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CRYOGENIC/ HIGH TEMPERATURE STRUCTURAL ADHESIVES

by

R. W. Vaughan and C. H. Sheppard

TRW SYSTEMS GROUP

ONE SPACE PARK • REDONDO BEACH • CALIFORNIA

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center

Contract NAS3-[illegible]

FOREWORD

This document constitutes the final report for the work accomplished between 29 June 1972 and 30 June 1973 by TRW Systems Group for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-16780 on Cryogenic/High Temperature Structural Adhesives.

This work was conducted under the technical direction of Dr. Tito T. Serafini of the Lewis Research Center, Cleveland, Ohio.

The Applied Chemistry Department of the Chemistry and Chemical Engineering Laboratory, Applied Technology Division was responsible for the work performed on this program. Dr. E. A. Burns, Manager, Applied Chemistry Department provided overall program supervision and Mr. R. W. Vaughan, Head, Product Development Section was Program Manager. Mr. C. H. Sheppard provided the major technical effort throughout the program in adhesive formulary and the evaluation of adhesives systems, and Dr. K. Berg, Whittaker R&D Corporation was responsible for all cryogenic testing throughout the program.

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SUMMARY

This document is the final program report describing work performed by TRW Systems for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-16780. The objective of this program was to develop technology for a cryogenic/high temperature structural adhesive system for application to Space Shuttle structures. This objective was accomplished by 1) conducting a literature survey in order to identify potential adhesive candidates and assessing the processing characteristics and performance properties of the candidate systems, 2) performing a screening evaluation of selected candidate adhesive systems and 3) performing a detailed evaluation of the most promising candidate adhesive systems.

The first phase of the work established that adhesive systems based on polyimide, polyphenylquinoxaline, polyquinoxaline, polybenzothiazole and polybenzimidazole polymers all possessed potential for providing useful properties over the required temperature range. However, the polyquinoxaline, polybenzothiazole and polybenzimidazole systems were not selected for further evaluation because their processing requirements were not conducive to production procedures. Consequently, three polyimide adhesive systems (TRW P4/A5F, American Cyanamide BR34/FM34 and DuPont NR150B) and one polyphenylquinoxaline [Boeing Aircraft Corporation PPQ II (IMW)] were selected for screening evaluations. During this phase, adhesive formulary and processing development studies were performed with the P4/A5F, NR150B and PPQ II (IMW) systems. It was established during these studies that NR150B system requires further development to provide a suitable adhesive system based on this resin.

The second phase of the work provided detailed property information on the P4/A5F (P4A/A5FA for stainless steel substrates) and BR34/FM34 systems. Initial information also was obtained for the PPQ II (IMW) system although sufficient quantity of PPQ II (IMW) resin was not available to complete the evaluation. Property information was obtained during this effort pertaining to static shear strength over the 20°K to 589°K temperature range; stressed and unstressed thermal aging at 477°K, 533°K and 589°K; and thermal shock and coefficient of thermal expansion over the 20°K to 589°K temperature range.

Differences between coefficient of thermal expansion values for the FM34 and A5FA adhesives systems were related to differences between shear strength values of the two adhesives at temperature extremes. The results from the detailed evaluations indicated that both adhesive systems, *i.e.* BR34/FM34 and P4/A5F or P4A/A5FA provide structural adhesive joints that are suitable for service applications in the 20°K to 589°K temperature range. However, the P4/A5F adhesive system was easier to process than the BR34/FM34 adhesive and the P4/A5F adhesive system provided void-free bondlines in large surface area adhesive joints.

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1. INTRODUCTION

This final report presents the work accomplished by TRW Systems for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-16780 during the period 29 June 1972 through 30 June 1973. The objective of the program was to develop technology for a cryogenic/high temperature structural adhesive system for application to Space Shuttle structures.

Structural adhesive systems capable of production line fabrication and suitable for cryogenic (20°K) and high temperature (589°K) applications are needed for the Space Shuttle. The desired lightweight, high structural efficiency requirements for this vehicle necessitate the use of adhesive bonding for both primary and secondary structures. A high degree of reliability for this adhesive is a key factor, therefore, a material that provides sound safety margins in structural designs is highly desirable.

Prior to commencing this program, a limited number of high temperature adhesive systems previously had been evaluated at cryogenic temperatures but sufficient data to afford a sound system selection for the Space Shuttle were not available (Reference 1). Because the thermal performance range is very large (approximately 810°K), thermally induced stresses are of great concern. Consequently, a screening evaluation program of potential candidate adhesive systems was necessary to identify the most promising adhesive system to meet the use requirements.

Several studies had been performed that had shown the polyimides (PI) and polyphenylquinoxalines (PPQ) possessed high potential for applications in the 20°K to 589°K temperature range. However, detailed performance data for these polymers as adhesives were not available and were necessary in order to select candidate materials for the Space Shuttle applications. Other polymers that also had shown potential for this application were the polybenzothiazoles (PBT), polyquinoxalines (PQ) and polybenzimidazoles (PBI). Although these systems all had been evaluated for high temperatures, evaluation for cryogenic temperature applications had not been performed. Because these data were an unknown factor, these materials also were considered as potential candidates. However, evaluation of technical information pertaining to the processing requirements of these systems indicated that these systems were not suitable for production applications. Consequently, adhesive systems based on these resin systems were not included in the screening studies.

During the course of this program, structural adhesive systems were evaluated for bonding titanium alloy and stainless steel adherends. The systems evaluated were:

- Adhesives based on P4/A5F polyimide adhesive developed by TRW Systems under Contract NAS1-9532 (Reference 2)
- American Cyanamide's BR34/FM34 polyimide adhesive
- Adhesives based on polyphenylquinoxaline (PPQ) resin developed by Boeing Aircraft Corporation, and
- Adhesives based on Dupont's NR150B polyimide resin varnish.

Detailed screening studies which included evaluation of adherend surface treatments, bondline thickness variations and cure cycle variations were conducted during the initial phase of the program. The two most promising systems (P4/A5F and BR34/FM34) then were selected for detailed evaluation. These evaluations included long term, elevated temperature stress rupture tests, unstressed isothermal aging tests, determination of shear strength at temperatures from 20°K through 589°K and coefficient of thermal expansion determinations over the temperature range 20°K through 589°K.

This program was performed in three tasks. During Task I, candidate adhesive systems were screened from which the two most promising adhesive systems were selected. These two systems then were evaluated to provide detailed property data during Task II. Reporting requirements were provided as the Task III activity.

This report is divided into sections covering the following subjects:

- Selection of adhesive systems for evaluation, and
- Detailed evaluation of adhesive systems.

The significant conclusions reached and assessments of the results are listed together with recommendations for activities that warrant further investigations. The information presented in the main body of this report is supplemented by appendices covering detailed descriptions of procedures used in specimen preparation, specimen processing and testing.

2. SELECTION OF ADHESIVE SYSTEMS

Several polymer and adhesive systems were available at the onset of this program which possessed the potential for providing acceptable performance over the service temperature range 20°K (-423°F) to 589°K (600°F). Consequently, in order to select the most promising systems for screening, a literature search was performed and an evaluation made of the systems considered most applicable (see Table I).

TABLE I.

POLYMER/ADHESIVE SYSTEMS POSSESSING POTENTIAL FOR CRYOGENIC TEMPERATURE SERVICE

Polymer Type	Trade Name	Manufacturer/Developer
Polyimide	BR34/FM34	American Cyanamide Bloomingdale Dept. Havre de Grace, Md.
	Metlbond 840	Whittaker Corp. Narmco Materials Div. Costa Mesa, Ca.
	NR150A	E. I. Dupont de Nemours Co. Plastics Dept., Wilmington, Del.
	P4/A5F[a)]	TRW Systems
Polyquinoxaline	PQ	Whittaker Corp. Research Div. San Diego, Calif.
Polyphenylquinoxaline	PPQ II (IMW)	Boeing Aircraft Corp. Seattle, Wash.
	PPQ 401	Whittaker Corp. Research Div. San Diego, Calif.
Polybenzimidazole	Imidite 850	Whittaker Corp. Narmco Materials Div. Costa Mesa, Calif.
Polybenzothiazole	PBT	Abex Corp. Columbus, Ohio

[a)] Developed under Contract NAS1-9532, Reference 2.

An earlier evaluation of structural adhesives for spacecraft applications had been reported in Reference 1 which included adhesive systems based on polyimide, polyamide-imide, polybenzimidazole, polyquinozaline, polyphenylquinoxaline and polyimide-azoquinazoline polymer systems. From these systems, one polyimide adhesive (FM34), one polybenzimidazole (Imidite 850) and one polyquinoxaline (Whittaker PQ) were evaluated; all others, except for the amide-imide, were not evaluated because they were not available commercially. The amide-imide system was rejected because of reported poor elevated temperature performance.

In the studies reported in Reference 1 titanium alloy 6A14V lap-shear specimens were prepared and subjected to a thermal shock cycle (see Figure 1). The results of lap-shear tests on the thermally shocked specimens strength were higher than the other two high temperature adhesives at both room temperature and at 200°K (-100°F) (see Table II). Testing at 533°K (500°F) also showed the superiority of the FM34 adhesive (see Figure 2).

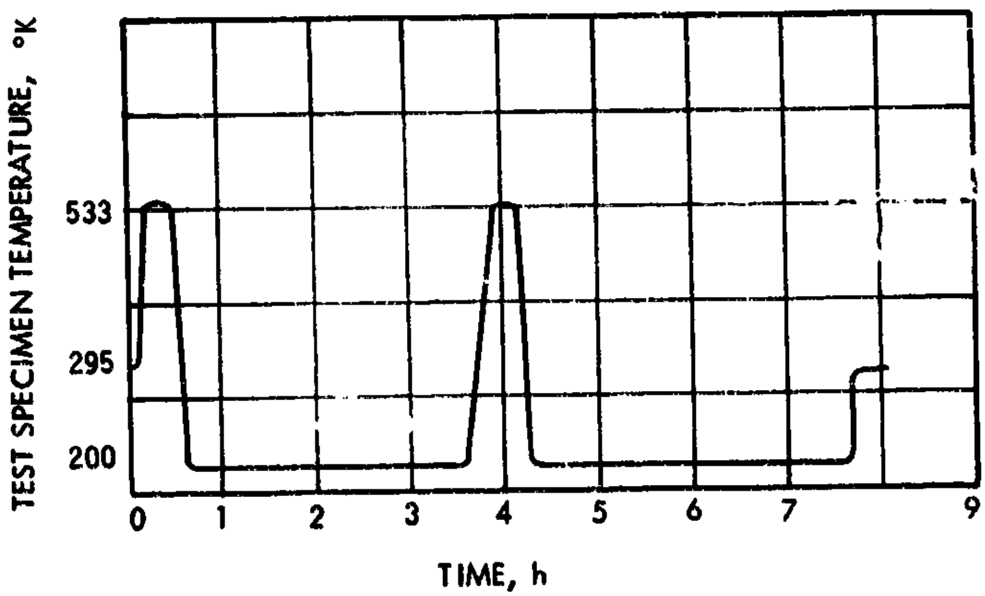

Figure 1. Thermal Shock Test Cycle

TABLE II.

THERMAL SHOCK TEST DATA

Adhesive System	Shear Strength, MN/m^2			
	Cycle 1[a]		Cycle 2[a]	
	295°K	200°K	200°K	295°K
Imidite 850 (PBI)	10.4	8.1	8.0	8.3
FM34 (PI)	16.0	18.5	18.5	13.0
Polyquinoxaline (PQ)	11.8	11.6	9.6	14.5
EA 913 (Epoxy)	27.0	13.1	12.2	26.5

[a] See Figure 1.

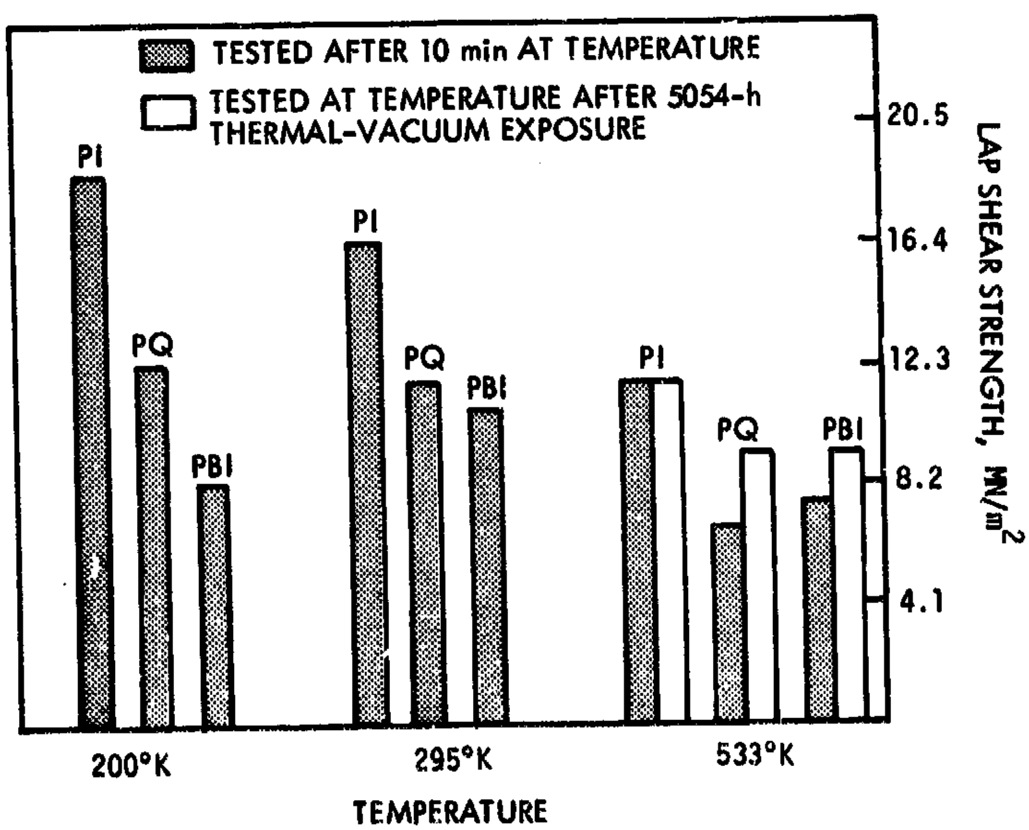

Figure 2. Adhesive Strength Test Data

The author of Reference 1 concluded that the polyimide adhesive system (FM34) was an excellent candidate for future spacecraft applications. Also, he concluded that the PQ and PBI systems offered no advantage over the polyimide system when used to bond titanium adherends. He noted that "aside from their lower adhesive strength on titanium, they also are considerably more difficult to process into adhesive bonds".

An evaluation of polybenzothiazole (PBT) adhesives reported in Reference 3 showed these systems to possess outstanding properties at 775°K (900°F) (see Figure 3). However, aging studies at 589°K (600°F) showed these systems had no advantage over the polyimide adhesives (see Figure 4).

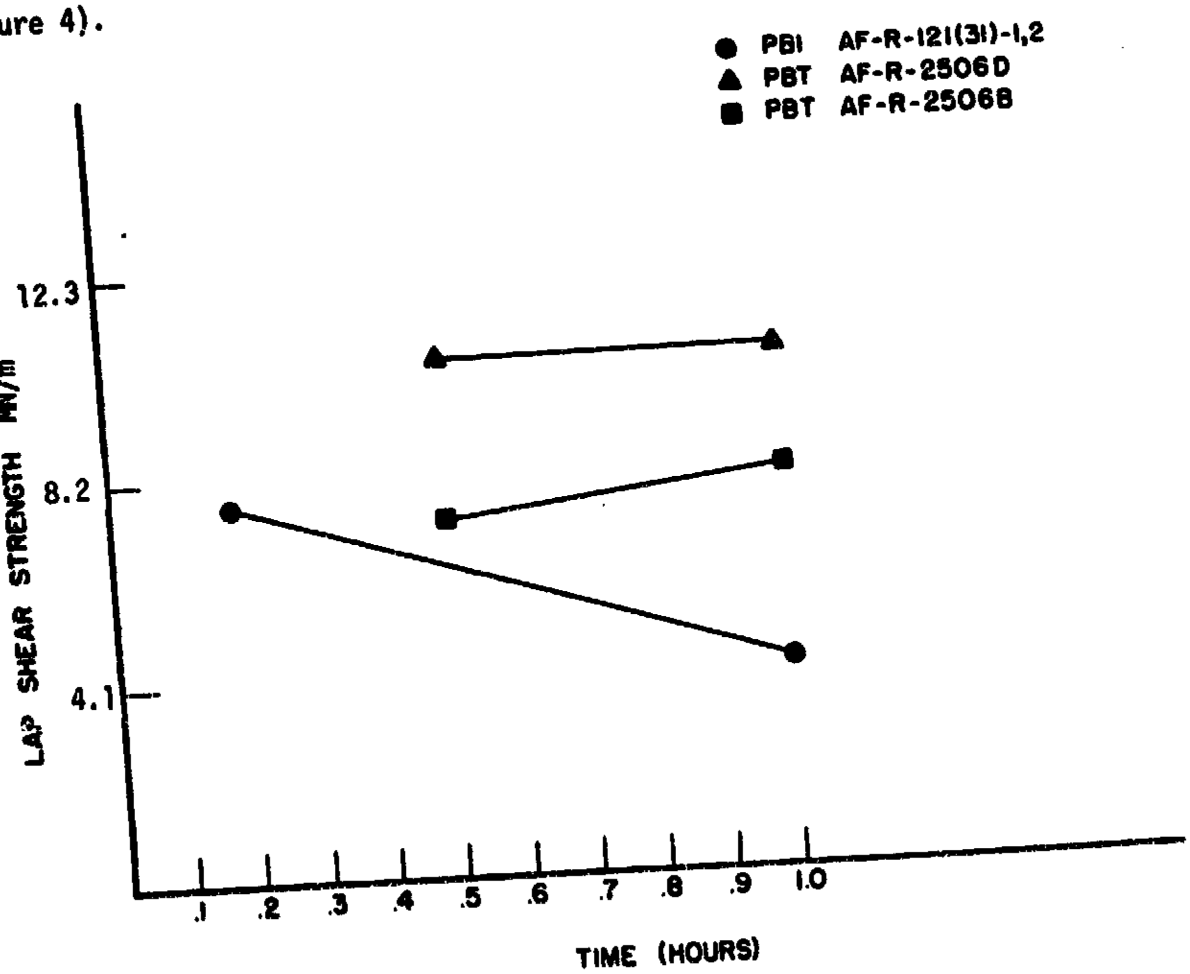

Figure 3. 775°K Lap-shear Strength of Titanium Alloy Joints Bonded With Various High Temperature Adhesives

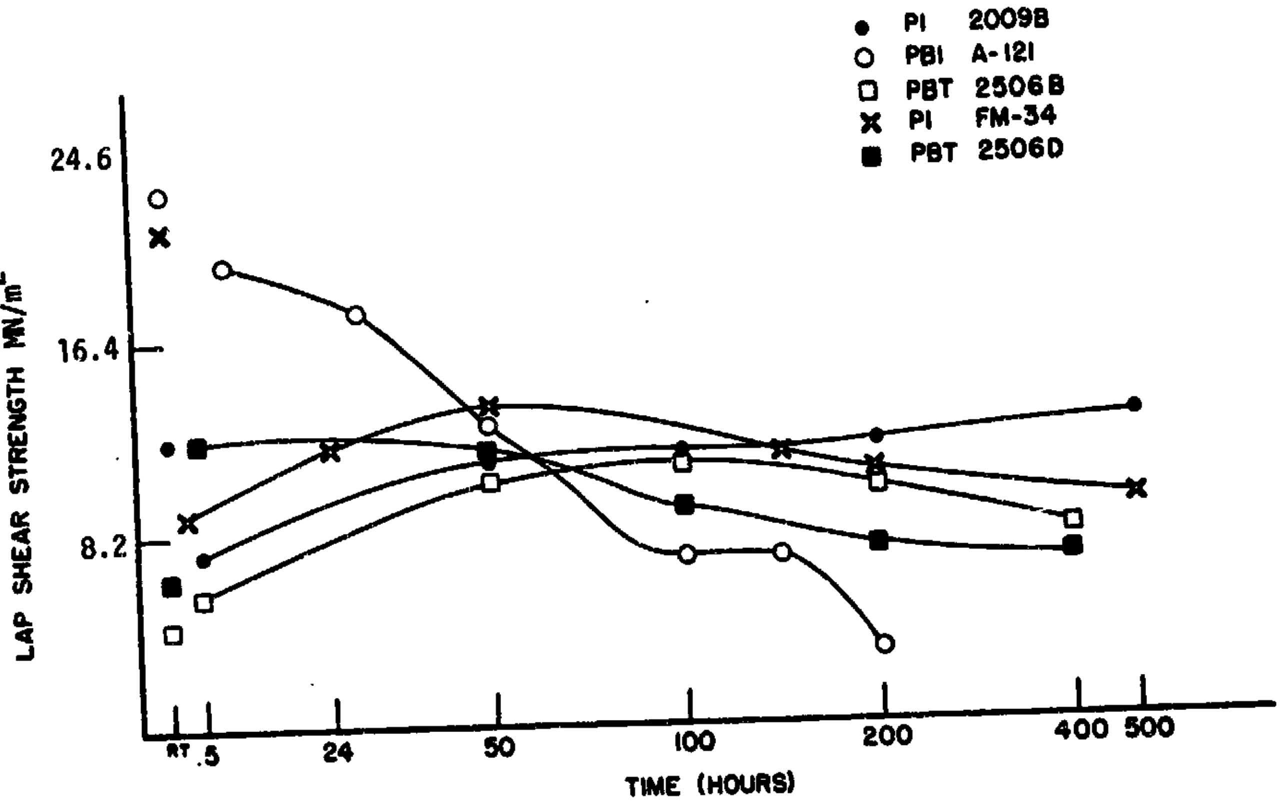

Figure 4. 589°K Lap-shear Strengths of Titanium Joints Bonded With Various High Temperature Adhesives

A program performed by TRW Systems for the NASA Langley Research Center (Reference 2) had developed an adhesive system (P4/A5F) based on a blend of TRW A-type addition-cure polyimide resin technology developed originally for NASA Lewis Research Center (Reference 4) with Amoco AI-1137 amide-imide resin. During this program it was demonstrated that the P4/A5F adhesive system produced zero-void, crack-free large surface area bondlines; a feature previously not obtained with other polyimide adhesive systems. Lap-shear strengths of titanium alloy 6Al4V joints produced during this program showed that the P4/A5F system also provided higher shear strength than other polyimide adhesive systems (see Table III).

TABLE III.

COMPARISON OF STRENGTHS OF ADHESIVE BONDED TITANIUM ALLOY JOINTS

Adhesive System	Lap Shear Strength, MN/m² at 295°K	Lap Shear Strength, MN/m² at 589°K
P4/A5F	24.0	12.3
FM34	21.0	8.5
AF-A-2009[a]	12.3	8.0

[a] See Reference 3.

Based on the findings of this evaluation, the following systems were selected for screening:

BR34/FM34 - Bloomingdale Department, American Cyanamid Corp.

NR150B - Dupont De Nemours

P4/A5F - TRW Systems

PPQ II (IMW) - Boeing Aircraft Corp. (BAC)

These systems were selected because:

- Data reported in Reference 1 showed that the BR34/FM34 system was the condensation cure polyimide adhesive system that provided the highest shear strength over a broad temperature range.
- Work performed under Contract NAS1-9532 (Reference 2) had shown that the P4/A5F system provided property and processing improvements over the BR34/FM34 system.
- Private communication with Dr. P. M. Hergenrother, BAC, had indicated that room temperature shear strength values of titanium alloy joints bonded with PPQ II (IMW) resin were $\sim$25.0 MN/m².
- Published data sheets for the DuPont NR150B polyimide resin indicated that high strength, low void content, thermally stable composites were produced from this resin which consequently indicated high promise for this resin as a structural adhesive.

The PQ, Imidite 850 and PBT systems were not selected because the processing requirements for fabricating bonded joints with these systems were too severe and not conducive to production techniques. Also, the earlier work (References 1 and 3) had not provided property improvements from joints bonded with these systems over those bonded with polyimide adhesive systems. Whittaker Corporation's Metlbond 840 and PPQ 401 systems were considered similar to the BR34/FM34 and PPQ II (IMW) systems, respectively, and therefore parallel screening of these systems would in essence have been a duplication of effort.

Prior to commencing screening of the selected polymer/adhesive systems, it was necessary to establish surface preparation procedures for both the titanium alloy and stainless steel substrates. Also, two of the selected systems [NR150B and PPQ II (IMW)] were not formulated adhesive systems. Consequently, it was necessary to perform adhesive formulary and processing studies with these two systems. The P4/A5F adhesive system was developed by TRW Systems under a NASA Langley Research Center contract for bonding titanium alloy substrates. In order to use this adhesive system with ferrous substrates it was necessary to incorporate an antioxidant which again required adhesive formulary studies.

2.1 EVALUATION OF SURFACE TREATMENTS

Test specimens conforming to Figure 5 were prepared in accordance with the screening matrix in Figure 6 using 17-7PH stainless steel and 6Al4V titanium alloy. The faying surfaces were prepared by procedures described in Appendix A. Adhesive tape manufacture, drying cycles and curing schedules for the various adhesive systems were performed in accordance with Appendix B.

Two titanium surface preparation procedures appeared to provide equivalent properties during these studies (see Table IV), *i.e.* Method A (Pasa-Jel) and Method C (Turco 5578). However, because previous studies (Reference 2) had shown that the Pasa-Jel method provided excellent long term elevated temperature aging properties and similar information pertaining to the Turco 5578 method was not available, the Pasa-Jel method was selected for use throughout this program.

Similarly, for stainless steel, Method A (Prebond 700) and Method C (Sulfuric Acid-Sodium Dichromate Bath) appeared equivalent (see Table IV). However, Method C was selected because it was the simplest for production applications.

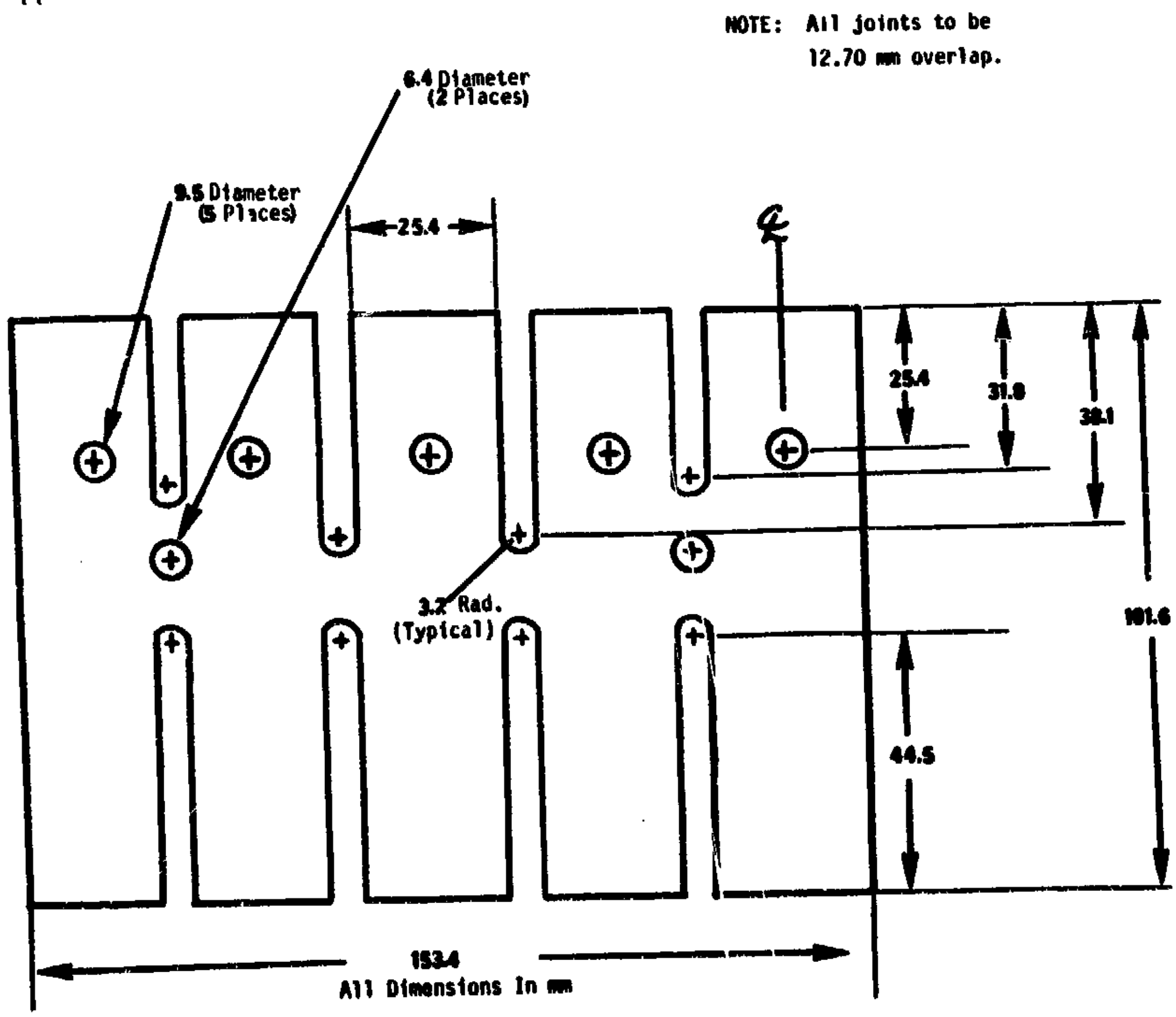

Figure 5. Lap Shear Panel

Surface Treatment		Adhesives	
		BR34/FM34	P4S/A5FS
	D	Ti	SS
	C	SS	Ti
	B	Ti	SS
	A	SS	Ti

Figure 6. Preliminary Screening of Surface Treatments

TABLE IV.

SUMMARY OF DATA FROM PRELIMINARY SCREENING OF SURFACE TREATMENTS

Substrate	Cleaning Method[c]	Shear Strength		Adhesive	Failure Mode
		MN/m^2	Standard Deviation[e]		
Ti[a]	A	11.7	0.02	P4S/A5FS	Adhesive
Ti	C	9.8	0.04	P4S/A5FS	Adhesive
SS[b]	B	12.9	0.21	P4S/A5FS	Adhesive
SS	D	15.1	--	P4S/A5FS	Adhesive
Ti	B	14.5	0.18	BR34/FM34	Combination Adhesive and Cohesive
Ti	D	(d)	--	BR34/FM34	Adhesive
SS	A	17.6	0.05	BR34/FM34	Cohesive
SS	C	18.1	0.12	BR34/FM34	Cohesive

a) Ti - 6A14V Titanium Alloy

b) SS - 17-7PH Stainless Steel

c) See Appendix A

d) Test Specimens debonded

e) Five replicates

2.2 ANTIOXIDANT STUDY OF P4/A5F ADHESIVE SYSTEM

An antioxidant is an essential component of adhesive systems used for bonding ferrous alloys, *e.g.* stainless steel, in joints intended for high service temperature applications. The antioxidants selected for screening in this program were arsenic thioarsenate (As_2S_4) and arsenic pentoxide (As_2O_5) both at 5 phr concentrations. Data from this study are presented in Table V and demonstrate that the formulations containing both of the antioxidants (*i.e.*, P4S/A5FS with As_2S_4 and As_2O_5) lowered the initial shear

TABLE V.

ANTIOXIDANT STUDY USING P4/A5F TYPE ADHESIVES

Substrate[a)]	Antioxidant	Antioxidant phr	Shear Strength MN/m^2	Shear Strength Standard Deviation[e)]	Failure Mode
Ti[b)]	As_2S_4	10	16.9	0.11	Adhesive
Ti[b)]	--	--	21.7	0.29	Adhesive
Ti[b)]	As_2O_5	5	18.8	0.12	Adhesive
Ti[c)]	As_2S_4	10	11.7	0.02	Adhesive
Ti[c)]	As_2S_4	5	11.6	0.09	Adhesive
Ti[c)]	--	--	17.7	0.12	Adhesive
SS[d)]	--	--	25.7	0.05	Cohesive
SS[d)]	As_2O_5	5	21.5	0.07	Combination Adhesive and Cohesive
SS[d)]	As_2S_4	5	19.1	0.13	Combination Adhesive and Cohesive

a) Ti - 6Al4V Alloy
SS - 17-7PH Stainless Steel

b) Surface preparation per Appendix A.2.1 except surfaces first were grit blasted with aluminum oxide.

c) Surface preparation per Appendix A.2.1.

d) Surface preparation per Appendix A.1.2, Method C.

e) Five replicates

properties of the P4/A5F system on both substrates. The lower values recorded with adhesives containing arsenic thioarsenate (P4S/A5FS) fit the same pattern as values reported in the literature for other polyimide systems (References 3 and 5). Consequently, the arsenic pentoxide containing adhesive formulation P4A/A5FA was selected for this program. Because the data presented in a previous report (Reference 2) indicated that antioxidants were not essential for retention of properties during thermal aging of titanium alloy joints but essential for stainless steel alloy joints (Reference 1), it was decided that two separate formulations would be used during subsequent evaluations, one for stainless steel alloys, *i.e.* P4A/A5FA, and one for titanium alloys, *i.e.* P4/A5F.

2.3 NR150B PROCESSING STUDY

Lap shear test specimens were prepared from NR150B adhesive film (see Table B-1) using the same curing process as recommended by DuPont for glass composite fabrication. Because the first series of test panels demonstrated a complete lack of adhesion to the substrates, a short process study was conducted to determine whether a successful adhesive bonding procedure could be developed expeditiously. The processing conditions investigated were the imidizing cycle, cure temperature and cure pressure (see Table VI). Because the shear strength values obtained all were low (~7 MN/m^2 was the highest shear strength at room temperature), further attempts to develop an NR150B adhesive were terminated.

TABLE VI.

SUMMARY PROCESS PARAMETERS OF NR150B

Panel Number	Cleaning Method[b]	Substrate (c)	Precure Minutes At 472°K	Precure Minutes At 672°K	Pressing Cycle Time Minutes	Pressing Cycle Pressure MN/m^2	Pressing Cycle Temp. °K
7119-7-1	A.2.3	Ti	180	120	7	17.4	688
7119-7-2	A.2.1	Ti	180	120	7	17.4	688
7119-7-3	A.1.2	SS	180	120	7	17.4	688
7119-7-4	A.1.3	SS	180	120	10	34.8	699
7119-7-5	A.2.3	Ti	180	35	10	34.8	699
7119-13-1[a]	A.2.1	Ti	180	35	10	34.8	699

a) Adhesive contained 5 phr of arsenic thioarsenate

b) See Appendix A.

c) Ti - 6Al4V Titanium Alloy
SS - 17-7PH Stainless Steel

2.4 DEVELOPMENT OF BONDING PROCESS FOR BAC PPQ RESIN

The Boeing Aircraft Company (BAC) PPQ II (IMW) resin was evaluated for bonding lap shear test specimens using adhesive formulations described in Table B-1. These formulations did not provide promising results (*e.g.* <4 MN/m^2), therefore it was decided to investigate the use of neat PPQ resin as the primer and adhesive for bonding lap shear specimens. The shear strength values obtained from these bonded specimens were acceptable although considerable difficulty was encountered in reproducing the adhesive coating thickness during specimen fabrication. Most of the specimens provided a bondline thickness of 0.08 mm (0.003 inch) and attempts to obtain thicker coatings were frustrated by local unbonding of the coating from the faying surface prior to the curing operation. A processing procedure then was developed using the 5% w/w neat PPQ resin solution as a primer and the PPQ adhesive formulation shown in Table B-1. Although the unbonding problem that had been prevalent during the preparation of earlier specimens did not reoccur, this procedure did not provide reproducible 0.20 mm thick bondline thicknesses. Values obtained during these studies (see Table VII) indicated that differences in bondline thickness had little effect on room temperature lap shear strength but had significant effect on elevated temperature strength. This conclusion was drawn because bondline thickness was the only significant variable between test panels. Additional work on process development for the PPQ system was precluded because only a limited supply of resin was available from BAC (this resin was not available commercially).

TABLE VII.

SUMMARY OF PPQ ADHESIVE PRELIMINARY SCREENING

Bondline Thickness (mm)	Substrate (a)	Test Temp., °K	Shear Strength, MN/m^2	Percent Retention b)
0.20	Ti	295	18.2 c)	--
0.10	Ti	295	19.0	--
0.10	SS	295	23.8	--
0.20	Ti	533	12.8 c)	70
0.09	Ti	533	10.8	57
0.08	SS	533	5.5	23
0.20	Ti	589	10.5 c)	58
0.08	Ti	589	3.2	17
0.08	SS	589	2.1	9

a) Ti = 6Al4V Titanium Alloy
SS = 17-7PH Stainless Steel

b) $\text{Percent retention} = \frac{\text{Shear Strength @ Test Temperature}}{\text{Shear Strength @ 295°K (72°F)}} \times 100$

c) 100% adhesive failures

3. DETAILED EVALUATION OF CANDIDATE ADHESIVE SYSTEMS

Detailed evaluation of the candidate adhesive systems for service applications in the temperature range 20°K to 589°K consisted of:

- Static shear strength determination at 20°K (-423°F), 52°K (-353°F), 295°K (72°F), 533°K (500°F) and 589°K (600°F).
- Thermal shock tests over the 20°K (-423°F) to 589°K (600°F) temperature range.
- Static isothermal aging tests at 477°K (400°F), 533°K (500°F) and 589°K (600°F).
- Stress rupture tests at 50% of ultimate shear strength at 477°K (400°F), 533°K (500°F) and 589°K (600°F).
- Coefficient of thermal expansion determinations of the adhesive systems over the 20°K (-423°F) to 589°K (600°F) temperature.

Adhesive systems evaluated during these studies were BR34/FM34 and PPQ II (IMW) for both titanium alloy and stainless steel substrates, P4/A5F for titanium alloy substrates only and P4A/A5FA for stainless steel alloy substrates only. Full evaluation of the PPQ II (IMW) system was not completed because the resin was not commercially available.

3.1 STATIC SHEAR STRENGTH TESTING OF ADHESIVE SYSTEMS

Lap shear test specimens were bonded with PPQ II (IMW) P4/A5F, P4A/A5FA and BR34/FM34 adhesives. These specimens then were tested at 20°K (-423°F), 52°K (-353°F), 295°K (72°F), 533°K (500°F) and 589°K (600°F). Details of the test specimen preparation procedures, test procedures and test results are provided below.

3.1.1 Preparation of Test Specimens -

Test specimens were prepared (see Figure 7) using 17-7PH stainless steel and 6Al4V titanium alloy lap shear specimens. The surface preparations of the titanium and stainless steel substrates were performed in

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accordance with the procedures defined in Appendices A.2.1 and A.1.3, respectively. Tape manufacture, coupon priming, panel preparation and bonding cycles were in accordance with the procedures defined in Appendix B.

	Adhesive System/Bondline Thickness							
	P4A/A5FA		P4/A5F		BR34/FM34		PPQ	
	0.23 mm	0.40 mm	0.23 mm	0.40 mm	0.23 mm	0.40 mm	0.23 mm	0.40 mm[a]
6Al4V Titanium Alloy	--	--	4	4	4	4	4	4[b]
17-7PH Stainless Steel	4	4	--	--	4	4	--	--

[a] Bondline nominal thickness

[b] Number of replicates at each test temperature - 295°K (72°F), 533°K (500°F), 590°K (600°F).

Figure 7. Static Shear Strength Test Matrix

3.1.2 Test Procedures -

Lap shear test specimens were loaded in tension at a loading rate of 550 kg/minute. Simple clevis-pin grips were used for all tests except the cryogenic tests where a combination of serated, tapered tensile jaws and pins was necessary. Residence time at test temperature was ten minutes.

3.1.3 Test Results -

A summary of the static lap shear test data obtained is presented in Table VIII. Sufficient test specimens were not available for cryogenic testing of specimens bonded with the PPQ II (IMW) system; therefore, only room and elevated temperature results were obtained. Data obtained from testing specimens bonded with the BR34/FM34, P4/A5F and the P4A/A5FA systems were plotted graphically (see Figures 8 through 15). These graphs indicate that at the cryogenic temperatures, shear strengths of the BR34/FM34 adhesive are higher whereas at elevated temperatures the shear strengths of the P4/A5F and P4A/A5FA systems are higher.

TABLE VIII.

SUMMARY PRELIMINARY SCREENING OF ADHESIVES

Adhesive System	Bondline Thickness	Substrate (a)	Test Temperature, °K	Shear Strength MN/m²	Shear Strength σ(b)	Percent Retention c)
BR34/FM34	0.23	Ti	20	34.8	3.3	142.0
	0.39	Ti		34.9	1.8	150.4
	0.25	SS		33.5	5.7	140.7
	0.39	SS		33.6	3.3	171.4
P4/A5F	0.23	Ti		29.9	1.5	104.9
	0.36	Ti		21.9	0.5	79.9
P4A/A5FA	0.23	SS		23.0	2.5	125.0
	0.40	SS		23.5	1.5	124.3
BR34/FM34	0.23	Ti	52	30.4	6.8	124.1
	0.39	Ti		34.3	3.8	147.8
	0.25	SS		34.8	1.5	146.2
	0.39	SS		30.7	3.0	156.6
P4/A5F	0.23	Ti		33.3	2.5	116.8
	0.36	Ti		25.1	0.9	91.6
	0.23	SS		23.0	2.5	125.0
	0.40	SS		23.5	1.5	124.0
BR34/FM34	0.23	Ti	295	24.5	1.5	--
	0.39	Ti		23.2	1.2	--
	0.25	SS		23.8	0.6	--
	0.39	SS		19.6	1.4	--
PPQ	0.10	Ti		19.0	2.3	--
	0.15	Ti		23.2	--	--
P4/A5F	0.20	Ti		28.5	3.0	--
	0.40	Ti		27.4	1.1	--
P4A/A5FA	0.23	SS		18.4	0.2	--
	0.40	SS		18.9	0.2	--
BR34/FM34	0.25	Ti	533	11.8	0.2	48.2
	0.35	Ti		11.8	0.5	50.9
	0.23	SS		13.6	0.9	57.1
PPQ	0.39	SS		12.7	0.7	64.8
	0.09	Ti		10.8	2.3	57.0
	0.15	Ti		18.7	--	81.0
P4/A5F	0.23	Ti		21.9	2.5	76.8
	0.36	Ti		22.0	0.8	81.5
P4A/A5FA	0.23	SS		15.3	0.7	83.2
	0.40	SS		16.0	0.1	84.7
BR34/FM34	0.25	Ti	589	7.5	0.7	30.6
	0.36	Ti		7.7	0.3	33.2
	0.25	SS		7.3	0.4	30.7
	0.39	SS		6.5	0.4	33.2
PPQ	0.08	Ti		3.2	0.4	18.0
	0.15	Ti		3.0	--	31.0
P4/A5F	0.20	Ti		12.8	1.5	44.9
	0.31	Ti		12.5	1.4	45.6
P4A/A5FA	0.23	SS		11.3	1.1	61.4
	0.30	SS		9.8	0.7	51.9

a) Ti - 6Al4V Titanium Alloy
SS - 17-7 PH Stainless Steel

b) Standard deviations using 4 replicates.

c) Percent retention = $\frac{\text{Shear Strength @ Test Temperature}}{\text{Shear Strength @ 295°K (72°F)}} \times 100$

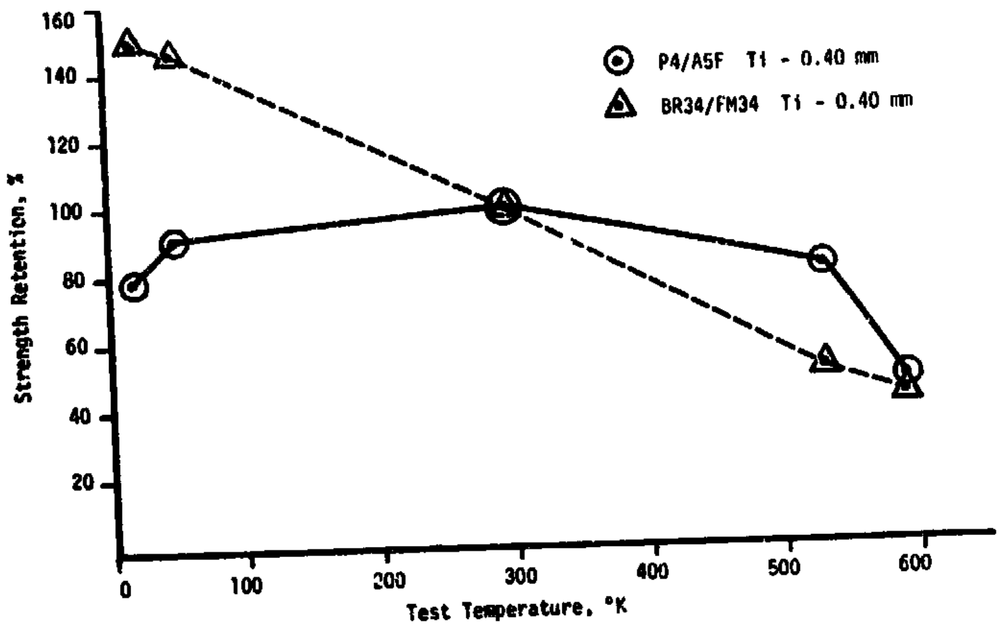

Figure 8. Lap Shear Strength Retention *vs* Test Temperature for 0.40 mm Thick Bondlines on Titanium Substrates

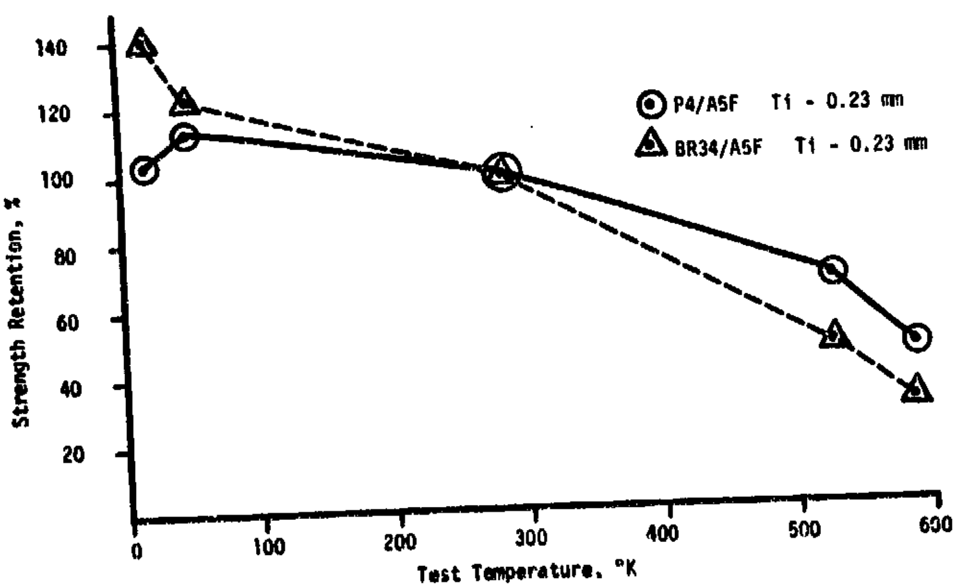

Figure 9. Lap Shear Strength Retention *vs* Test Temperature for 0.23 mm Thick Bondlines on Titanium Substrates

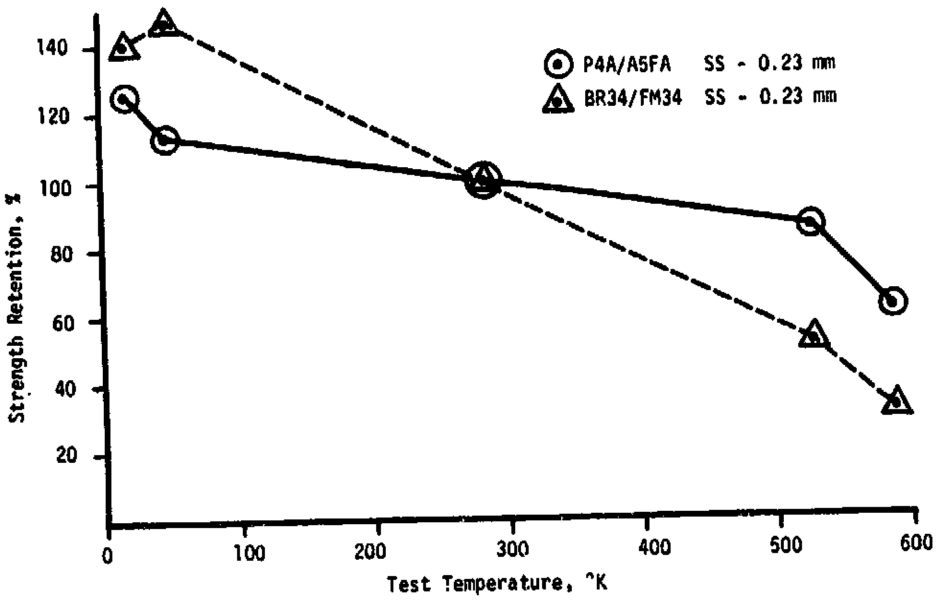

Figure 10. Lap Shear Strength Retention *vs* Test Temperature for 0.23 mm Thick Bondlines on Stainless Steel Substrates

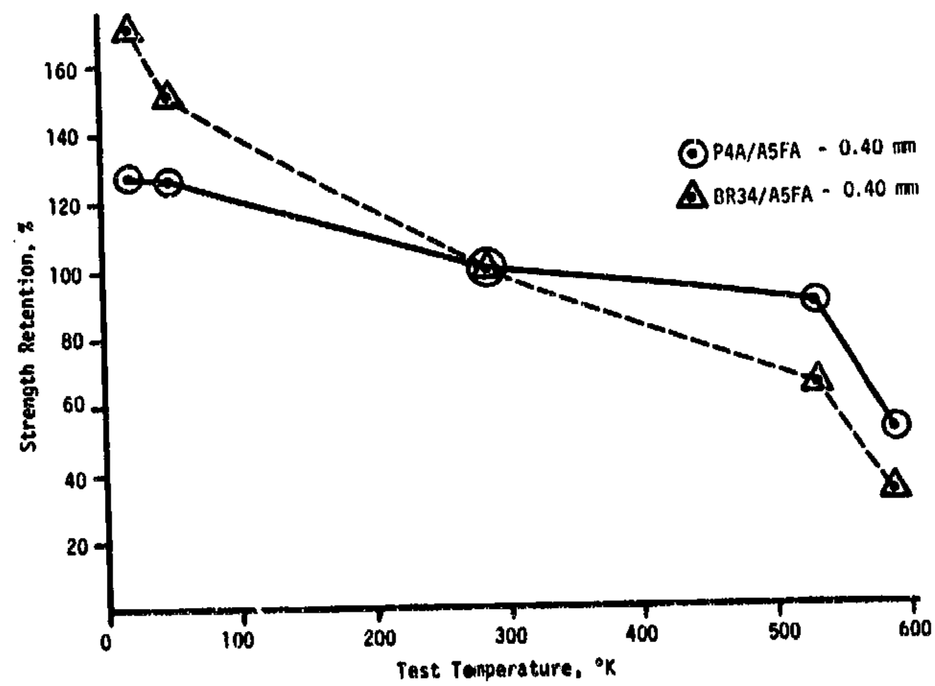

Figure 11. Lap Shear Strength Retention *vs* Test Temperature for 0.40 mm Thick Bondlines on Stainless Steel Substrates

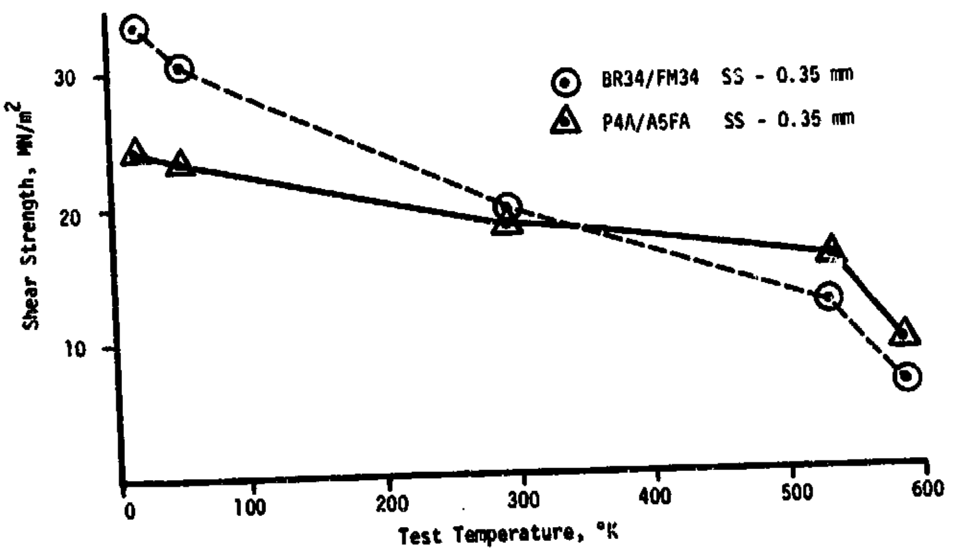

Figure 12. Lap Shear Strength *vs* Test Temperature for 0.35 mm Thick Bondlines on Stainless Steel Substrates

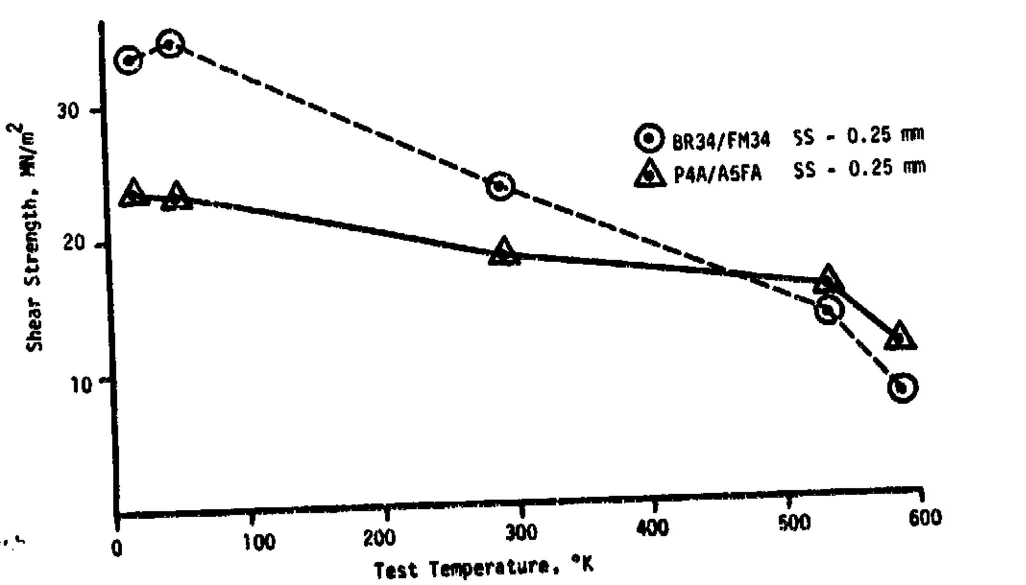

Figure 13. Lap Shear Strength *vs* Test Temperature for 0.25 mm Thick Bondlines on Stainless Steel Substrates

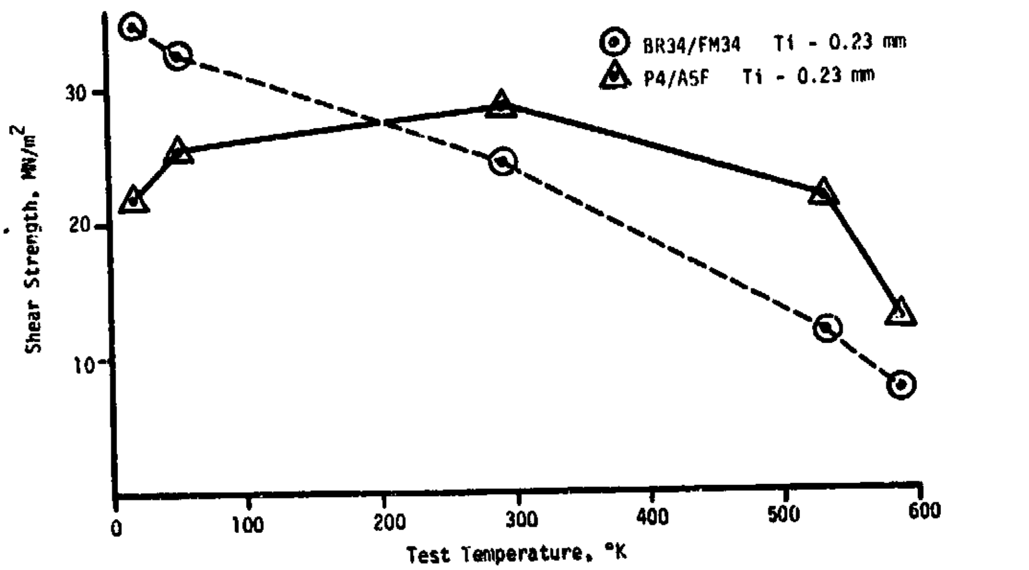

Figure 14. Lap Shear Strength *vs* Test Temperature for 0.23 mm Thick Bondlines on Titanium Substrates

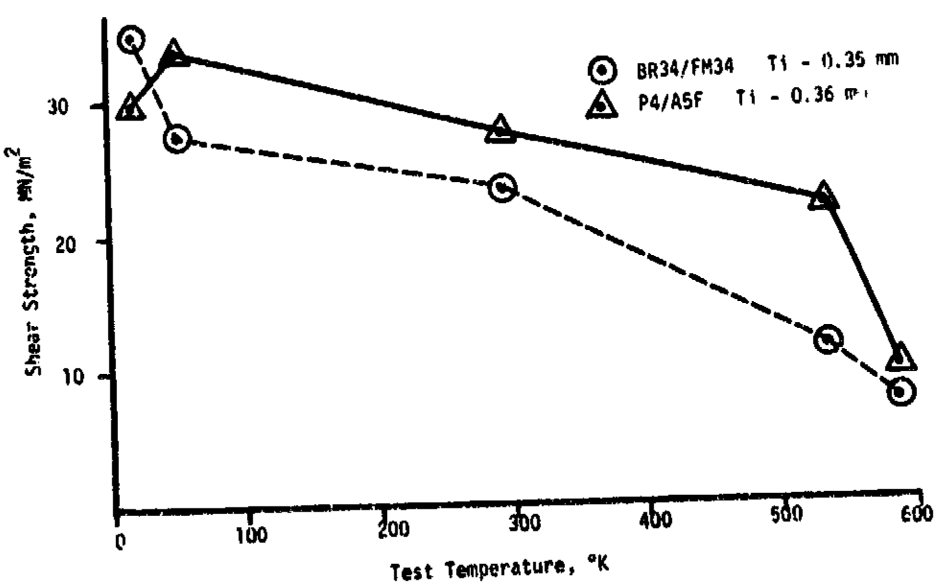

Figure 15. Lap Shear Strength *vs* Test Temperature for 0.35 mm Thick Bondlines on Titanium Substrates

3.2 THERMAL SHOCK TESTS

Stainless steel lap shear test specimens were bonded with P4A/A5FA and BR34/FM34 adhesives and subjected to thermal shock at 20°K (-423°F) and 589°K (600°F). All of the test specimens survived the thermal shock tests and subsequently were subjected to additional evaluation. Details of the test specimen preparation procedures, test procedures and test results are provided below.

3.2.1 Preparation of Test Specimens -

Stainless steel 17-7PH adherends were prepared in accordance with the procedure defined in Appendix A.1.3 and then bonded with P4A/A5FA and BR34/FM34 system by the procedures defined in Appendix B.2.1 and B.2.2, respectively. Sufficient specimens were prepared to meet the planned thermal shock test requirements (see Table IX) as well as for static thermal aging tests (see Section 3.3).

TABLE IX.

THERMAL SHOCK EVALUATIONS

Number of Specimens	Adhesive[a] System	Adherends[b]	Post-Test Use
1	P4A/A5FA	SS	Test at R. T.
1	P4A/A5FA	SS	Test at 477°K
1	P4A/A5FA	SS	Test at 533°K
1	P4A/A5FA	SS	Test at 589°K
10	P4A/A5FA	SS	Aging at 477°K
10	P4A/A5FA	SS	Aging at 533°K
10	P4A/A5FA	SS	Aging at 589°K
2	P4A/A5FA	SS	Stress rupture at 477°K
2	P4A/A5FA	SS	Stress Rupture at 533°K
2	P4A/A5FA	SS	Stress rupture at 589°K
1	BR34/FM34	SS	Test at R. T.
1	BR34/FM34	SS	Test at 477°K
1	BR34/FM34	SS	Test at 533°K
1	BR34/FM34	SS	Test at 489°K
10	BR34/FM34	SS	Aging at 477°K
10	BR34/FM34	SS	Aging at 533°K
10	BR34/FM34	SS	Aging at 489°K
2	BR34/FM34	SS	Stress Rupture at 477°K
2	BR34/FM34	SS	Stress Rupture at 533°K
2	BR34/FM34	SS	Stress Rupture at 589°K

a) Bondline thickness 0.23 mm nominal

b) SS = 17-7 PH Stainless Steel

3.2.2 Test Procedures -

The specimens were placed in a chamber and the temperature was elevated to 589°K (600°F) then, after stabilization of this temperature, the specimens were removed and immediately placed in a cryostat of liquid nitrogen (LN_2). After stabilization at the LN_2 temperature of 52°K (-320°F) the specimens were transferred immediately into a liquid hydrogen (LH_2) cryostat which then was purged and filled with liquid hydrogen. The specimens were allowed to stabilize at 20°K (-423°F) then removed and placed in a chamber at 589°K (600°F). After stabilizing at 589°K (600°F), the specimens were removed from the chamber and allowed to cool to room temperature (295°K). An idealized thermal shock cycle based on a temperature change rate of 11°K/minute minimum is shown graphically in Figure 16.

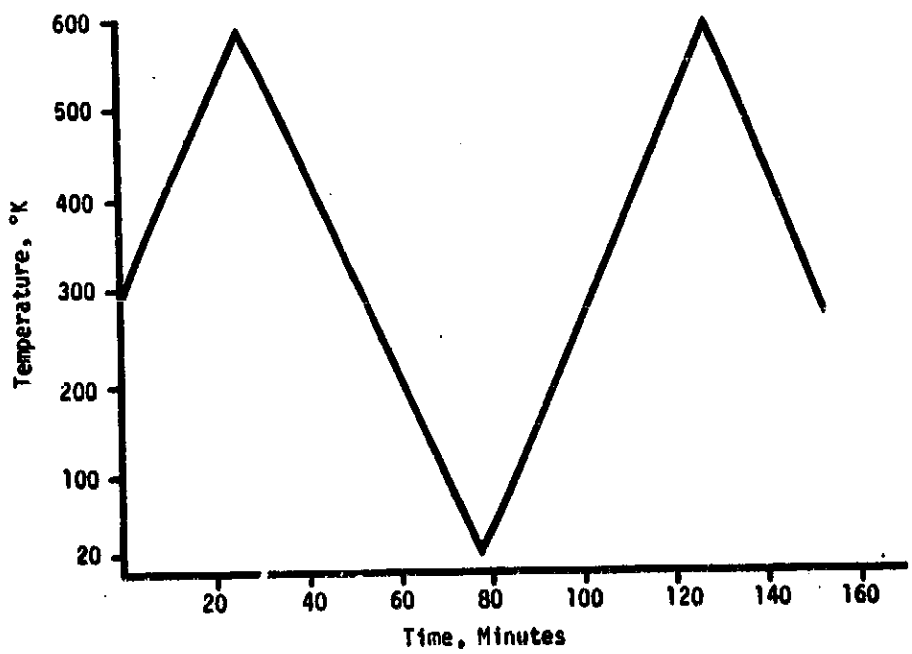

Figure 16. Thermal Shock Cycle

3.2.3 Test Results -

Post-test visual examination of specimens that had undergone the preceding thermal shock cycle provided no indication of adverse affects. Specimens then were selected for static lap shear tests to define whether mechanical property degradation had occurred as a result of thermal shock. Results from these tests (see Table VIII) indicated that no property degradation had occurred for the BR34/FM34 system as a result of thermal shock, although some degradation did occur with the P4A/A5FA system. The remaining specimens were used for thermal aging and stressed thermal aging tests in accordance with Table IX (see Sections 3.3 and 3.4).

TABLE X.
LAP SHEAR STRENGTH BEFORE AND AFTER THERMAL SHOCK

Adhesive System	Lap Shear Strength at 295°K (R.T.) MN/m^2 Before Thermal Shock	Lap Shear Strength at 295°K (R.T.) MN/m^2 After Thermal Shock
P4A/A5FA	19.1	15.9
BR34/FM34	21.7	21.7

3.3 STATIC THERMAL AGING TESTS

Stainless steel lap shear test specimens were prepared with P4A/A5FA and BR34/FM34 adhesives and, together with specimens surviving the thermal shock tests (see Section 3.2), then were subjected to thermal aging in air circulating ovens at 477°K (400°F), 533°K (500°F) and 589°K (600°F). After completion of the 1000-hour aging duration the specimens then were loaded to failure at room temperature. Details of the test specimen preparation procedures were provided in the preceding section and test procedures and results are provided below.

3.3 1 Test Procedures -

The test specimens were placed on metal shelves in three air circulating ovens each with an air velocity of 12.7 m/sec and an air change rate of 19.7 m^3/sec. Air temperature in each of the three ovens then was raised to each aging temperature, *i.e.* 477°K (400°F), 533°K (500°F) and 589°K (600°F). Specimens were withdrawn from the air circulating ovens after aging durations of 50, 100, 500, 750 and 1000 hours and their 295°K (R.T.) shear strength was determined.

3.3.2 Static Thermal Aging Test Results -

Strength retention *vs* aging duration plots at each test temperature were drawn (see Figures 17 through 22) from the shear strength values obtained from the post aging test results (see Tables XI through XIII). These

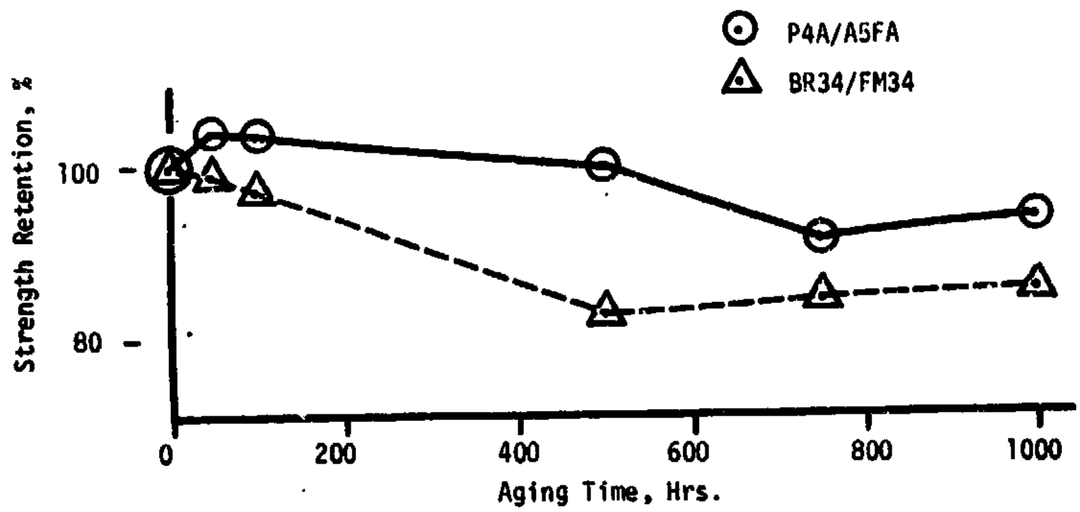

Figure 17. Unstressed Aging at 477°K of Stainless Steel Lap Shear Panels

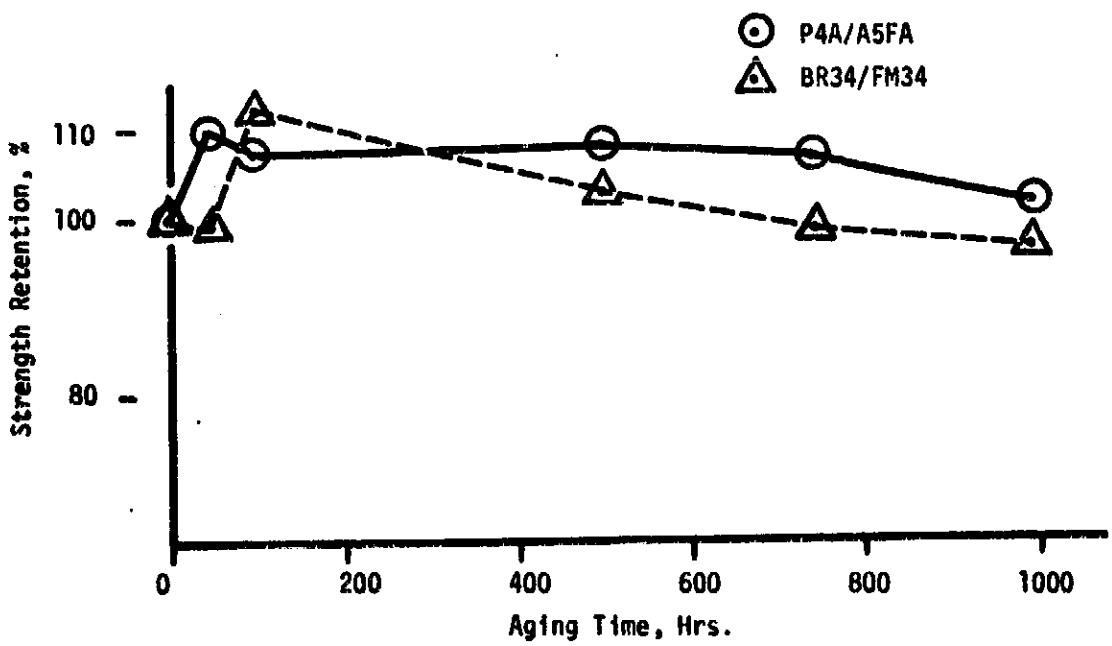

Figure 18. Unstressed Aging at 477°K of Stainless Steel Lap Shear Panels After Thermal Shock Tests

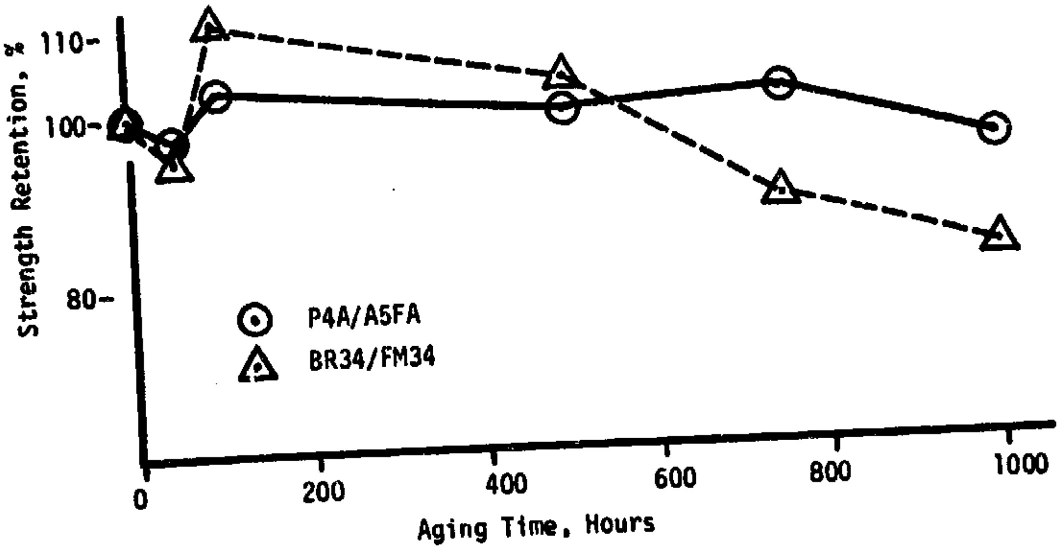

Figure 19. Unstressed Aging at 533°K of Stainless Steel Lap Shear Panels

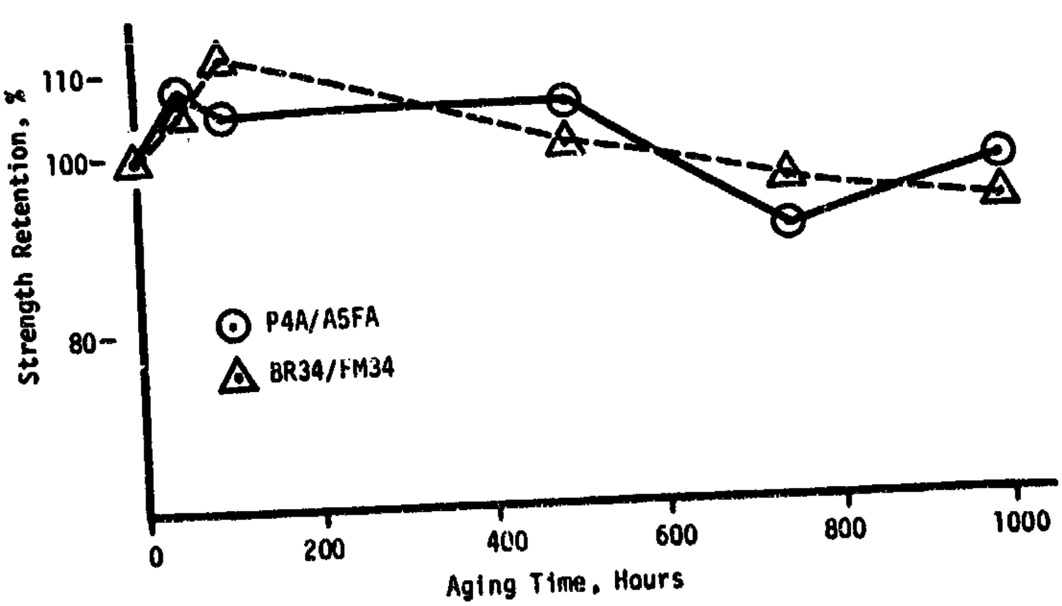

Figure 20. Unstressed Aging at 533°K of Stainless Steel Lap Shear Panels After Thermal Shock Tests

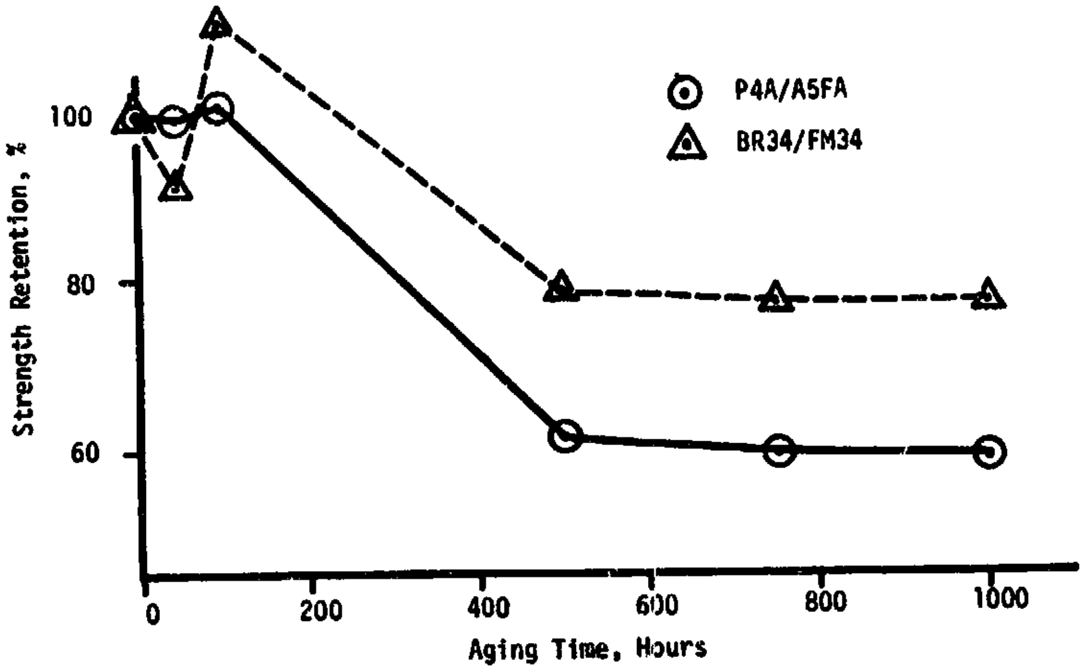

Figure 21. Unstressed Aging at 589°K of Stainless Steel Lap Shear Panels

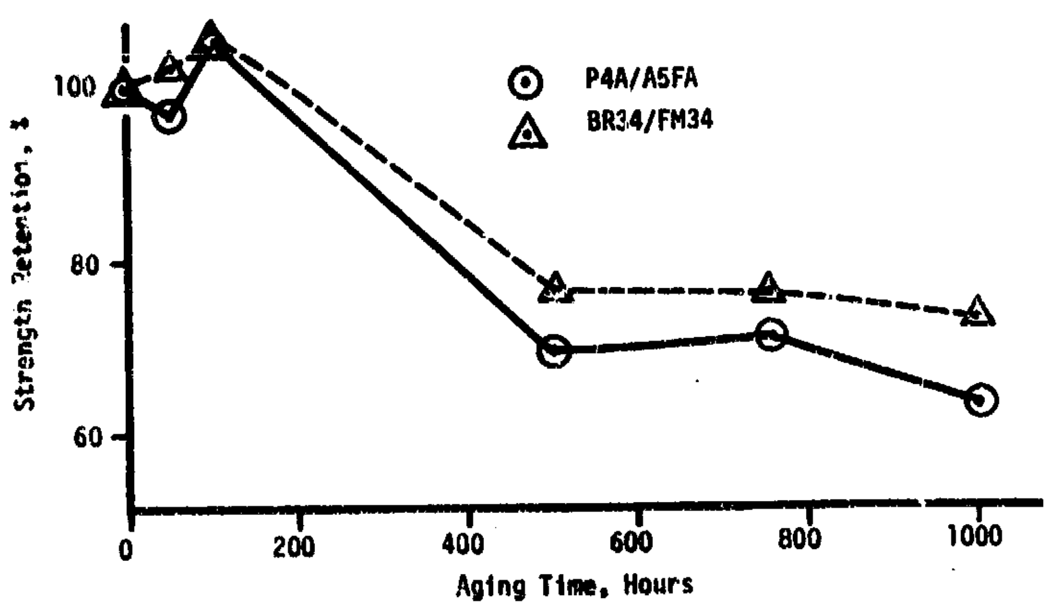

Figure 22. Unstressed Aging at 589°K of Stainless Steel Lap Shear Panels After Thermal Shock Tests

TABLE XI.

RESULTS FROM THERMAL AGING TESTS AT 477°K

Adhesive System	Aging Duration at 477°K, Hrs.	As Prepared Specimens		Specimens After Thermal Shock	
		Lap Shear[a] Strength, MN/m^2	Strength Retention, %	Lap Shear [a] Strength, MN/m^2	Strength Retention, %
P4A/A5FA	0	19.1	--	15.9	--
BR34/FM34	0	21.7	--	21.7	--
P4A/A5FA	50	19.8	104	17.5	110
BR34/FM34	50	21.5	99	21.5	99
P4A/A5FA	100	19.8	104	17.1	108
BR34/FM34	100	21.2	98	24.5	113
P4A/A5FA	500	19.1	100	17.2	108
BR34/FM34	500	18.2	84	22.5	104
P4A/A5FA	750	17.6	92	17.1	108
BR34/FM34	750	18.5	85	21.4	99
P4A/A5FA	1000	18.3	96	16.1	101
BR34/FM34	1000	18.7	86	21.1	97

[a] Determined at 295°K (R.T.)

TABLE XII.

RESULTS FROM THERMAL AGING TEST AT 533°K

Adhesive System	Aging Duration at 533°K, Hrs.	As Prepared Specimens		Specimens After Thermal Shock	
		Lap Shear[a] Strength, MN/m^2	Strength Retention, %	Lap Shear[a] Strength, MN/m^2	Strength Retention, %
P4A/A5FA	0	19.1	--	15.9	--
BR34/FM34	0	21.7	--	21.7	--
P4A/A5FA	50	18.7	98	17.1	108
BR34/FM34	50	20.8	96	23.0	106
P4A/A5FA	100	19.6	103	16.6	104
BR34/FM34	100	23.9	110	24.2	112
P4A/A5FA	500	19.0	100	16.6	104
BR34/FM34	500	22.5	104	21.8	101
P4A/A5FA	750	19.3	101	14.3	90
BR34/FM34	750	19.5	90	20.7	95
P4A/A5FA	1000	18.0	94	15.2	96
BR34/FM34	1000	18.0	83	20.3	94

[a] Determined at 295°K (R.T.)

TABLE XIII.

RESULTS FROM THERMAL AGING TESTS AT 589°K

Adhesive System	Aging Duration at 589°K, Hrs.	As Prepared Specimens		Specimens After Thermal Shock	
		Lap Shear[a] Strength, MN/m^2	Strength Retention, %	Lap Shear [a] Strength, MN/m^2	Strength [a] Retention, %
P4A/A5FA	0	19.1	--	15.9	--
BR34/FM34	0	21.7	--	21.7	--
P4A/A5FA	50	18.8	98	15.4	97
BR34/FM34	50	19.8	91	22.4	103
P4A/A5FA	100	19.1	100	16.6	104
BR34/FM34	100	23.9	110	22.7	105
P4A/A5FA	500	11.8	62	10.9	69
BR34/FM34	500	19.4	89	18.7	86
P4A/A5FA	750	11.3	59	11.3	71
BR34/FM34	750	16.7	77	16.5	76
P4A/A5FA	1000	11.2	59	10.1	64
BR34/FM34	1000	16.6	77	16.0	74

[a] Determined at 295°K (R.T.)

plots indicated higher strength retention for the P4A/A5FA adhesive joints aged at 477°K and 533°K and higher strength retention for BR34/FM34 adhesive joints aged at 589°K. No effects of thermal shock on either type of adhesive joint were observed.

3.4 STRESSED THERMAL AGING TESTS

Lap shear test specimens were bonded with PPQ II (IMW), P4/A5F, P4A/A5FA and BR34/FM34 adhesives. These specimens were loaded into stressed thermal aging test jigs at 50% of their ultimate strength and then subjected to thermal aging in air circulating ovens at 477°K (400°F), 533°K (500°F) and 589°K (600°F). After completion of a 1000-hour aging duration, those specimens that survived the test were loaded to failure at room temperature. Details of the test specimen preparation procedures, test procedures and test results are provided below.

3.4.1 Preparation of Test Specimens -

Lap shear test specimens were prepared using 17-7PH stainless steel and 6A14V titanium alloy substrates. The surface preparation of the titanium alloy and stainless steel alloy substrates was in accordance with the procedures described in Appendix A.2.1 and A.1.3, respectively. Panels were bonded with BR34/FM34, P4/A5F, P4A/A5FA and PPQ II (IMW) adhesive systems in accordance with the procedures described in Appendix B.

3.4.2 Test Procedures -

Test specimens prepared in accordance with Section 4.3.1 as well as stainless steel specimens which had survived thermal shock (see Section 3.2) were loaded into the stress rupture test fixtures and the predetermined load (see Tables XIV, XV and XVI) was applied (see Figures 23 and 24) by adjusting the weighted lever arm length by an adjustment screw. These test jigs were pre-located in air circulating ovens with an air velocity of 12.7 m/sec and an air change rate of 19.7 m^3/sec. The ovens then were heated to the test temperatures (*i.e.* 477°K (400°F), 533°K (500°F) and 589°K (600°F) and the test specimens and jigs were allowed to reach equilibrium before

TABLE XIV.

SUMMARY OF STRESSED THERMAL AGING STUDIES FOR TITANIUM ALLOY SPECIMENS

Adhesive System	Initial Shear Strength, 295°K	Shear Strength After Aging, 295°K	Strength[a] Retention, %	Failure Time, Hours	Stressed Thermal Aging Conditions		
					Test Temperature, °K	Test Load, KN	Test Shear Stress, MN/m^2
PPQ II (IMW)	24.6	19.6	80	N.F.	477	2.22	7.0
P4/A5F	32.5	24.9	77	N.F.	477	3.96	12.5
BR34/FM34	24.1	20.9	87	N.F.	477	1.96	6.2
PPQ II (IMW)	29.0	17.6[b]	61	2	533	2.58	8.2
P4/A5F	30.4	(c)	(c)	192 288	533	3.56	11.2
BR34/FM34	26.3	(c)	(c)	168 192	533	2.14	6.7
PPQ II (IMW)	27.9	4.9[b]	18	864	589	0.71	2.2
P4/A5F	27.7	(c)	(c)	360	589	1.91	6.0
BR34/FM34	24.4	(c)	(c)	2	589	1.18	3.7

a) % Retention = $\frac{\text{Shear Stress @ 295°K After Aging}}{\text{Shear Stress @ 295°K Before Aging}}$

b) Value represents one specimen. Other specimen failed during aging.

c) Neither specimen survived aging.

TABLE XV.

SUMMARY OF STRESSED THERMAL AGING STUDIES FOR STAINLESS STEEL SPECIMENS AFTER THERMAL SHOCK

Adhesive System	Initial Shear Strength, 295°K	Shear Strength After Aging, 295°K	Strength[a] Retention, %	Failure Time, Hours	Stressed Thermal Aging Conditions: Test Temperature, °K	Test Load, KN	Test Shear Stress, MN/m²
P4A/A5FA	15.9	18.3	115	N.F.	477	2.8	8.8
BR34/FM34	21.7	18.3	84	N.F.	477	2.3	7.0
P4A/A5FA	15.9	17.4	109	N.F.	533	2.5	7.7
BR34/FM34	21.7	20.3	94	N.F.	533	1.9	6.1
P4A/A5FA	15.9	12.8	81	950	589	1.8	5.6
BR34/FM34	21.7	13.9	64	N.F.	589	1.3	3.7

a) % Retention = $\frac{\text{Shear Stress @ 295°K After Aging}}{\text{Shear Stress @ 295°K Before Aging}}$

TABLE XVI.

SUMMARY OF STRESSED THERMAL AGING STUDIES FOR STAINLESS STEEL SPECIMENS

Adhesive System	Initial Shear Strength, 295°K	Shear Strength After Aging, 295°K	Strength[a] Retention, %	Failure Time, Hours	Stressed Thermal Aging Conditions: Test Temperature, °K	Test Load, KN	Test Shear Stress, MN/m²
P4A/A5FA	19.1	19.2	101	100 [b]	477	2.8	8.8
BR34/FM34	21.7	18.8	87	N.F.	477	2.3	7.0
P4A/A5FA	19.1	18.8	98	N.F.	533	2.5	7.7
BR34/FM34	21.7	18.0	83	N.F.	533	1.9	6.1
P4A/A5FA	19.1	13.3	70	N.F.	589	1.8	5.6
BR34/FM34	21.7	12.4	57	N.F.	589	1.3	3.7

a) % Retention = $\frac{\text{Shear Stress @ 295°K After Aging}}{\text{Shear Stress @ 295°K Before Aging}}$

b) Value represents one specimen. Other specimen failed during aging.

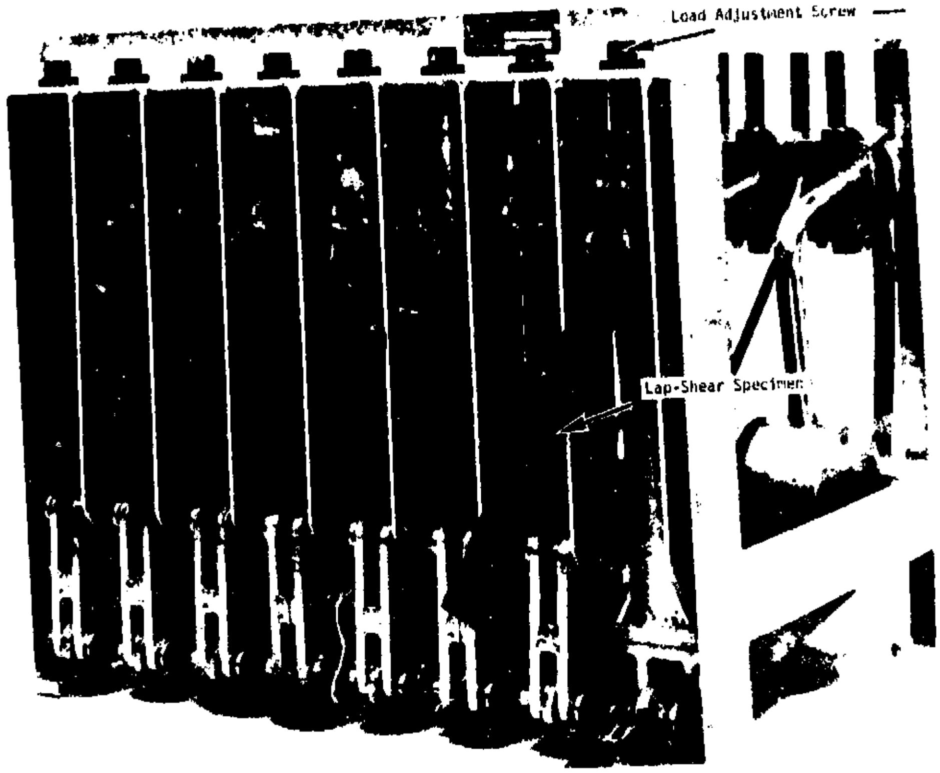

Figure 23. Loading Specimens in Stressed Thermal Aging Test Jig

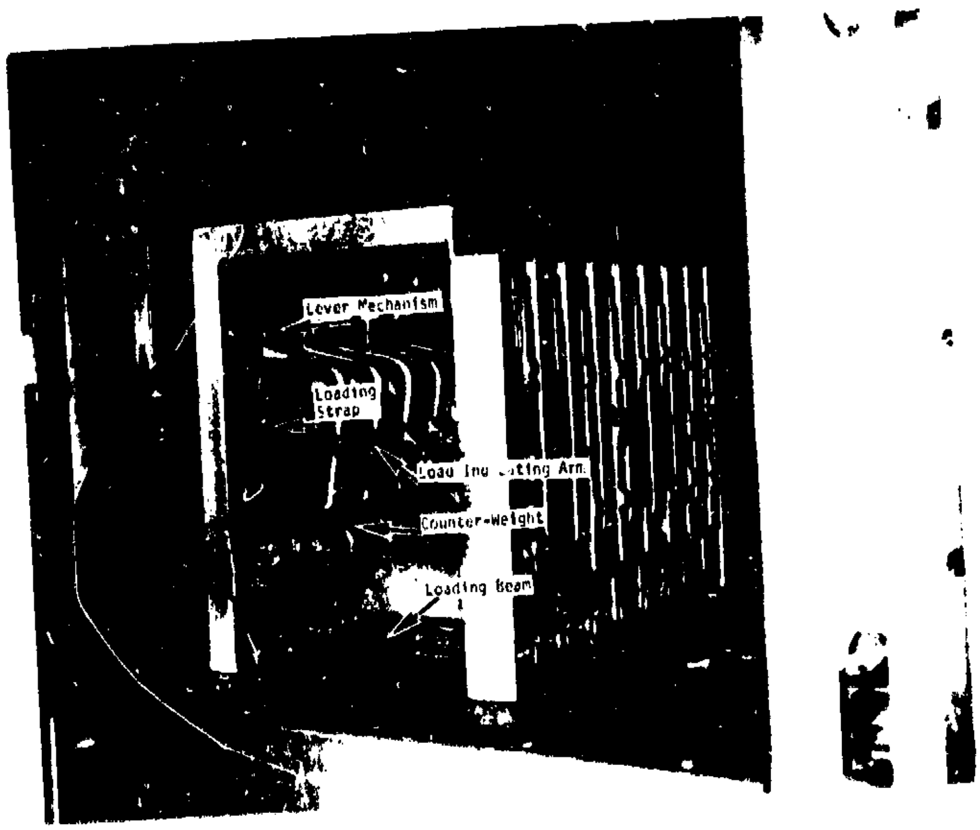

Figure 24. Stressed Thermal Aging Test Jig in Air Circulating Oven

the final load adjustments were made. Oven temperatures and specimen loads were monitored continuously and the loads were readjusted as necessary to the proper levels in order to compensate for test specimen creep. After completion of a 1000-hour aging duration, the load was released. The test fixtures and specimens were cooled to R.T. and the unfailed specimens were removed. Testing of the unfailed specimens then was performed at R.T. using a loading rate of 550 Kg/minute.

3.4.3 Stressed Thermal Aging Test Results -

Examination of the test results for the titanium alloy specimens indicated that the PPQ II (IMW) bonded specimens performed better than the other adhesive systems (see Table XIV). The stressed thermal aging tests on stainless steel alloy specimens were performed on specimens bonded with BR34/FM34 and P4A/A5FA adhesives only because sufficient quantity of PPQ II (IMW) resin for preparing these specimens was not available. These results (see Tables XV and XVI) indicated that the P4A/A5FA adhesive bonded specimens maintained their shear strength throughout the 1000-hour aging cycle better than the BR34/FM34 system. There were no apparent adverse affects caused by the thermal shock tests on either the P4A/A5FA or BR34/FM34 bonded specimens.

3.5 COEFFICIENT OF THERMAL EXPANSION DETERMINATIONS

The coefficient of thermal expansion was determined on specimens molded from the A5FA and FM34 adhesive films. These determinations were made over a 20°K (-423°F) to 589°K (600°F) temperature range. Details of the test specimen preparation procedures, test procedures and test results are provided below.

3.5.1 Test Specimen Preparation -

Test specimens were molded from A5FA and FM34 adhesive films using the procedures described in Appendix C. The resultant panels then were machined into plugs 2.0 mm thick by 12.7 mm wide and 50.8 mm long.

3.5.2 Test Procedures -

Coefficient of thermal expansion determinations were made using a standard quartz rod and tube with a liquid hydrogen cryostat for temperatures from 20°K (-423°F) to 295°K (R.T.) and electrical resistance heaters for temperatures from 295°K (R.T.) to 589°K (600°F). Dimensional changes in the specimens were measured with a linear variable transformer (LVT) which were plotted on a Mosley x-y recorder. Temperature changes were measured by a thermocouple attached to the specimen and plotted on the Mosley x-y recorder to provide strain *vs* temperature plots (see Figure 25).

3.5.3 Results of Coefficient of Thermal Expansion Determinations -

Strain measurements were taken for the four specimens over a temperature range of 20°K (-423°F) to 589°K (600°F) and plotted (see Figure 25). Taking incremental slopes from the data plotted in Figure 26, the incremental average coefficient of thermal expansion was calculated and plotted (see Figure 24). These data indicated a wider value range for the A5FA system ($\sim$22.86 X 10^{-6} to $\sim$59.44 X 10^{-6} cm/cm/°K) than for the FM34 system ($\sim$6.86 X 10^{-6} to 25.15 X 10^{-6} cm/cm/°K). Variations in the metallic filler content for either adhesive formulation could change these values and value ranges. Consequently, further formulary tailoring of either system could be performed to obtain coefficient of thermal expansion values to meet specific requirements.

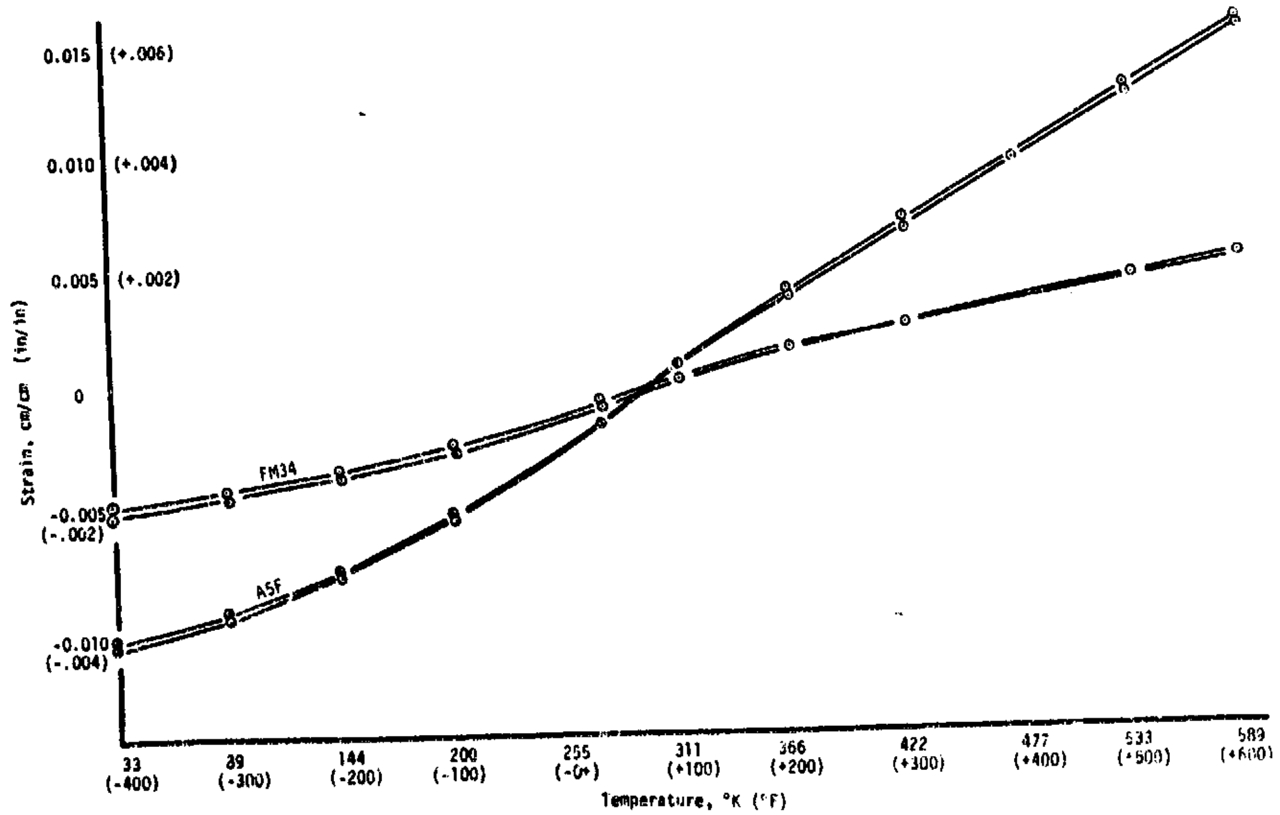

Figure 25. Strain *vs* Temperature Plots For Adhesive Plugs

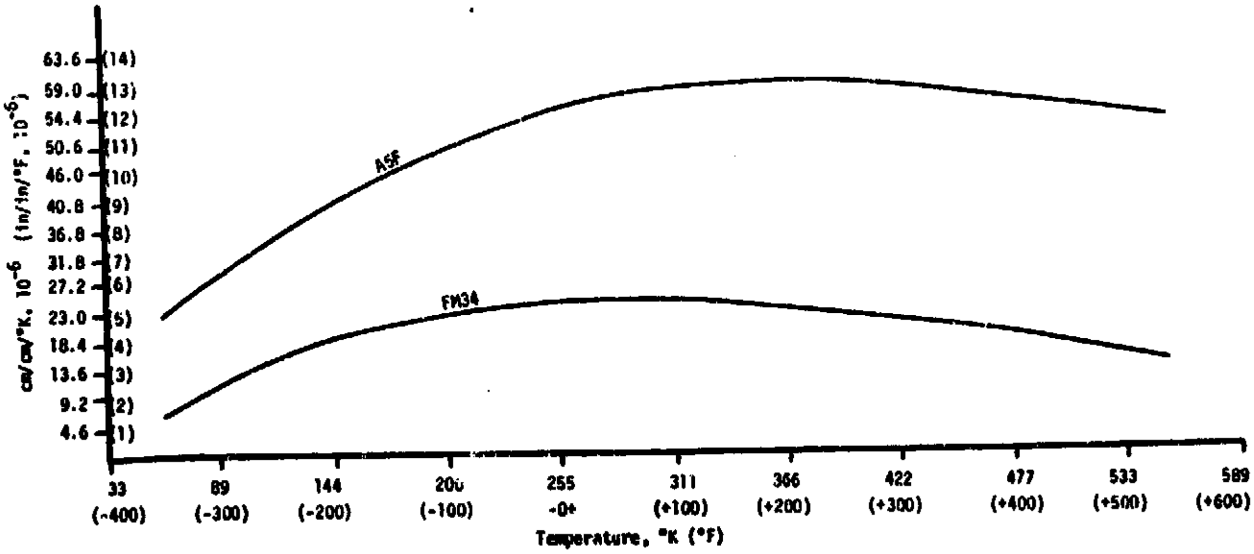

Figure 26. Coefficient of Thermal E..ansion

3.6 SUMMARY OF TEST RESULTS

Results from the static lap shear tests indicated that all of the adhesive systems evaluated, *i.e.* P4/A5F or P4A/A5FA, BR34/FM34 and PPQ II (IMW) provided similar room temperature values (see Table VIII). However, at 589°K (600°F) the P4/A5F or P4A/A5FA systems provided significantly higher strength retention values than did either the BR34/FM34 or PPQ II (IMW) systems. Superior strength retention for the PPQ II (IMW) system after thermal aging at 589°K was indicated by the results from stressed thermal aging tests with titanium alloy specimens (see Table XIII). Because a sufficient quantity of the PPQ II (IMW) resin was not available for preparing specimens for other tests such as unstressed thermal aging, stressed thermal aging or static tests at cryogenic temperatures, a thorough evaluation of this experimental resin was not performed. Unstressed thermal aging tests on the other two adhesive systems, *i.e.* BR34/FM34 and P4A/A5FA showed slightly higher strength retention values for the P4A/A5FA system at aging temperatures of 477°K (400°F) and 533°K (500°F) and slightly higher strength retention values for the BR34/FM34 system at 589°K (600°F).

Static tests at 20°K (-423°F) showed that the BR34/FM34 shear strength values increased more than the P4/A5F or P4A/A5FA system (see Table VIII). The BR34/FM34 values at 20°K were 42% higher than the room temperature values whereas the P4/A5F and P4A/A5FA values were 5% and 25% higher, respectively. Shear moduli determinations were not made during this program therefore it was not possible to ascertain whether significant resin embrittlement accompanied the high shear strength increase for the BR34/FM34 system.

Stressed thermal aging tests indicated that the titanium alloy adherends bonded with the P4/A5F system survived for longer durations at 533°K (500°F) and 589°K (600°F) than those bonded with BR34/FM34 (see Table XIV) although those bonded with the PPQ II (IMW) system survived the whole 1000-hour test duration. Most of the stainless steel alloy specimens prepared with the P4A/A5FA and BR34/FM34 systems also survived the whole 1000-hour test duration. However, the room temperature shear strength retention of specimens surviving the stressed thermal aging tests was higher for the P4A/A5FA system than for the BR34/FM34 system (see Table XV). Thermal shock tests had no apparent adverse affects on stressed thermally aged specimens bonded with either system (see Table XVI).

Thermal shock tests did not appear to affect the room temperature lap shear strength of specimens bonded with the BR34/FM34. There was some strength degradation for the P4A/A5FA system caused by thermal shock. Thermal shock had no apparent effects on properties determined by other tests, such as stressed thermal aging tests.

Coefficient of thermal expansion determinations on molded A5FA and FM34 specimens indicated a wider range of coefficient of thermal expansion values for the A5FA system than the FM34 system (see Figure 26). At the elevated temperatures the coefficient of thermal expansion for A5FA is above that of titanium and stainless steel substrates which indicates that less stresses occur at elevated temperatures in the bondline of specimens bonded with P4A/A5FA. This should result in higher strength retention at elevated temperatures. Observed elevated temperature values (see Table VIII) confirmed this deduction. The data also led to the deduction that the BR34/FM34 system should provide higher shear strength values at room temperature and higher shear strength retention values after thermal shock than the A5FA system. These deductions also are confirmed in the test results described in Section 3.4 (see Tables XIII, XIV and XV). As discussed previously in Section 3.5, adhesive formulary adjustments can change the coefficient of thermal expansion values. Consequently, optimization of either system formulation could be performed to suit specific performance requirements, such as improved thermal shock resistance, higher cryogenic or higher elevated temperature strength retention.

4. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this effort to identify a structural adhesive system for cryogenic and high temperature service applications. Based on these findings, recommendations are given for further material improvement and evaluation studies.

4.1 CONCLUSIONS

1. Two polyimide adhesive systems, *i.e.* BR34/FM34 and P4/A5F or P4A/A5FA were identified for applications at cryogenic (*i.e.* 20°K) and elevated (*i.e.* 589°K) service temperatures. These systems provided sound structural joints with both titanium alloy and stainless steel substrates. Both systems provided approximately equivalent properties. However, the P4/A5F system is easier to process and provides better quality bondlines (*e.g.*, lower void contents) particularly in large surface area joints.

2. The results from long term (*i.e.*, 1000-hour) stressed and unstressed thermal aging tests from joints bonded with the BR34/FM34 and P4/A5F or P4A/A5FA adhesive systems demonstrated the suitability of both systems for carrying sustained loads at elevated temperatures, *i.e.*, 477°K (400°F), 533°K (500°F) and 589°K (600°F) as well as surviving at these temperatures in the unloaded condition.

3. Determinations of the coefficient of thermal expansion values for the FM34 and A5FA adhesive systems indicated that different values and value ranges exist for these two systems. Because this property can affect the performance of adhesive bondlines in different thermal environments, it was suggested that variations in adhesive formulations could be made in order to optimize this property for a specific application.

4. Evaluation of a polyphenylquinoxaline resin [BAC PPQ II (IMW)] indicated high promise of this generic class of polymers for structural adhesive applications. However, detailed adhesive developmental studies are necessary to obtain suitable adhesive systems based on this type of polymer which will provide suitable bonded joints for detailed evaluation.

5. A commercial, proprietary surface preparation material, Pasa-Jel 107, was identified for preparing titanium alloy substrates for adhesive bonding. Processing procedures for preparing titanium alloy substrates with Pasa-Jel 107 are simple and amenable to production applications. Titanium alloy 6AL4V substrates prepared with Pasa-Jel 107 survived long term aging at air temperature extremes up to 589°K (600°F).

6. A standard sulfuric acid - sodium dichromate pre-etch procedure was identified for preparing stainless steel alloy for adhesive bonding. Processing procedures for preparing stainless steel substrates by this process are simple and amenable to production applications. Stainless steel 17-7PH substrates prepared by the sulfuric acid - sodium dichromate etch survived long term aging in air temperature extremes up to 589°K (600°F).

4.2 RECOMMENDATIONS

1. Studies to evaluate the effects of adhesive formulation changes on coefficient of thermal expansion values as well as companion studies on the effect of variations in coefficient of thermal expansion values on other properties are warranted in order to optimize an adhesive system for specific applications. Such studies should attempt to define optimum adhesive formulations (*i.e.* metallic filler contents) required to obtain highest thermal shock resistance, highest cryogenic and highest elevated temperature strength values.

2. Developmental studies on adhesive formulations based on polyphenylquinoxaline polymer systems are warranted in order to obtain improved high temperature strength retention and also to evaluate these systems for cryogenic temperature service.

3. Further property evaluation studies on structural joints bonded with the BR34/FM34 and P4/A5F adhesive systems are warranted to obtain detailed design information. Studies should include determination of shear modulus, creep, fatigue strength and stressed thermal aging at cryogenic temperatures and at different stress levels over the complete temperature range, *i.e.* 20°K (-423°F) to 589°K (600°F).

5. NEW TECHNOLOGY

Methods of preparing adhesive joints with BAC PPQ II (IMW) polyphenylquinoxaline resin were developed that demonstrated promise for this system as a structural adhesive. The relationship between coefficient of thermal expansion values of two polyimide adhesive systems (A5FA and FM34) and their mechanical properties, *i.e.* thermal shock and stressed thermal aging strength retention were established. Definition of this relationship can provide meaningful guidance in future adhesive formulary studies for specific applications.

The above concepts have been described in New Technology Disclosures submitted to the TRW Patent Office. The subject matter of these disclosures is listed below:

Docket Number	Title
73-112	Structural Adhesive Compounds Based On Polyphenylquinoxaline Resin
73-113	Process For Forming Structural Joints With Polyphenylquinoxaline Adhesives
73-114	Method For Predicting the Thermal Behavior of Structural Adhesives by Coefficient of Thermal Expansion Determinations
73-115	Autoclavable Structural Adhesive For Bonding Ferrous Alloys For High Temperature Applications

APPENDIX A.

SURFACE PREPARATION PROCEDURES

A.1 PREPARATION OF 17-7PH STAINLESS STEEL ALLOY FOR BONDING

A.1.1 Method A - Prebond 700

Step 1. Solvent clean with acetone.

Step 2. Immerse in Prebond 700 at 368°K (200°F) for 15 minutes. (75 Kg/m^3 distilled water)

Step 3. Cold water rinse at 295°K (72°F).

Step 4. Immerse in an aqueous solution of 4% w/w H_2SO_4 and 4% w/w HCl at room temperature for 20 minutes.

Step 5. Cold water rinse at 295°K (72°F).

Step 6. Immerse in an aqueous solution of 12% w/w HNO_3 and 2% w/w HF at room temperature for 15 minutes.

Step 7. Cold distilled water rinse at 295°K (72°F).

Step 8. Dry in an air circulating oven at 339°K (150°F).

A.1.2 Method B - Solvent Clean and Vapor Honed

Step 1. Solvent clean with acetone.

Step 2. Vapor hone faying surfaces.

Step 3. Cold distilled water rinse at 295°K (72°F).

Step 4. Dry in an air circulating oven at 339°K (150°F).

A.1.3 Method C - Sulfuric Acid - Sodium Dichromate Bath

Step 1. Solvent clean with acetone.

Step 2. Immerse in a bath of 96.6% v/v concentrated sulfuric acid (1.84 sp. gr.) and 3.4% v/v saturated aqueous solution of sodium dichromate (2.380 kg/liter distilled water) at 339°K (150°F) for 15 minutes.

Step 3. Air dry in an air circulating oven at 339°K (150°F).

A.1.4 Method D - Solvent Clean

Step 1. Thoroughly wash faying surfaces with acetone and wipe dry.

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A.2 PREPARATION OF 6Al4V TITANIUM ALLOY

A.2.1 Method A - Pasa-Jel

Step 1. Solvent clean with methyl ethyl ketone (MEK).

Step 2. Alkaline clean at 355°K (180°F) for 15 minutes in a solution of Turco HTC (428 g/liter).

Step 3. Rinse in hot tap water at 339°K (150°F) then cold tap water at 295°K (72°F).

Step 4. Immerse in an aqueous bath of nitric acid 15% w/w and hydrofluoric acid 3% w/w at room temperature for 30 seconds.

Step 5. Rinse in tap water at 295°K (72°F).

Step 6. Immerse faying surfaces in Pasa-Jel 107 for 15 minutes at room temperature.

Step 7. Rinse in distilled water at 295°K (72°F).

Step 8. Dry in an air circulating oven at 339°K (150°F).

A.2.2 Method B - Turco 5578

Step 1. Solvent clean with methyl ethyl ketone (MEK).

Step 2. Alkaline clean at 355°K (180°F) for 15 minutes in a solution of Turco HTC (428 g/liter).

Step 3. Rinse in hot tap water at 339°K (150°F) then cold tap water at 295°K (72°F).

Step 4. Immerse in an aqueous bath of Turco 5578 (544 Kg/m^3 distilled water) at 366°K (200°F) for 20 minutes.

Step 5. Wash with 366°K (200°F) distilled water.

Step 6. Dry in an air circulating oven at 339°K (150°F).

A.2.3 Method C - Phosphate Fluoride Treatment

Step 1. Solvent clean with methyl ethyl ketone (MEK).

Step 2. Alkaline clean at 355°K (180°F) for 15 minutes in a solution of Turco HTC (428 g/liter).

Step 3. Cold water rinse at 295°K (72°F).

Step 4. Immerse in an aqueous bath of nitric acid 15% w/w and hydrofluoric acid 3% w/w for 30 seconds at room temperature.

Step 5. Cold water rinse at 295°K (72°F).

Step 6. Immerse in an aqueous bath of 5% w/w trisodium phosphate, 2% w/w potassium fluoride, 3% w/w hydrofluoric acid at room temperature for 2 minutes.

Step 7. Cold distilled water rinse at 295°K (72°F).

Step 8. Immerse in 339°K (150°F) distilled water for 15 minutes.

Step 9. Cold distilled water rinse at 295°K (72°F).

Step 10. Dry in an air circulating oven at 339°K (150°F).

A.2.4 Method D - Solvent Clean

Step 1. Thoroughly wash faying surfaces with methyl ethyl ketone (MEK) and wipe dry.

APPENDIX B.

DETAILED PROCESSING PROCEDURES

B.1 PREPARATION OF ADHESIVE FORMULATIONS

The adhesive formulations were prepared using the constituents listed in Table B-1 by the following process.

B.1.1 P4/A5F Series of Formulations

The A-type polyimide and Amoco AI-1137 amide-acid varnishes first were blended together. Aluminum powder then was added and blended together with Cab-O-Sil for adhesive pastes and the arsenic compounds where applicable. The primer formulations then were diluted with DMF. Adhesive film was prepared by immersing Style 104 A1100 glass scrim in the adhesive paste and drawing the resultant film through wiper bars with a 0.45 mm gap. The resultant films then were air dried for 30 minutes and then dried in an air circulating oven for 15 minutes at 408°K (275°F) plus 5 minutes at 450°K (350°F).

B.1.2 NR150B Formulation

The NR150B polyimide resin first was diluted to 40% w/w resin solids by the addition of DMF. Aluminum powder then was added and blended together with Cab-O-Sil for the adhesive paste. The primer formulations were obtained by diluting the formulations with DMF. The adhesive film was prepared by immersing Style 104 A1100 glass fabric in the adhesive paste and allowing to drip dry over a period of 5 minutes. The adhesive film then was air dried in an air circulating oven at 472°K (390°F) for 3 hours and then precured an additional 1 hour at 672°K (750°F).

B.1.3 PPQ II (IMW) Adhesive Formulation

To the 20 percent resin solids PPQ II (IMW) resin, aluminum powder was added and blended together with Cab-O-Sil for the adhesive paste. The adhesive film was prepared by mounting the Style 104 A1100 glass scrim over a picture frame and coating the scrim with a 5% w/w PPQ resin and xylene/*m*-cresol mixture. The resultant film then was air dried for 20 minutes at room temperature plus 4 hours at 355°K (180°F). A second coating then was applied using adhesive paste and air dried for 16 hours at 355°K (180°F).

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TABLE B-1
ADHESIVE/PRIMER FORMULATIONS

Constituents[a)]	Parts by Weight of Constituents in Adhesive/Primer Formulation									
	P4	P4SX	A5FSX	P4S	A5FS	P4A	A5FA	NR150B Primer	NR150B Adhesive	PPQ II (IMW) Adhesive
P11BA (Resin Solids)	50	50	50	50	50	50	50	--	--	--
AI-1137 (Resin Solids)	50	50	50	50	50	50	50	--	--	--
NR150B (Resin Solids)	--	--	--	--	--	--	--	100	100	--
PPQ II (IMW) (Resin Solids)[c)]	--	--	--	--	--	--	--	--	--	100
Aluminum Powder, Grade 101	100	100	175	175	175	175	175	100	175	175
Cab-O-Sil M-5	--	--	5	5	5	5	5	--	5	5
Arsenic Thioarsenate	--	10	10	5	5	--	--	10	10	--
Arsenic Pentoxide	--	--	--	--	--	5	5	--	--	--
DMF	400	400	150	400	150	400	150	400	400	--
o-xylene/m-cresol (1:1 v/v)	--	--	--	--	--	--	--	--	--	150
Glass Scrim	--	--	b	--	b	--	b	--	b	b

a) P11BA - TRW A-type polyimide, 1100 FMW NA/80MPD:20TDA/BTDA
AI-1137, Amoco Corporation
Aluminum Powder - Aluminum Co. of America, Grade 101
Cab-O-Sil - Cabot Corporation
DMF - Dimethyl formamide, Baker Reagent Grade
Arsenic pentoxide - Baker Chemical Reagent Grade
Arsenic thioarsenate - ALFA Inorganics, Inc.
Glass Scrim - Style 104 glass scrim, A1100 amino-silane coupling agent
NR150B - Polyimide resin, Dupont

b) One layer of scrim coated with adhesive paste.

c) PPQ II (IMW) - Polyphenylquinoxaline resin PPQ II (IMW), Boeing Company

B.2 PREPARATION OF BONDED LAP SHEAR SPECIMENS

B.2.1 P4/A5F Series of Adhesives

Step 1. Prepare steel and titanium lap shear coupons for bonding using applicable cleaning procedures (See Appendix A).

Step 2. After applying an approximate 0.125mm primer coat to the prepared faying surfaces, dry as follows: 30 minutes 295°K (72°F) plus 15 minutes at 408°K (275°F) plus 5 minutes at 450°K (350°F).

Step 3. Assemble panels in bonding jig using previously prepared adhesive tape.

Step 4. Prepare vacuum bag assembly in accordance with Appendix D, NASA Report CR-112003 (Reference 1).

Step 5. Install assembly in an autoclave.

Step 6. Evacuate air out of the vacuum bag to provide a pressure of $\sim$100kN/m^2.

Step 7. Apply 610kN/m^2 nitrogen gas pressure.

Step 8. Heat assembly to 589°K (600°F) at a heat-up rate of 2-4°K per minute.

Step 9. Cure for 60 minutes under pressure.

Step 10. Release pressure and cool the assembly to room temperature in the vacuum bag ($\sim$100kN/m^2).

Step 11. Remove lap shear specimens and postcure in an air circulating oven for 16 hours at 561°K (550°F).

B.2.2 BR34/FM34 Adhesive System

Step 1. Prepare steel and titanium lap shear coupons for bonding using applicable cleaning procedure (See Appendix A).

Step 2. After applying a 0.8mm primer coat to the prepared faying surfaces, dry as follows: 30 minutes at 295°K (72°F) plus 35 minutes at 394°K (250°F).

Step 3. Assemble panels in bonding jig using commercially prepared adhesive film.

Step 4. Prepare vacuum bag assembly using conventional vacuum bagging techniques (*i.e.*, zinc chromate sealant, nylon film, etc.).

Step 5. Install assembly in an autoclave.

Step 6. Evacuate air out of vacuum bag assembly and heat at rate of 1-4°K/minute to 405°K (270°F) then reduce rate to 0.5-1°K/minute up to 450°K (350°F). When the temperature of the assembly is 427°K (310°F) apply 305kN/m^2 nitrogen gas pressure. Hold temperature at 450°K (350°F) for 60 minutes.

Step 7. Release pressure and cool the assembly to room temperature in the vacuum bag (∿100kN/m^2).

Step 8. Remove lap shear specimens and postcure as follows: 30 minutes at 450°K (350°F), then raise temperature to 561°K (550°F) at 7°K/minute for 2 hours at 561°K (550°F).

B.2.3 NR150B Adhesive System

Step 1. Prepare steel and titanium lap shear coupons for bonding using applicable cleaning procedure (See Appendix A).

Step 2. After applying a 0.8mm coating to the prepared faying surfaces dry as follows: 30 minutes at 295°K (72°F) plus 3 hours at 472°K (390°F) plus 2 hours at 672°K (750°F).

Step 3. Assemble lap shear coupons and adhesive film onto a preheated assembly jig at 689°K (780°F) and load into preheated press. Apply 17.5MN/m^2 (2500 psig) pressure and hold for 7 minutes.

Step 4. Cool press to below 589°K (600°F) prior to release of pressure.

Step 5. Remove lap shear specimens from assembly jig and cool to room temperature.

B.2.4 PPQ II (IMW) RESIN

Step 1. Prepare titanium lap shear specimens for bonding using the Pasa-Jel cleaning method. (See Appendix A.2.1.)

Step 2. Using a 5% solution of PPQ II (IMW) and xylene-*m* cresol (50/50 v/v) apply a thin coating and dry 4 hours at 355°K (180°F).

Step 3. Using the PPQ II (IMW) adhesive paste (Table B-1) apply another coating to the lap shear specimens and dry for 16 hours at 355°K (180°F).

Step 4. Prepare adhesive film in accordance with Appendix B.1.3 and apply to the faying surfaces.

Step 5. Assemble lap shear coupons onto a preheated assembly jig at 643°K (700°F) and load into a preheated press. Apply 0.35 MN/m^2 (50 psig) pressure and hold 60 minutes.

Step 6. Cool press to below 423°K (300°F) prior to release of pressure.

Step 7. Remove lap shear specimens from assembly jig and cool to room temperature.

APPENDIX C.

PREPARATION OF COEFFICIENT OF THERMAL EXPANSION SPECIMENS

C.1 PREPARATION OF A5FA ADHESIVE PLUGS

Step 1. Lay-up a 10-ply laminate of adhesive film prepared in accordance with Appendix B.1.1.

Step 2. Install lay-up in a cold press and apply 0.7 MN/m^2 (100 psig) pressure. Raise platten temperature to 589°K (600°F) and cure for one hour. Cool laminate under pressure.

Step 3. Postcure laminate in air for 16 hours at 589°K (600°F).

C.2 PREPARATION OF FM34 ADHESIVE PLUGS

Step 1. Lay-up a 10-ply laminate of adhesive film.

Step 2. Install lay-up in a vacuum bag as described in Appendix B.2.2.

Step 3. Cure laminate in an autoclave as described in Appendix B.2.2.

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