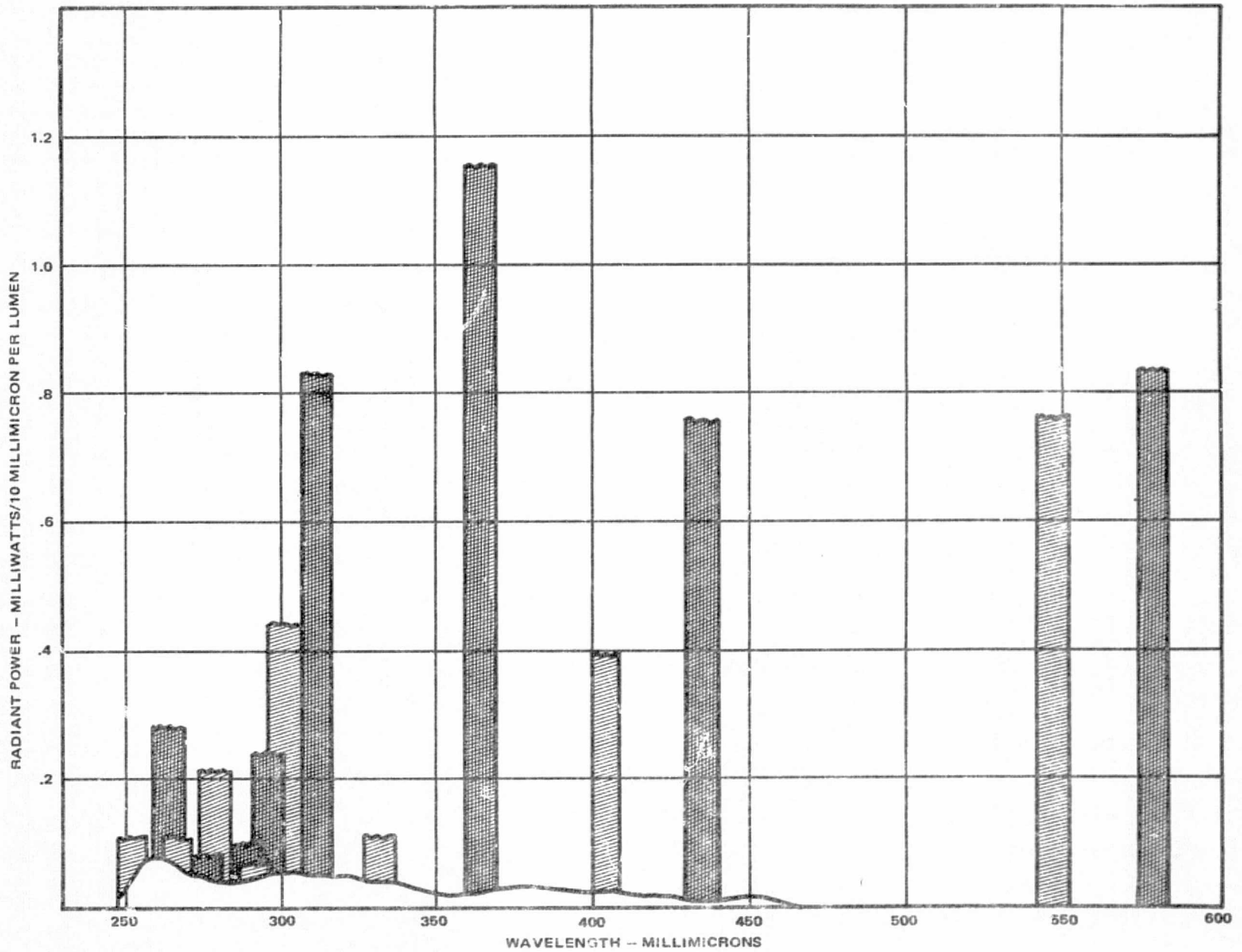


Figure 1. Spectral energy distribution Mercury T-3 Lamps.

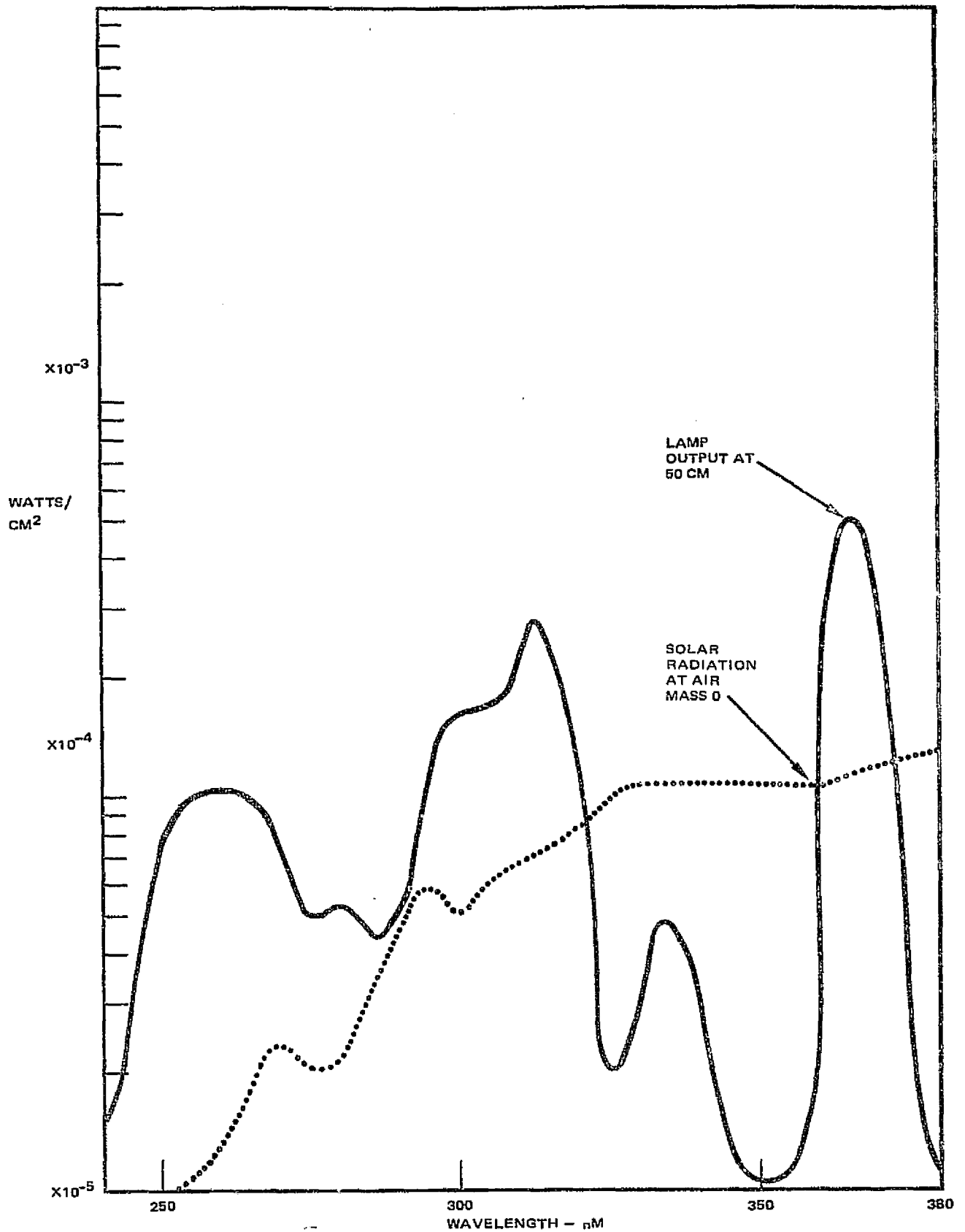


Figure 2. Ferro UVFR-101 Lamp Output at 50 cms (Mercury Vapor Lamp - Quartz housing)

(10)

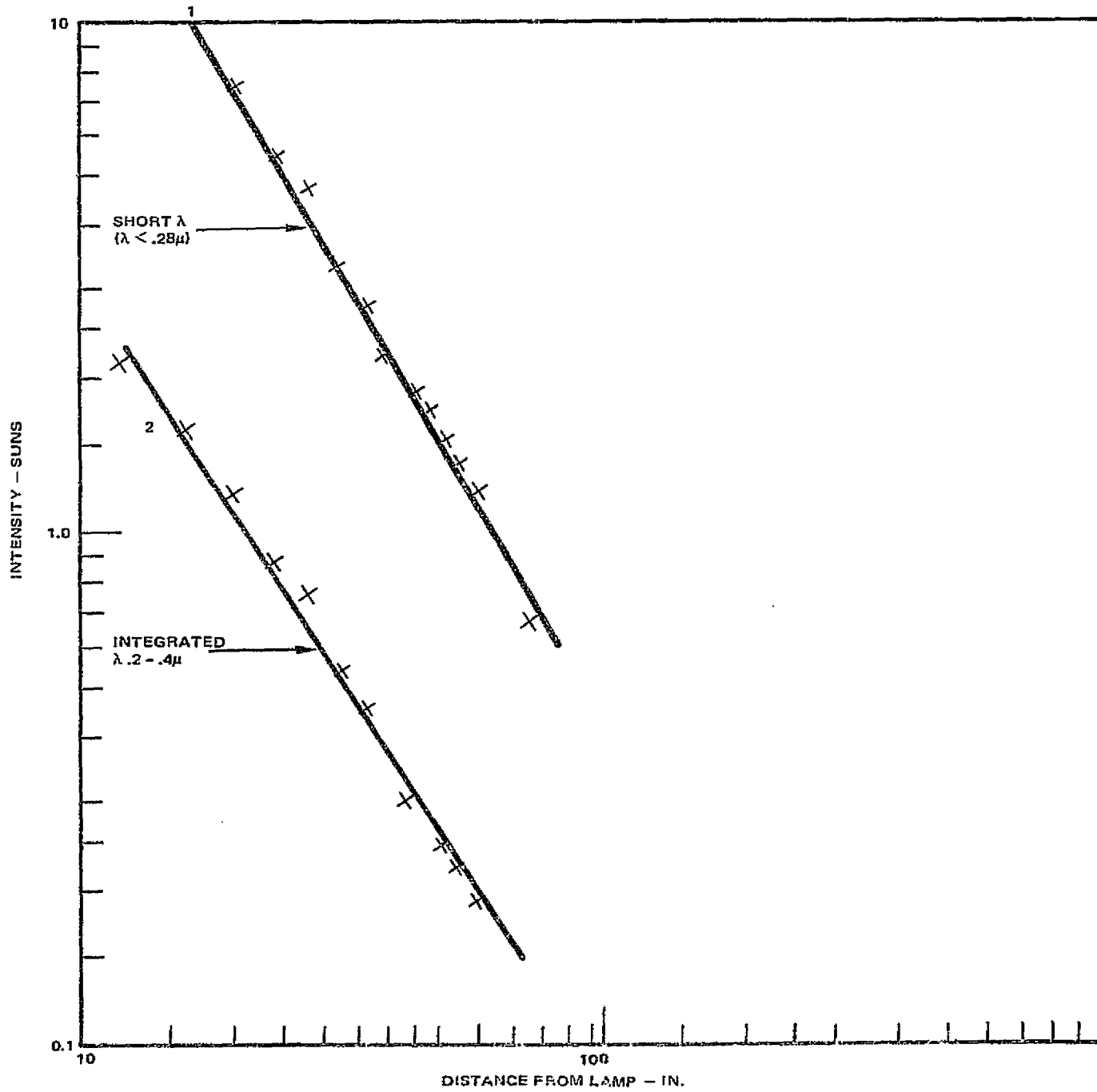


Figure 3. Intensity vs. distance of Ferio U.V. Lamp UV FR-101.

Commercial Polymers

An investigation indicated that there were five main classes of thermosetting polymers currently being cured by UV. These were: (a) polyesters, (b) epoxies, (c) acrylics, (d) epoxy-acrylics, and (e) urethanes. The commercially available materials shown in Table 2 were procured. Most of the resins were internally catalyzed, as furnished. Those which were not, were catalyzed with various commercially available catalysts.

The first tests, (with each resin except the Silmar S-389A solid alkyd resin), were to saturate two inch diameter discs of 181 glass fabric and determine if each would set up in a one hour exposure under the UV lamp. All samples, either internally catalyzed or catalyzed with 2% of benzoin derivative, did cure, thus indicating that each was, or could be, UV catalyzed.

A second series of tests were made with most of the resins to determine thick specimen capabilities. Four and eight ply 181 fabric laminates were used. These specimens were made 1-1/4 inches by 5-1/2 inches so they could, after rigidization, be used for flexural strength determinations. The fabric plies were brush impregnated with each resin to an approximate resin content of 50 percent. A 1-1/2 mil polyethylene film was used as a parting agent on top and on the bottom of each laminate. All the laminates, one 4 ply and one 8 ply of each type, were exposed at atmospheric pressure to UV for fifteen minutes, then removed and tested for either Barcol or Shore D hardness. A second fifteen minute exposure was again made to determine if any difference in hardness occurred.

In addition to testing the laminates, 10 gm of each resin were placed in an aluminum cup and exposed to the UV lamp. The 10 gm samples were approximately 1/8 inch thick in each case.

Table 3 shows the results of the laminate tests, and Table 4 the results of the cup tests. It should be noted that the Barcol results vary widely, in the same specimen, due, it is believed, to the fact that the samples were wrinkled from the heat generated during exposure thus preventing full pressure from being applied by the instrument. The values obtained, however, are enough to be very representative, indicating the materials which cured rapidly and those which cured slowly, or not at all, during the exposure time. The Shore D hardness tests likewise are only indicative and the values also vary widely from area to area on the specimen. In both cases, at least five readings were taken on each side of the specimen. The Shore D readings, while only meaningful on the softer specimens, nevertheless are in agreement with the Barcol readings, which only showed readings for the harder, more fully cured materials.

TABLE 2. UV RIGIDIZABLE MATERIALS TESTING

Material Designation	Source	Chemical Type	Catalyst
ATLAC 580-0SL	ICI Americas Inc.	Vinylmaleate-urethane modified polyester/ polystyrene crosslinker	Internal
ATLAC 4010L	ICI Americas Inc.	Bisphenol A-fumaric acid polyester/poly- styrene crosslinker	Internal
ATLAC 382-05L	ICI Americas Inc.	Bisphenol A-fumaric acid polyester/poly- styrene crosslinker	Internal
Ferropreg UVR	Ferro Composites	Chlorinated-phthalic- maleic polyester/ diallyl phthalate crosslinker	Internal
CBJ-62 3527A	Ferro Composites	Chlorinated-phthalic- maleic-polyester/ diallyl phthalate crosslinker (contain- ing acetone)	Internal
S-389-A	Silmar Div. of Vistron Corp.	Isophthalic-maleic polyester (alkyd por- tion only)	Benzoin Ether
Solar Resin (LR-6482)	3M Co-Solar Labs	Isophthalic-maleic polyester/vinyl toluene crosslinker	Internal
UVE 1001	General Elec. Co.	Epoxy, with no vinyl unsaturation. (Cationic polymerization).	Internal
Epocryl 370	Shell Chem. Co.	Epoxy	Benzoin or derivative
Reactomer 110	Thiokol Chem. Div.	Acrylic	Benzoin Ether
Lee Seal	Lee Pharmaceuticals	Epoxy-acrylic hybrid	Internal
XA2464	3M Company	Epoxy-acrylic hybrid	Internal
XA2466	3M Company	Epoxy-acrylic hybrid	Internal
Uvithane 788	Thiokol Chem. Div.	Urethane	Benzoin de- rivative

TABLE 3
RESULTS OF INITIAL LAMINATE TESTS

Material	Exposure Time, Min.	Barcol Readings				Shore D Readings				Remarks
		4 Ply Samples		8 Ply Samples		4 Ply Samples		8 Ply Samples		
		Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	
Lee Seal	15	25-55	45-55	25-35	20-30	80	80	80	80	
Lee Seal	30	25-55	45-55	25-35	20-30	85	90	80	80	
Atlac 580-05L	15	45-58	0	45-55	0	80	80	50	60	
Atlac 580-05L	15	45-60	30-55	45-55	25-40	85	85	65	75	
Atlac 4010L	15	45-50	30-45	50-55	15-25	65	75	85	75	
Atlac 4010L	30	45-50	30-45	45-60	35-45	70	80	80	75	
Atlac 382-05L	15	40-50	40-55	50-55	20-45	75	80	80	65	
Atlac 382-05L	30	40-50	40-55	50-55	20-45	85	70	75	80	
Ferro CBJ-62	15	0	0	0	0	50	50	60	30	Sticky & delam.
Ferro CBJ-62	30	0	0	0	0	65	60	60	50	Sticky & delam.
Ferropreg UVR	15	0	0	0	0	70	65	70	40	
Ferropreg UVR	30	0	0	0	0	70	70	70	55	
3M XA2464	15	0	0	0	0	75	65	70	30	
3M XA2464	30	12-20	0	10-15	0	75	65	70	35	
3M XA2466	15	0	0	0	0	0	0	0	0	Soft & sticky
3M XA2466	30	0	0	0	0	0	0	0	0	Soft & sticky

(13)

TABLE 4
RESULTS OF ALUMINUM CUP TESTS

Material	Exposure Time, Min.	Barcol Readings		Remarks
		Top	Bottom	
Lee Seal	15	40	30	Top slightly sticky. Air inhibition (?).
Lee Seal	30	45	38	
Atlac 580-05L	15	0	0	No air inhibition noted on top.
Atlac 580-05L	30	30	30	
Atlac 4010L	15	9-10	0	No air inhibition noted on top.
Atlac 4010L	30	12	0	
Atlac 382-05L	15	22-27	15-20	Possibly degraded from too rapid exotherm during 30 minute exposure.
Atlac 382-05L	30	15-22	5-10	
Ferro CBJ-62	15	0	0	Soft; no cure. Acetone still in resin.
Ferro CBJ-62	30	0	0	
3M XA2464	15	0	0	Soft, slight cure on top.
3M XA2464	30	0	0	
3M XA2466	15	0	0	Soft, slight cure on top.
3M XA2466	30	0	0	

(14)

Another series of tests were made to determine the effect of a vacuum on each resin formulation. Approximately 10 gm of each resin, in an aluminum cup, were placed in a vacuum desiccator and exposed to a vacuum for fifteen and thirty minutes. The weights before and after exposure to vacuum were determined, thus giving an estimate of the crosslinker weight loss. Table 5 shows the results.

From the results of the initial resin evaluations, a series of analytical tests were made on the polymers considered the most promising. The tests made included viscosity, specific gravity, uncured and cured colors, vacuum weight loss and curing characteristics after 30 minutes exposure to vacuum. Table 6 shows the results of these tests.

As a result of the initial screening tests, the 3M resin XA-2464, the Ferro CBJ-62, the General Electric Co. UVE-1001, and Thiokol Uvithane 788 were all dropped from further investigation since they did not harden sufficiently. The Thiokol Reactomer 110 was also dropped since it was of such a low viscosity as to make it very difficult to obtain adequate resin content in the composite sample. Attempts to lower the viscosity of the Uvithane 788, and at the same time raise its cured hardness were tried in several formulations, but no success was obtained.

Additional characterization tests were made on the Lee-Seal and the Epocryl 370 resins to determine the thermal characteristics and to determine if a complete cure had been obtained. The tests made included Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and a Rheovibron dynamic mechanical analysis. The TGA tests corroborated the simpler Barcol and Shore hardness tests; however, the DSC and Rheovibron tests were inconclusive. Therefore, these tests were discontinued.

Flexural property determinations at ambient and elevated temperature were made on composite samples using the three most promising resins; Epocryl 370, Solar Resin and XA-2466. In preparing the composites, which utilized both 181 style glass fabric and a special open weave glass tape, an attempt was made to obtain the same resin content in all the samples. Unfortunately, this was not accomplished because of the wide diversity in viscosities. The Epocryl 370 and the Solar resin was adjusted to almost the same viscosity with acetone, so that impregnation was done under somewhat the same conditions. However, since the XA-2466 has a very low viscosity as received, it was not possible to increase its viscosity to match the other two. Lowering the viscosity of the Epocryl 370 and the Solar resin was judged impractical. Table 7 shows the results of the flexural testing.

Curing Agents

An investigation was made to determine the optimum commercially available curing agent which might be used with the polyesters and/or other unsaturated resins. The materials procured are shown in Table 8.

The liquids were found easiest to incorporate into the resins, and of the liquids, Vicure 10 was found to give the best results, when used at a concentration of 2% by weight.

TABLE 5
VACUUM WEIGHT LOSS TESTS.

Material	Weights, Gms			Loss, %	
	Original	15 Min. Exposure	30 Min. Exposure	15 Min. Exposure	30 Min. Exposure
Lee Seal	9.8	9.7	9.7	1.02	1.02
Atlac 580-05L	9.3	9.0	8.6	3.2	7.5
Atlac 4010L	8.7	8.4	8.1	3.4	6.9
Atlac 382-05L	9.1	8.9	8.6	2.2	5.5
Ferro CBJ-62*	9.3	7.9	7.5	15.0	19.4
Ferropreg UVR	4.0	4.0	4.0	0	0
3M XA2464	9.9	10.0**	10.1**	+1.0	+2.0
3M XA2466	9.4	9.6**	9.6**	+2.0	+2.0

* Contains acetone.

** Unexplained increase in weight.

TABLE 6 - ANALYTICAL TESTS - UNCURED RESIN

Resin	Type	Source	Viscosity ^d c.p.s.	Sp.Gr.	Color		Weight Loss, % 30 min. Vacuum	Gel Time and Qual. Hardness Changes, Min. Radiation ^b				
					Initial	Final		gel	15	30	60	240
580-05L	Polyester ^a	ICI America	430	---			6.0	10 min gel	gelled	hard	hard	hard
XA-2464	Epoxy	3M Company	(1674) 370	1.15	amber	yellow	0.0	2 min skin only	skin	skin	skin	hard skin
XA-2466	Epoxy	3M Company	(2209) 1450	1.18	amber	lt brown	0.0	12 min skin only	skin	skin	skin	hard
Epicryl 370	Acrylate- bis phenol- A-epoxy	Shell Chemical	(900,000) 1,530,000	1.20	amber	yellow	0.7	3 min gelled	hard	hard	hard	hard
UVE 1001	Epoxy	General Electric	---		amber	yellow	0.98	4 min skin	skin	hard skin	hard skin	hard
Solar LR 6482	Polyester	Solar Labs	58,000		clear	yellowish	--	3-min gelled	hard	hard	hard	hard
RC-110	Acrylic	Thiokol Chem.	4.5	1.07	clear	yellow	--	5-min gel	hard	hard	hard	hard
Lee-Seal	Epoxy- acrylic	Lee Pharm.	148	--	clear	light yellow	0.0	4-min hard	hard	hard	hard	hard ^c

- a. Styrene cross-linking agent.
 b. Behavior of samples after 30 minutes in vacuum - irradiated in air.
 c. Small amount of liquid on top - believed due to air inhibition.
 d. Values in parentheses are vendor's data. Other values shown were determined at HAC with Brookfield LVT & RVF viscometers.

TABLE 7. MECHANICAL PROPERTIES DETERMINATIONS

Resin	Fabric	No. Plies	Barcol Hard.	Av. Breaking Load, lb.		Load Decrease % at 160°F	Av. Flexural Strength, psi x 10 ³		Flex Str. Decrease % at 160°F	Av. Flexural Modulus, psi x 10 ⁶		Modulus Decrease % at 160°F	Average Thickness In.	Av. Resin Content %
				RT	160°F		RT	160°F		RT	160°F			
Epocryl Solar Lab XA-2466	181-glass	4	60	64	55	-14	74	62	-16	3.9	2.9	-26	.0361	33.1
	" "	"	52-58	79	71	-10	65	57	-12	1.4	1.9	+35	.0438	39.1
	" "	"	62-68	35	26	-26	59	42	-29	4.1	2.6	-27	.0302	25.2
Epocryl Solar Lab XA-2466	181-glass	8	60-61	241	138	-43	62	43	-31	2.3	2.2	-4	.0753	34.7
	" "	"	60-62	247	224	-9	65	56	-14	2.4	2.0	-17	.0780	35.7
	" "	"	62-68	163	69	-58	68	31	-54	3.5	2.1	-40	.0606	24.9
Epocryl Solar Lab XA-2466	Solar-glas	1	-	40	23	-42	18.2	9.4	-48	.77	.31	-60	.0551	38.6
	" "	"	-	(37)**	(24)**	(-35)	(19.6)*	(11.3)*	(-42)	(.80)*	(.40)*	(-50)*	.0566	40.5
	" "	"	-	37	37	0	15.6	15.1	-3	.77	.56	-27	.0566	40.5
Solar Lab XA-2466	" "	"	-	(45)**	(45)**	(-24)	(19.8)*	(19.8)*	(0)	(.78)**	(.73)**	(-6)**	.0483	29.6
	" "	"	-	32	13.2	-58	18.8	6.9	-63	3.7	1.3	-65	.0483	29.6

* These samples were made with 2% Vicure 10 and 3% Cab-O-Sil.

** These samples were "B" staged 3 min. @ 160° prior to UV cure.

Table 8. Curing Agents

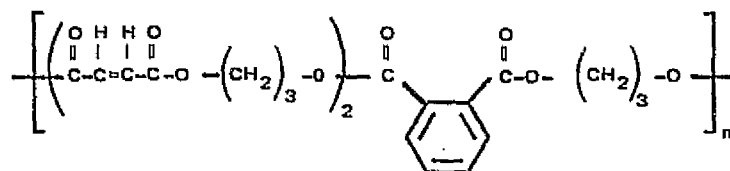
Generic Name	Trade Designation	Form	Source
Benzoin	Vicure 10	Powder	Ram Chemical Co.
Benzoin ether		Liquid	Stauffer Chem. Co.
Benzoin ethyl ether	Trigonal 14	Powder	Crescent Chem. Co.
Butylpropylbenzoin ether		Yellow Liquid	Noury Chemical Co.
Benzophenone/ Michler's Ketone		Powder	Biddle-Sawyer
Benzophenone amine	Ultracure I-100	Flakes	UOP, Inc.
2-chlorothioxanthone		Yellow Powder	Sherwin Williams Co.

Hughes' Synthesized Materials

A short period of time was spent on the syntheses of two classes of resins believed amenable to UV rigidization. One class consisted of polyester resins, using phenylglyoxylic acid (PGA) as the photo sensitizing agent. The second resin class was a photoactive polyimide.

Polyester Resins

Two types of polyester resins were synthesized for use in this investigation. One type was derived from maleic anhydride (98 g, 1 mole), phthalic anhydride (74 g, 1/2 mole), and 1,3-propanediol (115 g, 1.5 moles). Polymerizations were all catalyzed by H₂SO₄ and ultimately neutralized by NH₄OH. The molecular weight of one of the four batches made (Lot 4) was 2,013. Its molecular structure is shown below:



The second type of polyester synthesized was homologous with the first, but was derived from ethylene glycol rather than propylene glycol. Its molecular weight by Vapor Phase Osmometry (VPO) was 2,778, thus indicating a degree of polymerization of 5.83.

Each of the five resins synthesized was formulated with phenylglyoxylic acid in various proportions. Also many of the formulations also contained diallyl phthalate. The resin to DAP ratios generally were 1 eq: 1 eq, but some were 1 eq: 2 eq.

Blended compositions were all exposed to 1 solar equivalent of UV radiation for periods of time ranging from two hours to twenty-four hours, but seventeen to twenty-one hours were generally used. In virtually all cases the compositions polymerized, but often it was primarily on the surface. Polymerized compositions ranged from crumbly, to tacky underneath, to elastomeric, to hard and firm. The best two compositions were coated onto strips of 181 glass fabric, stacked into four ply laminates, and exposed to 1 sun for twenty-four hours. Both laminates rigidized, but with hardnesses too low to be measured with the Barcol instrument. The compositions were:

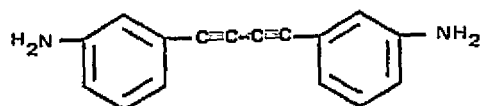
Resin #4 or 5	DAP	PGA
546 g (0.02 eq.)	2.45 g (0.02 eq.)	3.00 g (0.02 eq.)

Also studied was a solid, unstyrenated polyester obtained from the Sylmar Division of the Vistron Corporation. This material was a phthalic acid, maleic anhydride, propylene glycol based resin. Formulations were prepared with and without diallylphthalate, but all contained phenylglyoxylic acid. Solar exposures (1 sun) were carried out for two, seventeen, or twenty-one hours. The latter exposure period gave the best results with surface hardnesses of up to 60 (Shore A). Bottom layers were never completely hard.

It is evident from these studies that phenylglyoxylic acid can be used as a photosensitizing agent; however, difficulty is encountered in getting deep penetration. The reason for this stems largely from the fact that PGA requires 1 quanta of energy per molecule and the copolymerization thus is not a free radical chain propagation process.

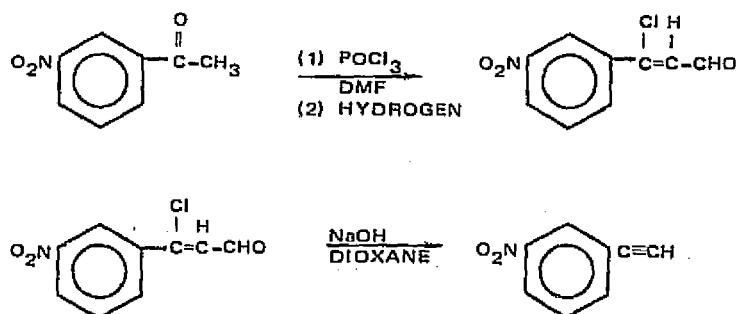
Polyimide Resin

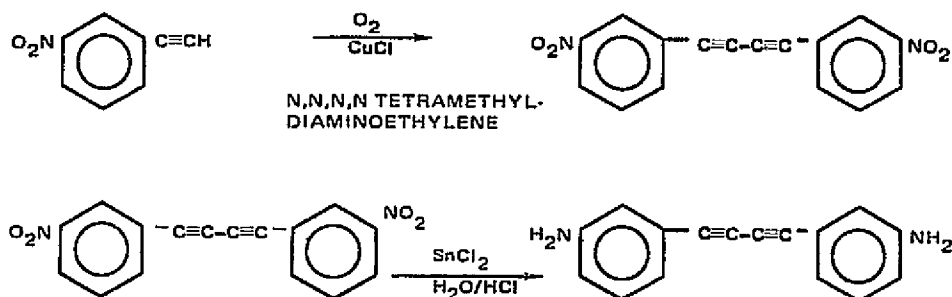
Investigation of the UV catalyzed polyimide was based on the knowledge that the diacetylene moiety ($-\text{C}\equiv\text{C} - \text{C}\equiv\text{C} -$) has been reported to be photosensitive (A.S. Hay, D. A. Bolton, K. R. Leima and R. F. Clark, Polymer Letters 8, 97-99 1970). We thus proposed to introduce this moiety into a polymer chain via the compound



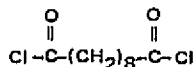
since the diamino derivative can be easily placed into a number of polymeric chains, for example polyamides and polyimides. The synthesis of an approximately 80 gram batch of this compound was made and the product was purified by recrystallization.

The following synthetic route was employed:





Upon further consideration of this structure, it was realized that if prepolymerized excessively, this would be an intractable oligomer which could not be impregnated into a fabric reinforcement. This consideration led to an analysis of those chemical structural features which would furnish a useful oligomer. The conclusion was that the backbone had to have more aliphatic carbon chains in order to have an impregnatable material. To prove the butadiyne cure concept, a simple polyamide rather than a polyimide was prepared by the reaction of sebacyl chloride



with the butadiyne in equal molar quantities. The resultant material was a tan powder moderately soluble in hot DMF. On exposure to UV, a thin film of the brown powder turned black in 10-20 minutes and, more importantly, was no longer as soluble. This indicated that the UV had definitely initiated cross-linking in the molecule.

We have thus demonstrated that the conceptual idea of causing photoinitiated cross-linking of polymeric moieties containing an acetylenic leakage is viable. The significance of this reaction is that the use of the butadiyne as a photosensitive cross-linking agent is unique and may presage an entirely new field of photocatalysis for polymers. Unfortunately, full exploitation of this system to result in an optimum product was beyond the scope of this project and further activity, was therefore, suspended.

Fabric Investigations

Braided Fabrics

The first samples were loose braided glass fiber tubing supplied by the Santa Fe Textile Company. It was found that while the tubing could be easily impregnated and then expanded by use of internal polyethylene tubing, it was not possible to uniformly cure the tube, since sufficient radiation

did not penetrate to the "far" surface of the tube. Thus, unless the structure was rotated during cure, braided tubing could not be used.

Solar Fabric, 15 Ounce

Samples were obtained from Solar Laboratories of a very open weave glass fiber 4-1/4 in. wide tape specially woven to be used with UV rigidizable resins. This material, shown in Figure 4 at a 10x magnification, had openings approximately 0.12 in. x 0.22 in. Expanded hand sewn tubes made with this fabric very satisfactorily cured throughout all surfaces without rotation, when irradiated for eight hours. This supported the premise to use open weave fabric in order to eliminate the shadowing effect.

The Solar fabric proved the efficiency of the open weave construction, but did not appear to be the optimum fabric because the axial fibers were not continuous, as shown in Figure 5 at 19x magnification. A close inspection of the fabric reveals that each axial bundle is composed of 9 individual fibers. The fibers are oriented so that each bundle has 3 pure axial fibers with 2 sets of two fibers shared equally with the neighboring bundles and giving transverse support. Two fibers are used to tie the axial fibers with the support fibers. (For future reference, fiber bundles will be designated with 4 numbers as follows; the first states the number of support fibers on the left, the second states the number of axial fibers, the third is the number of right supporting fibers and the fourth the number of fibers used to tie the bundle. Therefore, the Solar fabric tube would be designated as 2-3-2-2.)

Proceeding on the premise that for tubular constructions a higher proportion of axial fibers to transverse fibers would yield higher strength-to-weight ratio in the axial direction, a search was made to find such a fabric.

Fabrics With a High Content of Axial Fibers

In an effort to obtain an optimum material, Dr. Thomas Edman of the Philadelphia College of Textiles was contacted. He was asked if he could produce an open weave fabric having a construction of 1-3-1-1, 1-5-1-1 or 1-7-1-1.

Dr. Edman, who was the developer of the original open weave Solar fabric, stated that he could design an open weave fabric with a much higher percentage of axial fibers than transverse fibers. To do this, Dr. Edman eventually had to make 15 variations with the last being the only one judged suitable for impregnation. Type #15 was supplied as a glass fiber tape and non-seamed tubing. Unfortunately, in the fabrication technique used by Dr. Edman, the axial fibers were not straight, but had a number of waves, giving each axial member a slightly corrugated appearance. Thus, in compression, failure would occur at a lower load than would normally be expected. In preparing the flat and the tubular samples an attempt was made to hold the impregnated samples under tension during cure. This helped somewhat in straightening the axial fibers, but unfortunately did not result in completely straight axial fibers.

After the first attempts by Dr. Edman appeared unsatisfactory, a small contract

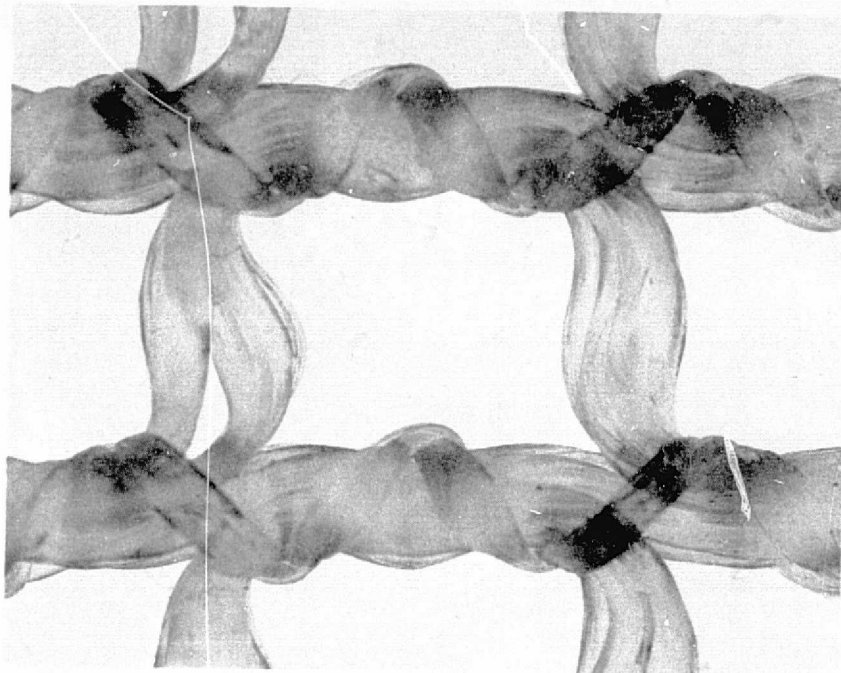


Figure 4, 10X Magnification of Solar Resin Fabric

ORIGINAL PAGE IS
OF POOR QUALITY

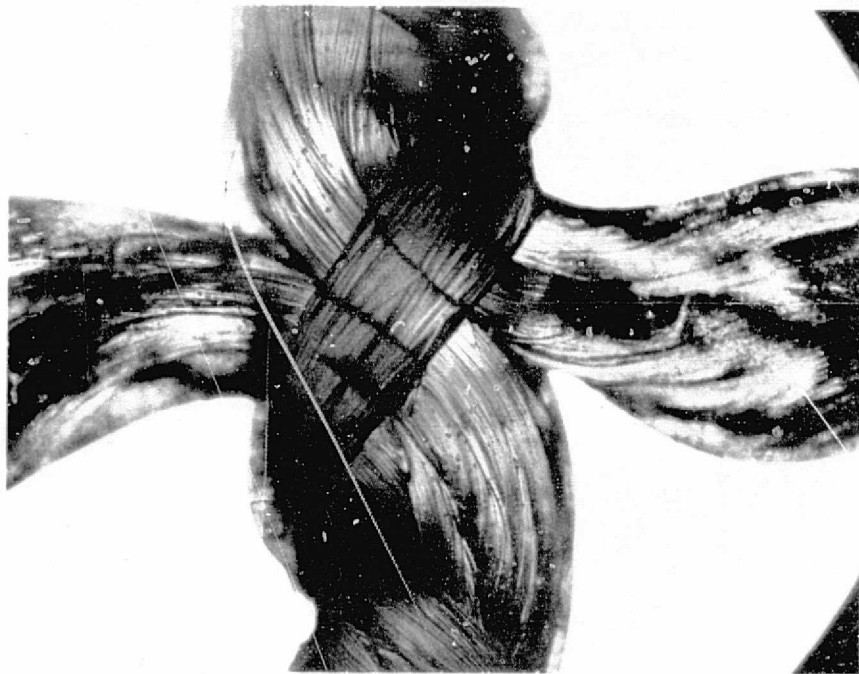


Figure 5. 19X Magnification of Solar Fabric Resin

was awarded to Textile Products of Stanton, CA to produce several types of leno weave fabrics. These types of fabric tapes were made, all 4-1/4 inches wide. Figure 6 is a sketch of the leno weave illustrating the single fiber strand used to wrap the axial fibers. Therefore, the nomenclature for a leno fabric with 8 axial fibers per bundle would be 0-8-0-1.

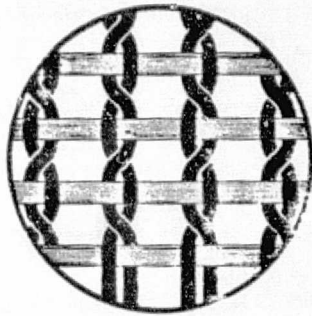


Figure 6. Sketch of Leno Weave

While these fabrics were not producible in the form of tubes, their production was considered valuable since, if they could be satisfactorily impregnated, they could be used to demonstrate the ultimate in axial strength-to-weight ratios.

Samples of several other glass fiber fabrics, with higher percentages of axial fibers to transverse, were also obtained from Solar Laboratories. These materials were, like the original Solar fabric, in the form of tape, in this case 2 in. wide. The best of these, Solar designation K-28, was impregnated as a flat tape, and as a hand sewn tube. Samples of machine sewn K-28 tubing were also made. These tubes were not satisfactory because of twisting. The twisting is a result of inadequate support in the transverse direction due to wider spacing of the transverse fibers and excessive loads brought on by additional axial fibers.

A few tests were also made to determine if graphite or Kevlar fabrics could be used with the UV system. Even very thin fabrics failed to cure completely on the "under" side of each fabric, indicating that in neither case did the UV penetrate completely.

Characterization Tests

The various fabrics described above were impregnated with the Solar resin, to resin contents ranging from 25 to 40 percent by weight. In all cases the fabrics were impregnated by immersing the fabrics in the resin from a minimum of 15 minutes to overnight, after which the composite was passed several times through a set of rubber rollers, mounted wringer style. This had the effect of removing most of the surface resin and at the same time homogeneously distributing the resin throughout the fabric. All samples were then irradiated for eight hours without rotation. The tubular samples were expanded by means of a pressurized polyethylene tube during irradiation.

Flexural strength and modulus samples were made by cutting specimens to sizes as indicated in ASTM D790, Method 1. (Size variations were in accordance with thickness values as given in ASTM D790.)

As expected, the 0-8-0-1 fabric from Textile Products exhibited the best flexural strength when compared to the Solar fabric and Dr. Edman's #15 fabric, hereafter referred to as E#15. However, as stated earlier, the Textile Products fabric was not suitable and therefore the candidates were reduced to the Solar fabric and the E#15 fabric. The fabric from Dr. Edman was studied in depth because of the higher axial-to-transverse fiber ratio and Dr. Edman's early but limited success.

Tubular samples of the E#15 fabric design were made in four foot lengths and cured while under a tensile load. This load was used to remove corrugations in the axial fibers caused by the folding of the fabric for shipment. It is important to note that the Solar fabric does not corrugate when folded. The corrugations are therefore thought to be caused by the lack of rigid transverse fibers. As a result of the corrugations, it was decided that the Euler buckling tests, originally proposed, would not give satisfactory results. Accordingly, the tubes were cut up (at the fold marks) and the short sections were used for compression, tensile and torsion tests. (Figures 7, 8 and 9.) The results are shown in Table 9. The results of similar testing for the Solar fabric reinforced system are presented in Table 10 & 11. Comparison of the specific flexural strengths for the Solar and E#15 fabric is presented in Table 12 and shows that both are essentially equivalent. The Solar fabric had another advantage in that it was easier to process and handle during impregnation.

Long term UV exposure data are presented in Table 13. These data indicate that 155 days of exposure to UV tends to toughen the composite since a slight increase in strength is accompanied by a significant drop in modulus. It is surmised that the UV radiation causes chain scission in the polyester matrix and the resultant short chain segments act as plasticizers which reduce the overall modulus values.

The project monitor requested that we determine the flexural strength of an expanded and rigidized tube section. The flexural strength of a 2.5 foot by 4" circumference Solar fabric tube impregnated with Solar resin was determined. As no known test method could be found for an open weave tubular material, a modified version of ASTM C-158, Method B, flexure testing of glass, was used as a close approximation. The test involves four point loading with 15 inches separating the lower points and 5 inches separating the upper points. The flexural load obtained was 72.5 pounds.

As a consequence of all the characterization studies of fabric and resin, it was decided to select the Solar fabric and Solar resin as the system to be used in the preprototype modeling study.

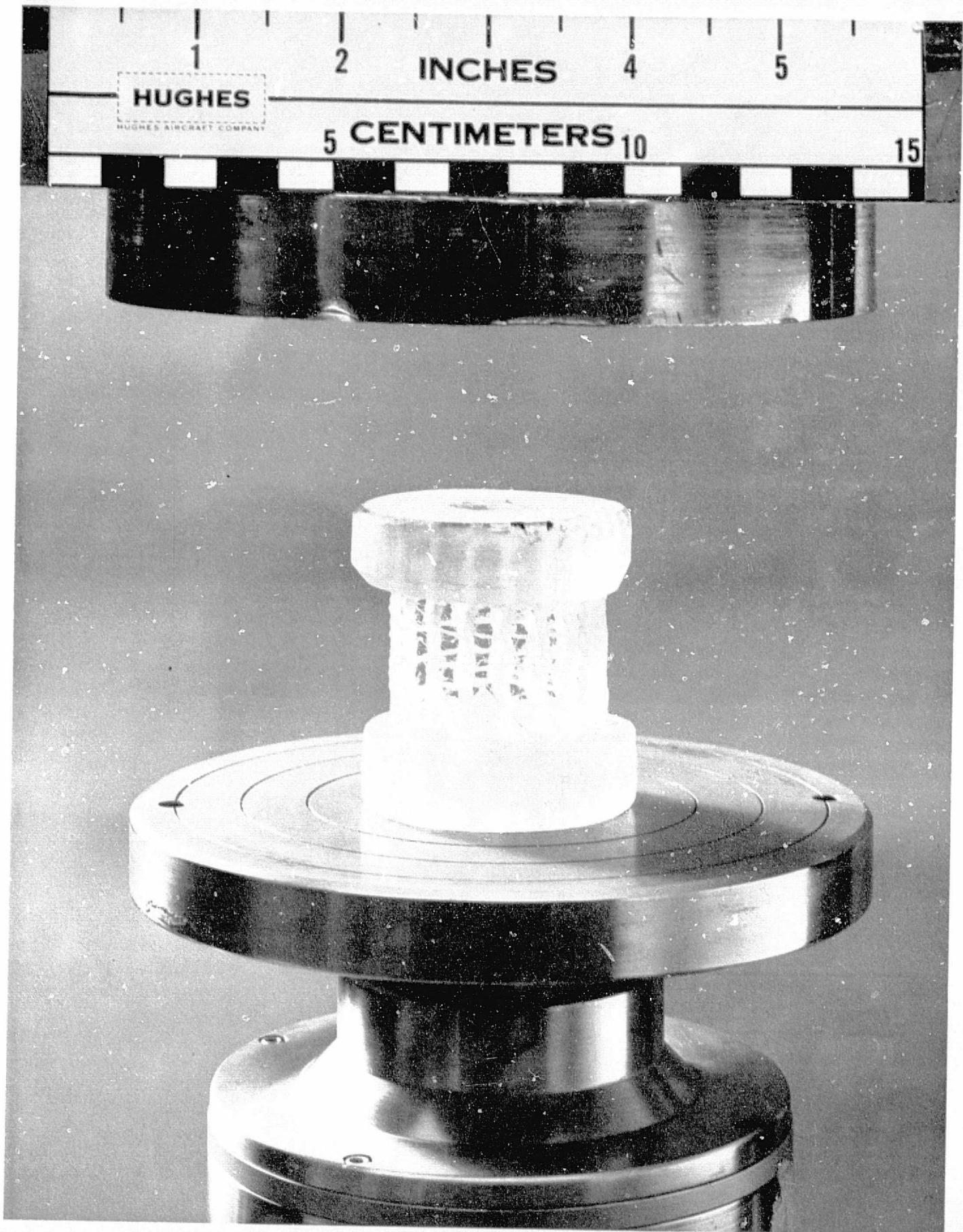


Figure 7. Compression Testing

ORIGINAL PAGE IS
OF POOR QUALITY

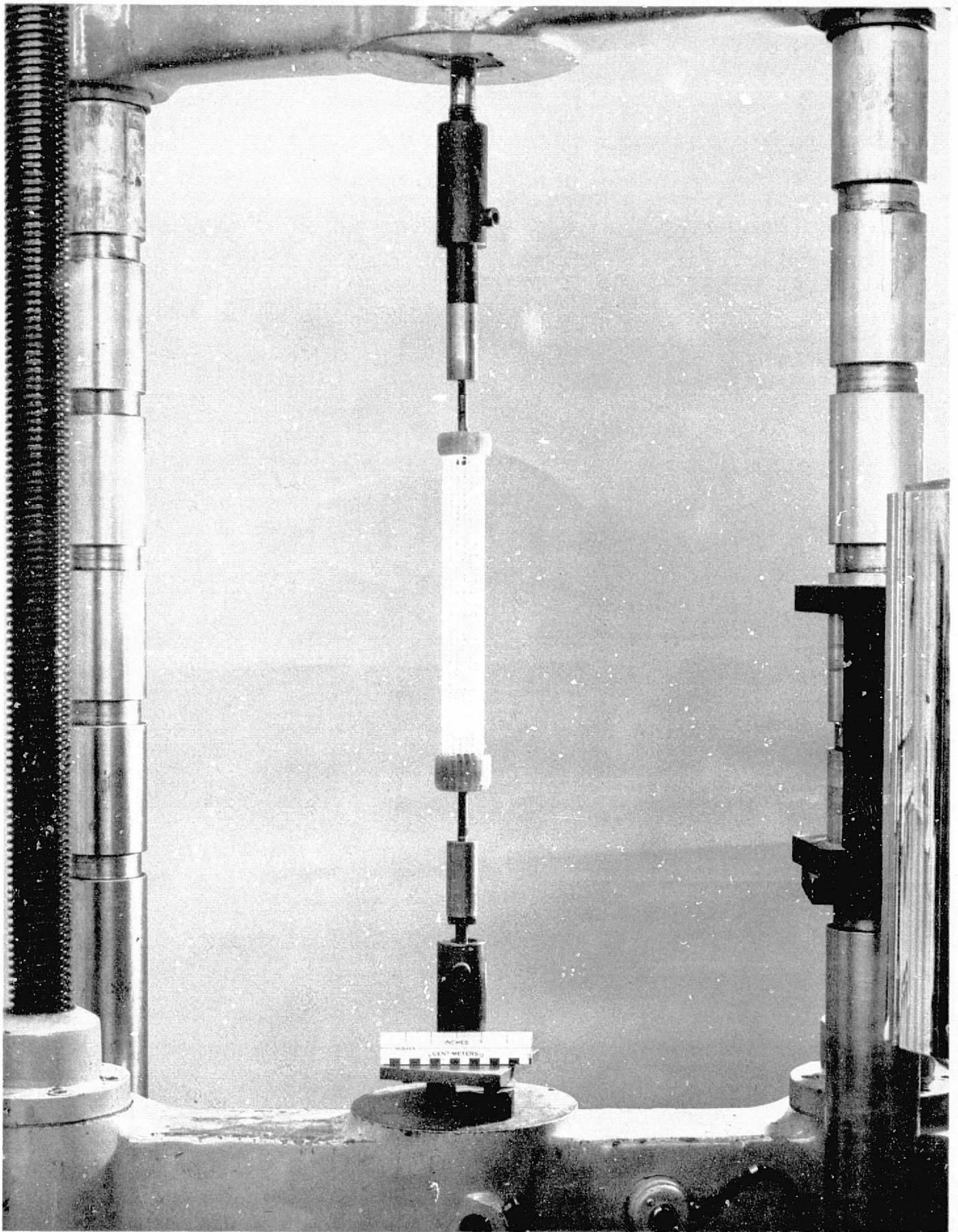


Figure 8. Tensile Testing

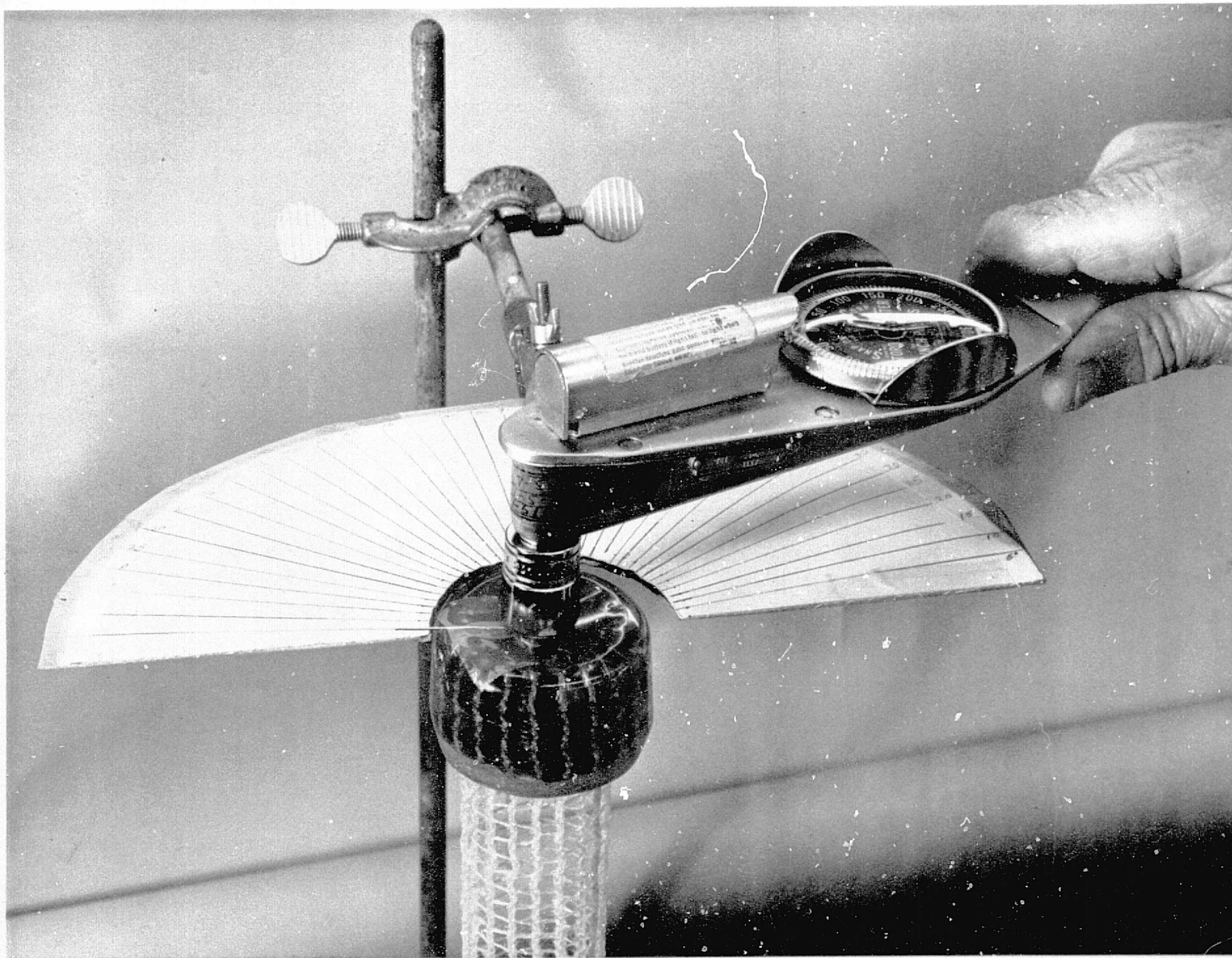


Figure 9. Torsion Test

(30)

ORIGINAL PAGE IS
OF POOR
QUALITY

TABLE 9

PHYSICAL PROPERTIES OF THE VARIOUS REINFORCEMENTS IMPREGNATED WITH SOLAR RESIN

Sample No.	Sample Type	Reinforcement		Impregnated		Material Resin Content, %	Ultimate Load,	Flexural Strength, psi x 10 ³	Flexural Modulus, psi x 10 ³	Specific Strength	
		Type	Weight, gm/yd ²	Weight, gm/yd ²	Thick-ness, in.					Ult. Load, wt./yd ²	Flex. St. wt./yd ²
108	Flat	0-4-0-1	139.1	232.4	.025	40.1	1.91	4.6	192	.0082	19.79
109	Flat	0-6-0-1	159.2	261.5	.025	39.1	2.31	6.0	317	.0088	22.94
110	Flat	0-8-0-1	197.7	311.1	.018	36.5	2.87	14.0	921	.0092	45.00
118	Flat	Solar K-28	360.2	627.3	.052	42.6	6.69	3.7	211	.011	5.84
121	Flat	1-5-1-1 (E#15)	490	774	.075	36.7	18.28	4.7	232	.023	6.07
124	Flat	1-5-1-1 (E#14)	483	748	.073	35.4	19.48	4.97	263	.026	6.64
125	Flat	1-5-1-1 (E#16)	736	1120	.096	34.3	28.17	7.06	338	.025	6.30
126	Flat	1-5-1-1 (E#17)	877	1422	.106	38.3	36.0	7.1	269	.025	4.99
122	Round 4" circumference 1" long	1-5-1-1 (E#15)	490	727	.075	32.6		Load at Failure Compression, lbs 338			
123		1-5-1-1 (E#15)	490	657	.075	25.4					
122	Round 4" circumference 12" long	1-5-1-1 (E#15)	490	727	.075	32.6		Load at Failure Tension, lbs 1400			
123		1-5-1-1 (E#15)	490	657	.075	25.4					
122	Round 4" circumference 12" long	1-5-1-1 (E#15)	490	727	.075	32.6		Torsion Test			
123		1-5-1-1 (E#15)	490	657	.075	25.4		twist, deg.	in lb., ult.		
122	Round 4" circumference 12" long	1-5-1-1 (E#15)	490	727	.075	32.6					
123		1-5-1-1 (E#15)	490	657	.075	25.4					

*Strength (lbs/in²) calculations were not made since there was no precise method of establishing an accurate value of the area upon which the load acted. These numbers, therefore, are for comparison only.

TABLE 10

PHYSICAL PROPERTIES OF SOLAR RESIN REINFORCED WITH 15 OZ SOLAR FABRIC*

SAMPLE TYPE	TEST TEMPERATURE	RESIN CONTENT %	TENSILE STRENGTH PSI	FLEXURAL STRENGTH PSI	FLEXURAL STRENGTH PSI	YOUNGS MODULUS PSI
Flat 5 Strands	75 ⁰ F	36.4	3.1×10^3	5.1×10^3	2.4×10^5	2.0×10^6
Flat 5 Strands	180 ⁰ F	36.4	3.0×10^3	5.0×10^3	3.0×10^4	—
Flat 5 Strands	250 ⁰ F	36.4	3.1×10^3	5.6×10^3	2.2×10^4	—
Flat 5 Strands	325 ⁰ F	36.4	3.1×10^3	5.6×10^3	2.0×10^4	—

* Average of 5 samples.

(32)

TABLE 11

COMPRESSIVE STRENGTH PROPERTIES OF SOLAR RESIN REINFORCED WITH 15 OZ SOLAR FABRIC*

SAMPLE TYPE	TEST TEMPERATURE	RESIN CONTENT %	COMPRESSIVE LOAD LBS**	COMPRESSIVE YIELD LBS**	MODULUS OF ELASTICITY PSI
ROUND 4 INCH CIRCUMFERENCE	75 ⁰ F	43.6	379	257	9 x 10 ⁴

* Average of 5 samples.

** See Footnote on Table 9.

TABLE 12

COMPARISON OF IMPREGNATED #15 AND SOLAR FABRIC PHYSICAL PROPERTIES

REINFORCEMENT TYPE	RESIN CONTENT %	SPECIFIC STRENGTHS FLEXURAL psi/gm/yd ²
EDMAN #15	36.7	6.07
15 OZ SOLAR FABRIC	36.4	5.80

TABLE 13

U.V. EXPOSURE OF 15 OZ SOLAR FABRIC SYSTEM

SAMPLE	FLEXURAL STRENGTH, PSI	FLEXURAL MODULUS, PSI
CONTROL	5.1 x 10 ³	2.4 x 10 ⁵
3700 HR. U.V.	6.0 x 10 ³	7.4 x 10 ⁴

Stowage Investigations

As previously stated, it was intended that the composite structures would be stored, prior to launch, in a rolled or folded condition. Therefore, in a stowed condition, it was required that the resin matrix be in a non-liquid "B staged" state in order that the material not run due to gravity or external pressure resulting in "starved" areas in the reinforcement; however, the matrix should be sufficiently limited in the cure so that the structure could be erected with reasonably low internal pressure.

The three most promising resins, Epocryl 370, 3M-XA2466 and Solar resin were selected for "B staging" tests to determine applicability to long term stowage. Several Epocryl 370 samples also had 2 percent of t-butyl perbenzoate added to (hopefully) act as a latent catalyst. The test samples consisted of impregnating 1 in. wide x 27 in. long glass tape sections. Each specimen was made by impregnation and "rubbing out" to insure thorough wetting and uniformity of impregnation. Depending on the polymer, resin contents varied from 30 to 40% in each fiber sample.

Two methods of "B" staging were tried; controlled, short duration UV radiation and heat curing at temperatures ranging from 70°C (160°F) to as high as 175°C (350°F).

"B" Staging By UV Exposure

UV "B" staging tests of the Epocryl 370 and XA-2466 impregnated tapes were made by incrementally irradiating them for 10, 20, 30, 40, 50 and 60 seconds. The 10 second irradiation (four feet from the lamp) effected a surface cure of the Epocryl 370 sample which removed tackiness, but did not harden the tape appreciably. Longer exposures definitely hardened the tape. A later four hour UV exposure appeared to cause complete hardening. Stowage tests, for several weeks, of the 10 second irradiated tape, showed some evidence of resin migration. The tests were made with tapes hanging vertically, folded and/or rolled up. In the case of the vertically hanging tape, there was definite evidence of resin concentration at the bottom end of the fabric due to gravity flow. Rolled up fabrics show some "starved" areas at points of maximum pressure. Resin deficiencies were very evident at folds in the fabric.

Similar irradiation tests were made with the 3M-XA2466 samples. Because of the appreciably lower viscosity of the XA-2466 it was found necessary to add up to 3-1/2 percent of pyrogenic silica (Cab-O-Sil, Cabot Corp.) in order to impart thixotropic properties to the resin. At 3-1/2 percent Cab-O-Sil addition, the resin apparently did not flow, or drip, in short time tests. Long time stowage tests of the filled XA-2466 tapes showed little evidence of gravity flow, but flow was very evident in the folded tape, and somewhat evident in the rolled tape. It was thus apparent that a 10 second UV irradiation was not sufficient in establishing a true "B" stage condition in either resin.

"B" Staging By Heat Exposure

Attempts were made to "B" stage both the Epocryl 370 and XA-2466 impregnated tapes by heating. Temperatures up to 350°F for short periods of time, e.g., 3-5 minutes had no apparent effect. Longer exposure times of up to four hours, in a circulating oven at 350°F, were tried. The Epocryl 370 impregnated fabrics, after 1-1/2 hours at 350°F, appeared to lose much of their surface tackiness, without any evidence of hardening. However, on exposure to UV, the samples appeared to set up much slower than usual, and remained slightly tacky on the surface of the fabric which was not facing the UV source. The XA-2466 system showed similar loss of tack after a 1-1/2 hour heat exposure at 350°F. No evidence of cure was found with this system after 4 hour exposure to UV radiation. It was concluded that the 350°F exposure caused a loss or deterioration of the catalyst.

Fabrics impregnated with Solar resin could be satisfactorily "B" staged by placing the impregnated fabric in an oven for 9-11 minutes at 160°F. The treated material was dry and only slightly tacky. Tapes hung vertically for up to five months showed very little evidence of resin flow. Rolled tapes also had satisfactory stowage results. Folded tapes did show some evidence of resin migration at the folds. Most significantly, Solar resin impregnated fabrics maintained for up to five months in a non-sealed, dark cabinet appeared to cure normally when exposed to UV radiation for eight hours.

Deployment Techniques

The composite structures to be made were planned to be tubular structures which would be expanded, from a rolled or folded shape, using thin (2 mil), polyethylene "lay-flat" tubing as a bladder. Since it was assumed that the UV radiation would have to penetrate two layers of polyethylene film, tests were made to determine the relative absorptivity of the film layers. The UV absorption tests were made using four ply, 181 glass fabric specimens impregnated with ICI-580-05L and Solar resin. Tests pieces 1 in. x 6 in. in size, were covered with one, two, three and four layers of the 2 mil polyethylene film. A section of each specimen was left uncoated to act as a control. After one hour exposure, the 580-05L specimens all showed a uniform hardness of approximately 41 Barcol. The Solar resin specimens showed approximately the same in 30 minutes. It was thus concluded that the UV absorption of the polyethylene film was negligible.

The bladder would contain a volatile solvent such as ethyl alcohol and would expand in the vacuum of space to erect the structure. This concept was evaluated on several one foot sections and proved satisfactory. However, several problems were encountered in the development of the preprototype development.

Preprototype Development

The fabrication of a tetrahedron approximately one meter in height was selected as the test configuration in conjunction with the project monitor. The open nature of a tetrahedral truss causes a minimum of member shadowing which is ideal for a UV rigidization system. It was also felt that a truss concept that featured basic repeating modules could be verified by environmental simulation testing of single repeating units of the larger structure.

The initial plan in the construction of the preprototype was to sew the joints. However, when this was tried it was found that a deterioration of the fabric occurred and presaged improper orientation on deployment. A decision was therefore made to develop and use rigid joints.

For fabrication of a large truss in the development of a prototype, the production of a large quantity of injection molded plastic joints would be most cost and property effective. Due to the high tooling costs for a mold as well as time considerations it was decided to use joints made from wooden dowels to simulate plastic joints as shown in Figure 10.

The impregnation of the six structural elements went smoothly, but several problems were encountered with the polyethylene bladders. The bladders were 1.05 meters in length and it was planned that as the bladder inflated, pressure would be applied in the longitudinal direction assuring complete erection. Each bladder had six grams of ethyl alcohol that was heat-sealed inside. The bladders were then placed inside a tube of Solar fabric and immersed overnight in Solar resin. The tubes were removed from the resin and run through a wringer twice. During the wringing operation, the bladders tended to twist or be held back and thereby folded over on themselves leaving areas where inner surfaces of impregnated fabric could touch each other.

The impregnated tubes were then "B" staged and a structure constructed and placed in a stowage configuration (Figure 11). An inspection of the bladders revealed that the ethyl alcohol had completely evaporated. Apparently the 2 mil polyethylene is not an adequate vapor barrier. Attempts made to replace the ethyl alcohol just prior to vacuum deployment were unsuccessful. It was therefore decided that the preprototype would be deployed by air pressure.

The deployment of the preprototype model, Figure 12, revealed two major problems. First, when the impregnated fabric was folded onto itself, the outer surfaces of the material would stick even though they were tack free. This self-adhering property was enough to inhibit a smooth deployment and indicates that resin migration may occur after long term stowage. Secondly, no significance was initially placed on the twisting and movement of the bladders during wringing. However, the bladder did not have enough strength, when inflated, to separate the top and bottom fabric layers where the bladder had been displaced. This resulted in elliptical rather than round members and in a flat member (back horizontal member in Figure 12), specifically where the bladder had been held back in the wringer and the two fabric inside surfaces contacted.

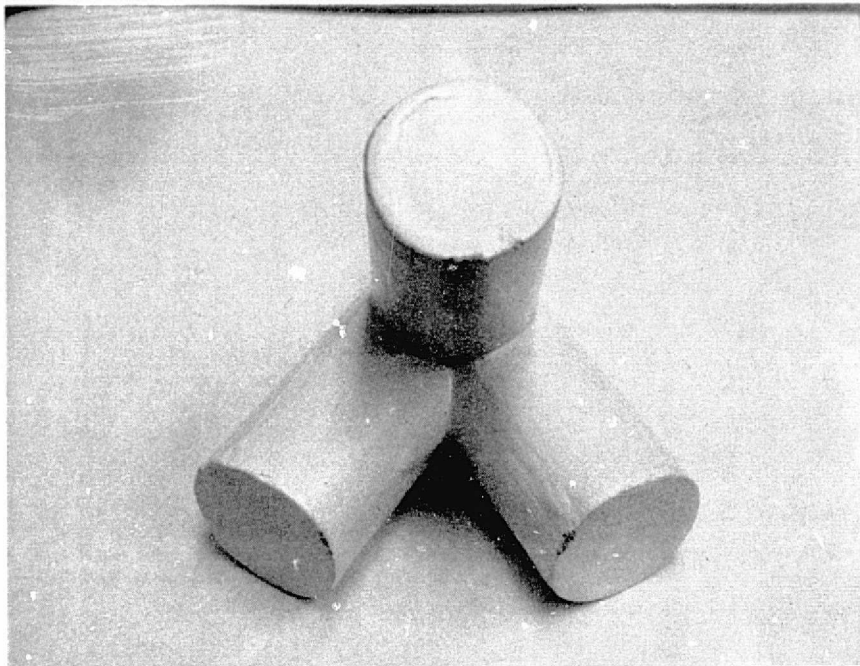


Figure 10. Tetrahedron Joints of Three Inches Height

ORIGINAL PAGE IS
OF POOR QUALITY

(38)



ORIGINAL PAGE IS
OF POOR
QUALITY

Figure 11. Stowed Preprototype Configuration

(39)

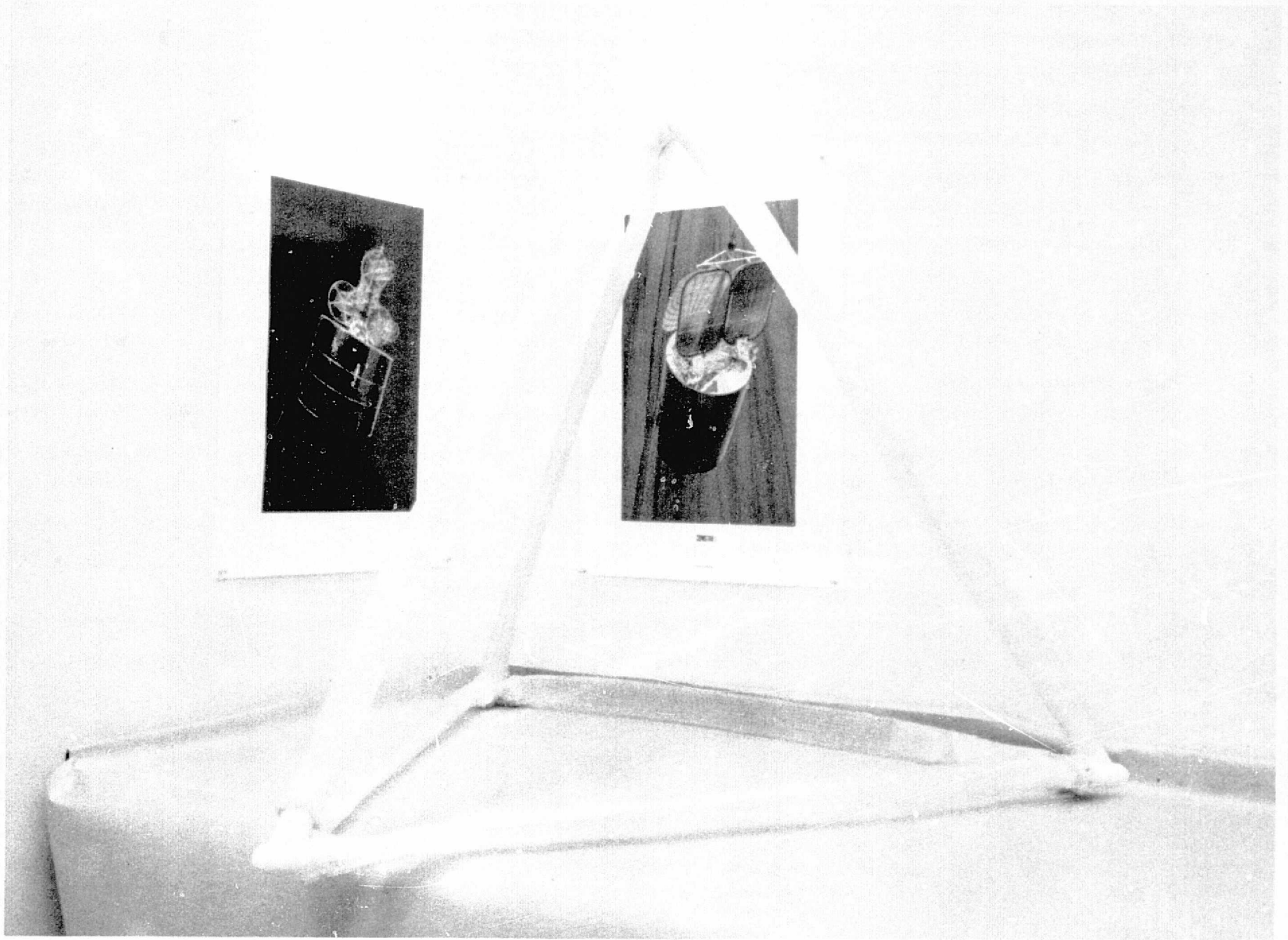


Figure 12. Expanded and Rigidized Preprototype

Conclusions

The ultimate aim of this project was to produce design information on a resin and a composite structure which could be used by engineers, designers and fabricators in production of expandable-rigidizable space structures. As part of an add-on contract, a meter high tetrahedron preprototype model was fabricated. The first objective, determination of an optimum resin, has been achieved. The Solar resin, based on its good physical properties, thermal performance, "B" staging and stowage is believed to meet all the requirements set forth for an optimum UV catalyzable resin for space structure usage. The second objective, design data on optimum structures, has not been achieved, because of fabric limitations. However, optimum design data was obtained on a composite system based on a state-of-the-art fabric, the 15 ounce Solar Reinforcing Fabric.

The fabrication of the preprototype model was based on Solar Laboratories resin and reinforcing fabric. Invaluable information pertaining to stowage and deployment problems was obtained on this model. The development of the prototype model will require prior resolution of these problems.

Recommendations

1. Evaluate the use of other bladders in place of the polyethylene bladder. New material must prevent evaporative loss of the expansion solvent. An example of such a bladder film might be a polyethylene/polyethyleneterephthalate coextrusion.
2. Evaluate the use of release paper, mold release or an external bladder on the outer surface of the tubular structure to prevent resin migration and self-adhesion of the structure before and during expansion.
3. Prepare a prototype model of larger scale to demonstrate the fabrication and design of rigidizable articles.