AD NUMBER
ADB007907
LIMITATION CHANGES
TO: **Approved for public release; distribution is unlimited.**
FROM: **Distribution authorized to U.S. Gov't. agencies only; Test and Evaluation; MAY 1975. Other requests shall be referred to Air Force Materials Lab., Wright-Patterson AFB, OH 45433.**
AUTHORITY
AFWAL ltr 3 Nov 1983

AD B00 907

AUTHORITY: AFWAL

Notice 3 Nov 83

AFML-TR-75-48

DEVELOPMENT OF IMPROVED CORE SPLICE ADHESIVES

LOS ANGELES AIRCRAFT DIVISION
ROCKWELL INTERNATIONAL

MAY 1975

TECHNICAL REPORT AFML-TR-75-48
FINAL REPORT FOR PERIOD JANUARY 1974 – JANUARY 1975

Distribution limited to U.S. Government agencies only; test and evaluation; May 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 Air Force Base, Ohio 45433.

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

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

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

THEODORE J. APONYI
Project Engineer

FOR THE COMMANDER

THEODORE J. REINHART, JR., Chief
Composite & Fibrous Materials Branch
Nonmetallic Materials Division

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: AFML-TR-75-48
2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): DEVELOPMENT OF IMPROVED CORE SPLICE ADHESIVES
5. TYPE OF REPORT & PERIOD COVERED: Final Technical Report, Jan [redacted] 74 – Jan [redacted] 75
6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): J. W. Mahoney, E. R. Crilly
8. CONTRACT OR GRANT NUMBER(s): Air Force F33615-74-C-5026
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Los Angeles Aircraft Division, Rockwell International Corporation, International Airport, Los Angeles, California 90009
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: Project 7340/Task 734002
11. CONTROLLING OFFICE NAME AND ADDRESS: AF Materials Laboratory, Air Force Systems Command, Wright-Patterson AFB, Ohio 45433
12. REPORT DATE: May 1975
13. NUMBER OF PAGES: 60p.
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): AF-7340; 734002
15. SECURITY CLASS. (of this report): Unclassified
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE: NA
16. DISTRIBUTION STATEMENT (of this Report): Distribution limited to U.S. Government agencies only; test and evaluation, May 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.
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(s)

Test Methods

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

A total of 16 test methods and associated target property values were selected and devised for determining the mechanical, physical, and handling characteristics of a 350°F service core splice adhesive. These were coordinated with knowledgeable people in the industry and subsequently used in the screening and characterization of various formulations. Approximately 90 materials were compounded by the formulator, of which 16 were screened for expansion ratio, →

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

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

408245 4B

20. ABSTRACT (CONT)

FROM slump, peak exotherm, volatile content, and uncured weight per square foot. Three of the most promising adhesives, identified as ADX-814, ADX-814.1, and ADX-815, were subject to all of the remaining tests to characterize them fully. All pertinent test procedures and data are included in this report.

FOREWORD

This technical report was prepared by the Los Angeles Aircraft Division of Rockwell International Corporation, Los Angeles, California, under U.S. Air Force contract No. F33615-74-C-5026. This contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials," and Task No. 734002, "Structural Adhesives." The work was administered under the direction of the Nonmetallic Materials Division, Air Force Materials Laboratory, with Mr. T. J. Aponyi (AFML/MB) as Project Monitor.

This report covers work performed from 2 January 1974 through 1 January 1975, and was submitted by the authors in February 1975.

The subject program was conducted by Materials and Producibility Engineering of the Los Angeles Aircraft Division of Rockwell International Corporation, Los Angeles, California. The performance of the program was under the general direction of Mr. N. Klimmek, Manager, Materials and Producibility Engineering. Work described in this report was performed under the direction of Mr. J. W. Mahoney, Program Manager. Mr. E. R. Crilly was the Principal Investigator for Rockwell. Formulation efforts were carried out by the Hysol Division of the Dexter Corporation, under Rockwell direction, with Mr. T. F. Mika being the original Principal Investigator for Hysol, followed by Mr. K. K. Rice under whose direction most of Hysol's effort was performed.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

Section I

INTRODUCTION

The major problems associated with core splice adhesives have been non-uniform foaming, excessive flow or slump, and uncontrolled exothermic cure reactions resulting in the charring of the adhesives and adjacent nonmetallic materials such as heat-resistant phenolic (HRP) core. These problems are especially acute for materials formulated to be compatible with modified epoxy structural adhesive systems curing in the 350° F range. The effect of high exotherm temperatures becomes most pronounced in splicing thick sections of nonmetallic core in that damage to the core as well as the adhesive can result. Lack of a suitable core splice adhesive can, in many cases, require design of parts to a single core density resulting in significant weight penalties. Likewise, where splicing is necessary because of configuration or other reasons, rejection rates can be high because of the aforementioned reasons. To provide adequate latitude in the use of a splicing adhesive, it should be available in a number of unexpanded calendered thicknesses from 0.025 to 0.100 inch, and should be procurable in a pourable paste version for more difficult applications.

It was the purpose of this program to develop core splice adhesives suitable for use at temperatures up to 350° F. The program was conducted in three phases, as follows:

- Phase I - Target Requirements. This phase was conducted by Rockwell and consisted of selecting suitable test methods for evaluating mechanical, physical, and handling and storage properties of foaming adhesives. Preliminary ranges for these properties were selected and coordinated with knowledgeable personnel in the aerospace industry, including the Program Monitor, to establish target properties.

- Phase II - Adhesive Formulation and Screening. This phase consisted of formulating various materials by Hysol based on the target requirements established in phase I. Hysol performed preliminary testing as required to support this effort. The best of these formulations were selected for screening by Rockwell using 0.10-inch material thickness film to determine expansion ratio, slump, peak exotherm, volatile content, and weight per square foot. Results were coordinated with Hysol to provide direction for formulation changes.

- Phase III - Adhesive Characterization. As a result of the screening tests performed in phase II, the three most promising formulations were selected for characterization in this phase of the program. They were subject to all of the tests for target requirements defined in phase I. These three materials were assigned experimental product numbers by Hysol (ADX 814, ADX 814.1, and ADX 815) and will be made commercially available as the demand develops.

Section II

SUMMARY

During the first quarter of this program, phase I (target requirements) was completed. This effort involved the establishment of target values and suitable test methods for the basic mechanical, physical, and handling and storage properties for foaming adhesives. Preliminary values and procedures were prepared and circulated to knowledgeable individuals in the industry for their comments. As a result of this survey and after consultation with the Project Monitor, several of the test procedures were modified and clarified, and some of the target values were changed. Several other target values were suspected of being too restrictive, but were not changed until results of subsequent phases of the program became available.

Phase II (adhesive formulation and screening) was started, with formulation studies beginning at Hysol immediately after the target properties were established. Approximately 90 formulations were compounded and subjected to preliminary testing by Hysol during the program. Of these, 16 were subjected to screening tests at Rockwell using nominal 0.10-inch-thick material. Tests used for screening were expansion ratio, slump, peak exotherm, volatile content, and uncured weight per square foot.

As a result of the screening tests performed in phase II, three materials were selected for phase III (adhesive characterization). The three adhesives have been subjected to all of the tests selected in phase I except for the storage life test which requires 6 months storage at 0° F and is still in progress. The three materials selected for phase III testing have been given the experimental designations ADX 814, ADX 814.1, and ADX 815 by Hysol. Samples of these materials were supplied in thicknesses of 0.10, 0.05, and 0.025 inch. All testing was performed with the 0.10-inch material except for the core size variation test in which all thicknesses were evaluated with

1/8-inch cell size core for uniformity of expansion, closed cell structure, and interlocking of core. With 3/16- and 1/4-inch cell size core, only the 0.10- and 0.05-inch-thick materials were evaluated. The availability of the 0.025-inch material provides additional flexibility for shop operations by permitting stacking plies for any required thickness.

Of the three materials selected for phase III testing, ADX 814.1 most closely meets all of the target requirements and is considered most satisfactory for use. It is capable of shearing the core over the temperature range from -65° to 350° F and, if sanded prior to bonding of facesheets with Plastilock PL 729 adhesive, will fail cohesively as evidenced by honeycomb flatwise tension tests. Another very strong point in favor of this material is that it possesses the best stability when exposed to 90° F for up to 10 days, retaining an expansion ratio in excess of 2:1 as well as satisfactory handling characteristics. ADX 814.1 is also adaptable to being made into a paste form which is desirable for certain applications.

Section III

TARGET REQUIREMENTS - PHASE I

Immediately after contract go-ahead, preliminary target requirements and test procedures were set up and sent to 23 individuals considered knowledgeable in the field for their comments. A list of those from whom comments were solicited is given in Appendix A, and those from whom replies were received are noted.

As a result of the comments received and after consultation with the Project Monitor, several of the test procedures were modified and clarified, and some of the target values were changed. In some cases, comments indicated that target values might be too optimistic, but no change was made until more conclusive information became available from subsequent phases of the program. As a result of other comments, a cold flow test was added. Since there was no known standard test for this property, a relatively simple test was devised and added to those for handling and storage properties. The test procedures as finally revised and used in this program together with the target values are given in Appendix B.

In general, the tests may be considered as falling into three categories: mechanical properties, physical properties, and handling and storage properties. It should be emphasized that the listed target values were considered as desired values of a foaming adhesive and not specification values. A brief description of each test selected, together with its significance and the reason for its inclusion in the program, is given here. Methods of calculation for quantitative properties are given in Appendix C.

TUBE SHEAR

Two concentric aluminum tubes having a 0.200-inch annular gap were bonded with 0.10-inch foaming adhesive film. Specimen thickness was 1/2 inch.

In practice, approximately 3-inch lengths of tubing were bonded at one time so that a minimum of five specimens could be thus obtained. (See Figure 1.) In testing, the outer tube was supported in a fixture, and the load was applied to the inner tube. (See Figure 2.) Ultimate stress was calculated using the mean annular circumference of the adhesive multiplied by the thickness of the specimen to determine the area. This test is a measure of the basic shear properties of adhesive and gives an indication of the strength that might be expected if it were used as a shear tie material for potting inserts or attachment of core to edge members. Since this test is relatively fast and inexpensive, it was included as a potential acceptance test for receiving inspection. The test itself, however, is considered of secondary importance because the primary purpose of a core splice adhesive is to provide sufficient strength to realize the core shear strength over the desired service temperature range of -65° to 350° F.

CORE SHEAR STRENGTH

This test is the standard short beam sandwich flexure test of MIL-A-25463 in which a splice is placed across the width of the core, 2 inches from one end. This places it in the maximum shear stress area of the sandwich during testing. The core used was 1/4-inch cell size, 0.004-inch 5052 aluminum foil, non-perforated, 1/2-inch thick. The faces were 0.063-inch-thick, bare 2024-T3 aluminum. The splice was cured prior to bonding of the face sheets. The plan dimensions of the sandwich were 3 x 8 inches with the ribbon direction of the core parallel to the 8-inch dimension. The purpose of this test was to determine if the core splice adhesive had a strength equal to the shear strength of unspliced core over the temperature range.

FLATWISE TENSION

Flatwise tension tests were performed in accordance with MIL-STD-401. A core splice was placed in the center of the 2- by 2-inch specimen and cured

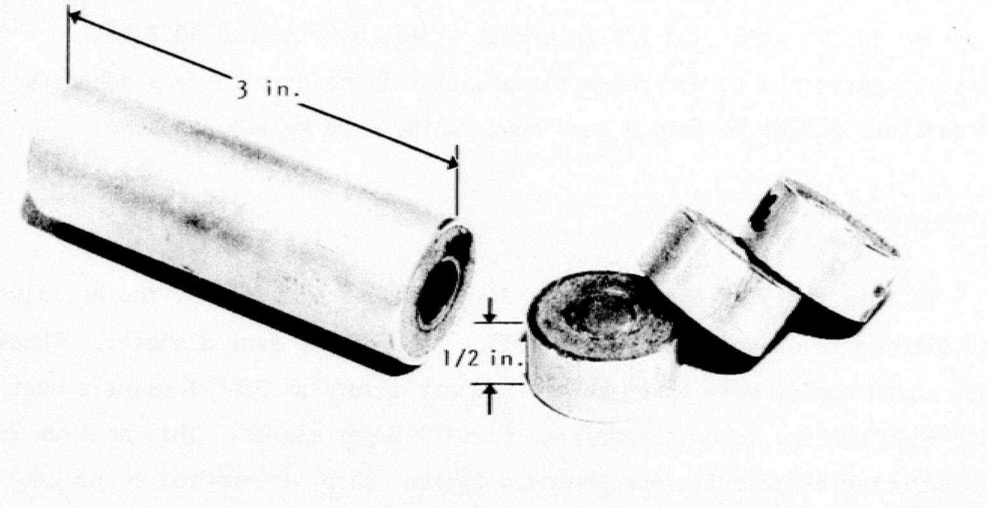


Figure 1. Tube shear specimens.

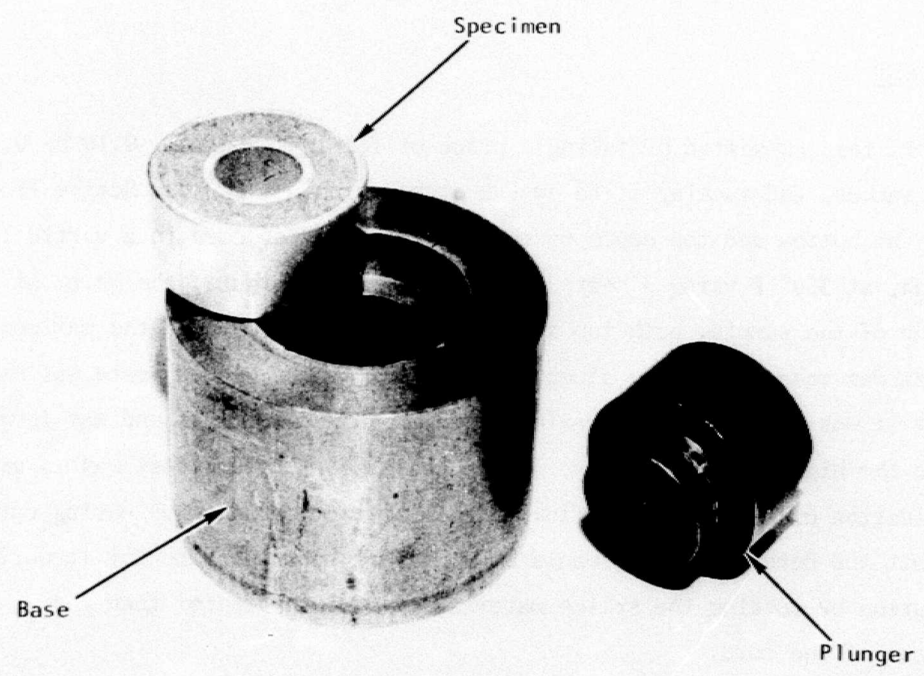


Figure 2. Tube shear test apparatus.

prior to bonding the face sheets. The core used in making the specimens was 1/2-inch thick, 3/16- and 1/4-inch cell sizes, 0.0015-inch 5052 foil. This test was performed to determine the ability of the core-to-face adhesive (Plastilock PL729) to form a good bond to the core splice adhesive.

EXPANSION RATIO

In this test, an approximately 2-inch-diameter circle of the adhesive was allowed to expand freely in a Teflon tube of the same diameter. Thickness measurements were taken before and after cure at 350° F using a heat-up rate from ambient to cure temperature of 2° F per minute. This heat-up rate was selected because it represented a typical shop minimum value and gave the most conservative results. The objective of this test was to obtain an indication of the size gap which the foaming adhesive could be expected to fill in actual applications.

SLUMP TEST

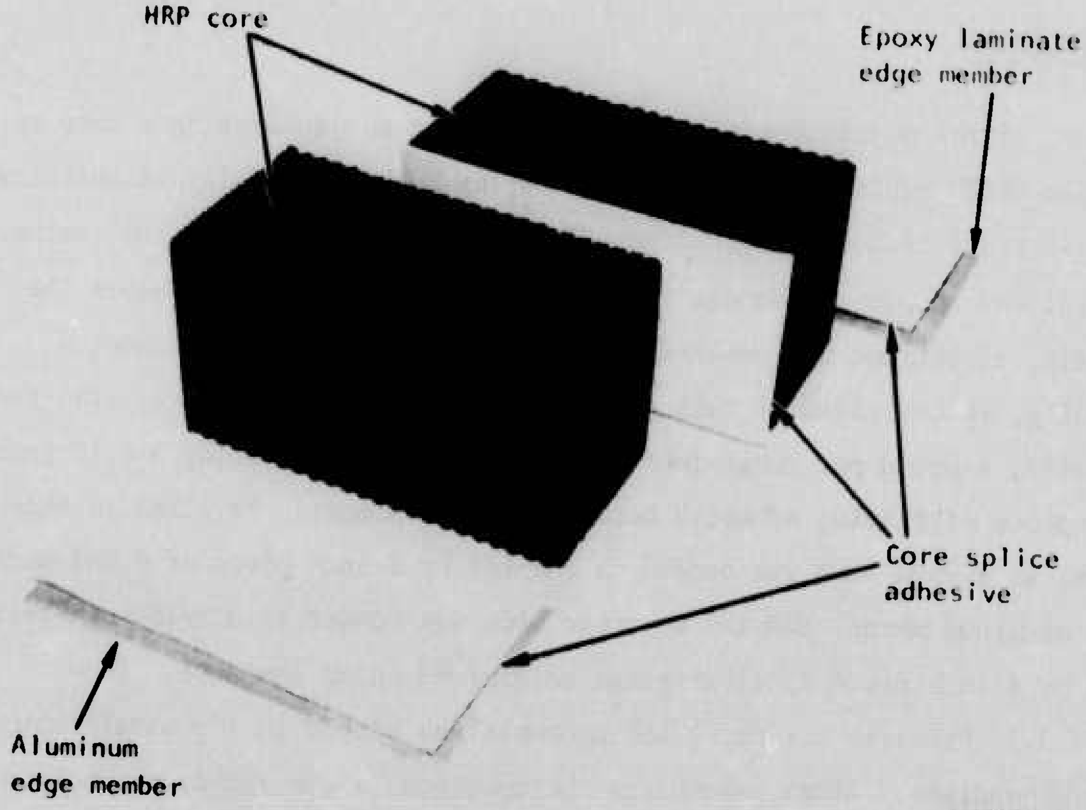
This test consisted of taking a piece of foaming material, 0.10 by 0.5 by 1.5 inches, and tacking it to an FPL etched aluminum sheet. Scribe lines marked the bottom and top edges of the specimen. After cure in a vertical position, at 350° F using a heat-up rate of 6° F per minute, the vertical movement of the sample, both top and bottom, was measured, and the maximum movement was recorded as the slump. A 6° F per minute heat-up rate was used because it was considered the maximum used in shop conditions and was found to give the highest slump values. The purpose of the slump test was to give an indication of the amount of flow of the core splice adhesive during cure of a part and determine if it would be necessary to compensate for it during fabrication by cutting the splice material to a width greater than the thickness of the core.

PEAK EXOTHERM

One of the major objectives of this program was to develop a core splice adhesive which had a low peak exotherm during cure, especially in splicing thick sections of nonmetallic core. The reason for desiring a low exotherm material was to prevent damage to the adhesive and core. To measure the exotherm, a specimen was devised to simulate a thick HRP core sandwich. Basically, it consisted of taking two pieces of 4 by 4 by 8 inch, 3/16-inch cell size, 4-pound-per-cubic-foot-density HRP core and placing a 0.10-inch-thick piece of foaming adhesive between the two pieces. Parallel to this splice, an 8-inch side was bonded to a 4-1/4 by 8-inch piece of 0.063-inch-thick aluminum sheet, and the opposite side was bonded to a 1/16-inch-thick, 4-1/4 by 8-inch piece of fiber glass reinforced epoxy laminate. (See Figure 3.) Prior to curing, a thermocouple was placed in the areal center of each bondline. After assembling the specimen as described, a simulated 1/8-inch aluminum face sheet coated with parting agent was placed on top and bottom of the sandwich. The assembly was wrapped peripherally with aluminum pressure-sensitive tape to prevent lateral movement of the core during cure. Specimens were cured in an autoclave at 350° F using a heat-up rate of 6° F per minute of the heating medium. The cure temperature was maintained at 350° (±10°) F until the peak temperature was observed in each bondline and began to drop off. Because of the insulating characteristics of the core, the temperature in the core splice area lagged other temperatures, but when the exothermic reaction took over, this was always the highest temperature. Figure 4 shows a sectioned specimen of a high exotherm specimen. The charred area is obvious in the adhesive.

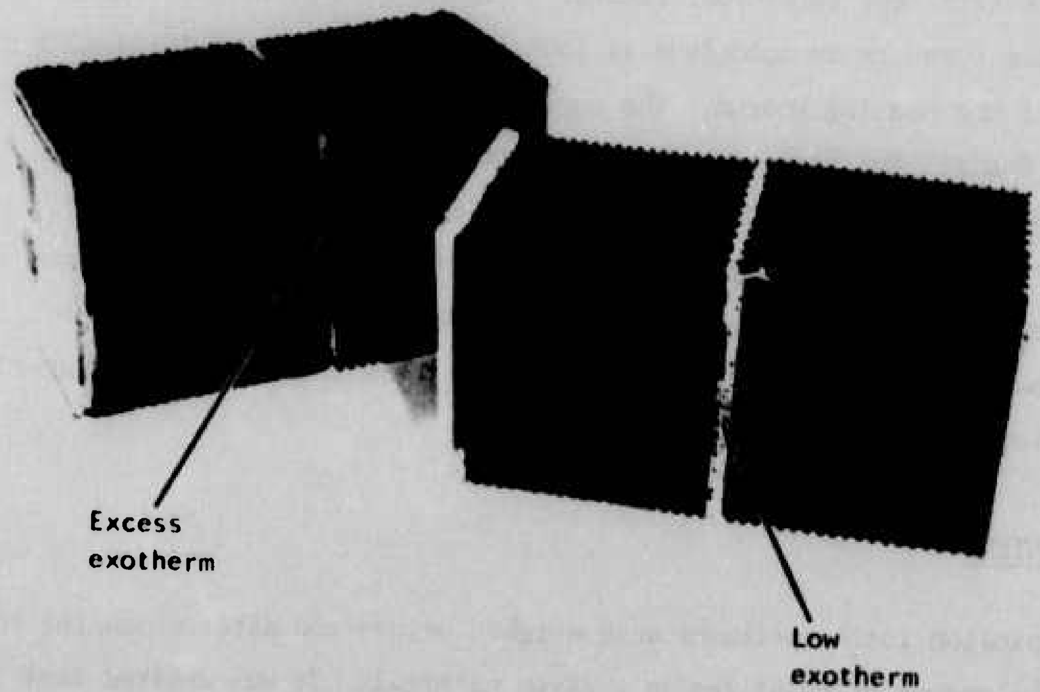
VOLATILE CONTENT

The expansion ratio specimens were weighed before and after expansion to determine the amount of volatiles in a given material. It was desired that



11166 95 1D

Figure 3. Peak exotherm specimen.



11166 95 1B

Figure 4. Peak exotherm specimens after test.

the volatile content be kept as low as possible to avoid any possible problem of volatile entrapment in a part during cure.

GEL TEMPERATURE

This test consisted of taking 2 by 2 by 0.10-inch-thick pieces of the adhesive and heating them up at the extreme rates of 2° and 6° F per minute. During heat-up, the specimens were probed periodically after foaming took place until no stringing occurred but the mass was still rubbery. This temperature was recorded as the gel temperature. The basic purpose of this test was to determine the effect of heat-up rate on gel temperature and to insure that gelation took place at a higher temperature than foaming. If it were, in fact, lower than the foaming temperature, then foaming could not occur at all and if it were too much higher than the point at which foaming took place, the foam could become unstable and collapse.

CELL STRUCTURE

Expansion ratio specimens and selected peak exotherm specimens were sectioned and the cell structure examined visually for foam quality and uniformity. Any tendency to produce voids or open cells was considered undesirable from the strength and durability standpoint.

DENSITY

Using the uncured weight of the expansion ratio specimens, the weight per square foot of 0.10-inch-thick material was determined. This value is of interest in calculating the weight of a part in which the core splice adhesive is used.

HANDLING CHARACTERISTICS

Handling characteristics were assessed by determining the ability of 0.10-inch-thick film to conform to a 1/8-inch-radius mandrel and exhibit sufficient tack to adhere to a properly cleaned and primed aluminum surface. In both of these cases, the film was heated, if required, to a temperature not exceeding 120° F to perform the tests. The reason for these tests was to determine the ability of the material to conform to radiused hard points in an assembly without cracking and to adhere to such members when pressed in place.

WORK LIFE

This test consisted of exposing adhesive specimens to ambient aging at 90° F for 4, 7, and 10 days. After these exposures, slump and expansion tests were performed. The basic reason for this test was to determine whether the material retained satisfactory characteristics if, after being placed in an assembly, a delay occurred between layup and the start of cure.

CORE SIZE VARIATIONS

Core splices were made using 1/8-, 3/16-, and 1/4-inch cell size aluminum cores, 1-inch thick, with controlled gaps equal to and twice the thickness of the films tested. The 0.10- and 0.05-inch-thick films were checked with all cores, and 0.025-inch-thick material was also used with 1/8-inch cell size core. The gaps were controlled by using appropriate thickness shims, 1/4-inch wide, coated with a parting agent so they could be easily removed after cure. Prior to curing, the assembly was wrapped around its periphery with pressure-sensitive tape to prevent lateral movement during cure. Subsequent to cure, the shims were removed and the splice was examined visually for uniformity of expansion, closed cell structure, and interlocking of the core. These tests were performed to determine the ability of the core splice adhesive to expand and interlock pieces of core of different cell sizes and with different gaps. Since this test consisted of a visual examination, qualitative terms were used to describe the results.

EDGE ATTACHMENT ADHESION

This series of tests was basically the same as the tube shear tests described previously except the inner adherend was varied to include 6Al-4V titanium alloy tubing, type 321 corrosion-resistant steel tubing, epoxy fiberglass tubing, and phenolic fiberglass laminate rods. The outer tube, in all cases, was 6061-T6 aluminum alloy. The purpose of this test was to determine adhesion of the foaming adhesive to various materials which might be used in edge attachments or inserts, and have results which could be compared to those obtained with aluminum over the expected service temperature range of -65° to 350° F.

STORAGE LIFE

This test consisted of storing the material at 0° F for 3 and 6 months, then exposing it to 90° F for 7 days, and determining the expansion ratio and slump after these exposures. The reason for including this test was to determine the stability of the material and obtain an indication of its useful life after prolonged sub-zero storage.

COLD FLOW

The cold flow test was used to measure the amount of slump that the uncured adhesive would exhibit when placed in an assembly and allowed to stand in a vertical position at 90° F for 7 days. The test consisted of pressing a 2- by 4-inch piece of 0.10-inch-thick adhesive to a cleaned piece of 4 by 6 by 0.063-inch-thick aluminum. The 2-inch dimension of the adhesive was placed even with a scribe line located 1-1/2 inches from the bottom of the aluminum sheet and parallel to the 6-inch dimension. The amount of adhesive flow was measured after 4 and 7 days at 90° F, and the 7-day measurement was recorded as cold flow.

Section IV

ADHESIVE FORMULATION AND SCREENING - PHASE II

Primary formulation studies were started at Hysol immediately after the basic requirements for the core splice adhesive were established. This effort continued for over 8 months with approximately 90 formulations being compounded. Initial efforts consisted of establishing the proper resin blend and ratios of thixotroping agents and blowing agents to produce the desired slump and expansion ratio characteristics. Subsequent to this, modifications were to improve the cell structure by increasing the toughness and elasticity of the resin. In the course of these studies, various blowing agents were studied, and it was determined that there was no advantage in changing from the original choice. Nucleating and foam stabilizing agents were subsequently investigated and although they offered some improvement in cell structure, this path was not actively followed in later work. Throughout the formulation effort at Hysol, continuing effort was expended in examining various curing agent/catalyst systems to lower the peak exotherm, improve stability at ambient conditions, and enhance mechanical properties.

As Hysol went through these formulation studies, they performed various preliminary tests and submitted the 16 most promising candidates to Rockwell for screening. The screening tests performed by Rockwell were expansion ratio, slump, peak exotherm, volatile content, and uncured weight per square foot for nominal 0.10-inch-thick film. Results are given in Table 1. As the screening tests were performed, the data were fed back to Hysol for use in their formulation efforts.

TABLE 1. SCREENING TEST RESULTS

Formulation No.	Thickness (in.)	Expansion ratio	Slump (in.)	Peak exotherm (°F)	Volatile content (%)	Uncured weight (lb/ft^2/ 0.100 in.)
Target	0.100 nom	2.5:1	0.50 max	450 max	1.0 max	0.62 max
073-145	0.104	2.60:1	0.35	402[a] 430[b] 605[c] 550[c]	0.32	0.61
0.73-158-1	0.114	2.52:1	0.50	425[a] 435[b] 650[c]	0.24	0.58
073-158-2	0.104	2.65:1	0.32	400[a] 380[b] 550[c]	0.45	0.57
073-158-8	0.106	2.47:1	0.17	415[a] 402[b] 565[c]	0.22	0.57
073-158-10	0.101	2.31:1	0.52, 0.35	410[a] 425[b] 575[c]	0.42	0.54
073-189-1	0.108	2.70:1	0.39	425[a] 420[b] 555[c]	0.22	0.55
073-189-2	0.106	2.20:1	0.16	385[a] 370[b] 400[c] 417[c]	0.20	0.54
073-189-3	0.124	2.05:1	0.10	370[a] 375[b] 380[c] 405[c]	0.39	0.51

(continued on next page)

TABLE 1. SCREENING TEST RESULTS (CONCL)

Formulation No.	Thickness (in.)	Expansion ratio	Slump (in.)	Peak exo-therm (°F)	Volatile content (%)	Uncured weight (lb/ft²/ 0.100 in.)
073-190-1	0.117	2.00:1	0.22	476[a] 430[b] 700[c]	0.03	0.62
073-190-2	0.101	2.55:1	0.12	370[a] 375[b] 430[c] 450[c]	0.44	0.58
073-190-3	0.116	2.00:1	0.40	400[a] 435[b] 580[c]	0.25	0.59
099-21	0.110	2.24:1	0.38	420[a] 426[b] 600[c] 560[c]	0.80	0.56
ADX 814 (099-22)	0.100	2.50:1	0.17	370[a] 371[b] 450[c]	0.70	0.55
ADX 814.1 (099-23)	0.105	2.74:1	0.22	425[a] 400[b] 450[c]	0.70	0.60
ADX 815 (099-36-1)	0.114	2.47:1	0.22	440,430[a] 425,420[b] 395,450[c]	0.00	0.56
099-36-2	0.110	2.10:1	0.15	390[a] 400[b] 510[c]	0.67	0.51

NOTES:

[a]Core-to-aluminum splice
[b]Core-to-epoxy fiber glass laminate splice
[c]Core-to-core splice

Details of procedures can be found in Appendix B.

In considering the data of Table 1, the primary variables associated with the different formulations are as follows:

- 073-145 — Original formulation establishing resin blend, thixotroping agent ratio and blowing agent ratio
- 073-158-X — Variations in resin blend, thixotroping agent ratio, and hardener ratio
- 073-189-X, 073-190-X — Variations in hardener/catalyst systems
- 099-21, -22, -23 — Use of new base resin and variation in hardeners/catalysts
- 099-36-1, -2 — Use of new base resin, variation in ratio of other resin components, and effect of different hardeners

During the formulation phase, a change in the base resin system was necessary. This was required because of the possibility of not being able to obtain one of the ingredients. Although the supplier committed himself to manufacturing this ingredient through 1975, the uncertainty of long-term availability resulted in the removal of this material from all further formulation. A replacement was found which met all program requirements and which is used in sizable quantities for other products by Hysol and other formulators. The manufacturer of this material has made assurances that it will be continuously available because of its widespread use.

Since reducing peak exotherm was one of the prime objectives of the program, Hysol examined various methods for determining this value rapidly and inexpensively rather than using the honeycomb core test used for screening purposes. Early attempts using a differential screening calorimeter showed no correlation between the values obtained with this instrument and those observed using the honeycomb core procedure. Subsequently, a test was devised in which approximately 7.5 grams of the adhesive (2 plies of 0.100-inch-thick film) are placed in the bottom of a 1.5-inch-diameter by 1-inch-deep tin soil can (nominal 1 ounce). (See Figure 5.) A thermocouple is positioned so that it will be approximately in the middle of the expanded mass. The can is then placed in a preheated 350° F oven which results in about a 45° F per minute temperature rise. The maximum temperature is observed and the sample cured for about 15 minutes. After cooling, the sample is cut through the center for observation of foam quality and possible charring. This test showed fair correlation with the honeycomb block procedure used by Rockwell. Balancing of sample size and insulation around the can to control heat-up rate could provide more accurate correlation of the soil-can method with the honeycomb core block procedure. The latter, however, should be considered as more applicable for qualification testing, whereas a refined soil-can procedure might be valuable for rapid checks for gross screening or quality control purposes.

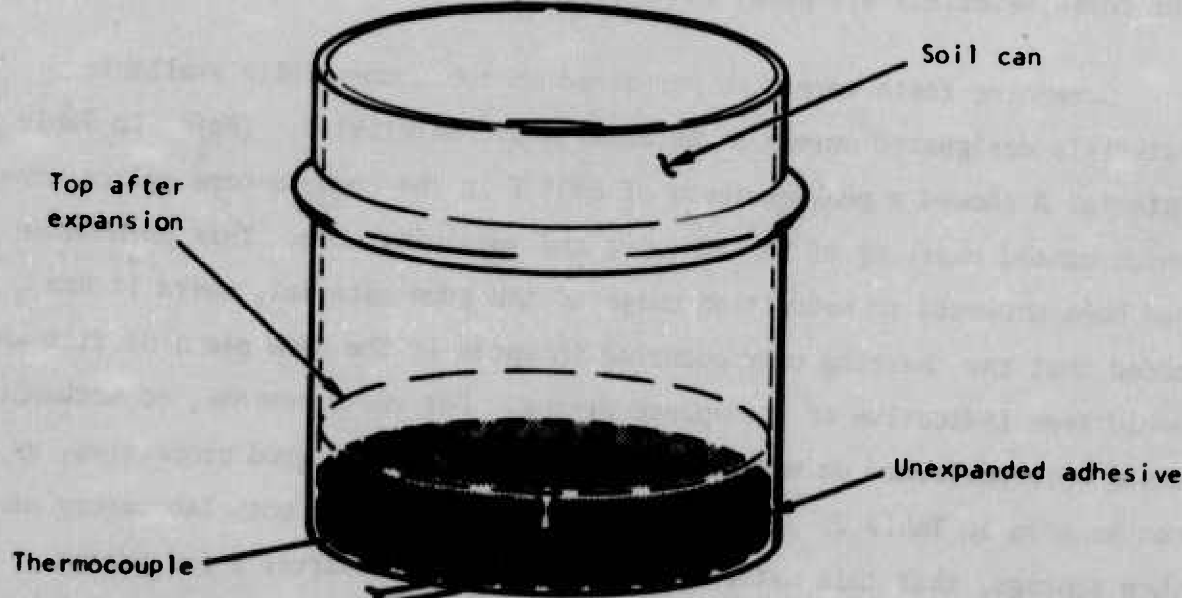


Figure 5. Soil can exotherm test apparatus.

In examining the screening test results of Table 1, it can be seen that 10 of the 16 formulations failed to meet the peak exotherm target value, 450° F maximum, and hence were not evaluated further. The 073-189-2 and -3 formulations had satisfactory exotherm properties but lower-than-desired expansion ratios. The main reason, however, for excluding them from further consideration was their poor room temperature stability in that they would crack on handling after 2 to 7 days exposure to ambient laboratory temperatures. The 073-190-2 formulation looked promising in the screening tests, but it was not considered for inclusion in phase III testing because the catalyst system used was known to yield erratic adhesion to aluminum. Attempts were made to overcome this deficiency by minimizing the catalyst concentration, but they were unsuccessful. This left three materials which were determined to be satisfactory for the adhesive characterization phase. All of these materials used the replacement base resin system discussed previously. Since they were to be characterized in phase III, they were given experimental designations: ADX 814 (099-22), ADX 814.1 (099-23), and ADX 815 (099-36-1). Preliminary data sheets for these materials are given in Appendix D.

Screening tests were also performed on two commercially available materials designated herein as material A and material B. (Refer to Table 2.) Material A showed a peak exotherm of 640° F in the core-to-core splice area which caused charring of the adhesive and adjoining core. This phenomenon had been observed in production usage of the same material, where it was noted that the charring only occurred in spots in the same piece of film which would seem indicative of incomplete mixing. For these reasons, no mechanical tests were performed on material A. Material B showed good properties, as can be seen in Table 2. It has been noted, however, in both laboratory and shop storage, that this material tends to crack even after a few months storage at 0° F. Its poor stability and handling characteristics are major deficiencies.

TABLE 2. TEST DATA ON TWO COMMERCIAL MATERIALS

Property	Unit	Material A	Material B
Thickness	in.	0.111	0.118
Expansion ratio	-	2.20:1	2:46:1
Slump	in.	0.06	0.13
Peak exotherm	° F	510[a] 545[b] 640[c]	312[a] 317[b] 355[c]
Volatile content	%	0.60	0.34
Uncured weight	$lb/ft^2/0.100$ in.	0.68	0.52
Core shear strength	psi	d	
Control			
-65° F			861
RT			836
350° F			306
Splice			
-65° F			821
RT			753
350° F			307
Tube shear strength	psi	d	
RT			852
250° F			451
300° F			103
350° F			60

NOTES:

[a]Core-to-aluminum splice
[b]Core-topepoxy fiber glass laminate splice
[c]Core-to-core splice
[d]Not tested because of high peak exotherm

Details of procedures can be found in Appendix B.

Section V

ADHESIVE CHARACTERIZATION - PHASE III

As a result of the screening tests performed in phase II of the program, three materials were selected for full characterization. These formulations have been assigned experimental product numbers by Hysol. They are ADX 814, ADX 814.1, and ADX 815. Preliminary data sheets for these materials are given in Appendix D.

In this phase, those tests not included in the screening were performed. They included tube shear, core shear, honeycomb flatwise tension, gel temperature, cell structure, handling characteristics, work life, core size variations, edge attachment adhesion, storage life, and cold flow.

Tube shear results are given in Table 3. The specimens for this test consist of two concentric aluminum tubes bonded together with the foaming adhesive. The outside diameter of the inner tube was 0.500 inch and the inside diameter of the outer tube was 0.900 inch, leaving an annular space of 0.200 inch to allow for the expansion of the 0.100-inch adhesive film. In testing, load was applied to the inner tube while the outer tube was supported in a fixture. (See Figures 1 and 2.) This induced a shear stress in the adhesive. In calculating the shear stress, the mean annular diameter of 0.700 inch was multiplied by the actual height of the specimen (nominally 0.5 inch) to determine the area. None of the materials met the preliminary 350° F target value of 550 psi, but ADX 814 and ADX 814.1 met the amended target. All three met -65° F and room temperature (RT) targets. This particular test is considered of secondary importance in that the materials were primarily formulated to provide good values for core splicing. It was included because it is a relatively fast and inexpensive test which offered the possibility of providing an acceptance procedure for receiving inspection if sufficient correlation can be established between it and core shear tests.

TABLE 3. ALUMINUM-TO-ALUMINUM TUBE SHEAR RESULTS

Test temperature	Target	Tube shear strength (psi) ADX 814	ADX 814.1	ADX 815
-65° F	Orig 750	1,766	1,452	1,100
		1,615	1,679	1,413
		2,080	1,773	1,579
	Rev 1,200	1,582	1,421	1,024
		1,875	1,437	1,447
	Avg	1,784	1,552	1,313
RT	Orig 750	1,132	996	1,120
		1,014	1,061	1,240
		1,043	1,136	1,237
	Rev 950	1,032	927	1,081
		1,144	1,110	1,021
	Avg	1,173	1,046	1,140
300° F	None	198	342	211
		252	348	219
		266	375	258
		231	307	242
		236	317	321
	Avg	237	338	250
350° F	Orig 550	150	129	54
		159	146	61
		147	137	84
	Rev 125	161	130	79
		172	140	89
	Avg	158	136	73

NOTES:

6061-T6 aluminum alloy tubing used for thest tests.

Details of procedure can be found in Appendix B.

In analyzing the core shear results of Table 4, it is obvious that the preliminary target values were set too high. They should have been at a value equivalent to the expected shear strength of the honeycomb core used in fabrication of the specimens. For example, at ambient temperature, using MIL-C-7438 requirements, the value should have been set at approximately 690 psi for the 7.9-1/4-40-5052 core used, making correction for flexural shear versus plate shear. this correction was based on data in Hexcel TSB 120. In testing ADX 814, core splice strengths were close to revised target values at RT and -65° F. Strength at 350° F was approximately 10 percent lower than the revised target. Tests showed ADX 814.1 to be well above target and slightly stronger than controls at -65° F and RT. The first series of tests at 350° F were 20 percent below the revised target values. ADX 815 was 15 percent below target at -65° F, but well above target at RT and 350° F.

In most cases where core shear was not obtained, little if any adhesion was noted between the core splice adhesive which had been precured, and the core-to-face adhesive. In such cases, a crack was observed in the core splice adhesive while the specimen was under load. Since the splice was in the area of maximum shear stress, the crack was probably caused by failure of the foaming adhesive to transmit load from one core segment to the other. This had been verified with ADX 814.1. When the precured core splice adhesive was sanded prior to bonding of the face sheets, strengths were obtained which were high enough to shear the core at both RT and 350° F. (Refer to Table 4.)

Honeycomb flatwise tension results are given in Tables 5, 6, and 7 for -65° F, RT, and 350° F, respectively. Specimens were made with both 3/16- and 1/4-inch cell size core, 0.0015-inch foil, 5052 alloy, 1/2-inch thick. The core splice adhesive was placed in the center of the specimen and cured prior to bonding the face sheets to the core. No attempt was made to prepare the surfaces of the cured core splice adhesives by scuff sanding or other means; thus, these tests were simulating the worst possible condition for obtaining a good bond between the splice adhesive and the core-to-face adhesive.

TABLE 4. HONEYCOMB CORE SHEAR RESULTS

Test temperature	Core shear strength (psi)				
	Target	Control (no splice)	ADX 814	ADX 814.1	ADX 815
-65° F	Orig 1,100 Rev 690	691 758 722	679 687 681	761 746 770	577 610 577
Avg		724	682	759	588
RT	Orig 1,100 Rev 690	685 767 708	696 681 710	761 728 743	710 722 -
Avg		720	696	744	716
350° F	Orig 800 Rev 290	337 332 323	240 255 296	216 246 232	323 318 348
Avg		331	264	231	330
RT Sanded	Orig 1,100 Rev 690	Not applicable	Not tested	914 915 873	Not tested
Avg				901	
350° F Sanded	Orig 800 Rev 290	Not applicable	Not tested	320 293 297	Not tested
Avg				303	

NOTES:

Core: 7.9-1/4-40-5052, 0.625-inch thick.
Face sheet: 2024-T3 bare, 0.063-inch thick.
Core-to-face adhesive: B. F. Goodrich Plastilock PL 729-3, 0.10 lb/sq ft.

Details of procedure may be found in Appendix B.

TABLE 5. HONEYCOMB FLATWISE TENSION RESULTS AT -65° F

Core splice adhesive	Target stress (psi)	Core	Failing stress (psi)	Failure mode	Core	Failing stress (psi)	Failure mode
None, Control	800	4.4-3/16-15-5052	975 988 978	100% cohesive	3.4-1/4-15-5052	923 945 925	100% cohesive
Avg			980	↓		931	↓
ADX 814	↓	↓	975 950 725	100% cohesive core to face, 100% adhesive at splice	↓	663 763 830	100% cohesive core to face, 100% adhesive at splice
Avg			850			752	
ADX 814.1	↓	↓	925 883 730	100% cohesive core to face, 100% adhesive at splice	↓	918 880 788	100% cohesive core to face, 100% adhesive at splice
Avg			846			862	
ADX 815	↓	↓	950 825 820	100% cohesive core to face, 50-100% cohesive at splice	↓	845 818 970	100% cohesive core to face, 50-100% cohesive at splice
Avg			865			878	

NOTES:

Face sheet: 2024-T3 bare, 0.020-inch thick.
Core-to-face adhesives: B. F. Goodrich Plastilock PL729-3.

Details of procedure can be found in Appendix B.

TABLE 6. HONEYCOMB FLATWISE TENSION RESULTS AT RT

Core splice adhesive	Target Stress (psi)	Core	Failing stress (psig)	Failure mode	Core	Failing stress (psi)	Failure mode
None, control	Original 1,000, revised 800 ↓	4.4-3/16-15-5052 ↓	988 975 935	Core ↓	3.4-1/4-15-5052 ↓	955 950 935	Core ↓
Avg			966			947	
ADX 814			863 850 845	50% core, 50% cohesive ↓		975 955 890	100% cohesive core to face, 100% adhesive at splice
Avg			853			940	
ADX 814.1			833 945 858	50% core, 50% cohesive 100% core 50% core, 50% cohesive		938 880 930	100% cohesive core to face, 100% adhesive at splice
Avg			879			916	
ADX 815			863 923 758	20% core, 80% cohesive 50% core, 50% cohesive 50% core, 50% cohesive		930 895 928	100% cohesive core to face, 100% adhesive at splice
Avg			848			918	
ADX 814.1 splice sanded			1,300 1,305 1,263	100% cohesive core to face, 100% cohesive at splice.	Not tested		
Avg			1,289				

NOTES: Face sheet: 2024-T3 bare, 0.020-inch thick. Core-to-face adhesive: B.F. Goodrich Plastilock PL729-3.
Details of procedure can be found in Appendix B

TABLE 7. HONEYCOMB FLATWISE TENSION RESULTS AT 350° F

Core splice adhesive	Target stress (psi)	Core	Failure stress (psi)	Failure mode	Core	Failure stress (psi)	Failure mode
None, control	550	3/16-5052-0.001SN	788	Core	1/4-5052-0.001SN	644	50% core, 50% cohesive
			780			793	20% core, 80% cohesive
			794			681	40% core, 60% cohesive
Avg			787			706	
ADX 814			580	90% core, 90-100% adhesive at splice		625	10% core, 100% adhesive at splice
			743			780	50% core, 50% cohesive at splice
			581			650	10% core, 10% cohesive at splice
Avg			635			685	
ADX 814.1			627	100% core, 100% adhesive splice		543	10% core, 90% adhesive splice
			640	100% core, 90% adhesive splice		510	20% core, 80% cohesive splice
			627	100% core, 100% cohesive splice		531	50% core, 50% cohesive splice
Avg			631			528	
ADX 815			575	80% core, 100% cohesive at splice		620	80-100% core, 100% cohesive at splice
			563			565	
			-			628	
Avg			569			604	

NOTES: Face sheet: 2024-T3 bare, 0.020-inch thick. Core-to-face adhesive: B.F. Goodrich Plastilock PL729-3

Details of procedure can be found in Appendix B.

In all cases, the reduction in strength of specimens containing the splice as compared to the core having no splice was in the order of magnitude of the area of the splice. This can be seen in the failure mode in which there was generally lack of adhesion between the core-to-face adhesive and the core splice adhesive. The cured ADX 815 core splice adhesive showed the best ability to adhere to the core-to-face adhesive with several partial cohesive failures noted. The ADX 814 specimens with 1/4-inch cell size core were the only ones failing to meet the target value of 800 psi at -65° F, whereas all of the materials met the revised RT target value of 800 psi. All 350° F values exceeded the target value of 550 psi. All of these values could undoubtedly be improved if the test procedure were modified such that the cured splice area was sanded prior to bonding the face sheets to the core. Evidence of this was apparent when the RT flatwise tension tests were repeated with ADX 814.1 adhesive using the 3/16-5052-0.0015N core and the values were increased in excess of 45 percent over the unsanded specimens 30 percent over the controls. In examining the failure mode, the failure in the splice area was 100-percent cohesive. The splice area essentially increased the total core-to-face bond area, thus accounting for the values being even higher than the controls.

Table 8 gives the work life characteristics of the three materials. Essentially, this testing consisted of exposing slump and expansion ratio specimens to a constant temperature of 90° F and then testing at 4, 7, and 10 days. Included as a matter of information is the uncured thickness at each of the test times which gives an indication of any reaction which may be occurring at the exposure temperature. In all cases, the expansion ratio was calculated on the basis of the initial thickness of the material prior to exposure. The heat-up rate used for the expansion ratio was approximately 2° F per minute, whereas that for the slump test was about 5° to 6° F per minute. These heat-up rates were used because initial testing showed them to represent the worst condition for these particular tests. ADX 814 and ADX 814.1 maintained tackiness up through the 10-day exposure period. The ADX 815 material lost its tack within the initial 4 days, and it was necessary

TABLE 8. WORK LIFE CHARACTERISTICS

Core splice adhesive	Exposure time (days at 90° F)											
	0			4			7			10		
	T_o (in.)	Expansion ratio	Slump (in.)	T_4 (in.)	Expansion ratio	Slump (in.)	T_7 (in.)	Expansion ratio	Slump (in.)	T_{10} (in.)	Expansion ratio	Slump (in.)
ADX 814	0.119	2.80	0.17	0.156	2.06	0.09	0.165	1.67	0.03	0.165	1.55	0.08
				0.157	2.06	0.05	0.169	1.64	0.03	0.162	1.62	0.07
				0.160	2.10	0.06	0.170	1.62	0.03	0.165	1.59	0.11
Avg				0.158	2.07	0.07	0.168	1.64	0.03	0.164	1.59	0.09
ADX 814.1	0.110	2.74	0.22	0.140	2.58	0.08	0.153	2.43	0.10	0.145	2.28	0.08
				0.138	2.61	0.06	0.148	2.40	0.08	0.148	2.22	0.09
				0.140	2.52	0.10	0.150	2.42	0.09	0.147	2.20	0.06
Avg				0.139	2.57	0.08	0.150	2.42	0.09	0.147	2.23	0.08
ADX 815	0.104	2.76	0.25	0.147	1.91	0.13	0.145	1.70	0.07	0.146	1.57	0.05
	0.100	2.75		0.151	1.79	0.12	0.148	1.72	0.11	0.152	1.58	0.06
	0.110	2.64		0.148	1.91	0.09	0.150	1.73	0.09	0.153	1.55	0.06
Avg	0.105	2.72		0.149	1.87	0.11	0.148	1.72	0.09	0.150	1.57	0.06

NOTES:

T_o = Initial uncured thickness
T_4 = Uncured thickness after 4 days exposure
T_7 = Uncured thickness after 7 days exposure
T_{10} = Uncured thickness after 10 days exposure

$$\text{Expansion ratio} = \frac{\text{Cured thickness after exposure}}{T_o}$$

Details of procedure can be found in Appendix B.

to use heat to generate sufficient tack to have it adhere to a plate in determining its slump. ADX 814 and ADX 814.1 exhibited very high tack and were therefore, somewhat difficult to handle. The formulations are such, however, that the tack can be controlled, to a somewhat lower level without suffering loss of other properties.

Edge attachment adhesion tests were run to check the adhesion of the three materials to epoxy fiber glass, phenolic fiber glass, titanium, and corrosion-resistant steel (CRES). These tests were essentially tube shear tests in which the inner tube was one of the aforementioned materials while the outer tube was aluminum. Annular dimensions were the same as those using both tubes of aluminum. Results are given in Table 9. The epoxy tubing was a standard glass fabric laminated material. The phenolic material could not be obtained in either tube or rod form as a glass phenolic molding material. Therefore, sections of a phenolic fiber glass laminate were machined into 1/2-inch-diameter rods for use in testing. Both of these glass reinforced materials were scuff sanded and solvent degreased with methyl ethyl ketone. The solvent was removed from the parts by air drying a minimum of 8 hours prior to bonding. The titanium tubing was 6Al-4V alloy, prepared for bonding using Turco 5578. The type 321 corrosion-resistant steel tubing used for this series of tests was cleaned in Turco Vitro-Kleen for 10 minutes at 160° F and then passivated in a 50-percent nitric acid solution at RT for 10 minutes.

In the case of the epoxy adherend tests, the values for all materials exceeded the target values at -65° F and room temperature, showing good adhesion. The phenolic adherend results were lower than anticipated for ADX 814 and ADX 814.1 at -65° F, with ADX 814 showing an abnormally high scatter and ADX 814.1 failing to meet the target value of 750 psi. The most apparent reason for this scatter with the ADX 814 and for the low values obtained with the ADX 814.1 was that the failures occurred at the inner adherend/adhesive interface rather than in the foamed adhesive. If this diameter of 0.5 inch had been used calculating the area rather than the mean annular diameter of

TABLE 9. EDGE ATTACHMENT ADHESION TEST RESULTS

Core splice adhesive	Tube shear strength (psi)														
	Target			Inner adherend material[a]											
				Epoxy fiber glass			Phenolic fiber glass			Titanium (6-4)			CRES (321)		
	-65° F	RT	350° F	-65° F	RT	350° F	-65° F	RT	350° F	-65° F	RT	350° F	-65° F	RT	350° F
ADX 814	Orig 750	Orig 750	Orig 550	1,469	796	99	1,088	1,396	62	920	955	35	1,189	554	46
				747	763	60	549	1,487	41	1,244	697	63	753	499	42
	Rev 900	Rev 650	Rev 50	1,547	1,079	100	1,027	1,339	63	708	892	47	784	672	49
				817	840	58	647	1,328	66	1,175	426	35	963	498	46
				1,307	1,034	80	1,110	1,320	73	1,100	578	47	970	450	47
Avg				1,177	902	79	884	1,374	61	1,029	710	45	932	535	46
ADX 814.1	Orig 750	Orig 750	Orig 550	1,347	926	73	558	1,091	43	1,248	567	48	807	793	49
				1,281	1,013	84	557	975	37	1,318	452	73	1,156	685	76
	Rev 900	Rev 650	Rev 50	1,324	997	89	474	1,098	39	1,462	490	43	969	536	65
				1,332	1,034	87	721	1,013	43	609	656	76	777	609	50
				1,303	1,139	100	481	1,006	23	1,230	464	71	926	1,041	57
Avg				1,317	1,022	87	558	1,037	37	1,173	526	62	927	733	59
ADX 815	Orig 750	Orig 750	Orig 550	1,650	1,262	61	1,238	951	63	1,105	979	62	973	540	47
				1,718	1,226	88	1,097	800	66	1,132	680	61	986	580	50
	Rev 900	Rev 650	Rev 50	1,708	1,074	95	1,152	739	64	1,295	879	67	880	732	60
				1,377	1,040	84	1,352	973	66	1,078	883	64	1,069	767	37
				1,436	1,196	74	912	852	-	1,223	715	69	885	669	56
Avg				1,578	1,160	80	1,150	803	65	1,167	827	65	959	658	50

NOTES:

[a]Outer tube 6061-T6 aluminum alloy

Details of procedure can be found in Appendix B.

0.7 inch, the failing stress would have been increased in the ratio of 7 to 5, or 40-percent higher. To give values comparable to those in Table 2, however, all calculations were made on the same basis. In general, better adhesion was obtained to titanium than corrosion-resistant steel with all materials at -65° F and RT.

Approximately 3-inch lengths of tubing were bonded from which 1/2-inch-long specimens were cut. (See Figure 1.) It was very difficult to cut these specimens without overheating them because of the toughness of the titanium and steel. Local overheating may have occurred in some cases and weakened the foamed adhesives thus resulting in some of the low values. It should be noted that, regardless of the adherend, all values were quite low at 350° F. This same phenomenon was observed with aluminum adherends.

Various properties including gel temperature, handling characteristics, core size variations, and cold flow are given in Table 10. Except for gel temperature and cold flow, descriptive terms have been used to give relative evaluation of the three selected adhesives. In the case of cell structure, all materials had closed cells, and the terms refer to the uniformity and size of the cells. The high tack of the ADX 814 and ADX 814.1 systems would make them somewhat difficult to handle, but the formulator states that this property can be controlled without affecting other properties. Checking the materials with various cell size cores and various thicknesses of the core splice adhesives with controlled gaps between segments of the core equal to and twice the thickness of the film tested showed varying degrees of expansion and interlock. The gaps were controlled with appropriate thickness shims, and tests were performed using 0.10- and 0.05-inch-thick film with 1/4-, 3-16-, and 1/4-inch cell size honeycomb and 0.025-inch-thick film with 1/8-inch core only. The cured splice was examined visually for degree of expansion and ability to fill the gap. It was also examined for interlock which describes the ability of the foaming adhesive to flow around small segments of the core and cause a good tie between pieces of core. Results are given in Table 10 using

TABLE 10. MISCELLANEOUS PROPERTIES

Property	Target	Formulation					
		ADX 814		ADX 814.1		ADX 815	
Cell structure	Closed, uniform	Good		Very good		Excellent	
Handling characteristics Pliability Tack	 Conform to 1/8 in. R Vertical adhesion	 Satisfactory Very high		 Satisfactory High		 Satisfactory Satisfactory	
Core Size Variation	Uniform expansion and interlocking of core	Expansion	Interlock	Expansion	Interlock	Expansion	Interlock
1/8 in. cell							
0.100 in. film							
0.200 in. gap		2	4	2	1	1	1
0.100 in. gap		2	2	1	1	1	1
0.050 in. film							
0.100 in. gap		4	3	1	2	2	2
0.050 in. gap		3	3	2	1	2	1
0.025 in. film							
0.050 in. gap		4	3	2	2	3	3
0.025 in. gap		4	4	3	2	2	4
3/16 in. cell							
0.100 in. film							
0.200 in. gap		3	3	2	2	2	1
0.100 in. gap		3	1	2	2	1	1
0.050 in. film							
0.100 in. gap		2	3	2	2	3	4
0.050 in. gap		2	2	2	2	2	2
1/4 in. cell							
0.100 in film							
0.200 in. gap		1	3	1	1	1	1
0.100 in. gap		1	1	1	1	1	2
0.050 in. film							
0.100 in. gap		3	4	3	2	1	1
0.050 in. gap		4	4	2	1	1	1
Gel temperature (°F)	180° F minimum						
2° F/min heat-up rate		275-280		270-275		250	
6° F/min heat-up rate		300-305		300-305		260-265	
Cold flow	Original 0 in. at 90° F						
4 days		0.015		0.010		0.025	
7 days	Revised	0.020		0.015		0.030	
10 days	0.050 in. at 90° F	0.020		0.015		0.030	

NOTES:

1 = Excellent; 2 = Very good; 3 = Good; 4 = Fair.

Details of procedures can be found in Appendix B.

descriptive terms ranging from fair to excellent. Except for special applications or for use laminated to other thicknesses, 0.025-inch-thick film would not be recommended for production use.

In measuring the gel temperature, all materials foamed as expected prior to reaching this temperature. No degradation of the foam was noted between the time of foaming and the time of resin gelation. These values are reported in Table 10 for the minimum and maximum heat-up rates of 2° F and 6° F per minute, respectively.

While the original target was no cold flow, it is reasonable to expect the adhesive to expand as much due to foaming in the edgewise direction as it expands in thickness. Adapting a conservative value of 0.050 inch for such expansion, it is observed that all three adhesives would accommodate their cold flow and, consequently, meet the revised target value.

Based on the work life characteristics reported in Table 8, it was concluded that only ADX 814.1 could provide the desired expansion ratio and slump after storage at 0° F followed by 7 days at 90° F. The results of 3 months storage are given in Table 11. The material, in addition to providing target expansion and slump properties after this exposure, still maintained pliability and tack. It is planned that these tests will be repeated after 6 months storage at 0° F.

TABLE 11. STORAGE LIFE TEST DATA

Material	Exposure	T_o (in.)	T_7 (in.)	Expansion ratio	Slump- (in.)
ADX 814.1	3 months at 0° F, followed by 7 days at 90° F	0.106 0.109	0.148 0.147	2.03 2.06	0.04 0.03
	Avg			2.05	0.035

NOTES:

T_o = uncured thickness after 0° F exposure

T_7 = uncured thickness after 0° F plus 7 days at 90° F exposure

$$\text{Expansion ratio} = \frac{\text{Cured thickness after exposure}}{T_o}$$

Details of procedure can be found in Appendix B.

Section VI

CONCLUSIONS

As a result of the test data accumulated in this program, certain of the original target values were found to be unrealistic. These included values for tube shear strength, core shear strength, RT flatwise tension strength, and edge attachment strengths. These have been revised as shown in Tables 3, 4, 6, and 9 as well as in the appropriate sections of Appendix B.

Those properties whose value depends in part upon the bond between the core shear adhesive and honeycomb face sheet (viz, core shear and flatwise tension) can be significantly improved if the core splice is sanded prior to bonding to the face sheet. (See Tables 4 and 6.)

Each of the three materials selected for phase III (adhesive characterization) had certain desirable characteristics which might lead to their selection depending upon requirements. From an overall point of view, however, ADX 814.1 is considered to be the most promising adhesive. In addition to exhibiting very acceptable strength characteristics, its cold flow (Table 10), work life (Table 8), and storage life (Table 11) indicate there will be little likelihood of manufacturing problems due to overaging on production delays (out-time) during layup.

Appendix A

PERSONNEL CONTACTED FOR PHASE I COMMENTS

Organization	Individual
AFML	
ASD[a]	J. Treadway
Bell Helicopter[a]	R. Hunter
Boeing Aircraft	
Boeing Vertol	
General Dynamics, Fort Worth[a]	W. Toothaker
General Electric, Albuquerque[a]	J. Tipton
Grumman Aerospace	
Kaman Aerospace	
Lockheed-California[a]	E. Hagberg
Lockheed-Georgia[a]	L. Meade
LTV[a]	G. Bourland
Martin Marietta Aerospace, Baltimore Div	
McDonnel-Douglas[a]	B. Upton
Northrop Corp., Aircraft Div[a]	R. Patton
NASA, Huntsville	
NASA, Langley[b]	R. Pride
Picatinny Arsenal	
Plastec[c]	H. Pebly
Rockwell International, Columbus[a]	J. Fasold
Rockwell International, Space[a]	F. Scott/H. Clancy
Rockwell International, Tulsa[a]	R. Sanders
Sikorsky Aircraft	

[a]Comments received
[b]Deferred to major contractors
[c]Deferred to Picatinny Arsenal

Appendix B

TEST PROCEDURES AND TARGET REQUIREMENTS

TUBE SHEAR

Tube shear specimens were fabricated using 3-inch lengths of 1- and 1/2-inch outside diameter FPL etched aluminum tubing both with 0.050-inch wall thickness. These dimensions gave a nominal 0.200-inch annular gap when the tubes were assembled. A 0.1-inch-thick film of the core splice adhesive was wrapped around the smaller tube with a butt joint down one side. This tube was then slipped into the larger tube. Edge holding devices were installed to maintain concentricity. After cure, five 1/2-inch-long specimens were cut from the 3-inch part, allowing a nominal 1/4-inch trim on each end (Figure 1). Testing consisted of supporting the outer tube and forcing the inner tube out, using a load displacement rate of 0.05 inch per minute (Figure 2). Stress was calculated based on the mean diameter of the annular space. (Refer to Appendix C.) Five specimens were tested at each of three temperatures: -67° F, room temperature (RT), and 350° F.

Target Requirement	Revised Requirement
-67° F - 750 psi	-67° F - 1200 psi
RT - 750 psi	RT - 950 psi
350° F - 550 psi	350° F - 125 psi

CORE SHEAR STRENGTH

Sandwich flexure specimens, 3 x 8 inches, were prepared using 0.063-inch-thick 2024-T3 bare FPL etched aluminum face sheets. The core was 1/4-inch cell size, 0.004-inch foil, 5052 alloy, nonperforated honeycomb, 1/2-inch thick. The ribbon direction of the core was parallel to the 8-inch dimension. A core splice extended across the 3-inch dimension, 2 inches from one end, and was cured prior to bonding the faces to the core. The splice was made so that each piece of the honeycomb was just touching the core splice adhesive prior to cure. Plastilock 729-3 adhesive was used in bonding the faces to the core. Triplicate specimens were tested in flexure at -67° F, RT, and 350° F. Results were compared with similar specimens combining no core splice. Method of calculation is described in Appendix C.

Target Requirement	Revised Requirement
-67° F - 1,100 psi	-67° F - 690 psi
RT - 1,100 psi	RT - 690 psi
350° F - 800 psi	350° F - 290 psi

FLATWISE TENSION STRENGTH

Flatwise tension tests using 3/16- and 1/4-inch cell size honeycomb core, both with 0.0015-inch foil, were conducted using the procedure of MIL-STD-401. Triplicate specimens having a core splice through the center of each specimen were tested at -67° F, RT, and 350° F. The splice was made so that each piece of the honeycomb was just touching the uncured core splice adhesive and was cured before bonding the FPL etched faces to the core. Plastilock 729-3 adhesive was used in bonding the faces to the core. Results were compared with similar specimens containing no splice. Method of calculation is given in Appendix C.

Target Requirement	Revised Requirement
-67° F - 800 psi	-67° F - 800 psi
RT - 1,000 psi	RT - 800 psi
350° F - 550 psi	350° F - 550 psi

EXPANSION RATIO

Specimens of adhesive 2 inches nominal diameter and 0.1-inch thick were placed on an aluminum sheet with a suitable parting film or a Teflon sheet, and free foamed in a Teflon tube having the same inside diameter as the specimen. Thickness measurements were taken along two diameters at right angles to one another on 1/2-inch centers starting approximately 1/2 inch from the edge of the specimen. Measurements were made before and after cure. Two heat-up rates were used in curing the specimens; namely, 2° and 6° F per minute. The average thickness before cure is the expansion ratio.

- Target requirement: 2.5: 1

- Revised requirement: 2.0:1

SLUMP TEST

Specimens of adhesive 0.5 by 1.5 inch and 0.1-inch thick were mounted on a vertical FPL etched aluminum surface, the long dimension positioned vertically. Scribelines marked the top and bottom of the specimen. After cure, the vertical movement of the top and bottom edges was measured, with the larger movement being recorded as slump. Specimens were cured using two heat-up rates; namely, 2° and 6° F per minute.

- Target requirement: 0.5 inch max

PEAK EXOTHERM MEASUREMENTS

Core splice and edge attachment bonds were produced in an 8 by 8 by 4-inch simulated honeycomb sandwich, using 3/16-inch RHP core 4-pound density. The core was split into two halves 4 by 8 inches and spliced together with a 4 by 8 by 0.1-inch specimen of adhesive. One remaining 8-inch edge was similarly bonded to an 0.063-inch thick aluminum sheet (4-1/4 by 8 inches), and the other

8-inch edge was similarly bonded to a 1/16-inch glass fabric epoxy resin sheet (4-1/4 by 8 inches). Simulated face sheets 1/8 by 8 by 8 inches were treated with a release agent and installed top and bottom between the aluminum and plastic edge members (Figure 3). A thermocouple was installed at the areal center of each of the three adhesive films to permit monitoring of the temperature during cure. A heat-up rate of 2° F per minute was used in curing specimens. The maximum recorded on each thermocouple represents the peak exotherm value for that configuration.

- Target requirement: 450° F max

VOLATILE CONTENT

Adhesive specimens used for expansion ratio tests were weighed before and after cure to determine volatile content.

- Target requirement: 1% max

GEL TEMPERATURE

A 2 by 2 by 0.1-inch specimen of adhesive was exposed to the standard 350° F adhesive cure cycle. During the heat-up cycle at 2° to 6° F minute from RT to 350° F, the pad was probed periodically after foaming occurred. The temperature at which resin stringing no longer occurs and the specimen had a rubbery consistency was recorded as the gel temperature. A minimum of three deterrnininations were made bracketing the permissible heat-up rates.

- Target requirement: 180° F min

CELL STRUCTURE

Foamed specimens were sectioned and visually checked for foam quality and uniformity. Any tendency to produce voids or other evidence of nonuniformity was noted.

- Target requirement: Closed cell, uniform

DENSITY

Average uncured film areal density was calculated using thickness and weight values derived from expansion ratio and volatile content tests. Method of calculation is given in Appendix C.

- Target requirement: 0.62 lb/ft^2 for 0.10-inch-thick unexpanded material

HANDLING CHARACTERISTICS

The material shall be capable of conforming to a 1/8-inch radius. It shall also exhibit sufficient tack to adhere to a properly cleaned/primed aluminum surface in a vertical position. Tack and conformability may be enhanced by heating the film with warm air to a temperature not exceeding 120° F.

WORK LIFE

Specimens were tested for expansion ratio and slump after extended periods out of storage. Selected periods were 4 days, 7 days, and then daily until properties appeared to drop off.

- Target requirements: 7 days at 90° F

CORE SIZE VARIATIONS

Core splices were made using 1/8-, 3/16-, and 1/4-inch cell size aluminum honeycomb, 1-inch thick, with controlled gaps between the core equal to and twice the nominal thickness of the core splice adhesive. Adhesive thicknesses to be checked were 0.100, 0.050, and 0.025 inch. The 0.025-inch adhesive was only checked with 1/8-inch cell size core. One specimen was prepared for each configuration.

Specimens were fabricated using two 4 by 4-inch squares of honeycomb for each. The desired gap was maintained by using a shim of the desired thickness, 0.25-inch wide by 4-1/2 inches long. The shim was coated with a parting agent and placed on edge on an aluminum sheet similarly treated. A 3/4 by 4-inch strip of core splice adhesive was tacked to the side of one piece of core even with the edge. This piece of core was then brought in contact with the shim, and the other piece of core was butted against the other side of the shim. The core-shim assembly was wrapped around its periphery with aluminum pressure-sensitive tape to prevent movement during cure. A simulated 0.063-inch skin treated with parting agent was placed on top of the taped core and the assembly cured. After cure, the simulated skins and shim were removed and the splice was visually examined.

- Target requirement: Uniform expansion, closed cell and interlocking of core.

EDGE ATTACHMENT ADHESION

Tube shear specimens were prepared as described under "Tube Shear" with the exception that the inner tubes were an adherend other than aluminum. Other adherends which were evaluated included epoxy-fiber glass, titanium, corrosion-resistant steel, and glass reinforced phenolic molding compound.

As in the tube shear test, aluminum adherends were FPL etched prior to bonding. Phenolic and epoxy reinforced plastic adherends were sanded lightly followed by wiping with methyl ethyl ketone. Parts were air dried 8 hours prior to bonding. The 6Al-4V titanium tubing was prepared using Turco 5578 at 180° to 200° F, for 8 to 10 minutes. The 321 CRS tubing was prepared using Turco Vitro-Kleen for 10 minutes at 160° F followed by passivation in 50-percent nitric acid at room temperature for 10 minutes. Method of calculation is given in Appendix C.

Target Requirement	Revised Requirements
-67° F - 750 psi	-67° F - 900 psi
RT - 750 psi	RT - 650 psi
350° F - 550 psi	350° F - 50 psi

STORAGE LIFE

Specimens were tested for expansion ratio and slump after extended periods of storage at 0° F or below followed by the work life as established under "Work Life."

- Target requirements: 6 months at 0° F plus ambient temperature work life

COLD FLOW

A 4 by 6-inch piece of aluminum, 0.063-inch thick, was scribed 1-1/2 inches from one edge parallel to the 4-inch dimension. A 2 by 4-inch piece of core splice adhesive, 0.100-inch thick, was pressed to the cleaned aluminum sheet with one 2-inch side even with the scribe line.

The adhesive film was in intimate contact with the aluminum over its entire area. The specimen was placed in a vertical position at a temperature of 90° F for 7 days. Each day for the first 4 days and at the end of 7 days, the movement of the adhesive beyond the scribe line was recorded.

- Target requirement: 0 in.
- Revised requirement: 0.050 in.

Appendix C

METHODS OF CALCULATIONS

TUBE SHEAR STRENGTH

$$\text{Tube shear strength, psi} = \frac{P}{\left(\frac{OD_i + ID_o}{2}\right) h \pi}$$

where

P = failing load, pounds
OD_i = outside diameter of inner tube, inches
ID_o = inside diameter of outer tube, inches
h - specimen height, inches

Nominal dimensions were

OD_i = 0.500 inch
ID_o = 0.900 inch
h = 0.50 inch

CORE SHEAR STRENGTH

$$\text{Core shear strength, psi} = \frac{P}{b\ (t + t_c)}$$

where

P = failing load, pounds
b = sandwich width, inches
t = total sandwich thickness, inches
t_c = honeycomb core thickness, inches

Nominal dimensions were

b = 3 inches
t = 0.75 inch
t_c = 0.625 inch

FLATWISE TENSION STRENGTH

$$\text{Flatwise tension strength, psi} = \frac{P}{\ell \times \omega}$$

where

P = failing load, pounds
ℓ = length of specimen, inches
ω = width of specimen, inches

Nominal dimensions were

$\ell = \omega = 2$ inches

EXPANSION RATIO

$$\text{Expansion ratio} = \frac{T_f}{T_i}$$

where

T_f = cured thickness, inches
T_i = uncured thickness, inches

SLUMP

Direct measurement in inches of movement of edge from position of scribe line.

PEAK EXOTHERM

Direct measurement in °F, measured by installed thermocouples.

VOLATILE CONTENT

$$\text{Volatile content, \%} = \frac{W_1 - W_2}{W_1} \times 100$$

where

W_1 = uncured weight of expansion ratio specimen

W_2 = cured weight of expansion ratio specimen

GEL TEMPERATURE

Direct measurement in °F, measured by installed thermocouple

CELL STRUCTURE

Direct visual examination

DENSITY

$$\text{Uncured weight, lb/sq ft/0.10 thickness} = \frac{W_1}{A} \times \frac{144}{454} \times \frac{0.10}{T_i}$$

$$= 0.0317 \frac{W_1}{A\ T_i}$$

where

W_1 = uncured weight of expansion ratio specimen, grams

A = area of uncured expansion ratio specimen, sq in.

T_i = uncured thickness of uncured expansion ratio specimen, in.

144 = sq in./sq ft

454 = gm/lb

0.10 = nominal thickness of specimen, in.

HANDLING CHARACTERISTICS

Pliability = ability to conform to 1/8-inch radius

Tack = ability to adhere to a cleaned/primed surface in a vertical position

WORK LIFE

Determine expansion ratio and slump after exposures to 90° F.

CORE SIZE VARIATIONS

Visual check for expansion and core interlock.

EDGE ATTACHMENT ADHESION

Same as for tube shear strength.

STORAGE LIFE

Determine expansion ratio and slump after 3 and 6 months storage at 0° F followed by 7-day exposure to 90° F.

COLD FLOW

Direct measurement in inches of movement of edge from position of scribe line.

ADHESIVES

PRELIMINARY DATA SHEET

ADX-814

INTUMESCENT ADHESIVE

DESCRIPTION: ADX-814 is a tacky, 350°F curing expandable film for use in gap filling applications or splicing a variety of metal or plastic core structures. ADX-814 is particularly useful where large sections are to be joined and high heats of reaction (exotherm) must be avoided.

This material is available as 25, 50 or 100 mil thick film.

PROPERTIES: The following is based on a 1 hour @ 350°F cure after a 2°F/minute heat up.

Cured density, lbs/ft^3	28
Expansion Ratio	2.8 : 1
Vertical Slump, in.	0.1
Volatiles, %	< 0.5

STORAGE: ADX-814 should be stored at 0°F or lower to prolong shelf life. It may remain at room temperature for several weeks without loss in properties.

SPI SKIN HAZARD: Class 2.

KKR:mem
1/8/75

ADHESIVES

PRELIMINARY DATA SHEET

ADX-814.1

INTUMESCENT ADHESIVE

DESCRIPTION: ADX-814.1 is a tacky, 350°F curing expandable film for use in gap filling applications or splicing a variety of metal or plastic core structures. ADX-814.1 is particularly useful where large sections are to be joined and high heats of reaction (exotherm) must be avoided. It has considerably better shelf life than ADX-814.

This material is available as 25, 50 or 100 mil thick film.

PROPERTIES: The following is based on a 1 hour @ 350°F cure after a 2°F/minute heat up.

Cured density, lbs/ft^3	28
Expansion Ratio	2.7 : 1
Vertical Slump, in.	0.1
Volatiles, %	< 0.5

STORAGE: ADX-814.1 should be stored at 0°F or lower to prolong shelf life. It may remain at room temperature for several months with only a minor decrease in expansion properties.

SPI SKIN HAZARD: Class 2.

KKR:mem
1/8/75

ADHESIVES

PRELIMINARY DATA SHEET

ADX-815

INTUMESCENT ADHESIVE

DESCRIPTION: ADX-815 is a tacky, 350°F curing expandable film for use in gap filling applications or splicing a variety of metal or plastic core structures. ADX-815 is particularly useful where large sections are to be joined and high heats of reaction (exotherm) must be avoided.

This material is available as 25, 50 or 100 mil thick film.

PROPERTIES: The following is based on a 1 hour @ 350°F cure after a 2°F/minute heat up.

Cured density, lbs/ft^3	28
Expansion Ratio	2.9 : 1
Vertical Slump, in.	0.2
Volatiles, %	$<$ 0.5

STORAGE: ADX-815 should be stored at 0°F or lower to prolong shelf life.

SPI SKIN HAZARD: Class 2.

KKR:mem
1/8/75

☆ U. S. GOVERNMENT PRINTING OFFICE: 1975 — 657-630/265