UNCLASSIFIED

AD NUMBER

ADB007909

LIMITATION CHANGES

TO:

Approved for public release; distribution is unlimited.

FROM:

Distribution authorized to U.S. Gov't. agencies only; Test and Evaluation; AUG 1975. Other requests shall be referred to Air Force Materials Lab., Wright-Patterson AFB, OH 45433.

AUTHORITY

AFWAL ltr 3 Nov 1983

THIS PAGE IS UNCLASSIFIED

AD B00 7909

AUTHORITY: AFWAL Notice 3 Nov 83

DEPARTMENT OF DEFENSE
UNITED STATES OF AMERICA

AFML-TR-75-90

② 16

DEVELOPMENT OF HIGH TEMPERATURE ADDITION - CURED ADHESIVES

ADVANCED TECHNOLOGY LABORATORY
AEROSPACE GROUPS
HUGHES AIRCRAFT COMPANY
CULVER CITY, CALIFORNIA 90230

AUGUST 1975

TECHNICAL REPORT AFML-TR-75-90
REPORT FOR PERIOD MARCH 1974 – MARCH 1975

Distribution limited to U.S. Government agencies only; test and evaluation, August 1975. Other requests for this document must be referred to the Air Force Materials Laboratory, Nonmetallic Materials Division, Composite and Fibrous Materials Branch, AFML/MBC, Wright-Patterson AFB, Ohio 45433.

AIR FORCE MATERIALS LABORATORY
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio 45433

NOTICE

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

Theodore J. Aponyi

Theodore J. Aponyi
Project Engineer

FOR THE COMMANDER

Theodore J Reinhart Jr

Theodore J. Reinhart, Jr., Chief
Composite and Fibrous Materials Branch
Nonmetallic Materials Division

AIR FORCE - 17-11-75 - 200

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

(18) 1. REPORT NUMBER (19)
AFML-TR-75-90 ✓

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER
(9) Technical rept.

4. TITLE (and Subtitle)
(6) DEVELOPMENT OF HIGH TEMPERATURE ADDITION - CURED ADHESIVES,

5. TYPE OF REPORT & PERIOD COVERED
1 Mar~~ch~~ ~~19~~74 ~~to~~ 31 Mar~~ch~~ ~~19~~75, 21

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
(10) Robert H./Boschan ~~and~~ Abraham L./Landis

See ad B000277L

8. CONTRACT OR GRANT NUMBER(s)
(15) F33615-73-C-5062 ✓

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Advanced Technology Laboratory
Aerospace Groups, Hughes Aircraft Company
Culver City, California 90230

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Project Task No. 7340
Task No. 734002,
"Structural Adhesives"

11. CONTROLLING OFFICE NAME AND ADDRESS
Air Force Materials Laboratory, Nonmetallic Materials Division
Composite and Fibrous Materials Branch
AFML/MBC, Wright-Patterson AFB, Ohio 45433

(11) 12. REPORT DATE
Aug~~ust~~ ~~19~~75

13. NUMBER OF PAGES
70
(12) 80p.

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)
(16) AF-7340
(17) 734002

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
Distribution limited to U.S. Government agencies only; test and evaluation, August 1975. Other requests for this document must be referred to the Air Force Materials Laboratory, Nonmetallic Materials Division, Composite Fibrous Materials Branch, AFML/MBC, Wright Patterson AFB, Ohio 45433.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Adhesive, high temperature, polyimide, titanium, weld-bonding, addition polymers, titanium adhesives, acetylene terminated polyimide

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Several modifications of the previously studied HR 600 adhesive were chosen for investigation as addition cured polyimide adhesives for titnium. All of the materials studied were acetylene terminated oligomers which were prepared by reacting an arylenediamine with benzophenonetetracarboxylic dianhydride (BTDA) and capping this product with either 3-aminophenylacetylene (I) or 3-(3-aminophenoxy)phenylacetylene (II), followed by imidizing in a →

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

172310

LB

refluxing benzene-cresol mixture or in acetic anhydride. The most promising oligomers from the standpoint of melting point, solubility, flow properties and adhesive strength were those from I, BTDA, and 1, 3-di-(aminophenoxy)benzene(III), designated HR 600 DP-2 (HR 600 oligomer), and from II, BTDA, and III, designated HR 650. The present manufacturing cost (labor + materials) of HR 600 oligomer is considerably less than that of HR 650. Measured ambient temperature titanium lap shear strengths have been in excess of 4200 psi for HR 650 and 3600 psi for HR 600 oligomer, and lap shear strengths as high as 2600 psi at 500°F have been measured for both materials. Elevated temperature air aging tests (90 percent RH at 160°F) are very encouraging. Weld-bond fatigue data, Pi-tension titanium honeycomb data and T-peel data are presented and discussed.

FOREWORD

This technical report was prepared by Hughes Aircraft Company, Aerospace Group, Culver City, California, under U.S. Air Force Contract F33615-73-C-5062. The contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials," and Task No. 734002, "Structural Adhesives." The studies reported here are a continuation of those reported in the previous summary report, AFML-TR-74-88, May, 1974. The work was administered under the direction of the Nonmetallic Materials Division, Air Force Materials Laboratory, with Mr. T.J. Aponyi (AFML/MBC) as the Project Engineer.

This report covers the work performed from 1 March 1974 to 31 March 1975 and is submitted in partial fulfillment of the contract.

The work was performed in the Advanced Technology Laboratory under the management of Mr. L. Brian Keller. The program manager was Dr. Robert H. Boschan. The principal investigator was Dr. Abraham L. Landis. Professional assistance was provided by Dr. Norman Bilow, Senior Scientist, Dr. Daniel A. Demeo, Dr. Thomas W. Giants and Albert M. Schwider. Professional consultation was provided by Mr. L. Brian Keller, Mr. Arnold J. Tuckerman, Dr. Richard I. Akawie and Mr. Harry Raech. Research assistance of a very high caliber was provided by Mr. Raymond E. Lawrence, Mr. Thomas J. Shudic, Mr. Jeff D. Lohoff and Mr. Arturo A. Castillo.

This report was submitted by the authors in April 1975.

CONTENTS

CONTENTS (Continued)

LIST OF ILLUSTRATIONS

LIST OF TABLES

LIST OF TABLES (Continued)

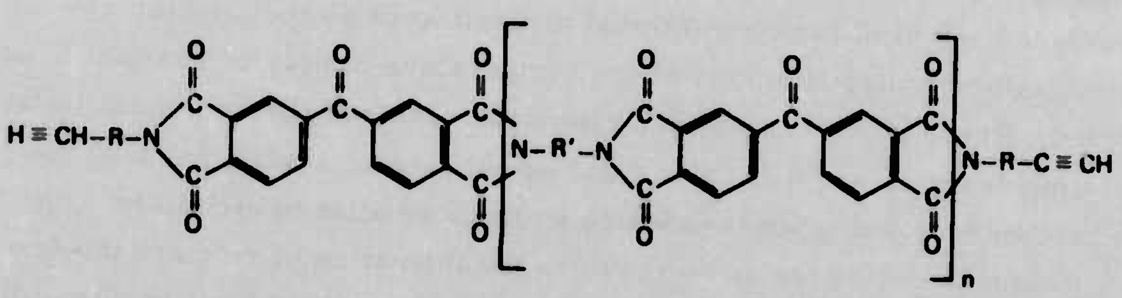
I. INTRODUCTION

Titanium is finding increasing use for aerospace applications, especially with the advent of supersonic aircraft. However, the adhesives which have been used for conventional aircraft such as the epoxies are unsuitable for bonding titanium where temperature ranges of 450-600°F are expected. Those polymers which do have the required thermal stability at these temperatures are difficult to use as adhesives, mainly because they cure by condensation processes which produce volatile by-products. The gases produced during the cure result in the formation of voids in the matrix with the serious consequence of impairing the strength and reliability of the bond. Also, the high cure temperature required for processing these adhesives further compounds the problem in that the volatiles produced have large volumes so that a relatively small amount of volatile by-products can have very serious consequences.

With these inherent difficulties of condensation type polymers in mind, Hughes Aircraft Company has, for several years, directed its efforts toward adhesive systems which cure by addition rather than condensation reactions. The investigation of addition curing oligomers was started early in 1971 after receipt of an AFML contract to develop thermally stable adhesives and laminating resins. Early in the investigation the addition reaction of terephthalonitrile N, N'-dioxide with cyano-substituted ethers and polyimides as well as acetylene-substituted polyimides were studied. Although they yielded thermally stable resins there were side reactions which produced some gaseous products. Also, they had to be employed as a slurry in a solvent to be effective as an adhesive. During this investigation it was discovered that the acetylene-substituted polyimides underwent homopolymerization when heated to yield exceptionally thermally stable resins.

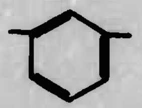
Furthermore, the homopolymerization of these oligomers did not produce any volatile by-products and as a consequence gave extremely low void content composites. Titanium lap-shear specimens bonded with an adhesive of this general type exhibited high strength, both at ambient temperature and at temperatures as high as 500°F. In the current program, titanium lap shear strengths as high as 4200 psi at ambient temperature and 2600 psi at 500°F have been found for these acetylene terminated polyimide oligomers.

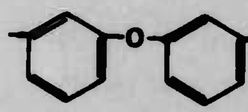
During the present program, acetylene-substituted polyimide oligomers were investigated with the general formula shown below.



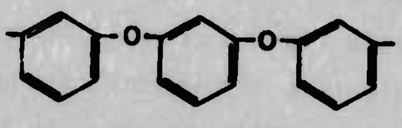
R and R' were chosen so as to optimize solubility, melting point, flow properties and other parameters leading to good ambient and elevated temperature adhesive strengths. The oligomers studied in this program had the following structures for R and R'.

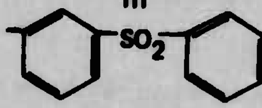
R


I

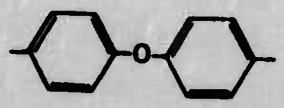

II

R'


III



IV


V

The two most successful oligomers studied in the current program were modifications of HR 600 (R = I and R' = III, n = 1). These were HR 600 DP-2 (R = I, R' = III, n = 2) and HR 650 (R = II, R' = III, n = 1).

Other oligomers were investigated with the objective of reducing the cost of the adhesive oligomer. These materials had R = I and R' = IV and R-I and R' = V.

Development work has included preparation of glass cloth adhesive prepregs, lap-shear tensile tests, air aging tests, humidity aging tests, weldbonding tests, Pi-tension titanium honeycomb tensile tests and T-peel tests.

II. SUMMARY

The work performed on high temperature adhesives during the past year is a continuation under Air Force Contract Number F33615-73-C-5062, "Development of High Temperature Addition-Cured Adhesives." The studies reported here are a continuation of those reported in the previous summary report, AFML-TR-74-88, May, 1974.

Several polyimide oligomer systems which cure thermally by addition reactions were studied as adhesives for titanium. Each oligomer was prepared by capping an anhydride terminated polyimide skeleton by reaction with either 3-aminophenylacetylene or 3-(3-aminophenoxy)phenylacetylene to yield, after imidization, a fully aromatic acetylene terminated monomer. Amine intermediates used in oligomer syntheses have previously been fully characterized by combustion analyses, infrared and nuclear magnetic resonance spectra, and amine titrations. In addition, infrared and nuclear magnetic resonance spectroscopy have been utilized as criteria for complete imidization, and for verification of the ratios of aromatic protons to acetylenic protons in the acetylene terminated oligomers.

Data from the previous program as well as the current program have indicated that HR 600 DP-1 oligomer is very effective as an adhesive for titanium, but that lowering the modulus of the adhesive resin will lead to higher strengths, both at ambient and elevated temperatures.

With this in mind, two new oligomers have been evaluated as adhesives for 6A14V titanium alloy. These two materials have been designated HR 650 and HR 600 DP-2. Both contain an increased number of aromatic ether linkages in the oligomer backbone and thus were expected to have greater flexibility in the cured resins by virtue of their lower crosslink densities.

As predicted, both HR 650 and HR 600 DP-2 were indeed superior to HR 600 DP-1 as adhesives at both ambient and elevated temperatures. The best values for ambient temperature titanium lap shear strengths were 4200 psi and 3600 psi, respectively, for HR 650 and HR 600 DP-2. At 500°F, strengths up to 2600 psi were measured for both materials. As previously observed, the presence of acetic anhydride imidized oligomer is necessary for good adhesive strength.

One of these oligomers, HR 600 DP-2, was selected for further evaluation including elevated temperature air aging, humidity aging, Pi-tension tensile strengths on titanium honeycomb specimens, and weldbonding tests. Economic considerations were given considerable weight in this selection, since the HR-600 DP-2 oligomer can be presently prepared at considerably less expense than the HR 650 oligomer.

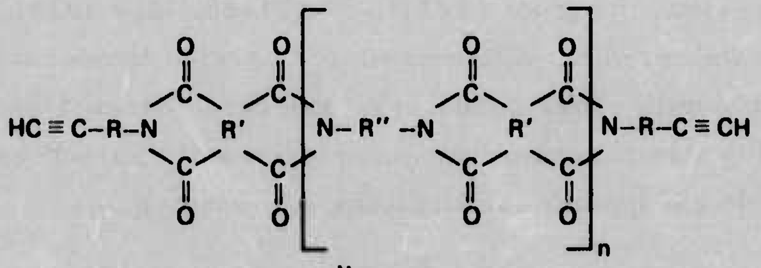
Elevated temperature air aging tests to 450°F and humidity aging tests were very encouraging, but indicated that additional work was necessary to optimize adhesive properties at temperatures of 500°F and higher.

In the previous program (AFML-TR-74-88, May 1974), the feasibility of polyimide weldbonding of titanium, for service temperatures in excess of those attainable with epoxy adhesives, was demonstrated with the DP-1 oligomer. During this program, encouraging results have been obtained with the use of the DP-2 oligomer for titanium weldbonding.

III. TECHNICAL DISCUSSION

A. ACETYLENE-TERMINATED POLYIMIDE OLIGOMERS

The successful use of homopolymerizable acetylene-terminated polyimide oligomers as laminating resins in the preparation of glass cloth and graphite reinforced laminates led to the belief that this type of resin would function as a one-component adhesive for 6Al4V titanium. These oligomers can be depicted by the general formula

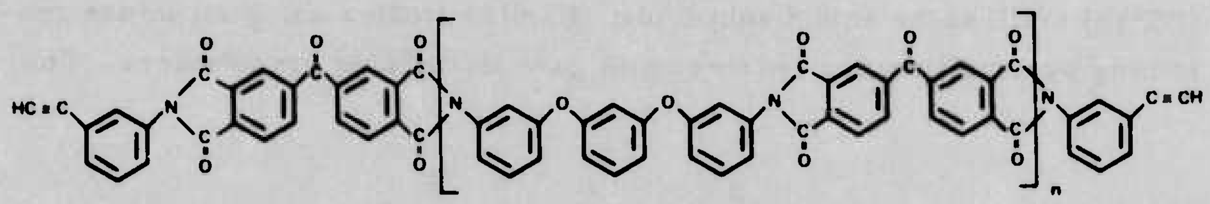


II

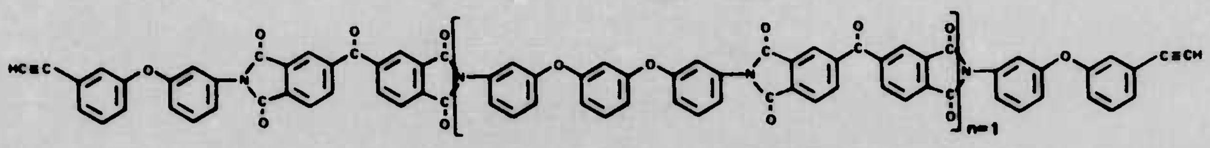
Depending on the structure of R, R' and R'' and the values of n, a variety of physical properties can be realized. For this study we have limited ourselves to aromatic structures for R, R' and R'' since aromaticity is considered necessary to achieve the high thermal stability required for the objectives of this study. We have studied oligomers in which n, the degree of polymerization (DP) was as high as 3. This allowed us to vary the crosslink density of the cured polymer and consequently the modulus and toughness of the cured resin. The results have been very promising in that lap shear strengths in excess of 4000 psi at ambient and 2600 psi at 500°F have been achieved with some of these resins.

The synthesis of these polyimide oligomers entails (1) the preparation of the polyamic acid and (2) imidization of the polyamic acid by either refluxing in a mixture of meta-cresol and benzene or in acetic anhydride.

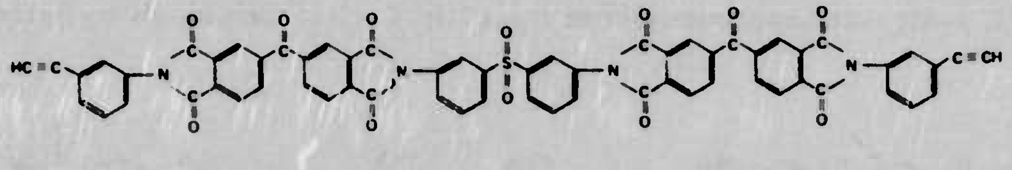
The resins studied in this program are shown by the following structures.



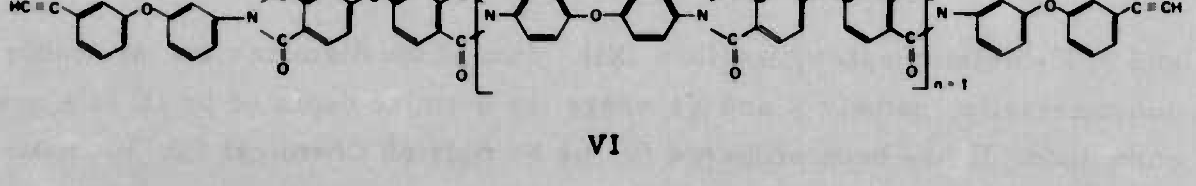
III HR600 Type Oligomers



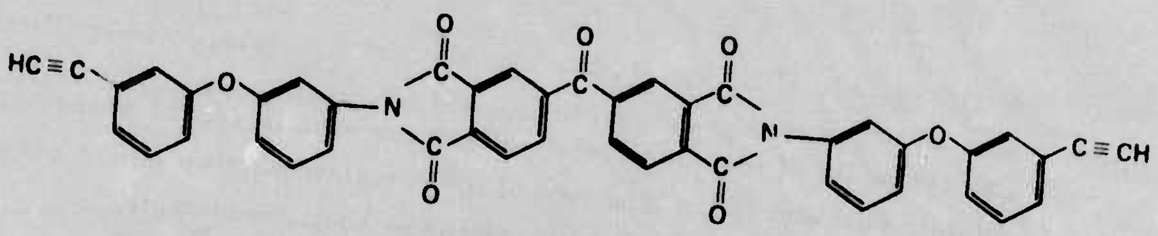
IV HR650 Type Oligomers



V

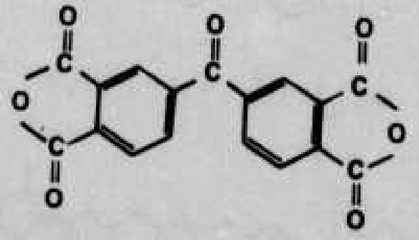


VI



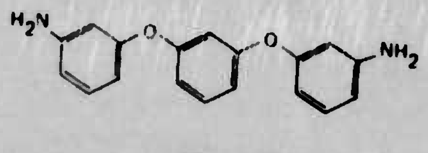
VII HR700 Type Oligomers

All the resins depicted above use benzophenonetetracarboxylic dianhydride (BTDA) (VIII) as the acid dianhydride. Earlier studies using structure containing pyromellitic dianhydride units gave intractable prepolymers. The

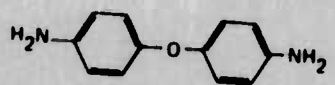


VIII (BTDA)

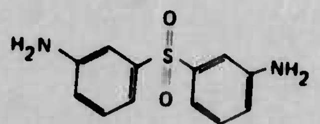
BTDA is readily available from Gulf Chemical Company and yields tractable and soluble oligomers. The diamines used in the preparation of the resins were 1, 3-di(3-aminophenoxy)benzene (IX), 4, 4'-bis(aminophenyl)ether (X)



IX

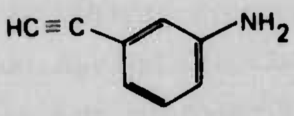


X

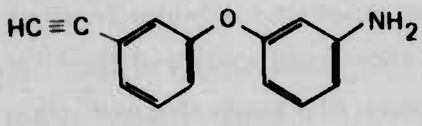


XI

and 3, 3'-bis(aminophenyl)sulfone (XI). Two of the diamines are available commercially, namely X and XI where the diamine depicted by IX is a new compound. It has been prepared for us by Aldrich Chemical Co. in small batches (500 grams) on a custom basis. The two acetylene compounds, 3-aminophenylacetylene (XII) and 3-(3-aminophenoxy)phenylacetylene (XIII) are new compounds and are prepared in this laboratory on a routine basis.



XII



XIII

Two of the resins described, VI and VII, were not used to prepare titanium lap shear specimens. In the case of VI, the oligomer before cure proved to be too viscous and it does not appear to have the necessary fluidity to give good adhesive bonds. The oligomer VII was not used because it was felt that the potentially high crosslinking density of such a structure would yield a bond with too high a modulus and therefore a brittle matrix.

1. HR600 Type Oligomer, DP of 1

This oligomer is depicted by structure III where n is equal to one. The outstanding properties observed in the glass-reinforced laminates from the homopolymer derived from III had earlier created considerable interest in the use of III as the base of a one-component adhesive for bonding titanium to titanium. At that time it was discovered that the method of imidization of the oligomer strongly influenced the strength of the bonded titanium. It was found that it was necessary to formulate the acetic anhydride imidized oligomer with the meta-cresol imidized oligomer to achieve good bond strength. In our earlier work the titanium lap shear specimens were prepared by sprinkling the oligomer onto the substrates, heating to melt the oligomer, and subsequently bonding pairs of tape-wrapped substrates together under a pressure of 15 psi. It was found that the use of a prepreg with 112 heat cleaned carrier cloth improved the strength and processing over the powder lay-up.

The work summarized here is a continuation of our earlier work with this resin. Aging and humidity tests were performed on adhesive bonded specimens using this oligomer.

a. Humidity Tests

A series of tests was performed to learn the effect of humidity on the lap shear strength of HR600 adhesive-bonded titanium test specimens. Twelve specimens were fabricated using a 50:50 mixture of HR600A (acetic anhydride imidized) and HR600C (meta-cresol imidized) impregnated Clark-Schwebel 112 heat-cleaned glass fabric. Dimethylformamide was used as the lacquer solvent for the resin. The titanium lap shear coupons were cleaned per Hughes Process Specification HP 9-30 described in the experimental section and the specimens made with 1/2-inch overlap, using spring clips to achieve 15 psi pressure. The specimens were cured at 600°F in air for 8 hours and separated into three groups of four each. The first group was placed in a desiccator, the second in the lab atmosphere, and the third in a 100 percent relative humidity chamber at 160°F, for 30 days, each. Table I gives the results. The humidity exposure decreased the ambient temperature lap shear strength about 20 percent and the 450°F lap shear strength 10 percent.

b. Aging Tests

A series of tests was performed to learn the effect of aging on the lap shear strength of HR600 adhesive bonded titanium test strips. Both filled (325 mesh aluminum) and unfilled prepregs were used. Thus, in preparing the filled prepregs, a resin mixture of acetic anhydride imidized HR600 designated HR600A, and meta-cresol/benzene imidized HR600 designated HR600C were blended in a 50:50 mixture with aluminum powder such that the mixture contained,

HR600 A/C	80 pbw
325 Mesh Aluminum Powder	20 pbw

A small amount of dimethylformamide was mixed with the filled resin mixture and applied to both sides of the starch-oil finished, heat cleaned 112 glass fabric. The solvent was removed by oven drying at 350°F for 15 minutes. This process was repeated until a 92 percent pickup of solids

TABLE I. EFFECT OF HUMIDITY ON LAP SHEAR STRENGTH HR 600 A/C TITANIUM SPECIMENS*

Conditions	Test Temp	Lap Shear Strength, psi
Dry desiccator, 30 days	RT	2360 2330 2345 ave
	450°F	2200 2110 2155 ave
Laboratory atmosphere, 30 days	RT	2210 2050 2130 ave
	450°F	2280 2140 2210 ave
100 percent RH, 160°F, 30 days	RT	1650 1760 1705 ave
	450°F	1950 1980 1965 ave

*The glue line was 0.003 ±0.0003 inch. All failures were cohesive. Cured at 600°F for 8 hours. Prepregs 112 heat-cleaned glass fabric.

was achieved. Titanium lap-shear coupons were cleaned per Hughes Process Specification HP9-30 and 60 lap shear specimens with 1/2-inch overlap were made using spring clips to achieve a 15 psi pressure. The specimens were then cured at 600°F for 8 hours.

Concurrently, sixty lap shear specimens were prepared using the same resin composition without the aluminum filler. The same 600°F cure at 8 hours was used.

The specimens made from both the filled and unfilled resins were divided into three batches and aged at room temperature, 450°F and 500°F. Aliquot portions were removed at specific time intervals until the last portion had been aged a total 1000 hours. Table II shows the values obtained for the filled, and Table III for the unfilled, specimens. The lap shear strength measurements were made at the temperature of aging. In both cases no changes were observed when the specimens were aged at room temperature. Aging at 450°F about 50 percent of the lap-shear strength was retained after 1000 hours, for both the filled and unfilled specimens. At 500°F, the unfilled specimens showed a much greater drop than the filled specimens. A possible explanation is that the aluminum acts as an antitoxidant at the higher temperature. Figures 1 and 2 show these trends.

2. HR600 Type Oligomer, Degree of Polymerization of 2

Our earlier work reported for the HR600 oligomer having a degree of polymerization (DP) of 1 indicated room temperature lap shear strengths of 2800 psi, 2600 psi at 450°F and 2000 psi at 500°F. It was felt that an increase in lap shear strength could be achieved if the resin were less brittle and tougher. This could be accomplished by increasing the degree of polymerization of the acetylene-terminated oligomer since this would effectively decrease the crosslink density. HR600 type of oligomers with a degree of polymerization of 2, i.e., where $n = 2$ in the formula depicted by III were prepared. This was accomplished by copolymerizing benzophenonetetracarboxylic dianhydride, 1, 3-di(3-aminophenoxy)benzene and 3-aminophenylacetylene in a 3:2:2 molar ratio. The polyamic acid was then

TABLE II. THERMAL AGING OF TITANIUM SPECIMENS BONDED WITH ALUMINUM 325 MESH FILLED HR600 A/C PREPREG ADHESIVES - LAP SHEAR STRENGTHS

Specimen	Aging Temperature $^{\circ}$F	Aging Time Hours	Glue Line Inches	Test Temperature $^{\circ}$F	Lap Shear Strength psi	Failure Mode (CO, Cohesive AD, Adhesive)
A1	R. T.	24	0.0099	R. T.	1730	CO
2	R. T.	24	0.0072	R. T.	1920	CO
3	R. T.	24	0.0087	R. T.	1680	CO
4	R. T.	24	0.0063	R. T.	1860	CO
5	R. T.	24	0.0086	R. T.	1660	CO
					1770 Ave	
B1	R. T.	1000	0.0093	R. T.	1960	CO
2	R. T.	1000	0.0096	R. T.	1640	CO
3	R. T.	1000	0.0074	R. T.	2030	CO
4	R. T.	1000	0.0130	R. T.	1860	CO
5	R. T.	1000	0.0079	R. T.	1490	CO
					1800 Ave	
C1	450	168	0.0076	450	2190	CO
2	450	168	0.0088	450	1964	CO
3	450	168	0.0078	450	2140	CO
4	450	168	0.0073	450	2160	CO
5	450	168	0.0078	450	2070	CO
					2100 Ave	
D1	450	336	0.0087	450	1870	CO
2	450	336	0.0102	450	1730	CO
3	450	336	0.0081	450	2060	CO
4	450	336	0.0075	450	2190	CO
5	450	336	0.0093	450	2100	CO
					1990 Ave	

(Continued next page)

(Table II, continued)

Specimen	Aging Temperature °F	Aging Time Hours	Glue Line Inches	Test Temperature °F	Lap Shear Strength psi	Failure Mode (CO, Cohesive AD, Adhesive)
E1	450	504	0.0078	450	1680	CO
2	450	504	0.0095	450	2140	CO
3	450	504	0.0097	450	2090	CO
4	450	504	0.0056	450	1560	CO
5	450	504	0.0130	450	1680	CO
					1830 Ave	
F1	450	720	0.0083	450	1530	AD/CO
2	450	720	0.0079	450	1660	AD
3	450	720	0.0078	450	1660	AD/CO
4	450	720	0.0115	450	1090	AD/CO
5	450	720	0.0105	450	1510	AD/CO
					1490 Ave	
G1	450	1008	0.0084	450	1150	CO
2	450	1008	0.0101	450	760	AD
3	450	1008	0.0082	450	1940	CO
4	450	1008	0.0127	450	1060	CO
5	450	1008	0.0065	450	900	CO
					1160 Ave	
H1	500	168	0.0119	500	1690	CO
2	500	168	0.0074	500	1980	CO
3	500	168	0.0079	500	2070	CO
4	500	168	0.0086	500	1780	CO
5	500	168	0.0083	500	2150	CO
					1930 Ave	

(Continued next page)

(Table II, concluded)

Specimen	Aging Temperature °F	Aging Time Hours	Glue Line Inches	Test Temperature °F	Lap Shear Strength psi	Failure Mode (CO, Cohesive AD, Adhesive)
I1	500	336	0.0080	500	1920	CO
2	500	336	0.0089	500	1940	CO
3	500	336	0.0090	500	1670	CO
4	500	336	0.0080	500	1430	CO
5	500	336	0.0157	500	870	CO
					1566 Ave	
J1	500	504	0.0073	500	1150	CO
2	500	504	0.0069	500	1120	CO
3	500	504	0.0082	500	1360	CO
4	500	504	0.0069	500	1790	CO
5	500	504	0.0094	500	1040	CO
					1290 Ave	
K1	500	720	0.0089	500	650	AD
2	500	720	0.0108	500	1400	CO
3	500	720	0.0082	500	1520	CO
4	500	720	0.0063	500	1460	CO
5	500	720	0.0072	500	1460	CO
					1298 Ave	
L1	500	1008	0.0116	500	1070	CO
2	500	1008	0.0102	500	810	AD
3	500	1008	0.0119	500	1190	CO
4	500	1008	0.0099	500	1010	AD
5	500	1008	0.0080	500	1020	AD
					1020 Ave	

TABLE III. THERMAL AGING OF TITANIUM SPECIMENS BONDED WITH HR600 A/C POLYIMIDE PREPREG ADHESIVES – LAP SHEAR STRENGTHS

Specimen	Aging Temperature °F	Aging Time Hours	Glue Line Inches	Test Temperature °F	Lap Shear Strength psi	Failure Mode (CO, Cohesive AD, Adhesive)
A1	R.T.	24	0.0025	R.T.	2250	CO
2	R.T.	24	0.0025	R.T.	2410	CO
3	R.T.	24	0.0029	R.T.	2100	CO
4	R.T.	24	–	R.T.	2350	CO
5	R.T.	24	0.0053	R.T.	2450	CO
					2310 Ave	
B1	R.T.	1008	0.0024	R.T.	2430	CO
2	R.T.	1008	0.0024	R.T.	2260	CO
3	R.T.	1008	0.0023	R.T.	2280	CO
4	R.T.	1008	0.0033	R.T.	2250	CO
5	R.T.	1008	–	R.T.	2080	CO
					2260 Ave	
C1	450	288	0.0052	450	2120	CO
2	450	288	0.0025	450	2500	CO
3	450	288	0.0028	450	2470	CO
4	450	288	0.0032	450	2560	CO
5	450	288	0.0032	450	–	–
					2410 Ave	
D1	450	336	0.0015	450	2080	CO
2	450	336	0.0035	450	2280	CO
3	450	336	0.0035	450	2160	CO
4	450	336	0.0014	450	1670	CO
5	450	336	0.0014	450	2140	AD
					2070 Ave	

(Continued next page)

(Table III, continued)

Specimen	Aging Temperature °F	Aging Time Hours	Glue Line Inches	Test Temperature °F	Lap Shear Strength psi	Failure Mode (CO, Cohesive AD, Adhesive)
E1	450	504	0.0023	450	1130	AD
2	450	504	0.0030	450	1570	AD
3	450	504	0.0018	450	1980	AD
4	450	504	0.0032	450	2300	AD
5	450	504	0.0030	450	–	AD
					1745 Ave	
F1	450	648	0.0029	450	1320	AD
2	450	648	0.0024	450	1090	AD
3	450	648	0.0022	450	1460	AD
4	450	648	0.0026	450	1230	AD
5	450	648	0.0014	450	1170	AD
					1254 Ave	
G1	450	1008	0.0018	450	1110	AD
2	450	1008	0.0028	450	920	AD
3	450	1008	0.0041	450	790	AD
4	450	1008	0.0041	450	2120	CO
5	450	1008	0.0045	450	940	AD
					1180 Ave	
H1	500	120	0.0031	500	2190	CO
2	500	120	0.0027	500	2390	CO
3	500	120	0.0025	500	2020	CO
4	500	120	0.0033	500	2550	CO
5	500	120	0.0036	500	2380	CO
					2310 Ave	

(Continued next page)

(Table III, concluded)

Specimen	Aging Temperature °F	Aging Time Hours	Glue Line Inches	Test Temperature °F	Lap Shear Strength psi	Failure Mode (CO, Cohesive AD, Adhesive)
I1	500	400	0.0030	500	1490	AD
2	500	400	0.0077	500	1610	CO
3	500	400	0.0029	500	1640	CO
4	500	400	0.0033	500	1010	AD
5	500	400	0.0050	500	1380	AD
					1430 Ave	
J1	500	568	0.0069	500	1010	AD
2	500	568	0.0034	500	1720	CO
3	500	568	0.0116	500	1180	AD
4	500	568	0.0026	500	1260	AD
5	500	568	0.0018	500	1090	AD
					1252 Ave	
K1	500	736	0.0018	500	930	AD
2	500	736	0.0038	500	830	AD
3	500	736	0.0050	500	—	AD
4	500	736	0.0032	500	840	AD
5	500	736	0.0031	500	900	AD
					875 Ave	
L1	500	1072	0.0023	500	320	AD
2	500	1072	0.0039	500	550	AD
3	500	1072	0.0042	500	290	AD
4	500	1072	0.0026	500	510	AD
5	500	1072	0.0064	500	400	AD
					410 Ave	

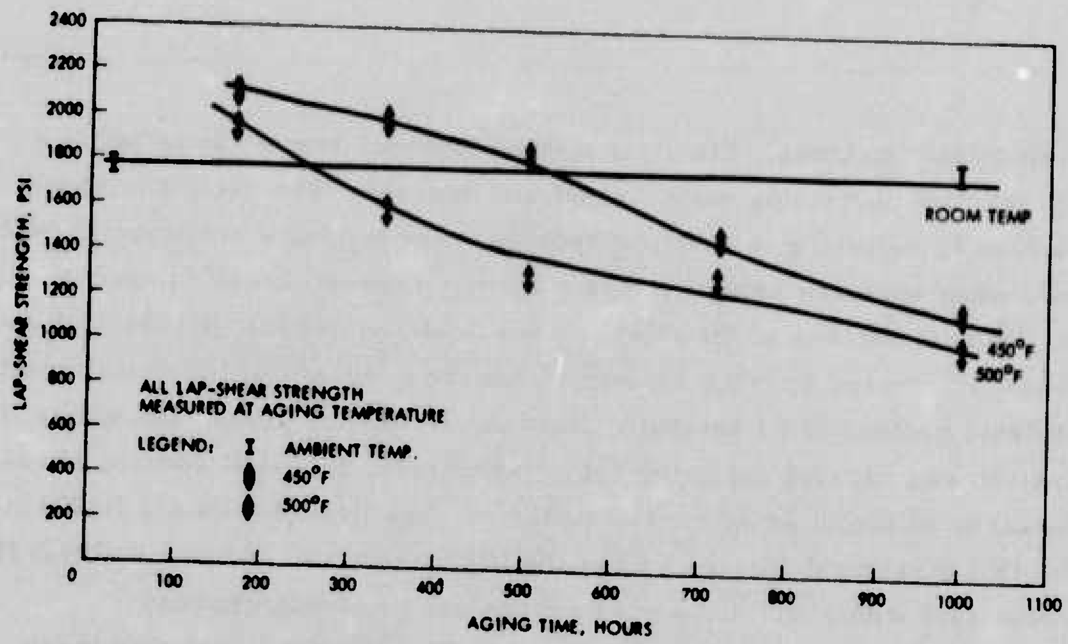


Figure 1. Thermal aging of titanium specimens bonded with aluminum (325 mesh) filled HR600 A/C polyimide prepreg adhesive.

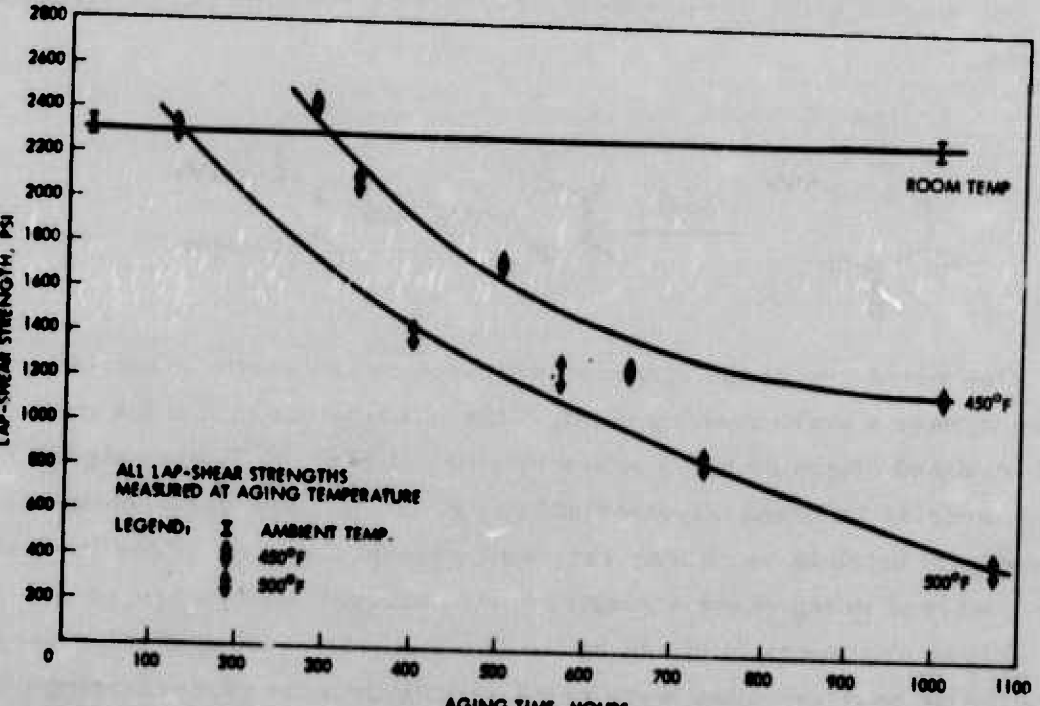
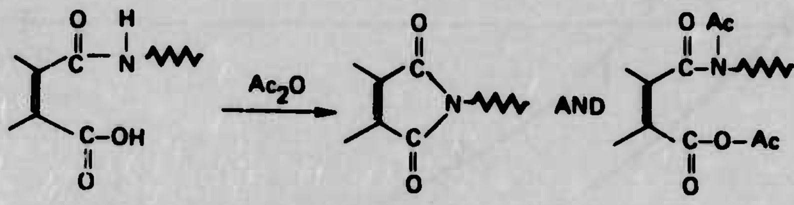


Figure 2. Thermal aging of titanium specimens bonded with HR600 A/C polyimide prepreg adhesive.

imidized by two methods. The first method involved heating at reflux in a solvent mixture containing meta-cresol and benzene. The second involved imidization by refluxing in acetic anhydride. The products prepared by both methods were analyzed using nuclear magnetic resonance (NMR) spectroscopy. Several batches of the meta-cresol imidized product (H1224-71A and H1224-85B) analyzed by NMR showed within the accuracy of the determination 2 acetylenic protons to 61 aromatic protons. However, in the case where the imidization was carried out using acetic anhydride, the NMR spectra showed the presence of acetyl groups. Two of the batches (H1224-71B and H1224-85A) showed this structural feature. Thus the NMR spectrum of batch H1224-71B was consistent with about 1.3 acetyl groups per molecule whereas batch H1224-85A showed 1.5 acetyl groups. The difference between these two values may be within the experimental error of the determination but the NMR nevertheless indicated the order of magnitude of the acetyl group content. Evidently, the acetic anhydride serves not only to imidize the oligomer, but also to form mixed anhydrides. Such a reaction can be visualized as follows.



One would expect the oligomer prepared by the acetic anhydride imidization to have a lower melting point. This is borne out in that the meta-cresol imidized oligomer has a softening point of 175-180°C whereas the acetic anhydride imidized oligomer softens at 150°C. The variation in acetyl contents from batch to batch may very well account for some of the inconsistencies observed in lap shear strengths when different batches are used.

These oligomers imidized by the two methods possessed some very interesting properties. They were more soluble than the corresponding oligomers having a DP of one. They were even somewhat soluble in chloroform, a solvent in which HR600 with DP of one is only very slightly soluble.

a. Adhesive Bond Strengths

The first group of experiments were carried out on a single batch of resin (the meta-cresol/benzene imidized resin H1224-71A and the acetic anhydride imidized oligomer H1224-71B) in order to avoid introducing a variable due to differences in composition of the resin. A detailed study was undertaken to optimize the strength of the bond by varying prepreg advancement time, postcure time and postcure temperatures. Lap shear tests were performed on titanium specimens (cleaned as per Hughes HP9-30) bonded with HR600-DP2 impregnated Clark-Schwebel 112 heat-cleaned glass fabric. These specimens were prepared from prepregs which had been advanced at 375°F for various times before being fabricated into lap shear specimens. The specimens were cured at both 560°F and 600°F in air at 15 psi for various lengths of time. In most cases single specimens were used rather than multiple specimens in order to conserve material and time. This type of experimental study was undertaken to indicate trends in adhesive strengths.

The specimens were fabricated from different blends of meta-cresol/benzene and acetic anhydride imidized resins. N-methylpyrrolidinone was used as the lacquer solvent to prepare the prepregs. The results of this study are shown in Table IV. From examination of the data certain trends can be discerned. These are as follows:

1. Acetic anhydride imidized resin is required to prevent adhesive type failure. The best results appear to be with the 50:50 blends of oligomers.
2. Excellent ambient and 500°F lap shear strengths are possible with this type of resin.

It is noteworthy that the presence of acetic anhydride imidized oligomer with the meta-cresol/benzene imidized oligomer is required to give a cohesive failure mode. Evidently the acetic anhydride imidized oligomer increases the wettability of the titanium by the resin. The mechanism of this is not understood at this time. It may be due to the presence of reactive acid anhydride sites which interact with the titanium.

Using a different batch of resin (H1224-85A and H1224-85B) gave different values for the lap shear strength of a 50:50 mixture. The latter batch

TABLE IV. EFFECT OF CURE SCHEDULE ON LAP SHEAR STRENGTH, HR600-DP2 TITANIUM SPECIMENS*

Wt. Ratio of Meta-Cresol/Benzene to Acetic Anhydride Imidized Oligomer	Prepreg Preconditioning Time (Min) at 375°F	Cure Temp., °F	Cure Time Hrs.	Lap Shear Strength, psi		Failure Mode Cohesive (CO); Adhesive (AD)	
				RT	500°F	RT	500°F
100:0	0	560	5	2800	-	CO/AD	-
	0	600	3	2300	-	CO/AD	-
	0	600	5	1700	-	CO/AD	-
	15	560	5	1800	-	CO/AD	-
	15	600	3	2600	-	CO/AD	-
	15	600	5	1500	-	CO/AD	-
	25	560	5	2300	-	CO/AD	-
	25	600	3	2600	-	CO/AD	-
	25	600	5	1300	-	CO/AD	-
	42	560	5	640	-	AD	-
	42	600	3	600	-	AD	-
	42	600	5	410	-	AD	-
	70	560	5	450	-	AD	-
	70	600	3	540	-	AD	-
	70	600	5	170	-	AD	-
90:10	0	560	5	2800	1900	CO/AD	CO/AD
	0	600	2	2200	2300	CO/AD	CO/AD
	15	560	5	2300	2400	CO/AD	CO/AD
	15	600	2	2200	2300	CO/AD	CO/AD
	25	560	5	2400	2100	CO/AD	CO/AD
	25	600	2	2100	1600	CO/AD	CO/AD
	42	560	5	1300	900	CO/AD	CO/AD
	42	600	2	1400	900	CO/AD	CO/AD
	70	560	5	600	200	AD	AD
	70	600	2	500	300	AD	AD
75:25	0	560	5	3000	1900	AD/CO	AD/CO
	0	600	2	2500	1900	AD/CO	AD/CO
	15	560	5	2500	2100	AD/CO	AD/CO
	15	600	2	2000	2100	AD/CO	AD/CO
	25	560	5	2400	1900	AD/CO	AD/CO
	25	600	2	1900	2100	AD/CO	AD/CO
	42	560	5	1800	1000	AD/CO	AD/CO
	42	600	2	1800	1400	AD/CO	AD/CO
	70	560	5	900	800	AD/CO	AD/CO
	70	600	2	800	700	AD/CO	AD/CO
50:50	0	560	5	2800	-	CO	-
	0	600	2	3000	-	CO	-
	15	560	5	3000	-	CO	-
	15	600	2	3000	-	CO	-
	25	560	5	3400	2000	CO	CO
	25	560	5	3000	-	CO	-
	25	560	10	3000	2500	CO	CO
	25	600	1	3200	1800	CO	CO/AD
	25	600	2	3000	-	CO	-
	25	600	3	2900	1800	CO	CO
	25	600	5	2600	2400	CO	CO
	42	560	5	2000	2100	CO	CO
	42	560	5	3200	-	CO	-
	42	560	10	3000	2600	CO	CO
	42	600	1	3600	1700	CO	CO/AD
	42	600	2	2000	-	CO	CO
	42	600	3	3100	2200	CO	CO
	42	600	5	2700	2600	CO	CO
	70	560	5	3000	-	CO	-
	70	600	2	3000	-	CO	-

*The glue line was 0.003 ±0.0003 inch. The lacquer solvent used to prepare the prepreg was N-methylpyrrolidinone. Prepregs were made with 112 heat-cleaned glass fabric. Resin identification numbers, H1224-71A and -71B. Titanium cleaned as per HP9-30.

appear to contain a higher concentration of mixed anhydrides compared to the earlier batch (1.5 acetyl groups per molecule compared to 1.3 acetyl groups per molecule). Lower values for the lap shear strength were found for the latter batch even though the processing into lap shear specimens were comparable for both batches. Thus the higher concentration of acetyl groups in the latter batch degrades the strength of the adhesive bond. The optimum value of the acetyl group concentration in the acetic anhydride imidized oligomer remains as yet to be resolved. The lap shear strengths thus far observed for this resin system can most certainly be increased.

Since it appears that the role of the acetic anhydride imidized oligomer is to improve the wettability of the titanium a group of experiments were carried out using the acetic anhydride imidized oligomer (H1224-85B) only as a primer for the titanium and the meta-cresol imidized oligomer as bonding resin. The results are shown in Table V and compares primed and unprimed substrates. The primed surfaces were not cured prior to assembly. It is noteworthy that priming of the titanium substrate increased both the room temperature and 500°F lap shear strengths. The ambient temperature results for the unprimed substrate are consistent with the meta-cresol imidized oligomer of the previous batch (H1224-71A). The results of the previous batch are shown in Table IV. Table VI compares the results of the two batches. Further investigation of the use of a primer is warranted from these results.

b. Titanium Honeycomb Structures

Titanium honeycomb specimens were prepared, using 3/4 inch titanium honeycomb between 50 mil 6Al4V titanium sheets. The honeycomb had 1/4 inch cells of 4 to 4.5 mil foil. The titanium was etched with the TURCO alkaline bath before assembly. Results of the Pi-Tension Honeycomb tests are shown in Table VII.

TABLE V. THE EFFECT OF ACETIC ANHYDRIDE IMIDIZED OLIGOMER AS A PRIMER ON LAP SHEAR STRENGTHS – HR600C-2DP RESIN*

Prepreg Conditioning Time at 360°F Min	No Priming – Lap Shear Strengths, psi		With Priming – Lap Shear Strengths, psi		Failure Mode			
					No Priming		With Priming	
	RT	500°F	RT	500°F	RT	500°F	RT	500°F
0	-	-	2500	970	-	-	CO	AD
	-	-	2500	1180	-	-	CO	AD
	-	-	2700	-	-	-	CO	
15	2800	610	3300	1340	CO	AD	CO	AD
	2500	870	3000	1490	CO	AD	CO	AD
25	2700	1100	2600	1070	CO	AD	CO	AD
	2600	890	2900	1240	CO	AD	CO	AD

*Specimens prepared using Type 6Al4V titanium, 112 heat cleaned glass cloth prepreg containing 75-80 percent resin (H1224-85B). Primer, resin H1224-85A. Cured at 600°F for 3 hours. Titanium etched with TURCO 5578 alkaline etchant.

TABLE VI. COMPARISONS OF LAP SHEAR STRENGTHS FOR DIFFERENT BATCHES OF HR600C-2DP RESINS – PRIMED AND UNPRIMED SURFACES – AMBIENT TEMPERATURE

Prepreg Conditioning Time (Min) at 375°F	Lap Shear Strengths, psi		
	No Primer		With Primer
	Resin H1224-71A	Resin H1224-85B	Resin H1224-85B
0	2300		2500 2500 2700
15	2600	2800 2500	3300 3000
25	2600	2700 2600	2600 2900

TABLE VII. PI-TENSION TENSILE STRENGTHS OF TITANIUM HONEYCOMB SPECIMENS (NOTES 1 AND 2)

Honeycomb Specimen	Ambient Temperature Tensile Strength psi	Remarks
-1 (Note 3)	150	Filleting (moderate)
-2 (Note 4)	99	Low to moderate filleting

Notes:
(1) Honeycomb specimens were prepared and tested in accordance with General Dynamics Corp. Specification FMS-1013. Give details of this Spec in an Appendix.

(2) Heat cleaned glass cloth 112E was employed as a reinforcement using a 50:50 mixture of resin H1224-71B (acetic anhydride imidized oligomer) and H1224-85B (meta-cresol imidized oligomer). Both specimens cured at 600°F for 3 hours.

(3) Prepared using 15 psi pressure on titanium faces in a 600°F oven.

(4) Prepared using only very moderate pressure (0.55 psi) on titanium faces in a 600°F oven.

Undoubtedly much higher tensile strengths can be obtained for this resin. Examination of the failed surfaces showed that only moderate to low filleting was present. In one of the specimens (specimen 2) a very low pressure (0.55 psi) was used and was probably responsible for the lower tensile strength (99 psi) compared to the 15 psi molding pressure (150 psi tensile strength).

c. Thermal Aging Tests

Thermal aging tests have been completed on the HR 600 resin having a degree of polymerization of 2. Titanium lap shear specimens were fabricated from 6Al4V titanium etched with the TURCO alkaline cleaner. The prepreg was made using 112E heated cleaned glass cloth impregnated with an equal weight mixture of meta-cresol imidized HR 600 DP-2 (H1224-70B) and acetic anhydride imidized HR 600 DP-2 (H1224-85A). No preconditioning was performed on the prepreg. The specimens were cured at 600°F for 3 hours in air. The tests were conducted at ambient, 300°F, 450°F and 500°F. The results are shown in Table VIII. This table depicts the lap shear strengths as a function of time. At 300°F, almost all of the lap shear strengths are retained over the 1000 hour interval. At 450°F, the lap shear strengths gradually decrease to about 80 percent of their value before aging. At 500°F, the strengths decrease to about 30-40 percent. Because of the scatter of the data it is difficult to obtain a more accurate interpretation of the retention of lap shear strengths as a function of aging time.

Table IX depicts the effect of long term aging in 90 percent relative humidity at 160°F. The results show that there is excellent retention of strengths. The results obtained at 450°F and 251 hours appear to be anomalous and could only be explained in that the specimens may have been poorly prepared. One would not expect the strengths to undergo a decrease and then an increase in values for this type of resin.

T-Peel Tests

T-peel specimens have been prepared by bonding one-inch strips of 5 mil 6Al4V titanium alloy with the prepreg fabric made using a 50:50 mixture of resin batches H2350-6A and -6B using a 3 hour cure at 600°F. T-peel strengths were determined according to ASTM T-Peel Method D1876.

The peel distance in each case was five inches. Two specimens were measured. One gave 2.0 lbs/in. and the other 1.8 lbs/in. average strength. Testing was done at ambient temperature.

TABLE VIII. EFFECTS OF LONG TERM AIR AGING ON LAP SHEAR STRENGTHS, 50:50 MIXTURE OF HR 600A AND HR 600C, DP-2*

Time, hours at Temperature	Lap Shear Strength, psi at Aging Temperature	Failure Mode
Room Temperature	3600	CO
300°F		
0	3200	CO
0	2500	CO
113	3000	CO
113	2500	CO
274	2400	CO
274	3100	CO
510	2900	CO
510	2900	CO
714	3300	CO
714	3200	CO
1000	2900	CO
1000	3100	CO
450°F		
0	2800	CO
0	2100	CO
113	2400	CO
113	2700	CO

*Titanium cleaned with Turco Alkaline Cleaner 5578; Prepreg, 112 heat cleaned glass cloth impregnated with 50:50 mixture of resin batches H1224-70B and H1224-85-A. No preconditioning of prepreg. Cure at 600°F for 3 hours in air at 15 psi pressure.

(Continued next page)

(Table VIII, concluded)

Time, hours at Temperature	Lap Shear Strength, psi at Aging Temperature	Failure Mode
450°F (cont)		
274	2800	CO
274	2800	CO
510	2600	CO
510	2500	CO
714	2600	CO
714	2200	CO
1000	1900	CO
1000	1900	CO
500°F		
0	1300	CO/AD
	1600	CO/AD
113	2300	CO
113	2100	CO
274	1700	AD/CO
274	2600	CO
490	1300	AD
490	1300	AD
750	1000	AD
750	600	AD
995	1600	AD
	800	AD

TABLE IX. EFFECT OF LONG TERM AGING IN 90 PERCENT RELATIVE HUMIDITY, 160°F ON LAP SHEAR STRENGTHS, 50:50 MIXTURE OF HR 600A AND HR 600C, DP-2*

Time, hours	Lap Shear Strength, psi		Failure Mode	
	R.T.	450°F	R.T.	450°F
0	2100 2400 2600	2100 2200	CO CO CO	CO CO
113	2300 2600	1800	CO CO	CO/AD
251	1900	1500 1000	CO/AD	CO/AD CO/AD
500	2100	2200 1800	CO	CO/AD CO/AD
929	1900 2100 2100	1400 1900 1900	CO CO CO	CO/AD CO/AD CO/AD

*Titanium cleaned with Turco Alkaline Cleaner 5578; Prepreg, 112 heat cleaned glass cloth impregnated with 50.50 mixture of resin batches H1224-70B and H1224-85-A. No preconditioning of prepreg. Cure at 600°F for 3 hours in air at 15 psi pressure.

It is recognized that bonded aluminum will have comparatively more peel strength than bonded titanium due to the lower modulus of the aluminum, which permits it to bend more as it peels. It is felt that even lower thickness of titanium than the 5 mil used here should be used to obtain useful T-peel data.

3. HR600 Type Oligomer, Degree of Polymerization of 3

The acetylene terminated polyamic acid having a degree of polymerization (DP) of 3 was prepared so as to learn if a further decrease in cross-link density would improve the lap shear strength of bonded titanium specimens. The oligomer having a DP of 3 is depicted by structure II when n = 3.

The acetylene terminated polyamic acid having a DP of 3 (n = 3) was prepared (H1224-86) by the reaction of benzophenonetetracarboxylic dianhydride, 1, 3-di(3-aminophenoxy)benzene and 3-aminophenylacetylene in molar ratios of 4:3:2. The oligomer was imidized in two ways, the first with meta-cresol/benzene mixture and the second by acetic anhydride.

For the 50:50 mixture of the imidized oligomer ambient temperature lap shear strengths up to 3500 psi were obtained. However, at 500°F the lap shear strength dropped to 600 psi or less. It appears that some flow had taken place at the higher temperature which contributed to the failure mode of the bonded joint. The use of the meta-cresol imidized oligomer by itself does not give good lap shear strengths. Only nominal values were obtained (800 psi or less). Upon examination of the failed bond, poor flow of the adhesive was apparent which resulted in poor contact of the adhesive with the titanium substrate. A series of titanium lap shear specimens was fabricated using acetic anhydride imidized HR600 oligomer with a DP of 2 as a primer. The meta-cresol imidized oligomer was used as the bonding resin in the form of a 112 glass cloth prepreg. Somewhat better strengths were obtained (up to 1700 psi) mainly because of better wetting of the adhesive. Again, the poor flow of the adhesive was responsible for only spot contact of the adhering substrates.

Further work with the DP-3 resin is not recommended at this time. It appears to be too viscous at cure temperatures to give a good bond. Also, the acetic anhydride imidized oligomer may possibly have too much flow at the higher temperatures (500°F) to impart good high temperature adhesive properties.

4. HR650 Type Oligomers

The relatively high modulus of the HR600 oligomers having a degree of polymerization of one made the cured resin somewhat brittle and therefore limited the lap shear strength. In order to decrease the modulus and thereby the brittleness of these types of oligomers, two extra ether linkages were introduced into the polymer backbone. This was accomplished by substituting 3-(3-aminophenoxy)benzene (XIII) for the 3-aminophenylacetylene (XII). The structure of such an oligomer is shown by formula IV. The extra ether linkages increased the solubility and fluidity compared to the HR 600. The melting point (140°C) was about 50°C lower.

As in the case of the HR600 type oligomer the best ambient temperature strengths were obtained using mixtures of acetic anhydride and meta-cresol/benzene imidized oligomers rather than the meta-cresol/benzene imidized oligomer alone. It appears that the role of the acetic anhydride imidized oligomer is to promote wetting of the titanium substrate by the adhesive. Even though the titanium had been cleaned by a fluoride-phosphate method the meta-cresol/benzene imidized oligomer lacks sufficient residual functionality to make as good an adhesive bond. The acetic anhydride imidized oligomer was found to contain mixed anhydrides. The amount of mixed anhydride varied from batch to batch and was found to affect the strength of the adhesive bond.

Lap shear strengths of titanium specimens bonded only with the meta-cresol imidized HR650 gave poor results, mainly due to the fact that the failure mode was adhesive. However, with the same cure cycle, the use of a 50:50 mixture of meta-cresol/benzene and acetic anhydride imidized oligomers gave higher lap shear strengths and the failure mode changed to cohesive/adhesive. These are shown in Table X.

A study was undertaken to optimize the lap shear strength of the 50:50 mixture using the same resins. These are shown in Table XI.

TABLE X. LAP SHEAR STRENGTHS OF TITANIUM SPECIMENS BONDED WITH HR650A/C (50:50 MIXTURE) AND HR650C

Test Temperature °F	HR650C Lap[a)] Shear Strengths, psi	50:50 Mixture[b)] HR650A/C Lap Shear Strengths, psi
Ambient	1520 1570 1730 2190 1750 ave	2600 2750 2730 2693 ave
450	2080 1750 2290 2230 2080 ave	
500	1390 1410 1350 1340 1370 ave	2340 2400 2400 2380 ave

All specimens cured at 600°F/8 hours, 0.003 glue line.

[a)] Clark-Schwebel 112 glass cloth – heat cleaned. 75 percent resin pickup from chloroform. Resin H1224-26.

[b)] Clark-Schwebel 112 glass cloth – heat cleaned. 50 percent resin pickup from chloroform. Resins H1224-35A and -35B.

TABLE XI. EFFECT OF CURE SCHEDULE ON LAP SHEAR STRENGTH, HR650A/C (50:50 MIXTURE) TITANIUM SPECIMENS*

Experiment No.	Prepreg Prepn Solvent, Final Resin Content, Percent	Prepreg Preconditioning Time, Min, at 375°F	Cure Temp, °F	Cure Time	Lap Shear Strength, psi		
					RT	450°F	500°F
H1550-02	Chloroform, 50	10	600	8 hrs	2600 2750 2730 2693 ave	- - - -	2340 2400 2400 2380 ave
H1550-05	Chloroform, 70	0	600	8 hrs	2310 2200 2255 ave	- -	- -
		10	600	8 hrs	-	-	2020 2043 2032 ave
		20	600	8 hrs	- -	- -	2110 2390 2250 ave
		30	600	8 hrs	3430 3430 3430 ave	- -	2500 2210 2350 ave

*Glue line 0.003 inch ±10 percent. Adhesive applied as a resin impregnated 112 heat-cleaned glass fabric. Resins H1224-35A and H1224-35B. A pressure of 15 psi was used during cure.

(Continued next page)

(Table XI, continued)

Experiment No.	Prepreg Prepn Solvent, Final Resin Content, Percent	Prepreg Preconditioning Time, Min, at 375°F	Cure Temp, °F	Cure Time	Lap Shear Strength, psi		
					RT	450°F	500°F
H1550-05 (continued)	Chloroform, 70 (continued)	60	600	8 hrs	1510 1150 <u>1330 ave</u>	- -	- -
		90	600	8 hrs	870 990 <u>930 ave</u>	- -	- -
	Chloroform, 50	120	600	8 hrs	540 590 <u>565 ave</u>	- -	- -
		150	600	8 hrs	490 540 <u>510 ave</u>	- -	- -
H1550-07	NMP, 70	0	600	17 hrs	1280	-	-
		10			1590	-	-
		20			1760	-	-
		30			1570	-	-
		40			1420	-	-
		50			1430	-	-
		60			1940	-	-
		70			1780	-	-
		80			1570	-	-
		90			1640	-	-

(Continued next page)

(Table XI, continued)

Experiment No.	Prepreg Prepn Solvent, Final Resin Content, Percent	Prepreg Preconditioning Time, Min, at 375°F	Cure Temp, °F	Cure Time	Lap Shear Strength, psi		
					RT	450°F	500°F
H1550-08	NMP, 70	0	600	3 hrs	2720	-	-
				4.5 hrs	2920	-	-
				6.5 hrs	2960	-	-
				8.5 hrs	1680	-	-
				20 hrs	1310	-	-
		30	600	3 hrs	2720	-	-
				4.5 hrs	3020	-	-
				6.5 hrs	2500	-	-
				8.5 hrs	1255	-	-
				20 hrs	1390	-	-
		60	600	3 hrs	3250	-	-
				4.5 hrs	2360	-	-
				6.5 hrs	2620	-	-
				8.5 hrs	1180	-	-
				20 hrs	1350	-	-
		90	600	3 hrs	2220	-	-
				4.5 hrs	2360	-	-
				6.5 hrs	1450	-	-
				8.5 hrs	670	-	-
				20 hrs	1310	-	-
		120	600	3 hrs	1065	-	-
				4.5 hrs	1000	-	-
				6.5 hrs	1550	-	-
				8.5	1110	-	-
				20 hrs	485	-	-

(Continued next page)

(Table XI, continued)

Experiment No.	Prepreg Prepn Solvent, Final Resin Content, Percent	Prepreg Preconditioning Time, Min, at 375°F	Cure Temp, °F	Cure Time	Lap Shear Strength, psi		
					RT	450°F	500°F
H1550-09	NMP, 70	45	450	24 hrs	530 640 585 ave	- -	- -
			500	2.5 hrs	2740 2870 2870 2827 ave	- - -	- - -
				5 hrs	3320 3680 3500 ave	- -	- -
				24 hrs	3440 3960 3040 3480 ave	- - -	- - -
			550	1 hr	3730 3420 3575 ave	- -	- -
				2 hrs	3940 3550 3745 ave	- -	- -

(Continued next page)

(Table XI, continued)

Experiment No.	Prepreg Prepn Solvent, Final Resin Content, Percent	Prepreg Preconditioning Time, Min, at 375°F	Cure Temp, °F	Cure Time	Lap Shear Strength, psi		
					RT	450°F	500°F
H1550-09 (continued)	NMP, 70 (continued)	45	550	4 hrs	2800 3400 3100 ave	- -	- -
				5 hrs	3960 4290 4125 ave	- -	- -
			600	1 hr	3870 3520 3695 ave	-	-
				2 hrs	3850 3460 3655 ave	- -	- -
				4 hrs	2520 2850 2685 ave	- -	- -
H1550-12	NMP, 70	0	560	2 hrs	4000 - -	1270 1250 1340 1287 ave	770 - -

(Continued next page)

(Table XI, concluded)

Experiment No.	Prepreg Prepn Solvent, Final Resin Content, Percent	Prepreg Preconditioning Time, Min, at 375°F	Cure Temp, °F	Cure Time	Lap Shear Strength, psi		
					RT	450°F	500°F
H1550-12 (continued)	NMP, 70	0	500	4 hrs	- -	- -	970 1010 990 ave
				8 hrs	- -	- -	1180 1120 1150 ave
				18 hrs	-	-	1080

Chloroform and N-methylpyrrolidinone (NMP) were investigated as lacquer solvents for the HR650. Prepregs made with NMP looked much better than those made with chloroform. The NMP could be easily removed at 325-350°F from the prepreg by drying in a hot air oven for approximately 10-15 minutes. The resulting prepreg was translucent and well impregnated with no voids. It was found that preconditioning the prepreg at 375°F before the specimens were fabricated improved the lap shear strengths. This may be due possibly to the combined effect of advancing the resin, which increases the viscosity so that it is not squeezed out of the bonded joint, and removal or residual traces of solvent from the prepreg.

Several important trends appear to be present. They are as follows:

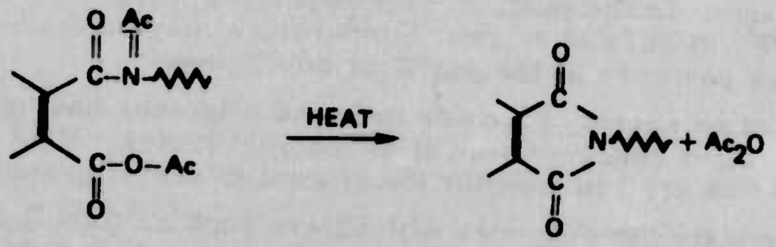
1. Preconditioning improves the lap shear strength of the bonded specimens possibly by removing residual solvent and by advancing the resin to an optimum viscosity.
2. Cure temperatures of 600°F improve the high temperature strength over that of lower cure temperatures (500 and 560°F) probably by increasing the crosslinking.
3. Cure temperatures less than 600°F give better ambient temperature strengths.

A new batch of resin (H1224-61) was prepared to study the effects of solvent and cure cycle on the lap shear strengths of titanium specimens bonded with this resin. Cure cycle experiments with this resin using cyclohexanone, chloroform, and N-methylpyrrolidinone as solvents for the preparation of prepregs with heat-cleaned Clark-Schwebel 112 glass fabric yielded lap shear strengths for titanium bonded samples which were inconclusive. The samples had an adhesive type of failure mode and the prepreg appeared to be resin-starved. Evidently the resin had been pushed out of the prepreg during the cure cycle.

A new batch of HR650 was prepared (H1224-72A and -72B) and both the meta-cresol/benzene and the acetic anhydride imidized oligomers were characterized by nuclear magnetic resonance (NMR) in order to gain insight as to the nature of the differences found from batch to batch. Based on NMR spectra, approximately 1.8 acetyl groups per oligomer molecule were found for the acetic anhydride imidized oligomer. Curing studies on a heated aluminum block with this oligomer showed that it cures more slowly than the m-cresol/benzene fraction. Upon melting on the block, some frothing of the resin took place. This may be due to reimidization of the oligomer by splitting of acetyl groups. No such frothing was noted for the meta-cresol/benzene imidized product. It is felt that the lack of reproducible lap shear strengths found between different batches of resin can be attributed to the different amounts of mixed anhydride present in the acetic anhydride imidized fractions. NMR offers a convenient method of monitoring the amount of mixed anhydride present in this fraction.

The lap shear strengths for the new batch of resin (H1224-72A and -72B) were measured. It was noted on the tested samples that many failed by the adhesive mode and almost none by cohesive modes. Microscopic examination of the failed bond showed the resin in the prepreg had been pushed out, possibly by some outgassing phenomenon. The flash from the adhesive joint was foam-like, further indicating outgassing. This phenomenon would be expected to degrade the strength of the adhesive bond.

The reimidization of the mixed anhydride during cure could account for any gaseous products. The reaction to account for this is shown below.



Nevertheless, fairly respectable values for room temperature lap shear strengths were seen, with values up to 2600 psi. The 500°F values were poorer, the best value being 1600 psi, which is considerably less than the 2600 psi for resin H1224-35A, and -35B. No significant differences were noted for lap shear strengths made from prepregs receiving varying amounts of preconditioning at 357°F. These observations are consistent with an oligomer containing a greater concentration of mixed anhydrides. It is also significant that blends of the two oligomers gave poorer strengths than those obtained using only the meta-cresol/benzene imidized oligomer.

The role of the acetic anhydride imidized resin in resin blend appears to make the oligomer better wet the titanium surface. However, the presence of the mixed anhydride could present difficulties in that the reimidization during cure would lead to volatile by-products.

The fact that lap shear strengths in excess of 4000 psi had been obtained for some of the 50:50 mixtures of acetic anhydride and metacresol imidized oligomers shows that the presence of the acetic anhydride imidized oligomer can result in high strength adhesive bonds. This suggests that the present batch of oligomer which gave poorer results had a greater concentration of mixed anhydrides.

These results suggest several approaches to increase the lap shear strength. These are:

1. Use the acetic anhydride imidized oligomer to prime the titanium substrate and the meta-cresol/benzene oligomer for the bonding resin.
2. Use a step temperature cure cycle to improve the lap shear strength. In the past, two temperatures were used – 560°F and 600°F. A cure at a lower temperature may be more desirable with a postcure at the 560°F or 600°F level.
3. Use of an acetic anhydride imidized oligomer having a carefully controlled concentration of mixed anhydrides. NMR spectra would be used to monitor the amount of acetyl groups present.
4. Formulate the oligomer with fillers such as Cab-O-Sil to improve adhesive qualities.

5. Mixtures of HR 600C and HR 650C Oligomers

In order to improve the processing characteristics of HR 600C resin a group of titanium lap shear specimens were fabricated using HR 650 as an additive. It was felt that the introduction of about 10 percent by weight of HR650C would improve the flow of the resin during cure and promote better adhesion. The titanium surfaces were primed with acetic anhydride imidized HR600 having a DP of 2. Table XII shows the results obtained. Excellent ambient temperature lap shear strengths were obtained. However, the lap shear strength at 500°F dropped down considerably. The failures were adhesive and it looked like the primer coat had softened. Evidently this batch of the primer had too high an acetyl group content. However, the approach using primers is very promising since the meta-cresol imidized HR600 oligomer by itself and without primer generally gave poorer room temperature lap shear strengths. It appears that the primer used in this study softens in the temperature range of 450-500°F. Solutions to this are the use of acetic anhydride imidized oligomers which have higher softening points, possibly the HR600 having a DP of 1.

It appears that blends of HR650C and HR600C are capable of giving good lap shear strengths and further work is justified.

6. Acetylene-Terminated Oligomer from the Reaction of Benzophenonetetracarboxylic Dianhydride, Bis-(3-aminophenyl)sulfone and 3-Aminophenylacetylene

Two of the three intermediates used in the preparation of HR600 and HR650 prepolymers are not yet available from commercial sources. As a means of reducing the cost of acetylene terminated polyimide, changes have been considered where commercially available aryldiamines are substituted for the 1,3-di-(3-aminophenoxy)benzene which is presently made in this laboratory. The use of commercially available bis-(4-aminophenyl)ether in the HR650 type resin as depicted by V as a substitution aryldiamine yielded an imide which melted 5°C higher than the HR600C. It was also less soluble in solvents such as dimethylformamide. It thus appears that para oriented aryldiamines makes the resin less processable.

TABLE XII. LAP SHEAR STRENGTHS OF A MIXTURE OF HR600C AND HR650C OLIGOMERS IN 90:10 WEIGHT RATIOS

Prepreg Preconditioning Time (Min) at 375°F	Lap Shear Strength, psi			Failure Mode		
	RT	450°F	500°F	RT	450°F	500°F
0	3200 3500	1800 2200	1100 700	AD/CO AD	AD AD	AD AD
15	3100 3300	1000 2000	800 800	CO/AD CO/AD	AD AD	AD AD
25	3300 3200	2100 2100	900 100	AD AD	AD AD	AD AD
42	3200 -	1900 -	300 500	AD	AD	AD AD

Specimens prepared using 6Al4V titanium, 112 heat cleaned glass cloth prepreg containing 75 percent resin (H1224-98, HR600C-DP-1 90pts, and H1224-96 HR650C, 10 pts), Primer HR600A-DP-2 (H1224-85A) – Cured at 600°F for 3 hours. Titanium etched with TURCO 5578 alkaline etchant.

A meta orientation of the functional groups was then considered. A search for a commercially available diamino aryl intermediate yielded the compound bis-(3-aminophenyl)sulfone (Aldrich Chemical Company, Inc. Cat. No. A7, 460-2). An HR600 type resin was prepared using this intermediate. A polyamic acid made by the reaction of 3-aminophenylacetylene, bis-(3-aminophenylsulfone and benzophenonetetracarboxylic dianhydride (Experiment H1224-54) was imidized two ways; the first with acetic anhydride and the second with meta-cresol/benzene. The imidized product had a lower melting point than HR600 and was more soluble. It was even soluble in chlorinated solvents such as chloroform, although not adequately soluble to make a useful lacquer.

The Clark-Schwebel 112 heat cleaned glass fabric impregnated with a 50:50 mixture of the acetic anhydride and meta-cresol/benzene imidized resin using cyclohexanone as a solvent was used to prepare some titanium bonded lap shear specimens. The best results to date showed ambient temperature lap shear strengths up to 2000 psi and 500°F lap shear strengths up to 1700 psi.

Further tests are required to learn its potential as an adhesive for titanium.

7. Weldbonding

Weld schedules have been established for spotwelding of titanium specimens and both spotwelded and weldbonded specimen have been prepared. All spotwelded lap shear specimens had a one-inch overlap. Weld schedules were established on three phase Sciaky Spot Welders with solid state controllers, and both spotweld and weldbonded specimens were prepared for S/N tests. The titanium was cleaned with Turco 5578 alkaline cleaner. The weld nugget was centrally located on the overlap and was approximately 1/4-inch diameter. This weld gave about 3000 psi for the lap shear strength. The adhesive mixture used in the weldbond had the following composition by weight: HR600A with a DP of 2 (H1224-85B), 25 percent; HR600C with a DP of 2 (H1224-85A), 25 percent; aluminum powder, 325 mesh, 50 percent; dimethylformamide, sufficient to make a readily applicable paste. After spotwelding through the adhesive, the specimens were dried at 350°F for 30 minutes to remove solvent and then cured at 600°F for 3 hours. Good spotwelds were obtained on lap shear specimens containing this formulation. These specimens were identified by the numbers H2350-01-A1 through -A25.

8. S/N Tests

S/N (fatigue) tests were run to evaluate the fatigue life of aluminum filled HR600AC-DP2 bonded spotwelded titanium. These tests were run on 1.0 inch overlap, 0.050 inch thick titanium specimens 1.0 inch wide. The specimens were adhesive bonded, spotwelded and weldbonded. The adhesive used in preparing the weld bond specimen was described in the previous section. The fatigue tests were run at 30 cycles per second. The S/N tests on the adhesive bonded, spotwelded and weldbonded specimens are shown in Figures 3, 4 and 5. The weldbonded specimens (Figure 5) clearly show increased fatigue resistance over the spotwelded specimens. No carrier cloth was used in any of the specimens used for the fatigue tests.

Figure 6 shows the four observed types of failure modes and Tables XIII, XIV and XV contain the applied loads, cycles to failure, and failure mode for adhesive bonded, spotwelded and weldbonded specimens.

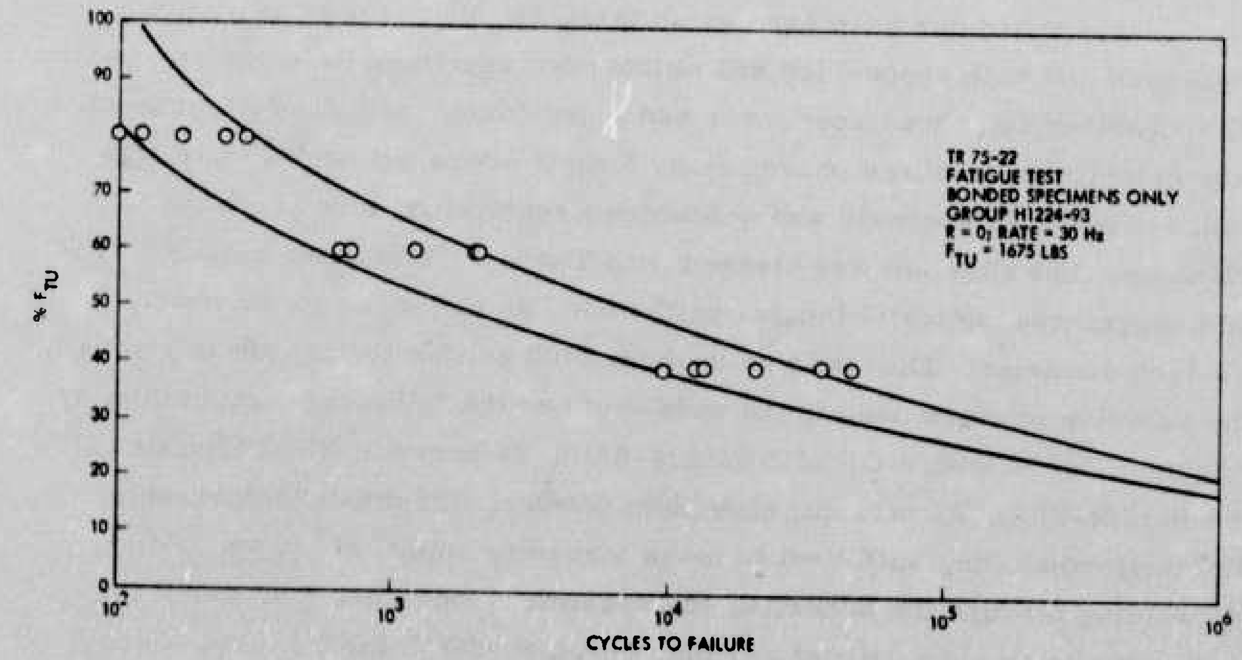


Figure 3. Fatigue (S/N) tests on adhesive bonded titanium specimens.

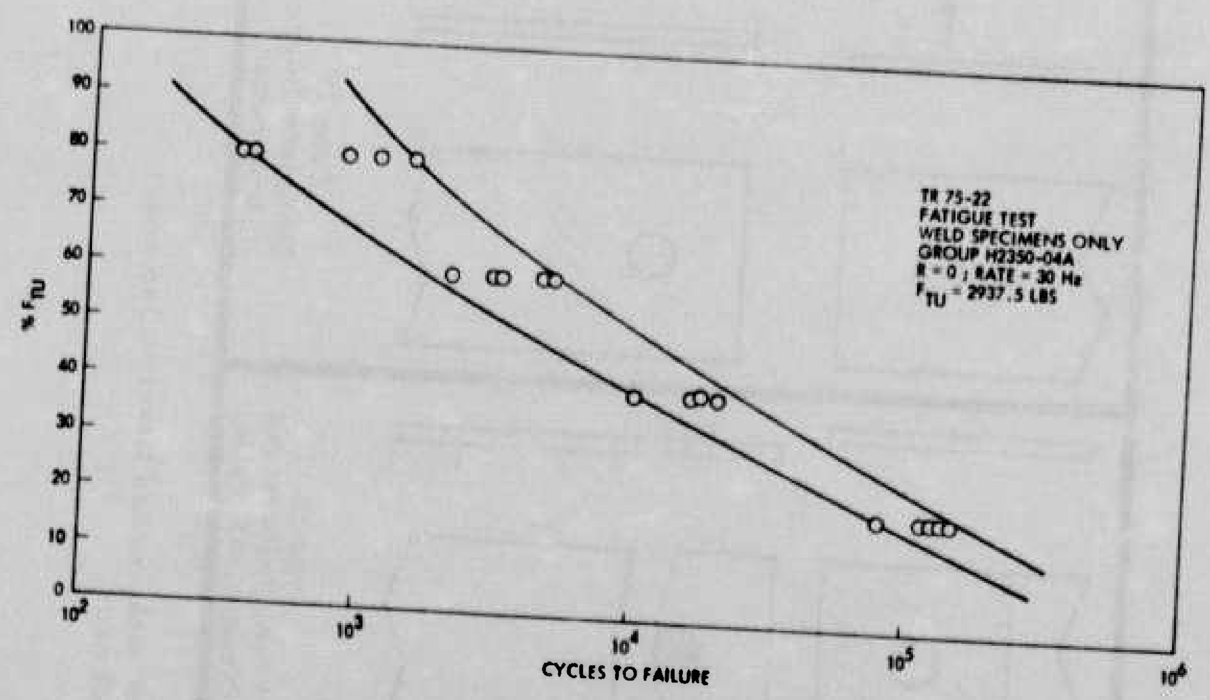


Figure 4. Fatigue (S/N) tests on welded specimens.

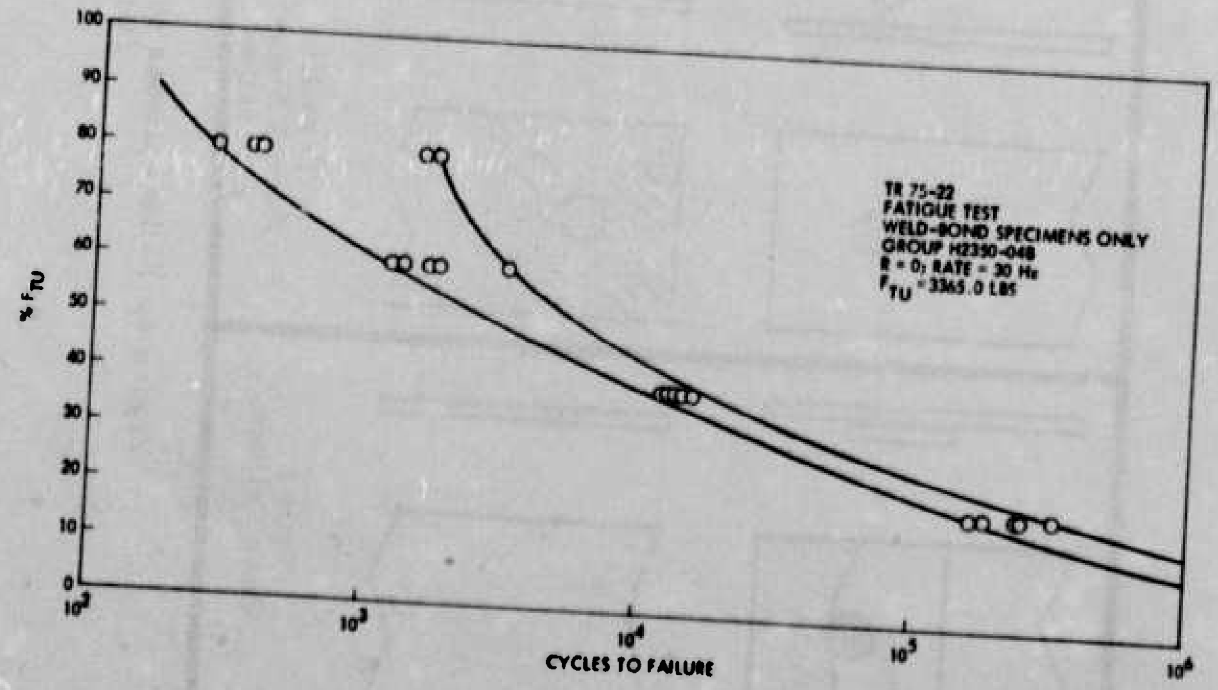


Figure 5. Fatigue (S/N) tests on weld bonded specimens.

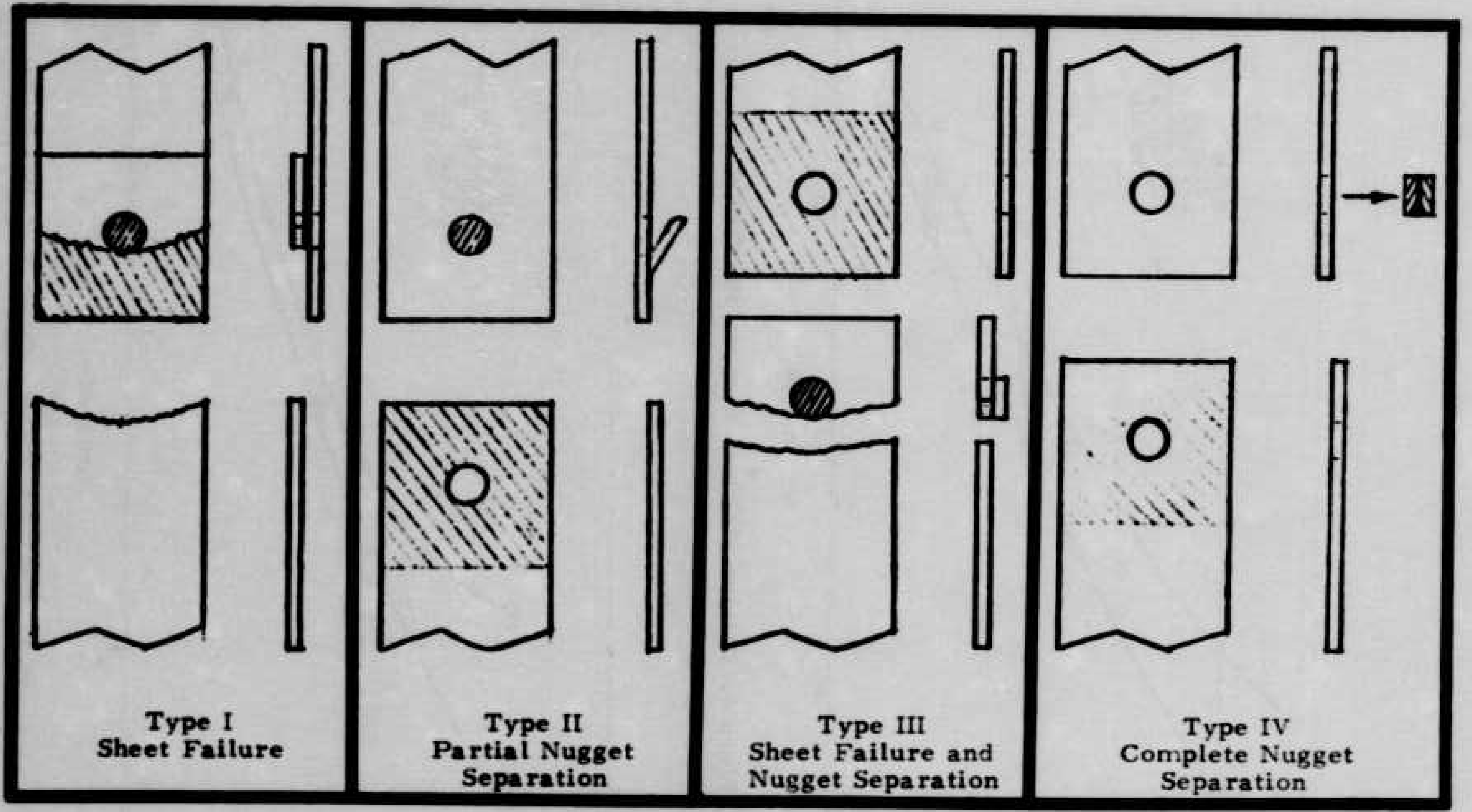


Figure 6. Failure modes observed on weldbonded titanium lap shear fatigue specimens.

TABLE XIII. FATIGUE TEST ADHESIVE BONDED TITANIUM SPECIMENS, F_{TU} = 1675 LBS, R = 0

Specification No. H1224-93		Load (lb)	N Cycles	Failure Mode	Comments
0.8 F_{TU}	3	0-1340	0	AD	
	4	0-1340	120	AD	
	5	0-1340	240	AD	
	6	0-1340	170	AD	
	7	0-1340	285	AD	
0.6 F_{TU}	8	0-1005	1,960	AD	
	9	0-1005	690	AD	
	10	0-1005	630	AD	
	11	0-1005	2,030	AD	
	12	0-1005	1,200	AD	
0.4 F_{TU}	13	0-670	13,260	AD	
	14	0-670	20,310	AD	
	15	0-670	12,300	AD	
	16	0-670	9,600	AD	
	17	0-670	46,000	AD	
	29	0-670	36,000	AD	
0.2 F_{TU}	18	0-335	2,504,000		No Failure
	19	0-335	2,542,000		No Failure
	20	0-336	2,504,000		No Failure
	21	0-335	10,185,000		No Failure
	22	0-335	8,498,000		No Failure

TABLE XIV. FATIGUE TEST SPOTWELDED TITANIUM SPECIMENS, F_{TU} = 2937.5 LBS, R = 0

Specification No. H2350-04A		Load (lb)	N Cycles	Failure Mode
0.8 F_{TU}	3	0-2350	840	II
	4	0-2350	375	II
	5	0-2350	360	IV
	6	0-2350	1,095	III
	7	0-2350	1,485	II
0.6 F_{TU}	8	0-1762.5	4,920	I
	9	0-1762.5	3,210	II
	10	0-1762.5	4,500	
	11	0-1762.5	2,070	II
	12	0-1762.5	3,000	II
0.4 F_{TU}	13	0-1175	20,000	I
	14	0-1175	10,000	I
	15	0-1175	17,000	I
	16	0-1175	17,000	I
	17	0-1175	16,000	I
0.2 F_{TU}	18	0-587.5	137,000	I
	19	0-587.5	141,000	I
	20	0-587.5	116,500	I
	21	0-587.5	78,000	I
	22	0-587.5	127,000	I

TABLE XV. FATIGUE TEST WELDBONDED TITANIUM SPECIMENS, F_{TU} = 3365.0 LBS, R = 0

Specification No. H2350-04B		Load (lb)	N Cycles	Failure Mode
0.8 F_{TU}	3	0-2692	270	
	4	0-2692	390	II
	5	0-2692	1,710	II
	6	0-2692	1,500	
	7	0-2692	360	
0.6 F_{TU}	8	0-2019	1,200	
	9	0-2019	3,120	
	10	0-2019	1,320	
	11	0-2019	1,620	II
	12	0-2019	1,770	
0.4 F_{TU}	14	0-1346	14,280	
	15	0-1346	12,660	
	16	0-1346	15,750	I
	17	0-1346	13,860	I
	23	0-1346	12,000	
0.2 F_{TU}	18	0-673	327,000	
	19	0-673	164,000	I
	20	0-673	248,000	I
	21	0-673	187,000	I
	22	0-673	250,000	

V. EXPERIMENTAL

Monomer Preparation

Preparation of 3-(3-nitrophenoxy)acetophenone – Experiment H1057-69

To a slurry of sodium sand (46.0 grams, 2.00 g-atoms) in dry tetrahydrofuran (1 liter), a solution of methanol (73.8 grams, 2.30 moles) in tetrahydrofuran (200 ml) was added dropwise with vigorous stirring. After all of the sodium had reacted, as evidenced by the absence of a grey color the slurry was added under argon to a solution of 3-hydroxyacetophenone (272.4 grams, 2.00 moles) in tetrahydrofuran. The reaction mixture was concentrated to dryness by distilling off the tetrahydrofuran using an oil bath as the heat source to prevent scorching. The last traces of solvent were removed by applying vacuum. Then, to the cooled product was added finely ground cuprous chloride (46 grams) and a solution of 3-bromo-1-nitrobenzene (505 grams, 2.50 moles) in deaerated pyridine (2 liters). The mixture was heated at reflux overnight under argon. The crude product was isolated by distilling off the pyridine and extracting the residue with benzene. The filtered benzene extract was washed successively with 1:1 hydrochloric acid, 10 percent aqueous sodium hydroxide and finally water. After drying the benzene extract with anhydrous potassium carbonate, the benzene was distilled off on the rotary film evaporator. The residue was triturated with absolute ethanol to remove unreacted 3-bromo-1-nitrobenzene to yield 192.9 grams (39 percent of theory) of product having a melting point of 72°C.

Experiment H1057-73

To a rapidly stirred slurry of sodium sand (46.0 grams, 2.00 g-atoms) in ether (1 liter) was added dropwise a solution of methanol (73.8 grams, 2.3 moles) in 200 ml of ether. The sodium methoxide was isolated by distilling off the ether using an oil bath as the heat source to prevent scorching. Then a solution of 3-hydroxyacetophenone (272.4 grams, 2.00 moles) in 2500 ml of ether was added dropwise under argon to the sodium methoxide. The mixture was heated at reflux for 2 hours and the ether distilled off using an oil bath as the heat source. To the dry sodium salt, finely ground cuprous chloride (46 grams) and a solution of 3-bromo-1-nitrobenzene (505 grams, 2.50 moles) in 2 liters of deaerated pyridine were added. The mixture was heated at reflux overnight. The pyridine was then distilled off on the rotary film evaporator. Then the residue was extracted with benzene and the benzene extract washed successively with dilute hydrochloric, 10 percent aqueous sodium hydroxide and water. The extract, after being dried with anhydrous potassium carbonate, was concentrated on the rotary film evaporator. The residue was triturated with cold ethanol, which extracted unreacted 1-bromo-3-nitrobenzene. The desired product, after drying under vacuum had a melting point of 75°C and represented a 46 percent yield (235.2 grams).

Preparation of 3-(3-nitrophenoxy)-α-chlorocinnamaldehyde (Experiment H1057-70)

Vilsmeier reagent was prepared by the dropwise addition of phosphorus oxychloride (175 grams, 1.16 moles) to dimethylformamide (260 ml) while maintaining the temperature at 20-25°C. Then a solution of 3-(3-nitrophenoxy)acetophenone (192.9 grams, 0.75 mole) in dimethylformamide (500 ml) was added dropwise to the Vilsmeier reagent while maintaining the reaction temperature below 20°C. After the addition, the reaction mixture was heated gently to 60°C and then allowed to cool to room temperature. After stirring at room temperature overnight, it was poured into a vigorously stirred cold saturated aqueous solution of sodium bicarbonate. The solids were filtered and extracted with benzene. The extract was dried with anhydrous potassium carbonate and concentrated to dryness on the rotary film evaporator. After triturating the product with isopropanol, it was vacuum-dried. The product (174.4 grams, 81 percent of theory) melted at 65°C.

Preparation of 3-(3-nitrophenoxy)phenylacetylene (Experiment H1057-71)

A solution of 3-(3-nitrophenoxy)-α-chlorocinnamaldehyde (174.4 grams, 0.60 mole) in dioxane (1200 ml) was added to an aqueous solution of sodium hydroxide (61.5 grams, 1.54 moles) in water (700 ml) while maintaining the reaction mixture at a gentle reflux rate. After the addition, the mixture was heated for an additional two hours. The reaction mixture was concentrated to about one-third of its volume by distilling off the dioxane on the rotary film evaporator. The concentrate was poured into 2 liters of ice water and the mixture extracted with benzene. The benzene extract, after being dried with anhydrous potassium carbonate, was concentrated to dryness on the rotary film evaporator to yield a yellow waxy looking product (114.6 grams, 80 percent of theory).

Preparation of 3-(3-aminophenoxy)phenylacetylene (Experiment H1057-72)

A solution of 3-(3-nitrophenoxy)phenylacetylene (114.6 grams, 0.48 mole) in ethanol (1200 ml) was added dropwise to a solution of ferrous sulfate heptahydrate (1396 grams, 4.98 moles) in water (700 ml) while maintaining the reaction mixture at a gentle reflux rate. The mixture was stirred at reflux for an additional two hours and then concentrated aqueous ammonium hydroxide (660 ml) was added and the mixture stirred at reflux overnight. After this time an additional portion of ammonium hydroxide (200 ml) was added and the stirring continued for another hour. The solids were removed by filtration and the filtrate extracted with ether. The extract was dried over anhydrous potassium carbonate and the ether was distilled off on the rotary film evaporator. The product was isolated by distilling the residue in a Hickman molecular still. The desired product was collected at 65°C-85°C/30-80 microns and represented a yield of 35 percent (35.3 grams).

Preparation of 3-nitro-α-chlorocinnamaldehyde (Experiment H1057-76)

The Vilsmeier reagent was prepared by the dropwise addition of phosphorus oxychloride (910 grams, 6.00 moles) to dimethylformamide (800 ml) while maintaining a temperature of 20-25°C. Then a solution of 3-nitroacetophenone (660 grams, 4.00 moles) in dimethylformamide (2000 ml) was added dropwise to the Vilsmeier reagent while maintaining the reaction temperature at 20-25°C. The mixture was kept at ambient temperature overnight. It was then poured into a vigorously stirred cold saturated aqueous solution of sodium bicarbonate taking care that the solution did not become acid. The product was immediately recovered by filtration and dissolved in benzene. The extract was dried over anhydrous potassium carbonate and the solid product recovered by distilling off the benzene on the rotary film evaporator. After triturating the solid residue with cold isopropanol it was dried under vacuum. The product (508.2 grams, 60 percent of theory) melted at 75-80°C and was converted to the acetylene derivative without further recrystallization.

Preparation of 3-nitrophenylacetylene (Experiment H1057-80)

A solution of 3-nitro-*o*-chlorocinnamaldehyde (417.7 grams, 2.00 moles) in dioxane (1600 ml) was added to an aqueous solution of sodium hydroxide (210 grams, 5.20 moles) in water (2000 ml) while maintaining the reaction mixture at a gentle reflux rate. After the addition, the mixture was heated for an additional 1.5 hours. The reaction mixture was concentrated to about one-half of its volume by distilling off the dioxane on the rotary film evaporator. The concentrate was poured into 4 liters of ice water and the mixture extracted with ether. The ether extract after being dried with anhydrous potassium carbonate, was concentrated on the steam bath. The concentrate was then vacuum distilled at 85-95°C/3 torr to yield 184.4 grams (63 percent of theory) having a refractive index of $N_D^{19} = 1.5882$.

Preparation of 3-aminophenylacetylene (Experiment H1057-81)

A solution of 3-nitrophenylacetylene (184.4 grams, 1.25 moles) in ethanol (2000 ml) was added dropwise under argon to a solution of ferrous sulfate heptahydrate (3150 grams, 11.3 moles) in water (5000 ml) while maintaining the reaction mixture at a gentle reflux. The mixture was stirred at reflux for an additional 2 hours and then concentrated aqueous ammonium hydroxide (1050 ml) was added and the mixture stirred at reflux overnight. After this time an additional portion of ammonium hydroxide (650 ml) was added and the stirring continued for another one-half hour. After cooling to room temperature the reaction mixture was extracted with ether. The ether extract was dried over anhydrous potassium carbonate and the ether was distilled off on the rotary film evaporator. The product was isolated by distillation in a Hickman molecular still. The desired product was collected at 35-55°C/60-100 microns, N_D^{22} 1.6171 and represented a yield of 93 percent (136.5 grams).

Preparation of Acetylene-Terminated Polyimides

a. HR-650 Prepolymer-Oligomer from the Reaction of 3-(3-Aminophenoxy)phenylacetylene, Benzophenonetetracarboxylic Dianhydride and 1,3-Di(3-aminophenoxy)benzene

Experiment H1224-26

A solution of 1,3-di(3-aminophenoxy)benzene (6.88 grams, 0.0239 mole) in dimethylformamide (70 ml) was added dropwise to a hot solution (heated at reflux temperature) of benzophenonetetracarboxylic dianhydride (14.43 grams, 0.0478 mole) in dimethylformamide (70 ml). After the addition was completed the solution was heated at reflux for an additional hour. Then a solution of 3-(3-aminophenoxy)phenylacetylene (10.5 grams, 0.502 mole based on experimentally determined neutralization equivalent) in dimethylformamide (50 ml) was added dropwise under argon. The solution was heated at reflux for an additional hour and then the solvent was distilled off on the rotary film evaporator. The polyamic resin was imidized by heating for 4 hours at reflux in a solvent mixture containing meta-cresol (200 ml) and benzene (100 ml). A Dean-Stark trap was used to remove the water. After distilling off the solvent on the rotary film evaporator the product was thoroughly washed with absolute ethanol and vacuum dried at 65°C. A yield of 29.5 grams of a golden yellow product, m.p. 140-145°C was obtained. This product was soluble in chloroform.

Experiment H1224-35

A solution of 1,3-di(3-aminophenoxy)benzene (11.4 grams, 0.0391 mole) in dimethylformamide (150 ml) was added dropwise to a hot solution (heated at reflux temperature) of benzophenonetetracarboxylic dianhydride (2515 grams, 0.0781 mole) in dimethylformamide (150 ml). After the addition was completed the solution was heated at reflux for an additional hour. Then a solution of

3-(3-aminophenoxy)phenylacetylene (18.0 grams, 0.0822 mole based on experimentally determined neutralization equivalent) in dimethylformamide was added all at once. The solution was heated under an argon atmosphere at reflux overnight. The solvent was distilled off on the rotary film evaporator to yield 54.3 grams of polyamic acid. This was divided into two parts and imidized in the following manner.

Meta-Cresol/Benzene Imidization – HR650C

A portion (30.0 grams) of the polyamic acid was heated at reflux for 4 hours in a mixture of meta-cresol (150 ml) and benzene (100 ml) using a Dean-Stark trap to collect the water. The solvent was distilled off on the rotary evaporator and the residue thoroughly washed with absolute ethanol and dried at 100°C in vacuum for 3 hours. A yield of 26.2 grams of imidized product, m.p. 145°C was obtained.

Acetic Anhydride Imidization – HR650A

A portion (24.3 grams) of the polyamic acid was heated at reflux in acetic anhydride (100 ml) for 8 hours. The acetic anhydride was distilled off on the rotary film evaporator and the imidized product thoroughly washed with absolute ethanol and dried at 80°C overnight under vacuum. A yield of 16.6 grams of a pinkish-yellow imidized product, m.p. 142-146°C was obtained.

Experiment H1224-44

A solution of 1,3-di(3-aminophenoxy)benzene (8.76 grams, 0.030 mole) in dimethylformamide (100 ml) was added dropwise to a hot solution (heated at reflux temperature) of benzophenonetetracarboxylic dianhydride (14.43 grams, 0.0478 mole) in dimethylformamide (70 ml). After the addition was completed, the solution was heated at reflux for an additional 0.5 hour. Then a solution of 3-(3-aminophenoxy)phenylacetylene (13.0 grams, 0.0617 mole based on experimentally determined neutralization equivalent) in dimethylformamide (100 ml) was added all at once. The solution was heated under an argon atmosphere for 1.5 hours and then stirred at room temperature overnight. The solvent was distilled off on the rotary film evaporator to yield 45 grams of resin. This was divided into two parts and imidized in the following manners.

Meta-Cresol/Benzene Imidization – HR650C

A portion (25.0 grams) of the polyamic acid was heated at reflux for 2 hours in a mixture of meta-cresol (100 ml) and benzene (50 ml) using a Dean-Stark trap to collect the water. The solvent was distilled off and the residue thoroughly washed with absolute alcohol and dried up to 160°C in vacuum overnight.

Acetic Anhydride Imidization – HR650A

A portion (20.7 grams) of the polyamic acid was heated at reflux in acetic anhydride (100 ml) overnight. The acetic anhydride was distilled off on the rotary film evaporator and the imidized product thoroughly washed with absolute ethyl alcohol and dried up to 160°C in vacuum overnight.

Experiment H1224-72

A solution of 1,3-di(3-aminophenoxy)benzene (9.63 grams, 0.033 mole) in dimethylformamide (100 ml) was added dropwise to a hot solution (heated at reflux temperature) of benzophenonetetracarboxylic dianhydride (21.5 grams, 0.066 mole) in dimethylformamide (200 ml). After the addition was completed, the solution was heated at reflux for an additional two hours. Then a solution of 3-(3-aminophenoxy)phenylacetylene (15.62 grams, 0.0777 mole based on experimentally determined neutralization equivalent) in dimethylformamide (50 ml) was added all at once. The solution was heated at reflux under argon overnight. Then the solvent was distilled off on the rotary film evaporator to yield 51.5 grams of polyamic acid. It was divided into two equal portions and imidized by the two ways described below.

Meta-cresol/Benzene Imidization – HR650C

A portion (25.7 grams) of the polyamic acid was heated at reflux for 4 hours in a mixture of meta-cresol (200 ml) and benzene (100 ml) using a Dean-Stark trap to collect the water. The solvent was distilled off on the rotary film evaporator and the residue thoroughly washed with absolute ethanol and dried at 115°C in vacuum for several hours. A yield of 23.0 grams (Identification number H1224-72A) of the imidized product, having a melting point around 140-145°C, was obtained.

Acetic Anhydride Imidization – HR650A

A portion (25.7 grams) of the polyamic acid was heated at reflux in acetic anhydride (190 ml) overnight. The acetic anhydride was distilled off on the rotary film evaporator and the imidized product thoroughly washed with absolute ethanol and dried at 115°C in vacuum for several hours. A yield of 18.3 grams (Identification number H1224-72B) of the imidized product, having a melting point around 110°-115°C, was obtained.

Experiment H1224-61

A solution of 1,3-di(3-aminophenoxy)benzene (9.34 grams, 0.032 mole) in dimethylformamide (100 ml) was added dropwise to a hot solution (heated at reflux temperature) of benzophenonetetracarboxylic dianhydride (20.67 grams, 0.0462 mole) in dimethylformamide (200 ml). After the addition was completed, the solution was heated at reflux for an additional two hours. Then a solution of 3-(3-aminophenoxy)phenylacetylene (14 grams, 0.0714 mole based on experimentally determined neturalization equivalent) in dimethylformamide (50 ml) was added all at once. The solution was heated at reflux under argon overnight. Then the solvent was distilled off on the rotary film evaporator to yield 50.6 grams of polyamic acid. It was divided into two equal portions and imidized by the two ways described below.

Meta-Cresol/Benzene Imidization – HR650C

A portion (25.0 grams) of the polyamic acid was heated at reflux overnight in a mixture of meta-cresol (120 ml) and benzene (60 ml) using a Dean-Stark trap to collect the water. The solvent was distilled off on the rotary film evaporator and the residue thoroughly washed with absolute ethanol and dried at 110°C in vacuum for several hours. A yield of 23.0 grams (Identification number H1224-61A) of the imidized product was obtained.

Acetic Anhydride Imidization – HR650A

A portion (25.6 grams) of the polyamic acid was heated at reflux in acetic anhydride (200 ml) overnight. The acetic anhydride was distilled off on the rotary film evaporator and the imidized product thoroughly washed with absolute ethanol and dried at 110°C in vacuum for several hours. A yield of 14 grams (Identification number H1224-61B) of the imidized product was obtained.

Experiment H1224-96

A solution of 1,3-di(3-aminophenoxy)benzene (10.0 grams, 0.0341 mole) in dimethylformamide (200 ml) was added dropwise to a hot solution (heated at reflux temperature) of benzophenonetetracarboxylic dianhydride (21.9 grams, 0.0683 mole) in dimethylformamide (200 ml). After the addition was completed the solution was heated at reflux for an additional hour. Then a solution of 3-(3-aminophenoxy)phenylacetylene (15.0 grams, 0.0717 mole) in dimethylformamide (40 ml) was added all at once. The solution was heated under an argon atmosphere at reflux overnight. The solvent was distilled off on the rotary film evaporator to yield the polyamic acid. The polyamic acid was imidized by heating at reflux overnight in a mixture of meta-cresol (300 ml) and benzene (150 ml) using a Dean-Stark trap to collect the water. About 0.4 ml of water was present in the trap. The solvent was distilled off on the rotary film evaporator and the residue thoroughly washed with absolute alcohol and dried at 120°C for 3 hours in a vacuum oven. The product (35.4 grams) started to melt at 158°C and was fairly fluid by 165°C. Upon further heating the melt cured.

b. HR600 Prepolymer-Oligomer from the Reaction of 3-Aminophenylacetylene, Benzophenonetetracarboxylic Dianhydride and 1,3-Di(3-aminophenoxy)benzene

Experiment H1224-98

A solution of 1,3-di(3-aminophenoxy)benzene (77.4 grams, 0.265 mole) in dimethylformamide (600 ml) was added to a solution of benzophenonetetracarboxylic dianhydride (170.8 grams, 0.530 mole) in dimethylformamide (800 ml) while maintaining the solution at reflux temperature. The addition took

90 minutes. Then a solution of 3-aminophenylacetylene (64 grams, 0.547 mole) in 50 ml of dimethylformamide was added all at once. The mixture was stirred at reflux temperature for 72 hours. The solvent was distilled off on the rotary film evaporator. The residue was then imidized by heating at reflux in a mixture of 725 ml of meta-cresol and 375 ml of benzene under an argon atmosphere using a Dean-Stark trap to collect the water. The mixture was heated for 16 hours during which time 3.2 ml of water was collected in the trap. The solvent was distilled off on the rotary film evaporator and the residue thoroughly washed with absolute ethanol using the high speed blender to insure intimate mixing. The residue was filtered and dried at 100°C for 16 hours in a vacuum oven. A yield of 261.4 grams of product was obtained.

Experiment H2350-08

A solution of 1,3-di(3-aminophenoxy)benzene (31.0 grams, 0.106 mole) in dimethylformamide (250 ml) was added to a solution of benzophenonetetracarboxylic dianhydride (68.4 grams, 0.212 mole) in dimethylformamide (500 ml) while maintaining the solution at reflux temperature. The addition took 45 minutes. After the addition the solution was heated for an additional 30 minutes and then a solution of 3-aminophenylacetylene (26.1 grams, 0.212 mole) in dimethylformamide (50 ml) was added all at once. After the addition the mixture was heated at reflux for 4.0 hours, the heat turned off and the solution allowed to stand over argon overnight. The solvent was distilled off on the rotary film evaporator. The residue was imidized in a mixture of 600 ml of meta-cresol and 300 ml of benzene under an argon atmosphere using a Dean-Stark trap to collect the water. The mixture was heated for 2 hours during which time 0.3 ml of water was collected in the trap. The benzene was distilled off from the solution until the pot temperature reached 135°C. The rest of the benzene was distilled off on the rotary film evaporator. A total of 325 ml of meta-cresol was then distilled off using a hot water bath of 90-95°C. The heavy viscous solution was added to 1200 ml of cold absolute ethanol which immediately precipitated the oligomer. The oligomer was filtered and thoroughly washed using the high speed blender to insure intimate mixing. The residue was filtered and dried overnight at 80°C in a vacuum oven. The product (84 grams) was a bright yellow powder which began to melt at 195°C. It was appreciably less viscous than the previous batch (H1224-98) and did not cure up as rapidly on a heated aluminum block.

c. HR600 Prepolymer-Degree of Polymerization of Two – Oligomer from the Reaction of 3-Aminophenylacetylene, Benzophenonetetracarboxylic Dianhydride and 1,3-Di(3-aminophenoxy)benzene

Experiment H1224-70

A solution of 1,3-di(3-aminophenoxy)benzene (25.0 grams, 0.0856 mole) in dimethylformamide (200 ml) was added dropwise to a hot solution (heated at reflux temperature) of benzophenonetetracarboxylic dianhydride (41.7 grams, 0.0856 mole) in dimethylformamide (400 ml). After the addition was completed, the solution was heated at reflux for an additional one-half hour. Then a solution of 3-aminophenylacetylene (11.0 grams, 0.0942 mole) in dimethylformamide (50 ml) added all at once. The solution was heated at reflux under argon overnight and then the solvent was distilled off on the rotary film evaporator. The residue weighed 93.6 grams, indicating some occluded solvent. It was then divided into two equal portions and imidized by the two methods shown below.

Meta-Cresol/Benzene Imidization – HR600C -2DP

A portion (46.8 grams) of the polyamic acid was heated for 4 hours in a mixture of meta-cresol (200 ml) and benzene (100 ml) using A Dean-Stark trap to collect the water. Only a few drops of water were observed in the trap after this time, which indicated that the major portion of imidization took place while preparing the polyamic acid. The solvent was distilled off on the rotary evaporator and the residue thoroughly washed with absolute ethanol and dried at 110°C in vacuum for several hours. A yield of 33 grams (Identification number H1224-71A) of imidized product was obtained. The resin started to soften at 175-180°C, about at the same temperature range as HR600 having a DP of one.

Acetic Anhydride Imidization – HR600A -2DP

A portion (46.8 grams) of the polyamic acid was heated at reflux in acetic anhydride (400 ml) overnight. The imidized product had completely dissolved after this time. Then the acetic anhydride was distilled off on the rotary film evaporator and the imidized product thoroughly washed with absolute ethanol and dried at 110-115°C for several hours. The yield was 29.8 grams (Identification number H1224-71B).

Experiment H1224-85

A solution of 1,3-di(3-aminophenoxy)benzene (28.5 grams, 0.0975 mole) in dimethylformamide (250 ml) was added dropwise to a hot solution (heated at reflux temperature) of benzophenonetetracarboxylic dianhydride (47.1 grams, 0.146 mole) in dimethylformamide (500 ml). After the addition was completed the solution was heated at reflux for an additional 45 minutes. Then a solution of 3-aminophenylacetylene (12.0 grams, 0.103 mole) in dimethylformamide (50 ml) was added all at once. The solution was heated at reflux under argon overnight and then the solvent was distilled off on the rotary film evaporator. The residue weighed 106 grams, indicating some occluded solvent. It was then divided into two equal portions and imidized by the two methods shown below.

Meta-Cresol/Benzene Imidization – HR600C -2DP

A portion (53 grams) of the polyamic acid was heated for 4 hours in a mixture of meta-cresol (400 ml) and benzene (200 ml) using a Dean-Stark trap to collect the water. Only a 0.3 ml of water was observed in the trap after this time, which indicated that the major portion of imidization took place while preparing the polyamic acid. The solvent was distilled off on the rotary evaporator and the residue thoroughly washed with absolute ethanol and dried at 140°C for 16 hours. A yield of 34 grams (Identification number H1224-85B) was obtained.

Acetic Anhydride Imidization – HR600A -2DP

The second portion (53 grams) of the polyamic acid was heated for 4 hours with acetic anhydride (400 ml). Then the acetic anhydride was distilled off on the rotary film evaporator and the imidized product thoroughly washed with absolute ethanol and dried at 140°C for 16 hours. The yield was 34 grams (Identification number H1224-85A).

Experiment H2350-06

A solution of 1,3-di(3-aminophenoxy)benzene (60.0 grams, 0.2054 mole) in dimethylformamide (600 ml) was added dropwise to a hot solution (heated at reflux temperature) of benzophenonetetracarboxylic dianhydride (98.2 grams, 0.3082 mole) in dimethylformamide (900 ml). After the addition was completed the solution was heated at reflux for an additional hour. Then a solution of 3-aminophenylacetylene (25.3 grams, 0.2162 mole) in dimethylformamide (50 ml) was added all at once. The solution was heated at reflux under argon overnight and then the solvent was distilled off on the rotary film evaporator. The residue weighed 212.5 grams, indicating some occluded solvent. It was then divided into two equal portions and imidized by the two methods shown below.

Meta-Cresol/Benzene Imidization – HR600C -2DP

A portion of the polyamic acid was heated for 16 hours in a mixture of meta-cresol (600 ml) and benzene (300 ml) using a Dean-Stark trap to collect the water. A total of 0.4 ml of water was collected in the trap which indicated that the major portion of imidization took place while preparing the polyamic acid. The solvent was distilled off on the rotary film evaporator and thoroughly washed with absolute ethanol and dried at 140°C for several hours in vacuum. A yield of 86 grams (Identification number H2350-06A) of imidized product was obtained.

Acetic Anhydride Imidization – HR600A -2DP

The second portion of the polyamic acid was heated at reflux in acetic anhydride (500 ml) for 4.0 hours. Then the acetic anhydride was distilled off on the rotary film evaporator and the imidized product thoroughly washed with absolute ethanol and dried at 140°C for several hours. The yield was 62 grams (Identification number H2350-06B).

d. HR600 Prepolymer – Degree of Polymerization of Three – Oligomer from the Reaction of 3-Aminophenylacetylene, Benzophenonetetracarboxylic Dianhydride and 1,3-Di(3-aminophenoxy)benzene

A solution of 1,3-di(3-aminophenoxy)benzene (42.7 grams, 0.146 mole) in dimethylformamide (400 ml) was added dropwise to a hot solution (heated at reflux temperature) of benzophenonetetracarboxylic dianhydride (62.8 grams, 0.195 mole) in dimethylformamide (600 ml). After the addition was completed, the solution was heated at reflux for an additional 45 minutes. Then a solution of 3-aminophenylacetylene (12.0 grams, 0.103 mole) in dimethylformamide (50 ml) was added all at once. The solution was heated at reflux under argon overnight and the solvent was distilled off on the rotary film evaporator. The residue weight 128 grams. It was then imidized by the two methods shown below.

Meta-Cresol/Benzene Imidization – HR600C -3DP

A portion (62.0 grams) of the polyamic acid was heated for 24 hours in a mixture of meta-cresol (400 ml) and benzene (200 ml) using a Dean-Stark trap to collect the water. About 0.4 ml of water was observed in the trap at this time, which indicated that the major portion of imidization took place while preparing the polyamic acid. The solvent was distilled off on the rotary film evaporator and the residue thoroughly washed with absolute ethanol and dried overnight at 120°C in vacuum. A yield of 47.7 grams (Identification number H1224-86A) of the imidized product was obtained. This product started to melt at ca 190°C almost the same temperature range as HR600 having a DP of one.

Acetic Anhydride Imidization – HR600A -3DP

The second portion (64 grams) of the polyamic acid was heated at reflux in acetic anhydride (400 ml) for 4.0 hours. Then the acetic anhydride was distilled off on the rotary film evaporator and the imidized product thoroughly washed with absolute ethanol and dried at 120°C overnight. The yield was 48.1 grams. It started to soften at 146°C.

e. Acetylene-Terminated Polyimide Oligomer from 3-Aminophenylacetylene, Benzophenonetetracarboxlic Dianhydride and Bis(3-Aminophenyl) Sulfone

Experiment H1224-54

A solution of bis(3-aminophenyl) sulfone (6.05 grams, 0.0243 mole) in dimethylformamide (50 ml) was added dropwise to a hot solution (heated at reflux) of benzophenonetetracarboxylic dianhydride (15.68 grams, 0.0487 mole) in dimethylformamide (50 ml). After the addition was completed, the solution was heated at reflux for an additional 20 minutes. Then a solution of 3-aminophenylacetylene (6.0 grams, 0.0521 mole) in dimethylformamide (25 ml) was added all at once and the mixture was heated at reflux for two hours. The solvent was distilled off on the rotary film evaporator to yield 33 grams of polyamic acid.

Meta-Cresol/Benzene Imidization

A portion (20.0 grams) of the polyamic acid was heated at reflux overnight in a mixture of meta-cresol (100 ml) and benzene (50 ml) using a Dean-Stark trap to collect the water. The solvent was distilled off on the rotary film evaporator and the residue thoroughly washed with absolute ethanol and dried at 90°C for several hours under vacuum. The imidized product (13.6 grams) melted around 175-180°C (Identification number H1224-54A).

Acetic Anhydride Imidization

A portion (12.5 grams) of the polyamic acid was heated at reflux in acetic anhydride (150 ml) overnight. The acetic anhydride was distilled off on the rotary film evaporator and the imidized product washed with absolute ethanol. It was dried in vacuum at 100°C for several hours to yield 9 grams of imidized product.

f. Acetylene-Terminated Polyimide Oligomer from 3-(3-Aminophenoxy)phenylacetylene, Benzophenonetetracarboxylic Dianhydride and bis(4-aminophenyl) ether

Experiment H1224-40

A solution of bis(4-aminophenyl) ether (7.3 grams, 0.0365 mole) in dimethylformamide (100 ml) was added dropwise to a hot solution (heated at reflux) of benzophenonetetracarboxylic dianhydride (22.8 grams, 0.0709 mole) in dimethylformamide (150 ml). After the addition was completed the solution was heated at reflux for an additional 0.25 hour. Then a solution of 3-(3-aminophenoxy)phenylacetylene (15.0 grams, 0.0717 mole based on experimentally determined neutralization equivalent of 209.2) in dimethylformamide (50 ml) was added dropwise under argon. The misture was heated at reflux overnight. The solvent was distilled off on the rotary film evaporator to yield 53.3 grams of polyamic acid.

Acetic Acid Imidization

A portion (30.0 grams) of the polyamic acid was heated at reflux in acetic anhydride (150 ml) overnight. The acetic anhydride was distilled off on the rotary film evaporator and the imidized product thoroughly washed with absolute ethyl alcohol and dried at 80°C in vacuum overnight. It softened at approximately 205°C when heated on an aluminum block. It cured much slower than the HR600 type resin.

A. PREPARATION OF ADHESIVE PREPREG AND BONDED TEST SPECIMENS

1. Materials

a. 112 Glass Fabric, starch-oil finish, heat cleaned. Source – Clark-Schwebel Fiber Glass Corp.

b. HR600 resin; meta-cresol/benzene imidized oligomers identified by lot numbers H1224-23, H1224-98; acetic anhydride imidized oligomer identified by lot number H1066-66.

c. HR650 resin; meta-cresol/benzene imidized oligomers identified by lot numbers H1224-26, H1224-35A, H1224-44A, H1224-72A, H1224-61A, H1224-96; acetic anhydride imidized oligomer identified by lot numbers H1224-35B, H1224-44B, H1224-72B, H1224-61B.

d. HR600 resin with a degree of polymerization of 2; meta-cresol/benzene imidized oligomers identified by lot numbers H1224-71A, H1224-85B, H2350-06A; acetic anhydride imidized oligomer identified by lot numbers H1224-71B, H1224-85A, H2350-06B.

e. Acetylene-terminated polyimide oligomer made by substituting bis(3-aminophenyl)sulfone monomer for 1,3-di(3-aminophenoxy)-benzene in HR600 type oligomer; meta-cresol/benzene imidized oligomer identified by lot number H1224-54A; acetic anhydride imidized oligomer identified by lot number H1224-54B.

f. N-Methyl-pyrrolidinone, practical grade (NMP).

g. N,N-Dimethylformamide, reagent grade (DMF).

h. Chloroform, reagent grade.

2. Process

a. Unfilled Resin

A typical prepreg was made by dissolving the resin in either NMP, DMF or other solvent such that the resin content of the solvent was sufficient to give the lacquer a syrupy viscosity (12-25 percent). An impregnation tank suitable for submerging glass fabric in strip form under the surface of the lacquer was heated to about 350°F. A hot solution of the lacquer was added to the preheated tank and the fabric passed through the solution in a continuous single impregnation mode. The prepreg was then dried in an air circulating oven for 15 minutes at 350°F. The resin content was checked by weighing before and after prepregging. It was redipped, redried in the same manner until the resin content was 70 percent. In the case where chloroform was used as a solvent the prepreg was placed through the lacquer at ambient temperature. The prepreg was then air dried at ambient temperature and finally oven dried at 185°F for 15 minutes.

b. Filled Resin

A mixture was made of the 50:50 mixture of acetic anhydride (HR600A) and the meta-cresol/benzene (HR600C) imidized polyimide resin with aluminum powder using the following proportions

HR600 resin mixture	80 pbw
325 mesh aluminum powder	20 pbw

To this mixture, approximately an equal weight of dimethylformamide was added and the paste thoroughly mixed. Both sides of a heat cleaned Clark-Schwebel 112 glass cloth were coated and oven dried at 350°F for 15 minutes until 92 pbw of resin mix was present on the cloth.

3. Lap Shear Specimen Preparation

a. The titanium specimens were cleaned either per Hughes Process Specification HP9-30 or by the TURCO alkaline etch process. Both are described below.

HP9-30

1) Remove organic soils by wiping surface clean with cellulose tissues soaked in toluene or methyl ethyl ketone; or by scrubbing with Ajax (Institutional Grade) or an equivalent abrasive cleaner followed by a rinse with tap, deionized, or distilled water to a water-break-free condition.

2) Pickle with the following tap water solution at room temperature for 30 seconds ±2 seconds.

Components	Parts by Volume ±10 Percent
Nitric acid, 70 percent	15.0
Hydrofluoric acid, 50 percent	3.0
Water, deionized or tap	82.0

3) Rinse in tap water at room temperature for 2 minutes minimum.

4) Immerse in the following tap water solution at room temperature for 2 to 2-1/2 minutes:

Components	Parts by Volume ±10 Percent
Trisodium phosphate (TSP)	5.0
Sodium fluoride	0.9
Hydrofluoric acid, 50 percent	1.6
Water, tap	92.6

5) Rinse in tap water at room temperature.

6) Soak in tap water at 150 ±10°F (66 ±6°C) for 15 minutes minimum.

7) Spray rinse with deionized or distilled water and dry at 120 to 150°F (49 to 66°C).

TURCO 5578 Alkaline Etchant for Titanium

1) Remove organics as per HP9-30 above.

2) Etch for 30 minutes at 190°F in solution containing 60 grams of TURCO 5578 in 1 liter of water

3) Rinse with hot tap water (160-180°F).

4) Wash with deionized water (160-180°F).

5) Air dry.

b. The prepregs were cut to 1-1/8 inches x 5/8 inch coupons.

c. The prepreg was placed between titanium coupons to achieve 1/2-inch lap.

d. The specimens were held in position using pressure-sensitive tape.

e. Spring clips were used to achieve 15 psi pressure.

f. The specimens were cured in a circulating air oven using a cure cycle described in the previous section.

☆ U.S. GOVERNMENT PRINTING OFFICE: 1975 — 657-630/236