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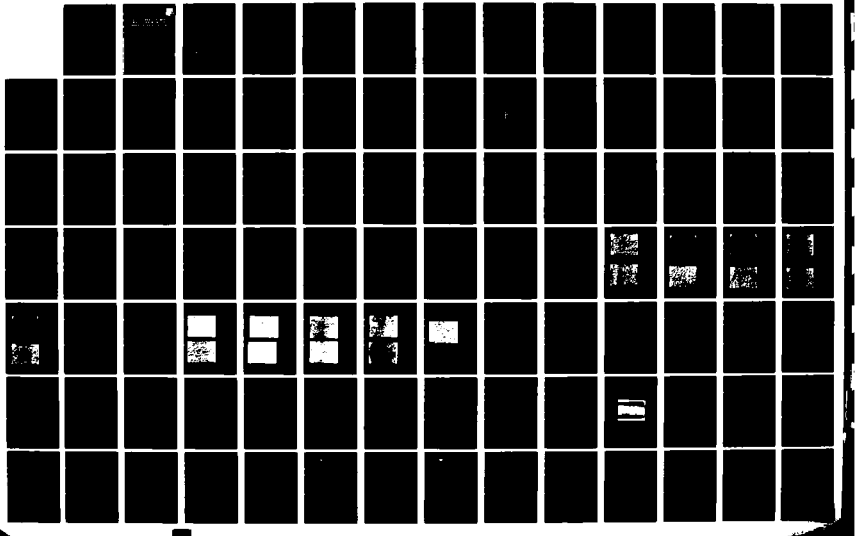

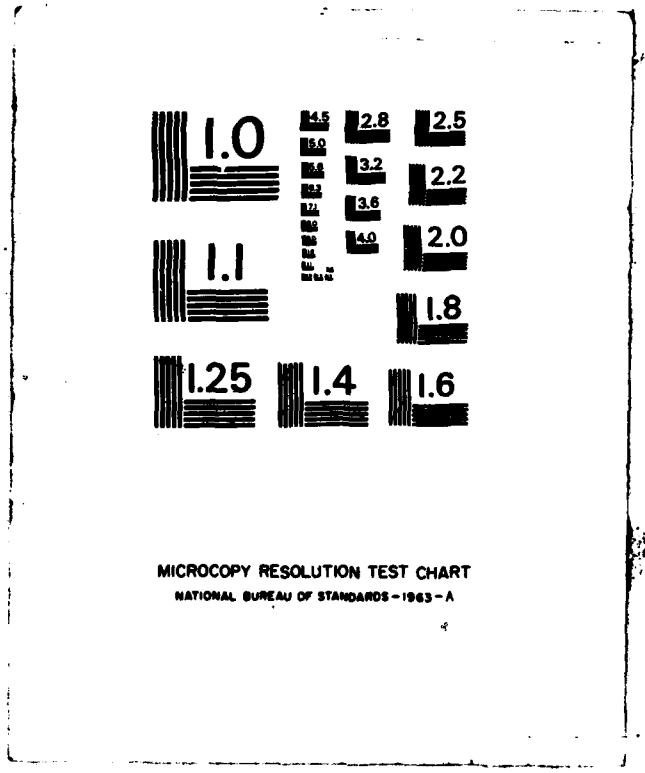
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DEVELOPMENT OF IMPROVED PRINTED WIRING BOARD INNER LAYER ADHESION

Thomas E. Baker
Raytheon Company
Equipment Division Laboratories
Sudbury, Massachusetts 01776

JUNE 1982

Final Report for Period 15 February 1980 to 15 February 1982

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

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

Herbert S. Schwartz

HERBERT S. SCHWARTZ, Project Engr
Composites, Adhesives & Fibr Matls Br

Robert L. Rapson

ROBERT L. RAPSON, Chief
Composites, Adhesives & Fibr Matls Branch

FOR THE COMMANDER:

F. D. Cherry

FRANKLIN D. CHERRY, Chief
Nonmetallic Materials Division

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

Polyimide multilayer printed wiring boards (MLPWB) offer much higher temperature resistance than epoxy MLPWB, however, their usage has been limited due to inner layer delamination problems. This study has determined the primary cause of delamination as adhesive failure to inner layer copper surfaces. Copper surface treatments based on sodium chlorite when used with a ferric chloride/hydrochloric acid pre-etch have been found to eliminate these delamination problems. A test specimen based on ASTM D2733 has been developed for measuring the inner

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layer adhesion of MLPWB. Also evaluated was a floating roller technique for measuring the peel strength of copper foil. This technique gave consistent, low-chatter peel strength values. Analytical techniques were also developed for characterizing polyimide pre-pregs. In general, the polyimide pre-pregs were of high quality and excellent consistency. MLPWB's fabricated to those materials and processes optimized per this study exhibited excellent moisture and thermal resistances when tested per applicable military specifications.

FOREWORD

This Final Technical Report covers the work performed on Contract No. F33615-79-R-5131, Project No. 2423, Task No. 242301 for the period 15 February 1980 through 15 February 1982.

This contract was performed by Raytheon Company, Equipment Division Laboratories Materials Engineering, Sudbury, Massachusetts for the Air Force Wright Aeronautical Laboratories (AFSC), Wright-Patterson Air Force Base, Ohio. This program was under the technical direction of Herbert S. Schwartz, AFWAL/MLBC. The project manager for Raytheon was Thomas E. Baker. Other key Raytheon contributors to the program were G. L. Fix, J. E. Breen, J. Howell, R. E. Keegan, R. T. MacNeil and W. Hall.

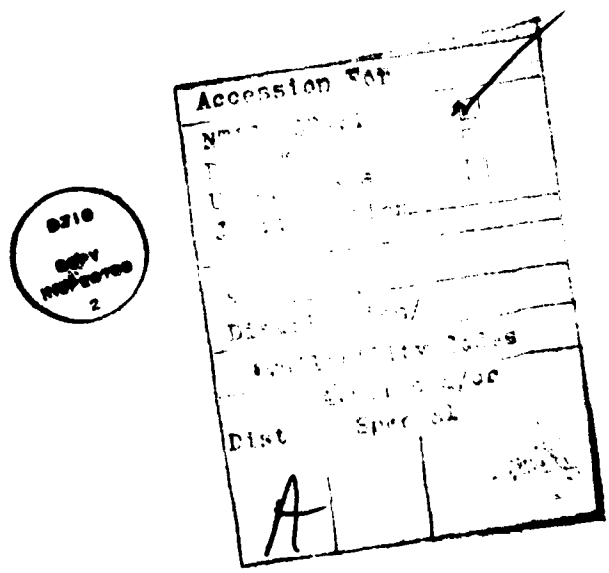


TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

SECTION I

INTRODUCTION

1. INTRODUCTION

Raytheon Company, Equipment Division Laboratories Materials Engineering conducted an Exploratory Development program for the improvement of printed wiring board inner layer adhesion. This program was conducted under Contract F33615-79-R-5131. This Final Technical Report describes the efforts performed during the period 15 February 1980 through 15 February 1982.

2. SUMMARY

The objective of this program was to define the primary mechanisms for inner layer adhesion failures of multilayer printed wiring boards (MLPWB) and to develop improved material and process control procedures and improved or modified materials and processes for improving the inner layer adhesion. The major tasks in this program were (1) conduct a comprehensive literature survey, (2) define inner layer adhesion degradation and failure mechanisms for contemporary materials and processes, (3) develop improved material and process control procedures and acceptance criteria, (4) develop improved or modified materials and processes, and (5) evaluate improved materials and processes in fabricated printed wiring boards. As a result of this investigation, guidelines were suggested for consideration in modifying existing applicable specifications for MLPWB.

The results of this study have produced several achievements which we feel are quite significant. The major program achievements include:

- Establishing the chief failure mechanism of MLPWB inner layer adhesion as adhesive failure to inner copper surfaces.
- Optimization of inner layer adhesion to the point where it is greater than the cohesive strength of C-stage portions within a MLPWB.
- Discovery of the synergistic effect of ferric chloride etch followed by red oxide treatment as a most effective means of treating inner copper foil surfaces to produce maximum adhesion.
- Demonstrated the consistency and high quality of polyimide prepreg material from several vendors qualified to applicable military specifications.
- Demonstrated the excellent moisture insensitivity of polyimide prepreg material.
- Confirmed the superior hydrolytic stability of polyimide MLPWB under bias humidity testing.

- Confirmed the excellent thermal shock/cycle and thermal aging resistance of polyimide MLPWB.
- Established the ASTM D2733 method of lap shear testing as a viable technique for measuring inner layer adhesion of MLPWB type laminates.
- Established the viability of ASTM D3167 floating roller technique for peel strength testing of copper foil from MLPWB.
- Established that a post-cure of 218°C (425°F) is sufficient for post-baking of polyimide MLPWB.
- Developed analytical techniques for the characterization of polyimide prepreg materials.

SECTION II

TECHNICAL EFFORT

1. SCOPE

Polyimide multilayer printed wiring boards (MLPWB) have been available for several years. Polyimides offer superior higher temperature resistance than epoxy MLPWB and also outstanding moisture resistance compared to epoxies. The acceptance and use of polyimide MLPWB for high reliability military equipment have been slow however. Polyimide MLPWB have been plagued with inconsistencies primarily because of inner layer adhesion failures within the laminate. These failures have surfaced many times during wave soldering operations, temperature cycling, elevated temperature exposure, and humidity testing. For that matter, delamination of polyimide MLPWB during fabrication and particularly after exposure to post-baking cycles was not an unusual occurrence.

In general, the state-of-the-art is that epoxy MLPWB's are limited to a maximum temperature of 125°C due to volume changes at the glass transition temperature (Tg). Cracks in plated-through holes can result by passing through the Tg. Polyimide MLPWB with a Tg of 240°C offer higher temperature capabilities. Because of poorer wetting and adhesion characteristics of the polyimides, MLPWB's fabricated from polyimide have been susceptible to many delamination problems. Other suspected causes of delamination in polyimide MLPWB technology included inconsistencies in the prepreg, moisture effects on prepregs, moisture effects on MLPWB prior to wave soldering, inadequate surface preparation and cleaning, inadequate treatment of copper foil surfaces, and improper lamination cycle. It is interesting to note that the results of this study will verify some of these suspected causes as being major contributors to inner layer adhesion failures while other suspects were found to be completely non-influential on adhesion.

The Air Force being cognizant of the limitations of polyimide MLPWB, initiated an exploratory development program to define MLPWB inner layer failure mechanisms and to develop improved materials and processes, as needed, to overcome the deficiencies of polyimide. In accordance with the overall program requirements established by the Air Force, this study was performed in five major tasks, namely, (1) conduct a literature survey to establish the state-of-the-art, (2) definition of inner layer adhesion degradation and failure mechanisms for contemporary materials and processes, (3) development of improved material and process control procedures and acceptance criteria, (4) development of improved materials and processes, and (5) evaluation of improved materials and processes in fabricated multilayer printed wiring boards.

2. LITERATURE SURVEY

A literature survey of publications and documentation relevant to the technical objectives of the contract was made. This survey included reviews of government and open literature, symposium presentations, technical and trade association documents, product data and other pertinent information.

Comprehensive searches of NASA and the Defense Technical Information Center (DTIC), formerly DDC, were made. The NASA search resulted in NASA Literature Search Number 43028, dated 11 March 1980, with 221 citations over the period of 1972 to present. The DTIC search resulted in DTIC Search Control Number 091892, dated 17 March 1980 with approximately 350 citations broad enough so that all areas regarding epoxy and polyimide lamination made to review only those references with relevancy to this program. Some reports on composite technology, i.e., polyimide graphite systems, have been included since many phases of that technology are appropriate to PWB technology.

A Lockheed Dialog information retrieval search was also performed and since the operator was in direct communication with the computer storage bank, a very selective and relevant search was possible. This search covered all significant scientific and technical journals and sources including Chemical Abstracts. The results of the Lockheed Dialog were particularly informative.

A Government-Industry Data Exchange Program (GIDEP) request for specific data on PWB inner layer adhesion technology was also made. The results of this effort were quite disappointing with only two responses. Our previous high responses from GIDEP on other programs lead us to believe that most of the GIDEP members are unaware of polyimide PWB interlayer adhesion problems since they are probably not users of them.

Letters were also sent to the major manufacturers of polyimide pre-preg materials as well as several of the largest users of polyimides. Response to our request was also quite limited. Subsequent private communications with some of the polyimide manufacturers resulted in their expression of interest in the study program, but they had little to offer on the question of interlayer adhesion of polyimide MLPWB's.

A summary of the highlights of the literature search is compiled in the Appendix. Based on this search four major generalizations appeared salient, namely,

- The inner layer adhesion of polyimide MLPWB's is a wide-spread problem.
- The use of vapor phase soldering (at $\sim$215°C) for the emerging leadless (hermetic) ceramic chip carrier technology may limit or exclude the use of epoxy MLPWB's.
- Polyimides offer lower life cycle costs and improved performance over epoxies particularly in adverse environments.
- Oxide surface treatments based on sodium chlorite look promising for treatment of copper surfaces.

3. STRUCTURAL EVALUATION METHODS OF INNER LAYER ADHESION

a. CONTEMPORARY MATERIALS AND PROCESSES

For the initial experimental work, two epoxy prepregs and two polyimide prepregs that qualified to applicable military specifications were chosen. The characterization data for these materials are found in Tables 26-28 and are discussed later in this report. It was the intent initially to direct about seventy percent of the experimental work towards the polyimides and the remainder on the epoxies. Subsequent experimentation indicated however that the emphasis should concentrate on the polyimides alone since polyimide MLPWB's were more sensitive to inner layer construction and as such more susceptible to inner layer adhesion failures.

A summary of the contemporary processes initially used is found in the Appendix. It is seen that some of the key processes used at the start of the program included either a red oxide treatment or ferric chloride/hydrochloric acid treatment for copper surfaces, and a 190°C (375°F) cure for laminating with a 232°C (450°F) post cure for polyimides. These are highlighted because they are some of the key factors which, after investigation, were to change.

b. DEFINITION OF INNER LAYER ADHESION DEGRADATION

Current Industry Methods for Evaluating Inner Layer Adhesion - Suprisingly, there are no industry - wide procedures available for measuring the inner layer adhesion of MLPWB's. Little effort has apparently been made by industry to develop a suitable technique. Short beam shear testing is used by several companies to determine inner layer shear strength but the non-homogeneity and anisotropy of composites such as MLPWB's creates many doubts as to the validity of such testing. A brief investigation of short beam shear testing gave results higher than a factor of 5 compared to the inner layer shear technique.

Initial Evaluation of Inner Layer Adhesion - Our previous experience with polyimide MLPWB's was one of reasonable success. Many times however a set of MLPWB's were below satisfactory and could be delaminated easily such as by striking on edge. We knew that adhesion to copper interlayers was critical but we did not know what the answer to overcoming this problem was at the time. Discussions with other fabricators of polyimide supported our findings. Delamination problems of this type were never a serious problem with epoxy MLPWB's. The exceptional adhesive characteristics of epoxies were usually enough to overcome inner layer adhesion problems. Epoxies do however exhibit delamination problems associated with moisture in the prepreg material. One of the first objectives was to establish a test procedure for measuring the inner layer shear strength of epoxy/copper and polyimide/copper laminates. The desired procedure had to be consistent in that samples from the same internal construction should not vary significantly. Initial testing was based on epoxy and polyimide laminates that were soldered to pull strips. The laminates were made by shearing 5 mil core, .005" thick, with 1 ounce copper on each side into 4"x4" squares. Preparation included pumice scrub, rinse, air dry, and copper surface treatment. The cores were then laminated with applicable prepreg material and post-baked (for polyimide) at 232°C for four hours. The laminates were processed and

solder plated at 20 amps per square foot for 10 minutes. The plated samples were then sheared into 1/2" squares. The pull strips which were cut into 1/2" by 4" long strips. The test specimens consisting of the laminate square and two pull strips were made by fixturing them and soldering for one-half hour at 232°C. Modified specimens similar to the original specimens were also made with the difference being that only 1/2" of one side of each pull strip was plated rather than the entire 4" length. The shear strengths were obtained by testing on a Tinius Olsen Universal Tester. The results as shown in Table 1 indicated that pull strips of copper/polyimide with double sides treated material were found to be better than any chemical surface treatment. When the solder joint did not fail, the results were consistent. However, the amount of bond degradation from soldering at 232°C was questionable, especially in the epoxy samples. Since one-fourth of the specimens failed at the solder joint, it was thought to use an adhesive rather than solder since this would eliminate any post heating which might degrade bond strengths. Further exploration of this technique showed inconsistent results and the obvious need for a better test was evident. As simplistic as this test was however, it was interesting to note that those samples that failed did so at the copper-epoxy or copper-polyimide interface.

Inner Layer Shear Strength Specimen - It was suggested by the Air Force that ASTM D2733, "Test Method for Interlaminar Shear Strength of Structural Reinforced Plastics at Elevated Temperatures", might be worthy of investigation for this program. The first of these samples were made using 5 mil polyimide laminates, however the 5 mil material was not strong enough and broke in tension. Further investigation led to the use of a sandwich construction consisting of two pieces of .062" "C" stage polyimide bonded with prepreg. A further refinement of this set-up was soon made and is shown in Figure 1. This configuration was subsequently used for all testing of inner layer lap shear. It proved to be very consistent giving reproducible results. The spring loaded plates as seen in Figure 2 minimize any twisting or bending so that forces exerted across the test zone are pure shear. The construction of the laminate as shown in cross-section in Figure 1 consisted of making a 6" x 6" laminate panel per the applicable procedures. The laminate was then cut into one-half inch wide specimens. The outer specimen pieces were not used for test purposes to insure that edge effects were not present. Notching of the sample was accomplished carefully to insure a uniform notch depth from sample to sample. A microscope was used to visually examine all samples.

Shear strength of samples tested using these specimens were calculated according to the formula

$$S_S = P/WA$$

where S_S = shear strength

P = applied load

W = width of specimen

A = distance between notches

TABLE 1 - SHEAR STRENGTHS FROM PULL STRIP TESTING

Material/Process	Test Results	Remarks
Epoxy; Hot Press cycle; Fe Cl/HCl etch; Polyclad prepreg - 108 (modified pull strips)	1) 130 lbs 2) 57 lbs 3) 22 lbs 4) 80 lbs	Failed at solder joint Failed at solder joint Failed at solder joint Failed at solder joint
Same as above except hot plate used for soldering pull strips to sample (modified pull strips)	1) 278 lbs 2) 310 lbs 3) 130 lbs 4) 104 lbs	Failed within pull strip Failed within pull strip Failed at solder joint Failed at solder joint
Epoxy; hot press; no special copper surface prep. Polyclad prepreg - (modified pull strips)	1) 66 lbs 2) 108 lbs 3) 40 lbs 4) Broke on Handling	Failed at solder joint Failed at Cu/Epoxy Failed at Cu/Epoxy N/R
Polyimide; hot press; post baked at 450°F for 4 hours Fe Cl/HCl etch (original pull strips)	1) 78 lbs 2) 45 lbs 3) 111 lbs 4) 120 lbs 5) 75 lbs	Failed at Cu/polyimide Failed at solder joint Failed at Cu/polyimide (slight twist to Sple) Failed at Cu/polyimide Failed at Cu/polyimide
Polyimide; modified hot press cycle; post bake at 450°F/4 hours Fe Cl/HCl etch (modified pull strips)	1) 98 lbs 2) 54 lbs 3) 86 lbs 4) 109 lbs (misalign)	Failed at Cu/polyimide Failed at Cu/polyimide Failed at Cu/polyimide Failed at Cu/polyimide
Polyimide; modified hot press cycle; post bake at 450°F/4 hours double sided treated material (modified pull strips)	1) 246 lbs 2) 340 lbs 3) 77 lbs 4) -------	Failed at Cu/polyimide Failed at Cu/polyimide Failed at solder joint ----------

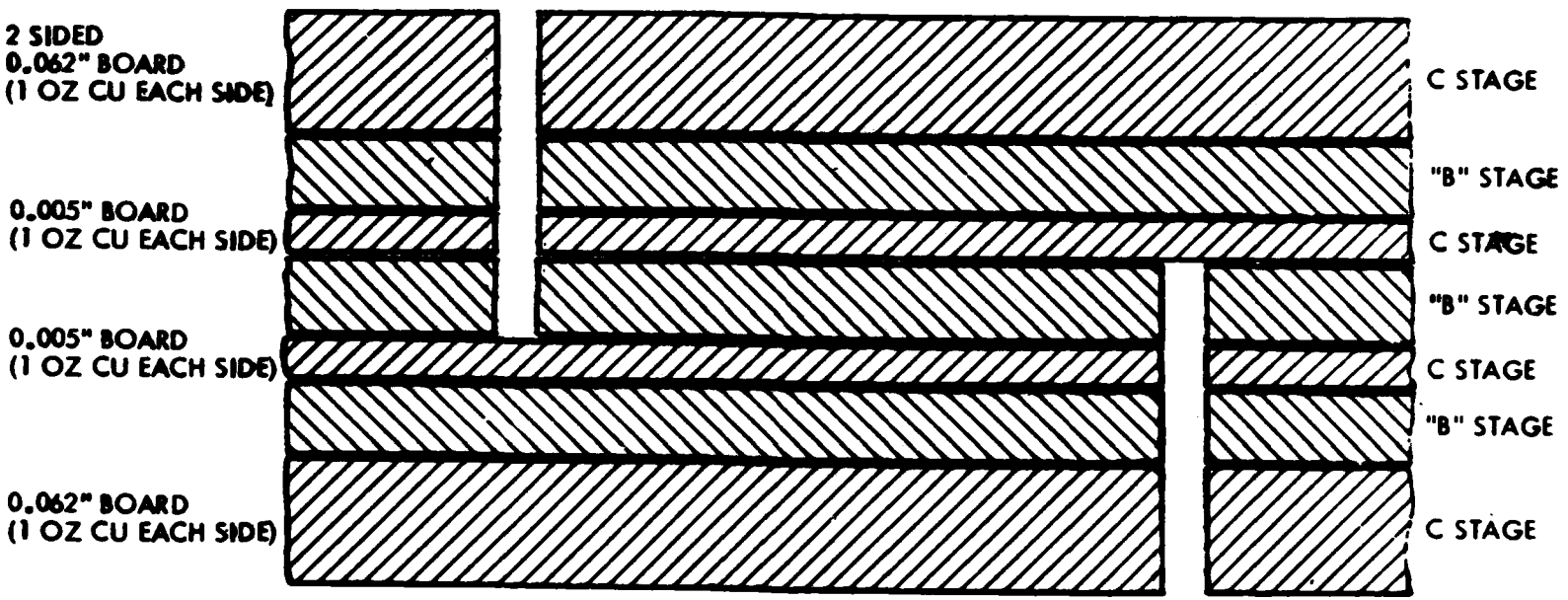


FIGURE 1 TRANVERSE SECTION OF LAP SHEAR SPECIMEN SHOWING LAYER BUILD-UP IN POLYIMIDE LAMINATE

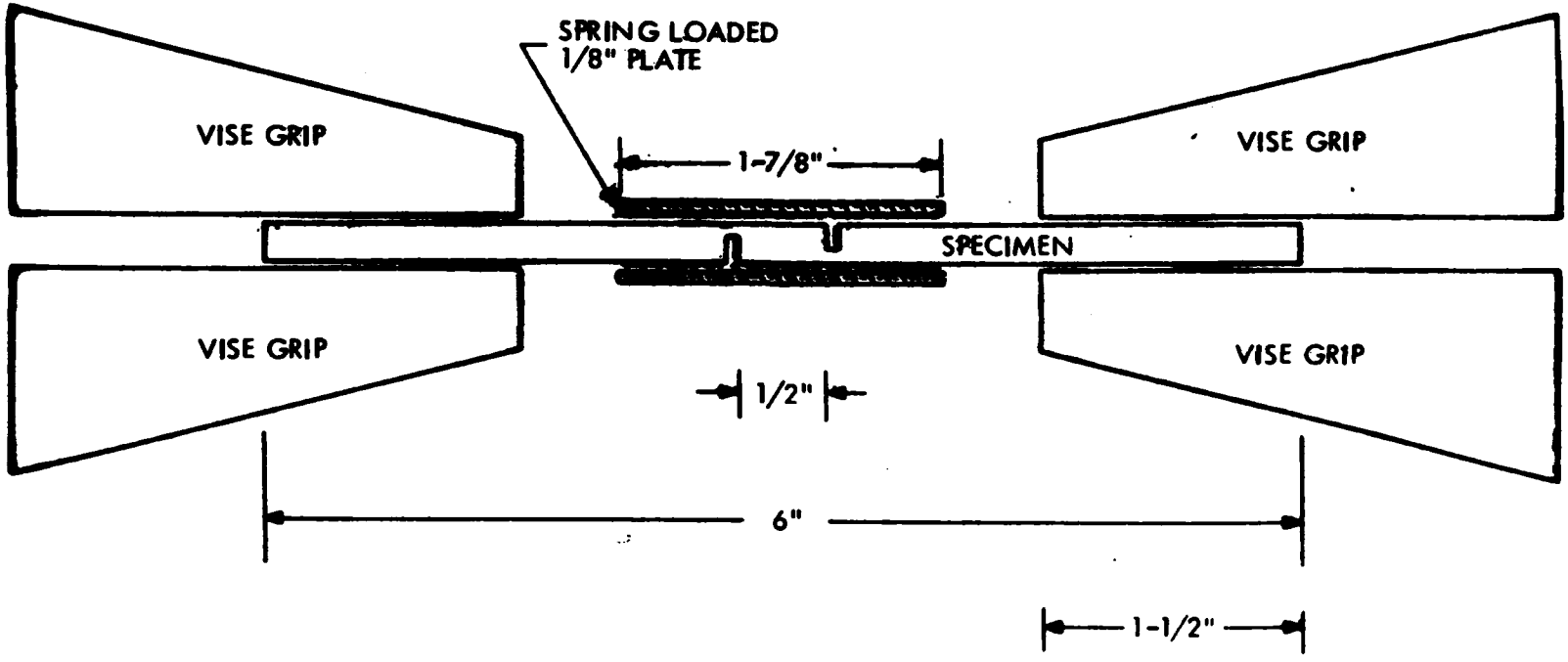


FIGURE 2 ASTM D2733 LAP SHEAR TEST SPECIMEN AND FIXTURING

Observation of the failure location and type, i.e., adhesive failure at copper/prepreg interface, etc., was noted and recorded. A copy of ASTM D2733 is included in the Appendix with permission from the American Society for Testing and Materials.

c. PEEL STRENGTH TESTER

It was believed and later found that a supplemental test to the ASTM D2733 interlaminar shear test was needed for determining the effects of minor processing changes. Once the interlaminar adhesion failure mode shifted from a copper/prepreg interfacial failure to a cohesive prepreg or C-stage material failure, the ASTM procedure was unable to detect variations at the copper interface. Peel strength testing was an obvious technique for measuring the effects of treatment on copper foil. It is surprising that the printed circuit industry does not have a standard peel test apparatus and procedure. It was felt that peel testing in accordance with ASTM D3167 which utilizes a floating roller peel tester appeared to be a desirable technique to use. While this peel tester was being fabricated, preliminary peel tests were made using a Hunter Spring Gauge. Assumedly, this technique would not be as reliable or reproducible as the floating roller tester. Surprisingly, however, the spring gauge technique is actually used by many laminate fabricators for measuring peel strength of clad laminates. We therefore used this method initially and considered it indicative of the peel strength value.

In discussions with the R&D director of an area supplier of high reliability prepreg and laminate materials, questions arose as to the accuracy of our set-up. A comparative test was therefore made of two test panels. These panels were made using Norplex prepreg and the ferric chloride red oxide treatment on the copper foil which is discussed later under surface treatments. The laminate supplier used a Luster-Jordan peel tester. The uniqueness of this system is that the spring gauge rides along on a 45° angle to horizontal at a controlled rate which translates to a constant 90° angle at the copper foil-laminate interface. A picture and description of the Luster-Jordan apparatus is included in the Appendix. With this set-up, the laminate supplier obtained an average peel strength of 4.2 pounds per linear inch (ppi). On the other panel, we used a Hunter Spring gauge, mounted to an Instron Universal Tester with loading rate of 0.2 inch/minute. The 90° angle was maintained by slowly moving the sample (by hand) using a perpendicular mark behind the unit as a reference. The values obtained are shown in Table 2 and are quite comparable. When the new peel tester fabricated to ASTM D3167 was obtained, a test to compare it to the hand-held method was made. Strips were peeled from each of four quandrants using the floating roller peel tester and also by holding samples by hand. Tests were run on the Instron Universal Test Machine using a cross-head speed of one inch per minute. Table 3 summarizes the results of these tests. It can be seen that the peel strength averaged 0.50 pounds force for the 1/8" wide strip held by hand and was 10% higher at 0.55 pounds for the fixture held strips. The roller drum peel strength tester not only gave consistent results but had a minimum of chatter and noise compared to the hand-held technique. These tests were performed using the standard Military specification specimen of 1/8" wide copper foil.

Peel strength values were also obtained using the peel strength tester with one-half (1/2) inch wide specimens which were approximately five inches long. This configuration made it much easier to handle than the shorter and narrower

Table 2 Peel Strength of Norplex Panel
(Instron Test Method)

	Peel Strength, ppi		
Strip No.	High	Low	Avg.
1	3.6	3.3	3.6
2	4.3	3.9	4.1
3	4.7	4.15	4.4
4	4.55	3.9	4.25
5	4.25	3.6	3.9
6	4.15	3.6	3.9
7	4.5	3.75	4.15
8	3.7	3.2	3.45
9	3.55	3.05	3.30
Avg.	4.14	3.61	3.89

Table 3 Peel Strength Testing

Board 24722-48 fabricated by standard procedure "B" stage 108 polyimide (Mica)
4 pieces 0.062 Polyimide "C" no copper, 1 oz. copper foil

	Force	
Sample ID	Hand Held	Fixture Held
1	0.49 lbs.	
2		---
3	0.51 lbs.	
4		0.57 lbs.
5	0.54 lbs.	
6		0.56 lbs.
7	0.52 lbs.	
8		0.55 lbs.
9	0.49 lbs.	
10		0.57 lbs.
11	0.48 lbs.	
12		0.49 lbs.
13	0.48 lbs.	
14		0.58 lbs.
15	0.46 lbs.	
16		0.51 lbs.
Avg.	0.50 lbs.	0.55 lbs.

standard MIL specimens. A comparison was also made to using a hand-held technique with the Instron Tester. Peel strength samples of one-quarter (1/4) inch width and five inches long were also measured using the hand-held technique.

The results of these tests are found in Table 19A. Generally, the values obtained using the roller drum peel tester averaged slightly higher than the hand-held technique. The scatter in variation is most likely due to a small sample base. At this time, we do feel that the floating roller peel tester is a definite improvement over industrial techniques such as an Instron tester using a spring gauge. A copy of ASTM D3167 is included in the Appendix with permission from the American Society for Testing and Materials.

d. SUMMARY/RECOMMENDATIONS

A lap shear test specimen based on the ASTM D2733 test technique appears to be an excellent means of determining the inner layer adhesion of MLPWB. This method is quite reproducible and allows for establishing quantitative data as well as providing a way for determining failure modes within a multilayer configuration.

Peel testing using a floating roller peel testing per ASTM D3167 also provides for a more controlled and reproducible method for determining the peel strength of copper foil to laminate materials.

It is recommended that the merits of each tester be evaluated by the recognized leader of printed circuit technology, namely, The Institute for Interconnecting and Packaging Electronic Circuits (IPC). If proven acceptable to IPC, most likely they would generate the proper specifications and documentation which would then be disseminated to the printed circuit board industry.

4. SURFACE TREATMENTS FOR COPPER

a. CURRENT INDUSTRY TREATMENTS AND THEIR COMPARATIVE ADHESION STRENGTH

At the beginning of this program, the primary surface treatment for inner layer copper surfaces of a MLPWB was based on cupric (black) oxide solutions. While such treatments had proved adequate for epoxy-copper interfaces, they were very inconsistent for polyimide-copper interfaces. The inadequacy of the black oxide when used with polyimide is most likely caused by two distinctly different elements. First, polyimides do not have the inherent high adhesive qualities of epoxies and as such do not produce high strength bonds. Secondly, it is believed that the long needle-like structure of the black oxide surface can break during the higher temperature processing required for polyimides. This obviously will lead to reduced bond strength at the polyimide-copper interface.

Double treated copper polyimide laminates have been available for several years and have peel strengths in the 6-9 pounds per inch width (ppi) range. A preliminary evaluation of double treated copper and two available commercial treatments for copper was performed. The results shown in Table 4 confirm the high peel strength of double treated copper and the poor peel strength of the other available treatments. The adhesion of double treated copper is attained by severe etching of the copper producing a very high surface area. Unfortunately,

Table 4 Peel Strength Tests (Material Mica)

Copper Surface Treatment (Ferric Chloride Plus)	Peel Strength, (Pounds per inch width)
1 minute immersion in Commercial Treatment No. 1 (Mixed Oxides)	0.72 avg. (14 specimens) (1.35 high; 0.35 low)
2 minutes immersion in Commercial Treatment No. 1	1.15 avg. (12 specimens) (3.0 high; 0.45 low)
10 minute immersion in Commercial Treatment No. 1	2.10 avg. (12 specimens) (2.45 high; 1.45 low)
1 minute immersion in Commercial Treatment No. 2 (Black Oxide)	2.27 avg. (12 specimens) (2.45 high; 1.95 low)
2 minutes immersion in Commercial Treatment No. 2	3.04 avg. (14 specimens) (3.45 high; 1.55 low)
10 minutes immersion in Commercial Treatment No. 2	1.87 avg. (14 specimens) (2.25 high; 1.55 low)
As Received Double Treated Copper	8.84 avg. (14 specimens) (9.25 high; 7.95 low)

TABLE 5 PREVIOUS STUDY DATA ON PEEL STRENGTH OF POLYIMIDE

Surface Treatment	Peel Strength, ppi
Power scrubbed, untreated	4.2 (epoxy for comparison)
Power scrubbed, untreated	.2
Double treated copper	3.5 - 6.4
Red oxide, low alkalinity	.5 - 1.1
Red oxide, high alkalinity	.5 - .9
Red oxide on scrubbed double treated copper	3.8
Ferric chloride/HCL etch	2.7
Copper sulfate	.7
Chromic acid	.1
Vapor honed	0 - .2
Ammonium persulfate (sulfuric acid)	.1

(450 psig; 365°F cure -2 hours; 450°F post-cure -4 hours)

such double treated copper is not normally amenable for inner layer copper surfaces of sophisticated MLPWB. The photoresist material of a film type will sit on the top of the spikes of the copper surface. Subsequent etching of circuits will result in an exceptional amount of undercutting of the copper. Liquid photoresists present problems in that they become entrapped in the high surface area and cannot be readily removed. In the late 1970's, several sources reported some success with cuprous (red) oxide solutions for polyimide-copper interfaces. These solutions based on sodium chlorite were reported to give improved peel strengths over the black oxide treatments. Our previous work in this time frame showed that the red oxide did not show any particular promise except when used on scrubbed double treated copper (see Table 5). Ferric chloride/HCL etch also appeared as a possible treatment for copper at the time.

b. MATRIX TEST OF COPPER SURFACE TREATMENT AND LAMINATING CONDITIONS

Evaluation of Polyimide Laminates - Our preliminary data indicated that ferric chloride or copper oxide treatment for copper, or a possible combination process using each treatment should be further explored. It was also not yet fully established as to what the optimum laminating temperature should be for polyimides. Therefore, a matrix was developed as shown in Figure 3 to explore these various combinations. The ferric chloride treatment was to be performed as follows:

1. Pumice Scrub
2. Water Rinse
3. Oven Dry 150°F
4. 30 sec. Immersion 50% Ferric Chloride/50% HCL at Room Temperature
5. Hot Water Rinse - 30 seconds
6. 30 Second Immersion 25% HCL
7. Hot Water Rinse
8. Blow Dry
9. Oven Bake 130°F - 15 minutes

The oxide treatment was to be performed as follows:

1. Pumice Scrub
2. Water Rinse
3. Oven Dry 150°F
4. 30 second Immersion in the Following Solution:
   30 gm/l Sodium Chlorite
   5 gm/l Sodium Hydroxide
   10 gm/l Tri-sodium Phosphate
   160° - 180° F
5. Hot Water Rinse
6. Blow Dry
7. Oven Bake 150°F - 15 minutes

The lamination lay-up for the samples fabricated in the matrix was chosen again because of the performance in previous work, and was as follows:

4 sheets Kraft paper .010" thick
Laminating Plate 6" x 8"

	COLD PRESS				HOT PRESS				TREATMENT
300 psi	Ambi-ent	275°F	312°F	340°F	Ambi-ent	275°F	312°F	340°F	
ATLANTIC LAMINATES									Red Oxide
									Ferric Chloride
									Red Oxide/$FeCl_3$
MICA CORP									Red Oxide
									Red Oxide/$FeCl_3$
									Ferric Chloride

FIGURE 3 MATRIX OF COPPER SURFACE TREATMENTS STUDY

1 sheet Teflon glass .010" thick
1 piece .062" polyimide 1/1
4 pieces 108 Polyimide "B" stage
1 piece .004" core Polyimide 1/1
4 pieces 108 Polyimide "B" stage
1 piece .062" Polyimide 1/1
1 sheet Teflon glass .010" thick
Laminating plate 6" x 8"
4 sheets Kraft paper .010" thick

A thermocouple was inserted into the center of the package and the rate measured. The second variable evaluated during this set of experiments was the lamination cycle. The final pressure of 300 psi would remain constant. The temperature at which the pressure was applied was from ambient to 340°F. For this set of experiments, the fastest (hot press) and the slowest (cold press) were chosen. After fabrication, the samples were post cured at 425°F for four hours and then tested. The lamination cycles for the cold and hot presses are shown in Figures 4 and 5.

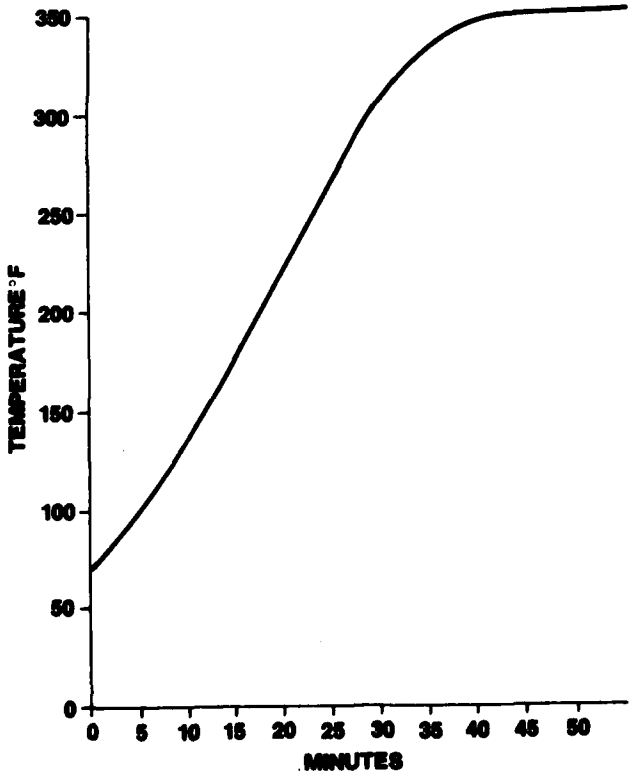


FIGURE 4 COLD PRESS CYCLE FOR LAMINATION

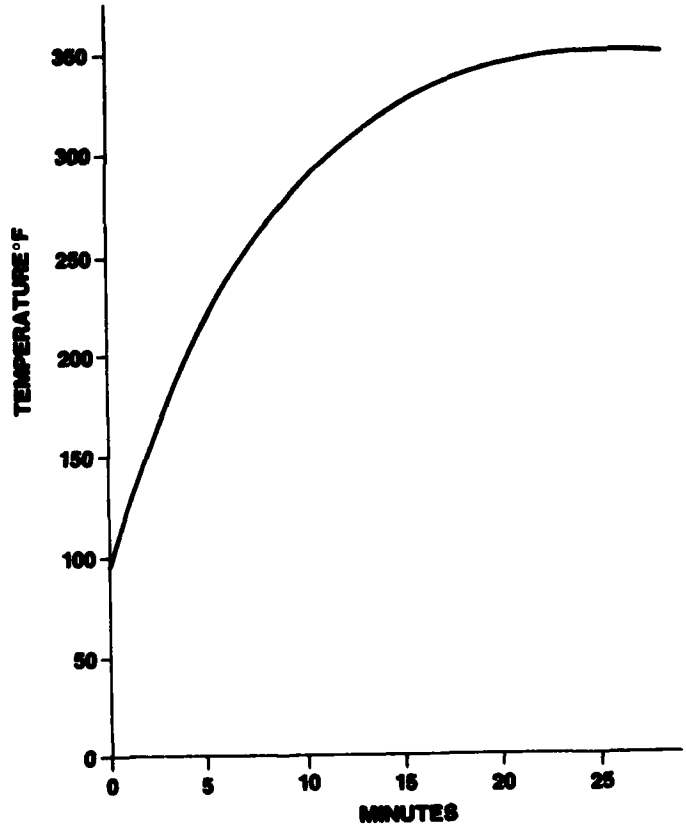


FIGURE 5 HOT PRESS CYCLE FOR LAMINATION

Eight samples were initially made per the matrix, all with ferric chloride surface treatment and the hot press cycle. A sample made with Atlantic laminate material with 300 psi applied at 275°F delaminated during post bake. The delamination occurred between the inner copper layer of the .062" material and the 108 "B" stage. A sample made with the Mica material with 300 psi applied at 340°F also delaminated after post bake during normal handling.

The samples which delaminated all exhibited bowing, i.e., the outer layer of 62 mil material appeared to have been in compression (see Figure 6). It was believed that not controlling the warp and woof orientations of the 0.062" sections of the adhesive sample lead to a greater thermal mismatch than expected. At the time, we believed that variations in the coefficient of expansion were the primary reason for delamination. Subsequent analysis however indicated that the induced stresses were relatively small and not a significant contributor to the delamination. Subsequent samples were then made using ferric chloride alone as the copper surface treatment and a set of samples using ferric chloride etch followed by the red oxide treatment were made. These results are shown in Tables 6 & 7.

From this data, it was seen that there is a higher shear strength for the laminate with the red oxide tratment in the range of 3 to 1. Tensile shear tests were run at temperatures up to 200°C. Specimens were put in the temperature chamber and allowed to soak for 15 minutes at temperature and then loaded. Test temperatures up to 200°C had no effect on the shear strength. The panel with only the ferric chloride had a tendency for lower shear strength the further the test specimen was taken from the edge. Figure 7 shows the effect.

Three other test panels were prepared with only the ferric chloride treatment. In these cases, pressure was not applied during the laminating cycle until the panel had reached 171°c (380°F), 156°C (312°F) and 135°C (275°F) respectively. All three panels delaminated either during the post cure bake at 232°C (425°F) or when cut into specimens. The delaminated panels bowed at the centers. This tendency to bow in the center is probably why the results in Table 7 show a decrease in shear strength the greater the distance from the edge. Additional samples were made to evaluate the effects of the copper surface treatments, namely ferric chloride alone, red oxide alone and a combination of these.

This data showed the red oxide treatment as satisfactory for achieving good adhesive bonding. The ferric chloride surface treatment did not result in as great an adhesive strength. However, a combination of a ferric chloride treatment followed by the red oxide had the highest strengths as shown by specimen No. 24722-2 in Table 8. In these specimens, the fracture occurred through the polyimide and not at the adhesive interface. Under these test conditions, this is the maximum adhesion strength that can be measured. For the lower strength ferric chloride treated material specimen groups 28117-7 and 28117-8 there is an indication that application of the laminating pressure at the lower temperature 135°C instead of 156°C resulted in higher shear strength. It should be noted that these values are well below those obtained for the red oxide treated material.

Comparing specimen groups 24722-1 and 28117-10, where the only difference was one was cooled under pressure from the laminating temperature and the other was not, there is no difference in shear strength. The surface treatment was the significant parameter not the pressure/temperature sequence during lamination. There was concern that heating the laminate under pressure to the final cure temperature as opposed to applying laminating pressure only after it reached the cure temperature may result in internal stresses at the adhesion interface. The data did not indicate that this was a factor. Cooling under pressure after laminating was not a factor either.

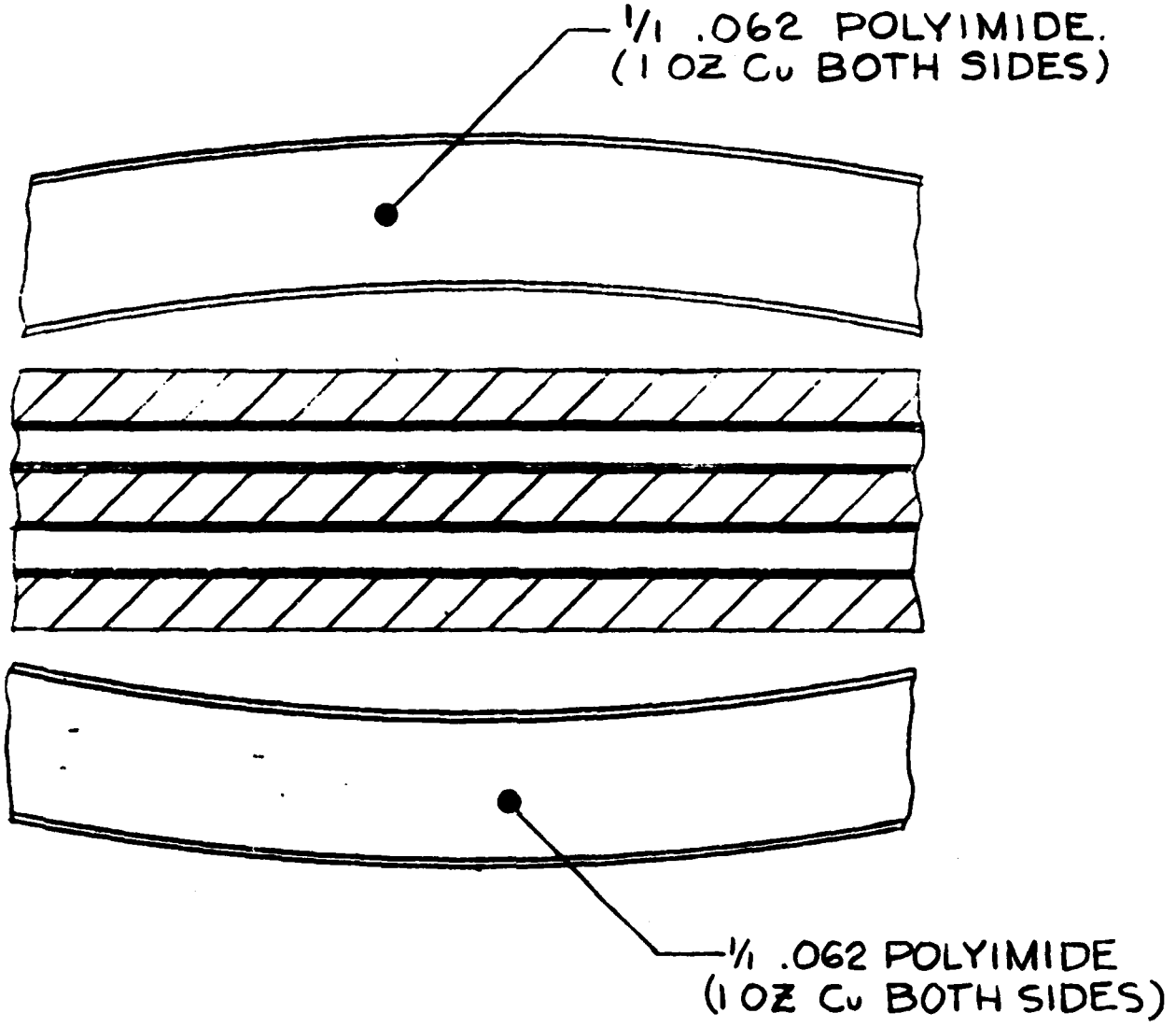


FIGURE 6 CROSS SECTION OF DELAMINATED POLYIMIDE

SAMPLE FROM
ANSI/ASTM D2733-70

4 PLY 108 POLYIMIDE PREPREG

1/1 .005 POLYIMIDE
(1 OZ Cu BOTH SIDES)

TABLE 6 - SHEAR STRENGTH OF LAMINATES WITH INNER COPPER SURFACES TREATED WITH $FeCl_3$ AND RED OXIDE

Oak-Atlantic Material

Polyimide Prepreg Standard Laminate

Low pressure (15 psig) to 135°C (275°F) then full pressure (300 psi) to final cure (182°C - 360°F) 1-1/2 hours

Post cure four hours @ 232°C (450°F)

Inner surfaces treated with $FeCl_3$ followed by red oxide treatment

Tensile Shear Test per ASTM D2733

Test Temp.	Max. Load (lbs.)	Calculated Shear Strength (psi)
23°C	309	1236
"	600	2400
100°C	Broke on Twisting	
"	340	1360
200°C	418	1677
200°C	464	1856

Fracture occurred in all cases between inner copper layer of 0.062" board and "B" stage.

SEM/EDAX analysis shows copper on both sides of fracture surface.

TABLE 7 - SHEAR STRENGTH OF LAMINATES WITH INNER COPPER SURFACES TREATED WITH FERRIC CHLORIDE ONLY

Oak - Atlantic Material

Laminated in Hot Press (182°C/360°F) at 300 psi for 1-1/2 hours.

Post Cure at 4 hours at 218°C/425°F

Surface given $FeCl_3/HCl$ Treatment only - NO Red Oxide

Tensile Shear Test per ASTM D2733

Test Temp., °C	Specimen* No. from Edge	Max. Load (lbs.)	Calculated Shear Stress (psi)
23	4	197	788
23	5	Broke on Handling	
23	6	142	568
100	3	210	840
100	7	94	376
200	8	Broke on Handling	
200	2	167	668

* half inch wide specimens were cut from 6" x 8" plate and numbered consecutively.

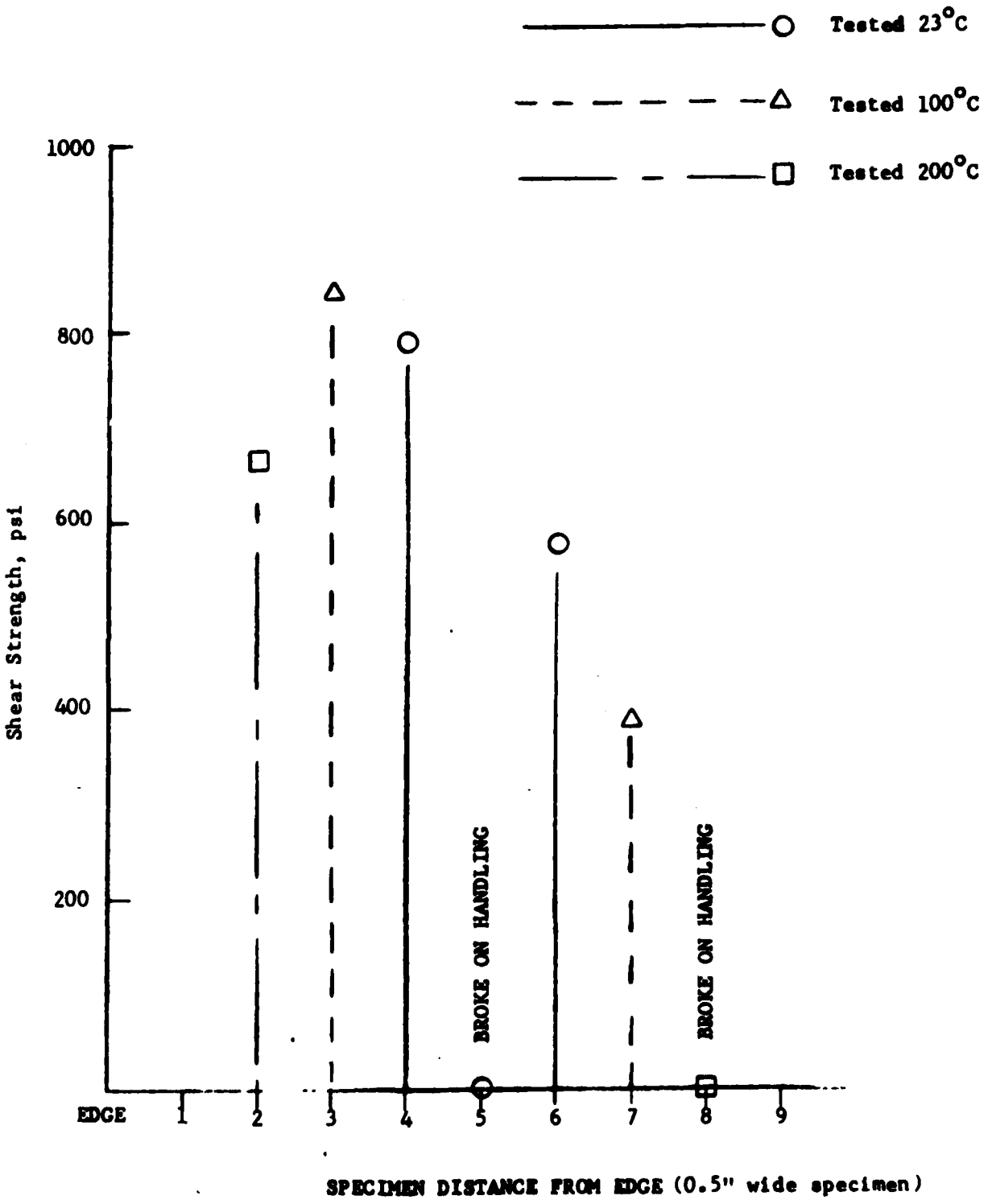


FIGURE 7 SHEAR STRENGTHS VERSUS DISTANCE OF SPECIMEN FROM THE EDGE

TABLE 8 - SHEAR STRENGTH OF LAMINATES WITH VARIOUS SURFACE TREATMENT AND PRESS CONDITIONS

Specimen ID	Material	Surface Treatment	Laminating Parameter	Test Temperature °C	Shear Stress at Bond Failure (psi)
28117-7	Mica 040019-1	Ferric Chloride (30 sec.)	A	23	348
				23	348
				100	340
				100	344
				200	300
				200	396
28117-8	Mica 040019-4	Ferric Chloride (30 sec.)	B	23	548
				23	569
				100	396
				100	436
				200	536
				200	416
28117-11	"B" Stage Atlantic 108	Red Oxide Treatment 30 Sec. - 88°C (190°F)	C	23	1304
				23	1464
				200	760
24722-1	"B" Stage Atlantic 108	Red Oxide Treatment 3 Min. - 93°C (200°F)	D	23	1040
				23	1240
				200	1240
24722-2	"B" Stage Atlantic 108	Ferric Chloride - 1 Min. Red Oxide 3 Min. - 93°C	D	23	1524
				23	1668
				200	1912
				200	1456
28117-10	"B" Stage Atlantic 108	Red Oxide Treatment 3 Min. - 88°C (190°F)	C	23	956
				23	1016
				23	1164

Table 8 (con't)

NOTE: Designation for Laminating Parameter

A. Heat press to 182°C (360°F)
Light pressure to 156°C (312°F)
300 psi at 156°C (312°F)
Full pressure for 2 hours
Post bake 218°C (425°F)/4 hours

B. Heat press to 182°C (350°F)
Light pressure to 135°C (275°F)
300 psi at 135°C (275°F)
Full pressure for 2 hours
Post bake 218°C (425°F)/4 hours

C. Heat press to 177°C (360°F)
Apply 300 psi immediately
Full pressure for 2 hours
Post bake 218°C (425°F)/4 hours

D. Heat press to 177°C (350°F)
Apply 350 psi immediately
Full pressure for 2 hours
Allow to cool under pressure
Post bake 218°C (425°F)/4 hours

As the experimentation continued, it was becoming apparent that the combined ferric chloride/red oxide treatment was superior to either treatment alone. To determine if this were true as process parameters were varied, additional samples were made as follows:

a. Material - Atlantic and Mica

b. Hot press vs. cold press

c. Post bake at 218°C/4 hours. vs. no post bake

d. Higher cure temperature (218°C) and longer cure time (5 hours) but with no post cure vs. normal 177°C cure and 2 hours cure time with post bake at 218°C for 4 hours.

e. Normal cure temperatures 177°C with longer cure time (5 hours) with and without post bake vs. normal time/temperature cure.

f. Red oxide treatment only (no ferric chloride) vs. combined surface treatment.

Specimens from all these samples were tested to failure in shear at 23°C and 200°C. The results are shown in Table 9.

There was no consistent difference in the strength of the Atlantic and Mica material. Shear strength and mode of fracture were approximately the same.

With the standard time/temperature for curing (177°C and 2 hours) and a post bake of 218°C for 4 hours, there was little difference in the hot press vs. the cold press samples (24722-4, -3, -5, -6). Strength values were slightly higher for the cold press samples but, all hot press samples were cohesion failures while two of the cold press samples had mixed adhesion/cohesion failures.

Post bake was necessary to achieve full adhesion strength. Lower strength values and adhesion failures in the non-post baked samples, given the same cure cycle, was evident in samples 24722-7, -8 as compared to 24722-4, -3. The higher strength values at 200°C as against the room temperature strength values for the non-post bake samples (-7, -8) suggested that the testing temperature caused some post bake effects even though the samples were only given a fifteen minute soak at room temperasture before being pulled. The overall average strength for bond strengths generally appear higher near the cure temperature than above or below it as has been previously observed in other systems (see T.E. Baker and J.S. Judge, "Adhesives in the Electronics Industry", Adhesives Age, 23, 15 (1980)).

Curing at higher temperature (218 vs. 177°C) for longer periods (5 hours vs. 2 hours) and eliminating the post cure bake did not achieve full adhesion strength as shown in samples 24722-11, -12 as compared to 24722-4, -3. The lower strengths and adhesion type failures are evident.

TABLE 9 - EFFECT OF VARIOUS PROCESS PARAMETERS ON INTERLAMINAR SHEAR STRENGTH AT ROOM TEMPERATURE AND 200°C

(All copper surfaces given Ferric Chloride and Red Oxide treatment except as noted)

Sample	Material	Hot Press or Cold Press	Cure Temp (°C)	Cure Time	Post Bake (218°C/6 hrs.)	Test Temp (°C)	Shear Stress (psi)	Fracture Mode	Cohesion Adhesion
24722-4	Atlantic	Hot Press	177	2 hrs	Yes	23	1456	Thru Outer "B" Stage	Cohesion
24722-4	Atlantic	Hot Press	177	2 hrs	Yes	23	1640	"B" Stage to Cu	Adhesion
24722-4	Atlantic	Hot Press	177	2 hrs	Yes	200	1760	Inner "B" Stage	Cohesion
24722-4	Atlantic	Hot Press	177	2 hrs	Yes	200	1968	Inner "B" Stage	Cohesion
24722-3	Mica	Hot Press	177	2 hrs	Yes	23	1596	Thru "C" Stage (0.005)	Cohesion
24722-3	Mica	Hot Press	177	2 hrs	Yes	23	1636	Thru "C" Stage (0.005)	Cohesion
24722-3	Mica	Hot Press	177	2 hrs	Yes	200	1828	Thru "C" Stage (0.005)	Cohesion
24722-3	Mica	Hot Press	177	2 hrs	Yes	200	1864	Thru "C" Stage (0.005)	Cohesion
24722-5	Atlantic	Cold Press	177	2 hrs	Yes	23	1728	Thru "C" Stage (0.005)	Cohesion
24722-5	Atlantic	Cold Press	177	2 hrs	Yes	23	2112	Thru "C" Stage (0.005)	Cohesion
24722-5	Atlantic	Cold Press	177	2 hrs	Yes	200	2276	Thru Inner "B" Stage	Cohesion
24722-5	Atlantic	Cold Press	177	2 hrs	Yes	200	2320	Thru Inner "B" Stage	Cohesion
24722-6	Mica	Cold Press	177	2 hrs	Yes	23	1776	Part thru "C" Stage, Part "B" to Cu	Mixed
24722-6	Mica	Cold Press	177	2 hrs	Yes	23	1936	Part thru "C" Stage, Part "B" to Cu	Mixed
24722-6	Mica	Cold Press	177	2 hrs	Yes	200	1568	Thru Inner "B" Stage	Cohesion
24722-6	Mica	Cold Press	177	2 hrs	Yes	200	2240	Thru Inner "B" Stage	Cohesion
24722-7	Atlantic	Hot Press	177	2 hrs	None	23	1424	"B" Stage to Cu	Adhesion
24722-7	Atlantic	Hot Press	177	2 hrs	None	23	1576	"B" Stage to Cu	Adhesion
24722-7	Atlantic	Hot Press	177	2 hrs	None	200	1576	Thru "C" Stage (0.002)	Cohesion
24722-7	Atlantic	Hot Press	177	2 hrs	None	200	1600	Thru "C" Stage (0.002)	Cohesion
24722-8	Mica	Hot Press	177	2 hrs	None	23	1120	Inner "B" Stage to Cu	Adhesion
24722-8	Mica	Hot Press	177	2 hrs	None	23	1364	Inner "B" Stage to Cu	Adhesion
24722-8	Mica	Hot Press	177	2 hrs	None	200	1920	Thru "C" Stage (0.005)	Cohesion
24722-8	Mica	Hot Press	177	2 hrs	None	200	1952	Thru "C" Stage (0.005)	Cohesion
24722-11	Atlantic	Hot Press	218	5 hrs	None	23	1576	Part thru "B" Stage, Part "B" Stage to Cu	Mixed
24722-11	Atlantic	Hot Press	218	5 hrs	None	23	1664	Part thru "B" Stage, Part "B" Stage to Cu	Mixed
24722-11	Atlantic	Hot Press	218	5 hrs	None	200	1336	Part thru "B" Stage, Part "B" Stage to Cu	Mixed
24722-11	Atlantic	Hot Press	218	5 hrs	None	200	1900	Part thru "B" Stage, Part "B" Stage to Cu	Mixed
24722-12	Mica	Hot Press	218	5 hrs	None	23	1120	"B" Stage to Cu	Adhesion
24722-12	Mica	Hot Press	218	5 hrs	None	23	1440	"B" Stage to Cu	Adhesion
24722-12	Mica	Hot Press	218	5 hrs	None	200	1412	"B" Stage to Cu	Adhesion
24722-12	Mica	Hot Press	218	5 hrs	None	200	1492	Thru "B" Stage	Cohesion
24722-14A	Atlantic	Cold Press	177	5 hrs	Yes	23	1608	Thru "B" Stage	Cohesion
24722-14A	Atlantic	Cold Press	177	5 hrs	Yes	23	1572	Part "C" Stage, Part "B" Stage to Cu	Mixed
24722-14A	Atlantic	Cold Press	177	5 hrs	Yes	200	1752	Tensile Fracture	-
24722-14A	Atlantic	Cold Press	177	5 hrs	Yes	200	1976	Thru "B" and "C" Stages	Cohesion

TABLE 9 - EFFECT OF VARIOUS PROCESS PARAMETERS ON INTERLAMINAR SHEAR STRENGTH AT ROOM TEMPERATURE AND 200°C (Cont'd)

(All copper surfaces given Ferric Chloride and Red Oxide treatment except as noted)

Sample	Material	Hot Press or Cold Press	Cure Temp (°C)	Cure Time	Post Bake (218°C/4 hrs.)	Test Temp (°C)	Shear Stress (psi)	Fracture Mode	Cohesion Adhesion
24722-14B	Atlantic	Cold Press	177	5 hrs	None	23	808	"B" Stage to Cu	Adhesion
24722-14B	Atlantic	Cold Press	177	5 hrs	None	23	600	"B" Stage to Cu	Adhesion
24722-14B	Atlantic	Cold Press	177	5 hrs	None	200	1544	Thru "B" Stage	Cohesion
24722-14B	Atlantic	Cold Press	177	5 hrs	None	200	1536	Tensile Fracture	-
24722-15A	Mica	Cold Press	177	5 hrs	Yes	23	1288	"B" Stage to Cu	Adhesion
24722-15A	Mica	Cold Press	177	5 hrs	Yes	23	1200	"B" Stage to Cu	Adhesion
24722-15A	Mica	Cold Press	177	5 hrs	Yes	200	1124	Part thru "C", Part "B" to Cu	Mixed
24722-15A	Mica	Cold Press	177	5 hrs	Yes	200	1340	Thru "B" Stage	Cohesion
24722-15B	Mica	Cold Press	177	5 hrs	None	23	1080	Thru "B" Stage	Cohesion
24722-15B	Mica	Cold Press	177	5 hrs	None	23	1072	Thru "B" Stage	Cohesion
24722-15B	Mica	Cold Press	177	5 hrs	None	200	1528	Thru "B" Stage	Cohesion
24722-15B	Mica	Cold Press	177	5 hrs	None	200	1680	"B" Stage to Cu	Adhesion
24722-16	Atlantic*	Cold Press	177	3 hrs	Yes	23	744	"B" Stage to Cu	Adhesion
24722-16	Atlantic*	Cold Press	177	3 hrs	Yes	23	1040	"B" Stage to Cu	Adhesion
24722-16	Atlantic*	Cold Press	177	3 hrs	Yes	200	1240	"B" Stage to Cu	Adhesion
24722-16	Atlantic*	Cold Press	177	3 hrs	Yes	100	1316	"B" Stage to Cu	Adhesion
24722-17	Mica*	Cold Press	177	3 hrs	Yes	23	1540	Thru "B" Stage	Cohesion
24722-17	Mica*	Cold Press	177	3 hrs	Yes	23	1480	"B" Stage to Cu	Adhesion
24722-17	Mica*	Cold Press	177	3 hrs	Yes	200	1520	"B" Stage to Cu	Adhesion
24722-17	Mica*	Cold Press	177	3 hrs	Yes	200	1288	"B" Stage to Cu	Adhesion

*Red Oxide Treatment Only/No Ferric Chloride

Samples 24722-14A, -14B, -15A, -15B show the longer curing time does not eliminate the need for the post bake with the cold press. The most consistent data in these series of tests emphasize the need for the post bake.

These studies indicated that best results are obtained with the ferric chloride treatment followed by the red oxide treatment, cold or hot press, laminate at 177°C for 2 hours and post bake at 218°C for 4 hours using either Atlantic or Mica material. In this case, the bonds formed will exceed the cohesive strength of the bonding material.

c. EFFECT OF SURFACE TREATMENT ON EPOXY LAMINATES

The effect of surface treatment on copper for epoxy laminates was also evaluated. One set of samples was made using no copper treatment except for a good cleaning. A second set was fabricated using the ferric chloride/hydrochloric acid pre-etch with a red oxide treatment. Table 10 shows the results with conventional epoxy glass materials. Again the superiority of adhesion at room temperature with the ferric chloride/red oxide treatment was apparent (Δ900 psi out of $\sim$2000 psi). In addition, the mode of failure changed from adhesive failure without the treatment to tensile (or cohesive) failure with the treatment. Again there was evidence of increased bond strength at elevated temperature (100°C) until at 200°C in all cases the "B" stage adhesion fails at very low values ($\sim$200 psi). This temperature is sufficiently above Tg for these materials and the epoxy has undoubtedly softened significantly. It was decided at this point in the study that all further efforts would be directed towards polyimide MLPWB since they posed the more difficult problem.

d. HYDROLYTIC STABILITY OF FERRIC CHLORIDE/RED OXIDE TREATED COPPER SURFACES

To obtain a rapid indication of the hydrolytic stability of the ferric chloride/red oxide treated copper surfaces, pressure cooker tests were conducted. Samples of the optimized system were subjected to steam in a pressure cooker at 121°C (250°F) at 15 psig for 8 hours and in some cases 16 hours.

These results are shown in Table 11. The previous results for unexposed panels are shown and directly underneath are the results after the panels have been pressure cooked. Mica and Oak-Atlantic material were used; panels with the standard surface treatment and those with the shorter one minute red oxide treatment were also used. In all cases, there was no evidence of bond deterioration even after 16 hours.

Some question was raised as to the reliability of this testing in the superheated steam because the outside copper sheet can act as a shield. However, the edges are exposed and it was subjected to the steam for 8 and in some cases, 16 hours. There was no deterioration at the edges. These tests indicated that the bond was stable.

e. STANDARD MATERIALS AND PROCESSES

From the studies to this point of the investigation the following materials and processes were considered as standard:

NOTE: The sodium chlorite used was technical grade and only 80% pure. The sodium hydroxide was also technical grade. The sodium phosphate was also technical grade and purchased as sodium phosphate, tribasic 12-hydrate.

TABLE 10 - SHEAR STRENGTHS OF EPOXY LAMINATES
WITH/WITHOUT OXIDE TREATMENT

Lap Shear Results for Epoxy Laminates

Sample #	Test Temp. (°C)	Surface Treatment	Shear Stress (psi)	Fracture Mode
8147-9-1	23	Clean Only	1768	Shear, "B" stage to Cu
	23		1788	
	100		2520	Tensile failure
	200		200	Shear, "B" stage to Cu
8147-9-2	23	Clean Only	1800	Shear, "B" stage to Cu
	23		2172	
	100		3000	Tensile
	200		120	Shear, "B" stage to Cu
8147-3	23	Clean Only	2248	Shear
	23		1840	
	100		2480	
	200		144	
8147-4	23	$FeCl_3$ + red oxide	3104	Shear
	23		2770	Tensile failure
	100		2380	
	200		128	Shear
8147-5	23	$FeCl_3$ + red oxide	2528	Tensile
	23		2856	
	100		2400	
	200		240	Shear

Table 11 Hydrolytic Stability of Selected Laminate Samples

Panel 24722-6 (Mica) - Standard Surface Treatment and Cure

Spec. No.	Test Temp, °C	Shear Strength	Fracture Mode
1	23	1776 psi	Mostly cohesive thru "C" stage
2	23	1936 psi	
3	200	1568 psi	Cohesive thru "B" stage
4	200	2240 psi	

Panel 24722-6 - Above Panel Subjected to 121°C (250°F) at 15 psig Steam for 8 Hours

1	23	1424 psi	Cohesive thru "C" stage
2	23	1416 psi	
3	200	1750 psi	
4	200	2008 psi	

Panel 24722-22 (Mica) - Standard Surface Treatment Except Only One Minute in Red Oxide Solution

1	23	1968 psi	Cohesive thru "B" stage
2	23	2060 psi	
3	200	1816 psi	Adhesive "B" stage to copper
4	200	1852 psi	Cohesive thru "B" stage

Panel 24722-22 - Above Panel Subjected to 121°C (250°F) at 15 psig Steam for 8 Hours

1	23	1720 psi	Cohesive thru "C" stage
2	23	1624 psi	
3	200	1840 psi	Cohesive thru "B" and "C" Stages
4	200	1976 psi	Cohesive thur "B" stage

Panel 28147-10-7 - Epoxy with Red Oxide Treatment

1	23	2448 psi	Mostly cohesive thru "B" stage
2	23	2592 psi	
3	100	2176 psi	Tensile
4	100	3328	Cohesive thru "B" stage

Table 11 Hydrolytic Stability of Selected Laminate Samples (Continued)

Panel 28147-10-7 - Above panel subjected to 121°C (250°F) at 15 psig steam for 8 hours (Epoxy)

1	23	2800 psi	Cohesive "B" thru "B" stage
2	23	3176 psi	
3	100	3200 psi	Tensile
4	200	280 psi	Cohesive thru "B" stage

Panel 24722-5 (Atlantic) - Standard Surface Treatment and Cure

1	23	1728 psi	Cohesive thru "C" stage
2	23	2112 psi	
3	200	2776 psi	Cohesive thru "B" stage
4	200	2320 psi	

Panel 24722-5 - Above panel subjected to 121°C (250°F) at 15 psig steam for 16 hours

1	23	2180 psi	Cohesive thru "C" stage
2	200	1880 psi	Cohesive thru "B" and "C" stage

Panel 24722-19 (Mica) - Standard surface treatment except only one minute in red oxide solution

1	23	2184 psi	Cohesive thru "B" stage
2	23	2212 psi	Cohesive thru "C" stage
3	200	2068 psi	Cohesive thru "B" and "C" stages
4	200	2128 psi	

Panel 24722-19 - Above panel subjected to 121°C (250°F) at 15 psig steam for 16 hours

1	23	2160 psi	Adhesion "B" stage to copper
2	200	1944 psi	Cohesion thru "B" and "C" stages

Panel 28147-10-6 - Epoxy with Ferric Chloride Etch

1	23	2208 psi	Tensile
2	23	2312 psi	
3	100	2080 psi	
4	200	228 psi	Cohesive "B" stage
5	200	232 psi	

The copper surface treatment which we had found optimum was as follows:

1. Pumice scrub (power brush recommended)
2. Water rinse - warm water
3. Blow dry
4. Ferric chloride/hydrochloric acid etch - 1 minute (50%-50% solution at R.T.)
5. Water rinse - hot water (120-140°F) spray 15-30 seconds
6. 25% hydrochloric acid dip - 1 minute
7. Water rinse - hot water spray
8. Red oxide treatment - 2 minutes @ 190-200°F
9. Water rinse - hot water spray
10. Blow dry

The preferred lamination cycle is as follows:

Hot press (350°F)
3 pieces .010" Kraft paper each side
Full pressure to 350 psi
Heat to 350°F (177°C)
Cure - 2 hours at 350°F
Cool under pressure

At this point, it appeared that the area that required the most attention to determine what controls would be needed, or what improvements if possible, was that of the red oxide treatment for copper. A large portion of the study remaining focused on this subject.

It should also be noted that power scrubbing has been used by us for several years. Proper cleaning of starting materials and also of materials that have been exposed during the photo-etch process is a must. We have not really discussed cleaning in any detail in this report because we feel that power scrubbing is an excellent technique. Many companies who do not power scrub or otherwise totally clean off photo-resist material stand the chance of inner layer delamination from unclean surfaces. Proper cleaning techniques cannot be overemphasized in the fabrication of MLPWB.

f. MODIFICATIONS OF RED OXIDE SOLUTION

Modifications of red oxide solution chemistry were initially made to determine their effects, if any, on the interlaminar adhesion. The chemical variations are shown in Table 12. For specimens 247222-30, and -31 only the sodium chlorite was lowered to 20% of its standard concentration.

Table 12 Modification of Standard Red Oxide Solution

Specimen ID	Sodium Chlorite (grams/liter)	Sodium Hydroxide (grams/liter)	Sodium Phosphate (grams/liter)
Standard Solution	30	5	10
24722-25	6	1.43	2.85
24722-26	12	1.43	2.85
24722-30	6	5	10
24722-31	12	5	10

All panels given a ferric chloride/HCl etch for one minute; two minutes in the Red Oxide solution, and the same laminating cycle.

Material: Mica

Lamination

Hot Press - 177°C (350°F)

Full Pressure - 350 psi

Cure for 2 hours

Cool under pressure

Post cure - 218°C (425°F)/4 hours

Table 13 shows the shear test results. All test panels had been given the same ferric chloride etch, the same two minute dip in the red oxide solution, and the same hot press laminating cycle. It can be seen that the concentration of the oxidizing agent ($NaClO_2$), or of all the chemicals can be lowered over a wide range with only slight effect on the interlaminar adhesion. It is interesting to note that the low chlorite solutions gave shear strengths typical of that obtained when using only ferric chloride. This was a strong indication of the importance of a proper oxide treatment on the copper foil.

To pursue this study in further detail, a matrix of red oxide solutions with wide variations in composition was made. Panels were then made with all copper foil being treated in respective red oxide solutions and peel strengths then measured. Table 14 lists the different variations of the composition used.

Table 14 also shows the analytical results for determining the composition of the bath analytically. We feel that the techniques developed for this analytical characterization are relatively precise. The difference noted in the table between the experimental analysis and the theoretical amount reflects real world conditions. The noted deviations reflect the imprecision built into this type of operation. Precise measurements would require more accurate volumetric equipment normally used in the analysis laboratory but not normally found in the standard printed circuit facility. Even under these conditions it is interesting to note that the deviations in the compositional tolerances are not great.

To study the effect of variations in the oxide bath and also to test the reliability of the new floating roller peel tester, panels were prepared using variations in the oxide bath as shown in Table 14. Each panel had sixteen one-eighth inch wide peel strips. Half of the strip was peel tested using the roller peel tester and the Instron Universal Test Machine and the other half was peel tested by holding the panel by hand on the Instron. Alternate strips were tested by the two fixturing methods.

Table 15 shows the results of the peel testing. The rolling peel tester gave consistently higher value but not ones that would change any conclusions. The adhesion varied considerably as a function of solution concentrations when measured by the peel test. Table 14 gives the solution concentrations "as prepared" and "analyzed". Solution 1, 3 and 4 give adhesion strengths well above those of the rest. Solution 1 had the highest value. Solutions 5 and 6 had the lowest values. Solutions 2 and 7 had intermediate values. The adhesion strength as measured by the peel test would indicate that the oxide solution was insensitive to variation in the sodium chlorite but was sensitive to low concentrations of the hydroxide. A summary of the data for the eight solutions showing descending peel strength, the red oxide solution composition and the weight percentage compositions of the three ingredients is shown in Table 16. Selected samples were also examined using the scanning electron microscope. Photomicrographs at 1200X of the copper foil surface and the polyimide laminate from which the foil was peeled are illustrated in Figures 8 through 17. Examination of these photomicrographs reveals that those solutions that produced the highest peel strengths (No. 1 and No. 8) show rather sharp discrete peaks

Table 13 Shear Strength of Laminates with Red Oxide Solution Modifications

Specimen ID	Test Temp	Shear Stress	Fracture Mode
24722-25-1	23°C	1840 psi	Cohesive thru "C" Stage
-2	23°C	2260	Mostly Cohesive Thru "B" Stage
-3	200°C	1840	Cohesive Thru "C" Stage
-4	200°C	1416	Cohesive Thru "C" Stage
24722-26-1	23°C	2000 psi	Cohesive Thru "B" Stage
-2	23°C	2032	Mostly Cohesive; Partly Adhesive B/Cu
-3	200°C	1784	Cohesive Thru "C" Stage
-4	200°C	1592	Cohesive Thru "C" Stage
24722-30-1	23°C	1336 psi	Cohesive Thru "C" Stage
-2	23°C	1444	Partly Adhesive/Cohesive
-3	200°C	1492	Partly Adhesive/Cohesive
-4	200°C	1264	Partly Adhesive/Cohesive
24722-31-1	23°C	1560 psi	Mostly Cohesive Thru "C" Stage
-2	23°C	1600	Mostly Cohesive Thru "C" Stage
-3	200°C	1840	Cohesive Thru "C" Stage
-4	200°C	1520	Cohesive Thru "C" Stage

Material: Mica

Table 14 Solutions of Red Oxide Bath of Varying Ingredients

	Theor.			Exper.		
Solution	$NaClO_2$	NaOH	Na_3PO_4	$NaClO_2$	NaOH	Na_3PO_4
1	15	10	5	13.7	9.6	5.3
2	30	10	5	28.3	10.8	4.8
3	60	10	5	54.3	10.2	4.8
4	30	5	5	25.4	5.3	3.8
5	30	20	5	27.3	20.7	4.5
6	30	10	2.5	26.6	10.1	2.7
7	30	10	10	26.2	10.5	7.7
8	30	5	10	28.3	5.3	7.8

Table 15 Peel Testing of Panels Made with Red Oxide Solution Variations

Sample	Force Hand	Force Fixture
24722-45-A Solution 1	.50 lbs.	.55 lbs.
	.55	.48
	.42	.56
	.48	.58
	.46	.62
	.50	.56
	.52	.59
	.51	.60
Avg.	.49	.57
24722-45-B Solution 2	.25 lbs.	.30 lbs.
	.25	.31
	.25	.31
	.25	.30
	.25	.30
	.25	.29
	.25	.26
	.25	.23
Avg.	.25	.29
24722-45-C Solution 3	.40 lbs.	.47 lbs.
	.43	.50
	.25	.25
	.50	.32
	.23	.55
	.49	.30
	.41	.45
	.40	.41
Avg.	.39	.41
24722-45-D Solution 4	.45 lbs.	.50 lbs.
	.41	.46
	.43	.49
	.40	.51
	.45	.48
	.45	.44
	.47	.44
	.45	.45
Avg.	.44	.47

Sample	Force Hand	Force Fixture
24722-45-E Solution 5	.08 lbs.	.09 lbs.
	.08	.10
	.07	.09
	.08	.09
	.07	.07
	.09	.23
Avg.	.08	.11
24722-45-F Solution 6	.19 lbs.	.16 lbs.
	.19	.16
	.16	.21
	.18	.17
	.20	.17
	.21	.16
	.19	.20
	.17	.17
Avg.	.19	.18
24722-45-G Solution 7	.33 lbs	.30 lbs
	.35	.27
	.33	.34
	.32	.36
	.30	.39
	.29	.36
	.32	.36
	.35	.35
Avg.	.32	.34

NOTE: The data is presented as force (pounds). The width of strips is 1/8" therefore peel strength may be obtained by multiplying force x 8 which equals pounds per inch width.

Table 16 Variation of Peel Strength as a Function of Varying Composition of Red Oxide Solution

Solution No.	Peel Strength ppi	Red Oxide Solution Composition					
		Grams/Liter			Weight %		
		$NaClO_2$	NaOH	Na_3PO_4	$NaClO_2$	NaOH	Na_3PO_4
1	4.6	15	10	5	50	33.3	16.7
8	4.4	30	5	10	66.7	11.1	22.2
4	3.8	30	5	5	75	12.5	12.5
3	3.3	60	10	5	80	13.3	6.7
7	2.7	30	10	10	60	20	20
2	2.3	30	10	5	66.7	22.2	11.1
6	1.4	30	10	2.5	70.8	23.6	5.8
5	0.9	30	20	5	54.6	36.4	9.1

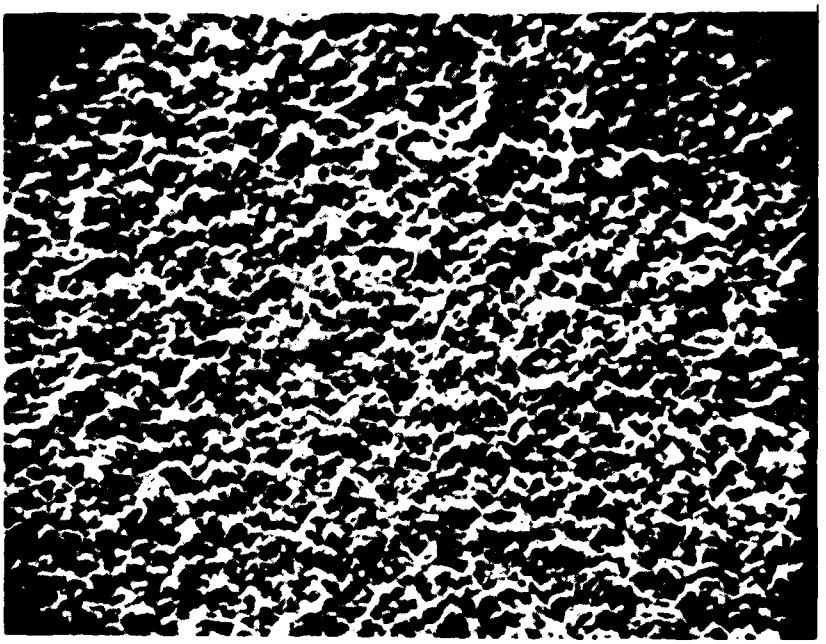


FIGURE 8

Solution No. 1
Copper foil surface
at 1200X.

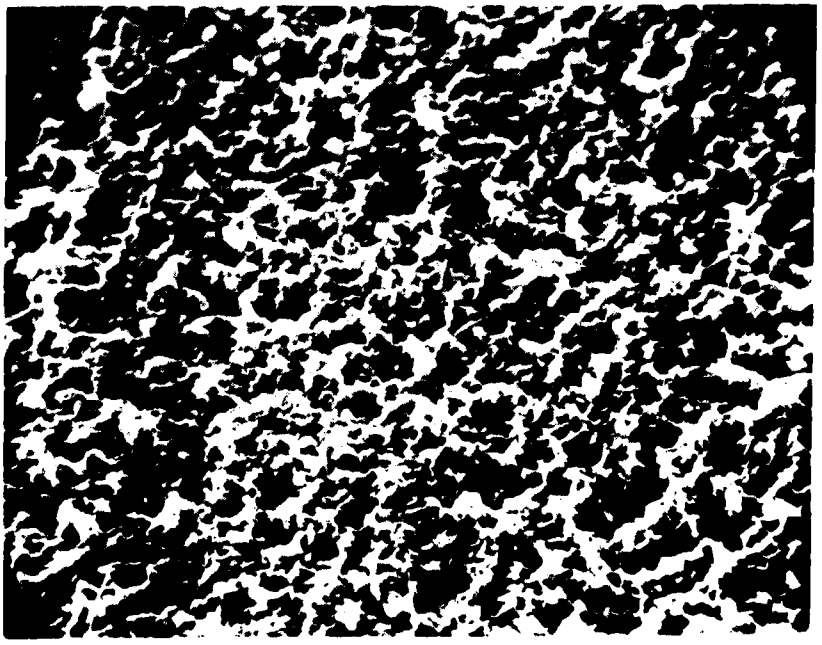


FIGURE 9

Solution No. 1
Polyimide laminate
surface at 1200X.

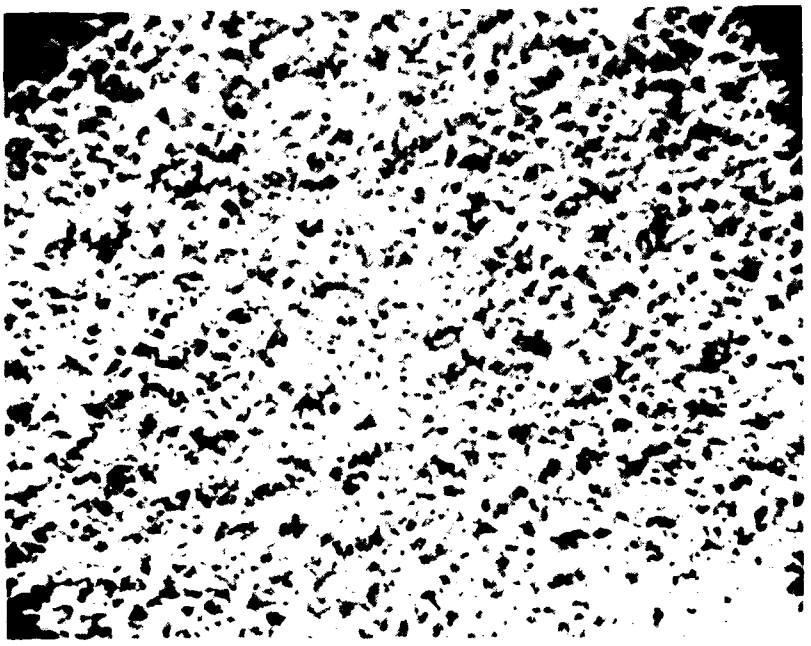


Figure 10

Solution No. 8
Copper foil surface
at 1200X.

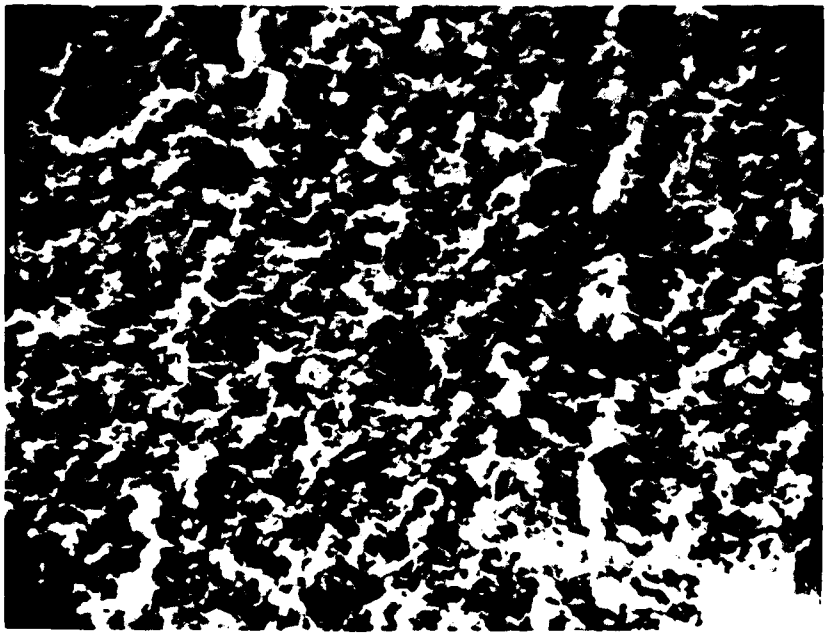


Figure 11

Solution No. 8
Polyimide laminate
surface at 1200X.

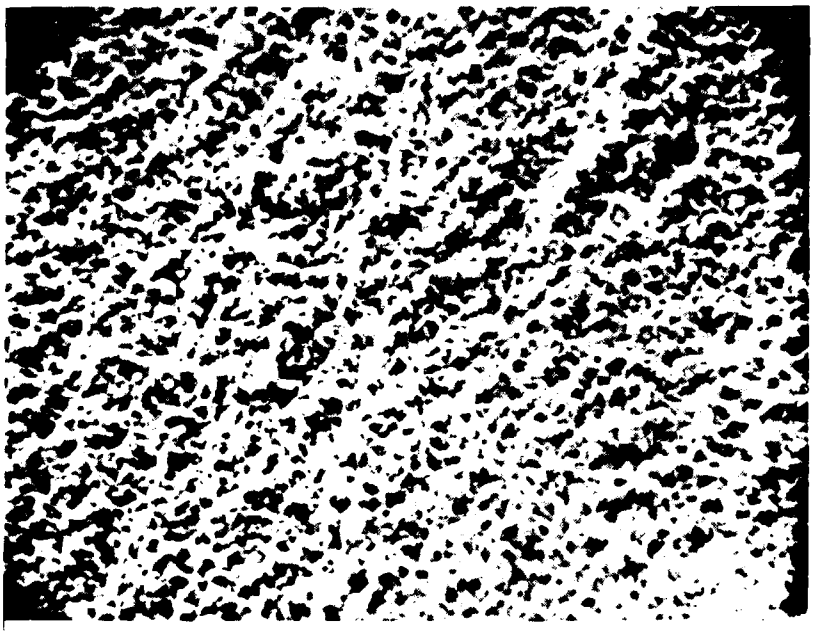


Figure 12

Solution No. 3
Copper foil surface
at 1200X.

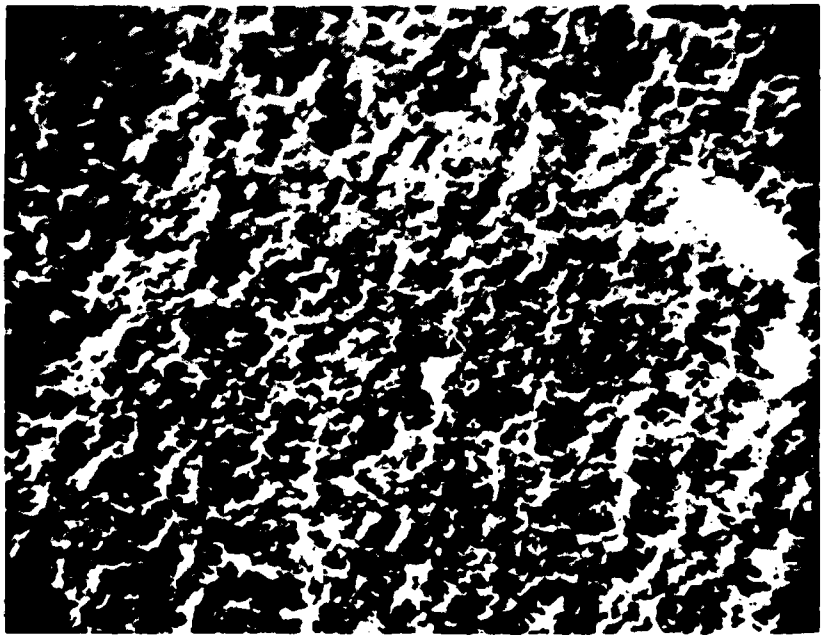


Figure 13

Solution No. 3
Polyimide laminate
surface at 1200X.

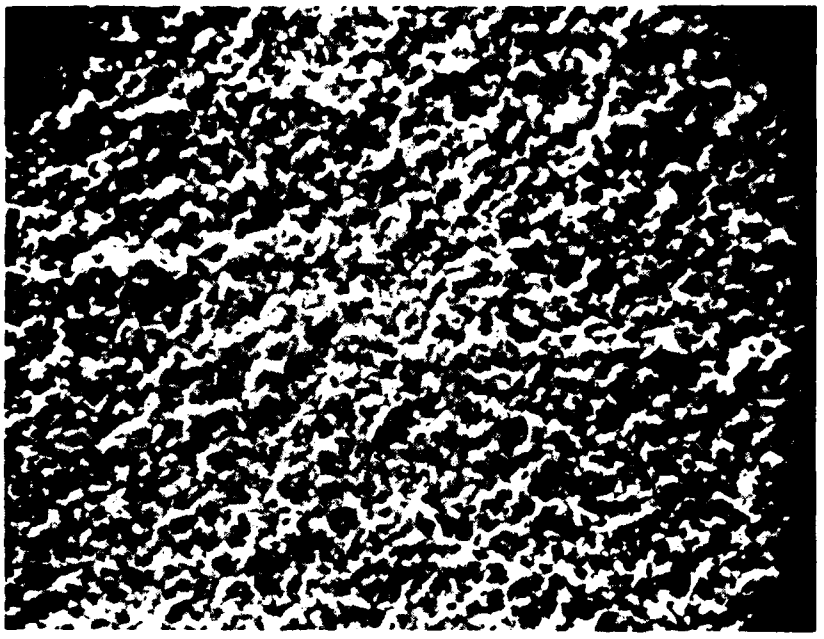


Figure 14

Solution No. 2
Copper foil surface
at 1200X.

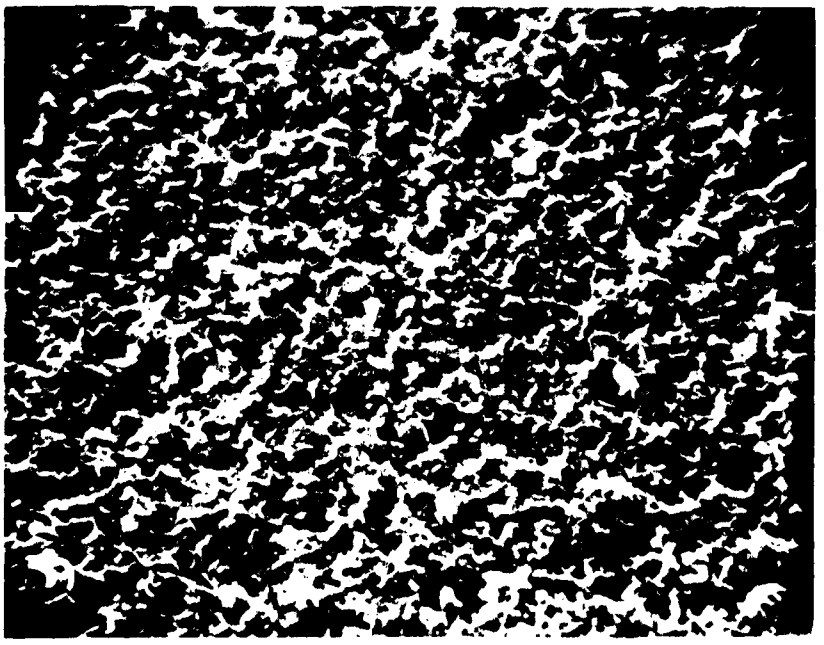


Figure 15

Solution No. 2
Polyimide laminate
surface at 1200X.

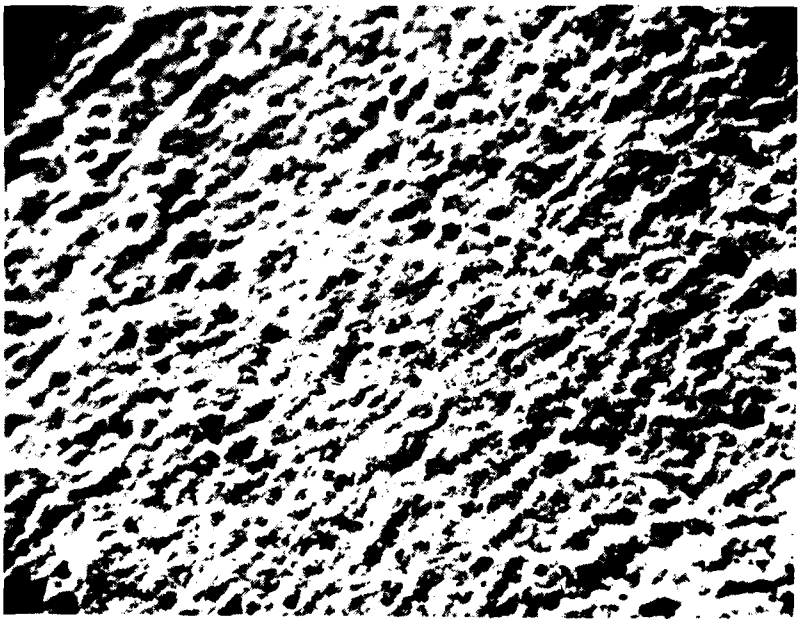


Figure 16

Solution No. 5
Copper foil surface
at 1200X.

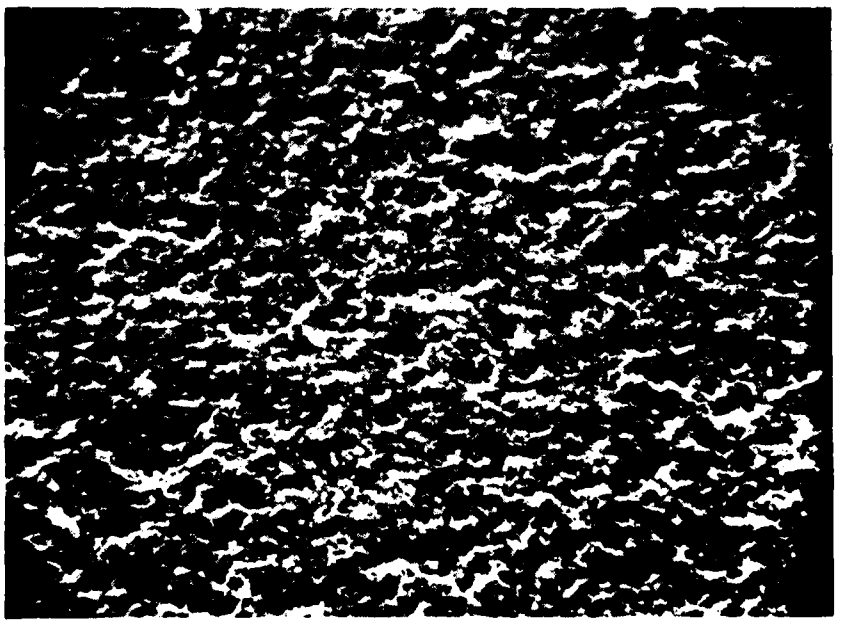


Figure 17

Solution No. 5
Polyimide laminate
surface at 1200X.

Table 17 Variations of Red Oxide Solution and Resultant Peel Strengths

		Red Oxide Solution Composition Grams/Liter		
Solution No.	Peel Strength	$NaClO_2$	NaOH	Na_3PO_4
8	4.4	30	5	10
9	4.7	30	0	10
10	3.5	30	5	0
11	3.5	30	0	0

in the oxide coating. As the peel strength decreases with the solution composition, these peaks become pronouncely more rounded. Figure 16 illustrates this quite clearly. One would assume therefore that the apparent increased surface area produced from Solutions No. 1 and 8 contribute significantly to the resultant peel strength. Also of interest is the corresponding photomicrographs of the polyimide laminates from each foil surface. These indicate that the polyimide has flowed very readily into the red oxide coating and replicated that surface. This of course indicates that the polyimide is readily wetting the red oxide which is a prime requisite for obtaining good adhesion.

Further variations were then made in which the sodium hydroxide was eliminated from the red oxide solution in one sample; sodium phosphate was eliminated in a second sample; and in a third sample, both were eliminated leaving only the sodium chlorite. The results of testing from panels made were quite surprising as shown in Table 17. The variation without sodium hydroxide produced the highest peel strength of all samples tested. The variation using only sodium chlorite also yielded a good peel strength. Photomicrographs of the treated copper and the polyimide laminate interfaces are shown in Figures 18-23.

Photomicrographs were also taken of a plain copper foil surface that had been cleaned by power scrubbing only and also of copper that was power scrubbed and then treated in the ferric chloride solution. Figure 24 shows that a cleaned copper surface has as very low surface area particularly when compared to ferric chloride etched copper as seen in Figure 25. The ferric chloride etched copper shows a dramatic change in topography which is quite striking at higher magnification as shown in Figure 26. The significant increase in surface area produced by the ferric chloride etch must certainly play a major role in producing the increased adheison obtained when using the ferric chloride-red oxide treatment system.

A study was also made to determine the variation of peel strength obtained as a function of the temperature of the red oxide solution. Using the standard red oxide solution of 30-5-10 (g/l sodium chlorite-sodium hydroxide-sodium phosphate) copper foil was processed (after ferric chloride etch) for two minutes in solutions at 180°F, 190°F, 200°F and 210°F. Panels for peel testing were then made using these treated foils. The results as shown in Table 18 indicate that optimum peel strength values were obtained from the 190°F solution. This data verifies previous studies which established a 190 - 200°F range for the temperature of the red oxide solution.

An evaluation of immersion time in the red oxide solution was also made. Copper foil was treated in standard red oxide solutions held at 200°F for immersion times of 1, 3, 5 and 10 minutes. Peel strengths of panels made with these treated copper foils are summarized in Table 19. This data is hard to explain. Optimum peel values are indicated at five minutes immersion time. Compared to the previous Table, 2 minutes in 200°F solution gives a comparable peel value of 5.3 ppi. Apparently six specimens are too small a base and the sampling size would have to increase to establish a more meaningful quantitative data.

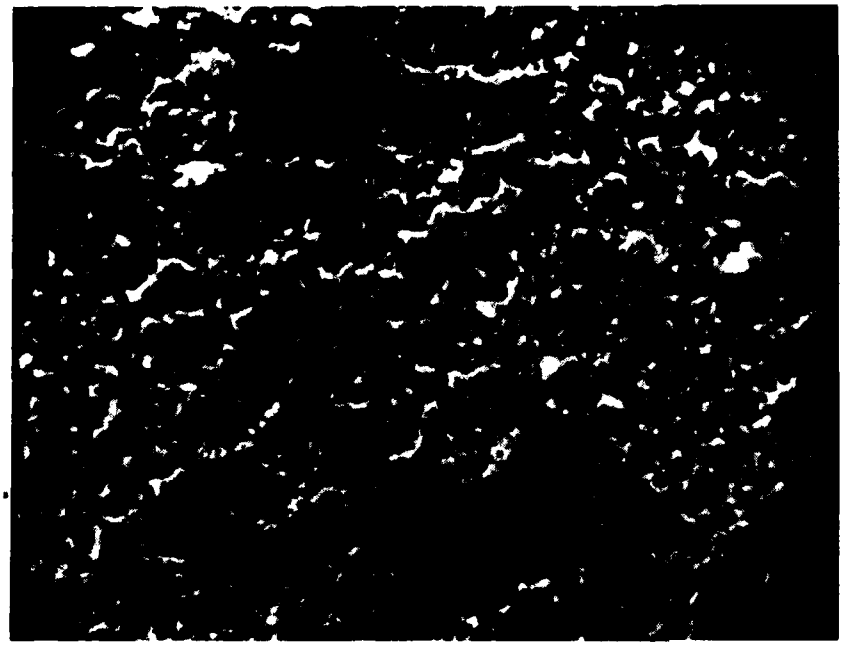


Figure 18

Solution No. 9 (No NaOH)

Copper foil surface
at 1200X.

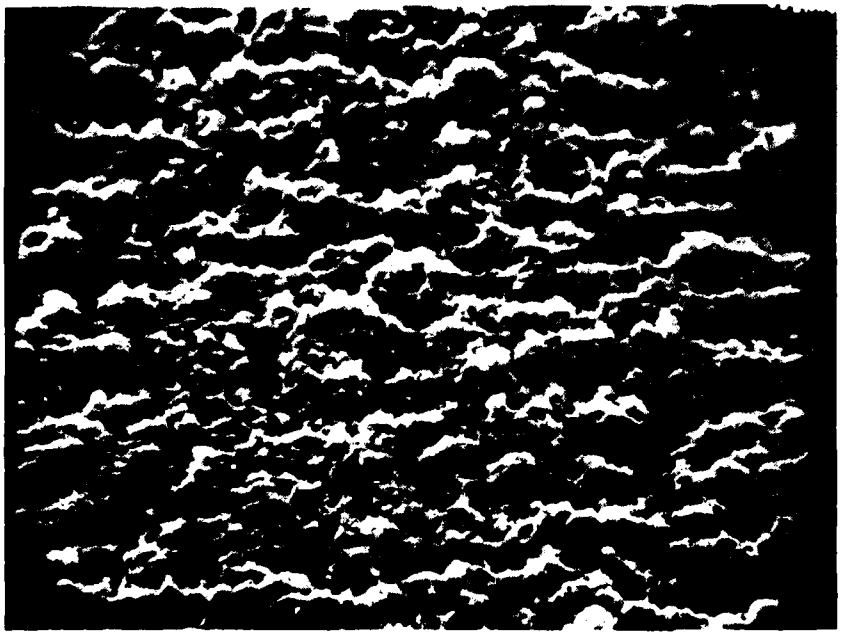


Figure 19

Solution No. 9 (No NaOH)

Polyimide laminate surface
at 1200X.

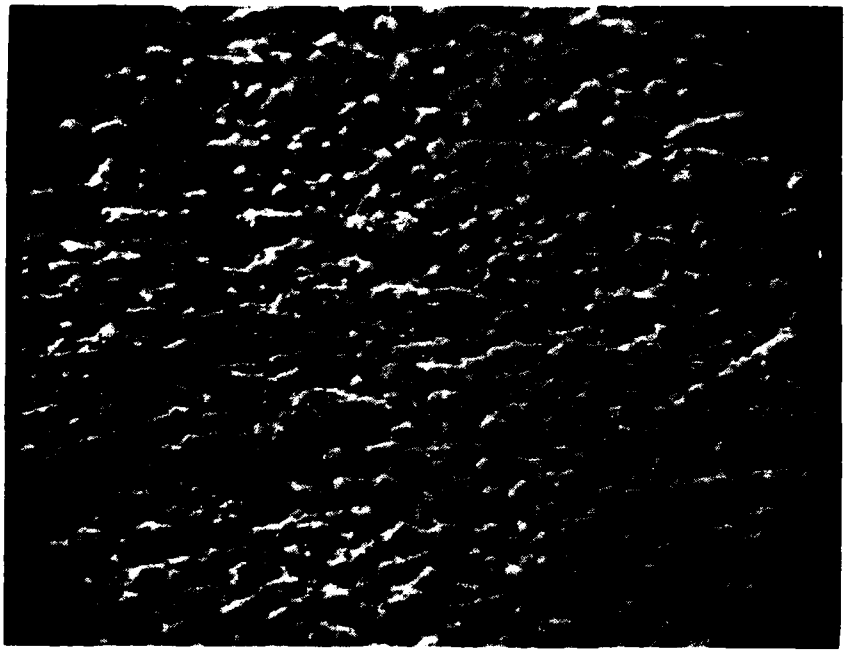


FIGURE 20

Solution No. 10 (No Na_3PO_4)

Copper foil surface at 1200X.

Figure 21

Solution No. 10 (No Na_3PO_4)

Polyimide laminate surface at 1200X.

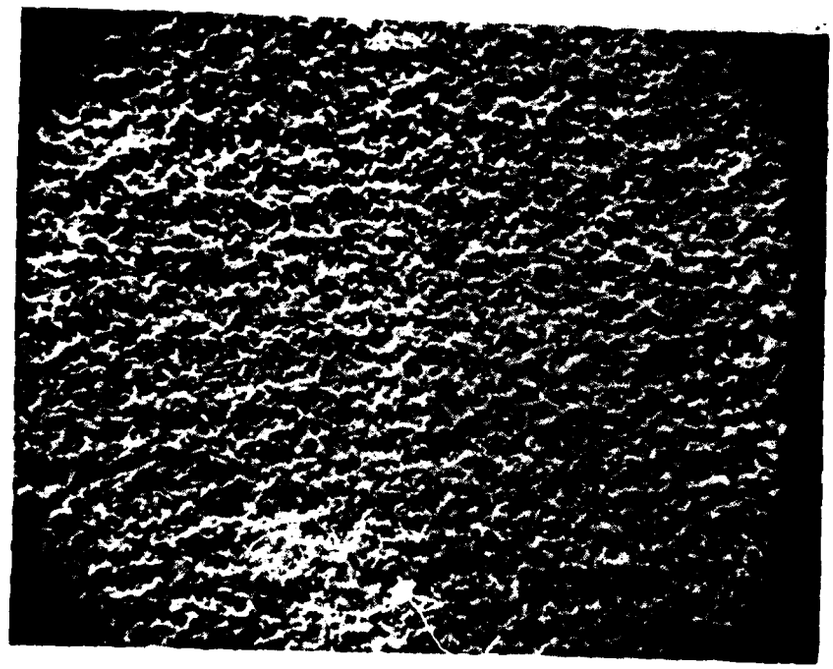


Figure 22

Solution No. 11 (No NaOH, No Na_3PO_4)

Copper foil surface at 1200X.

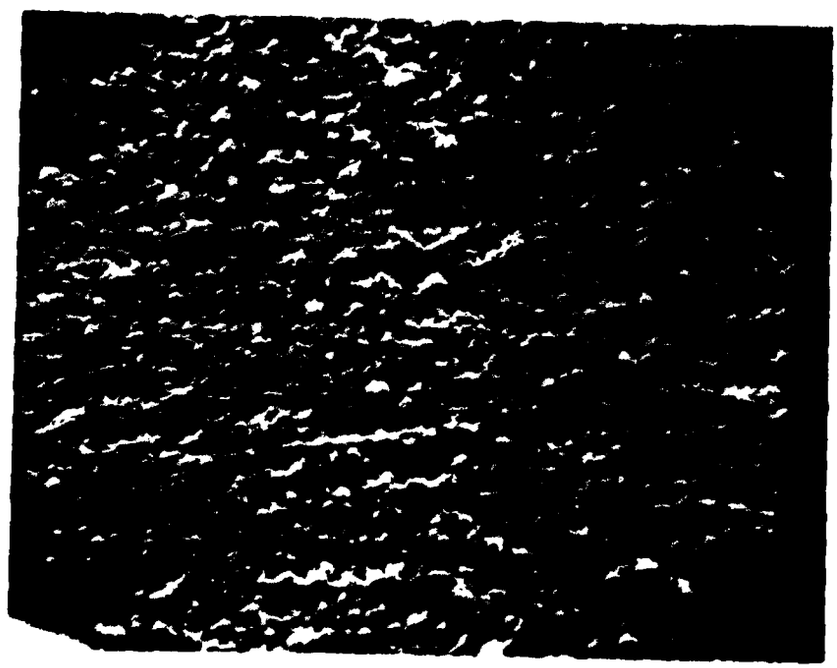


Figure 23

Solution No. 11 (No NaOH, No. Na_3PO_4)

Polyimide laminate surface at 1200X.

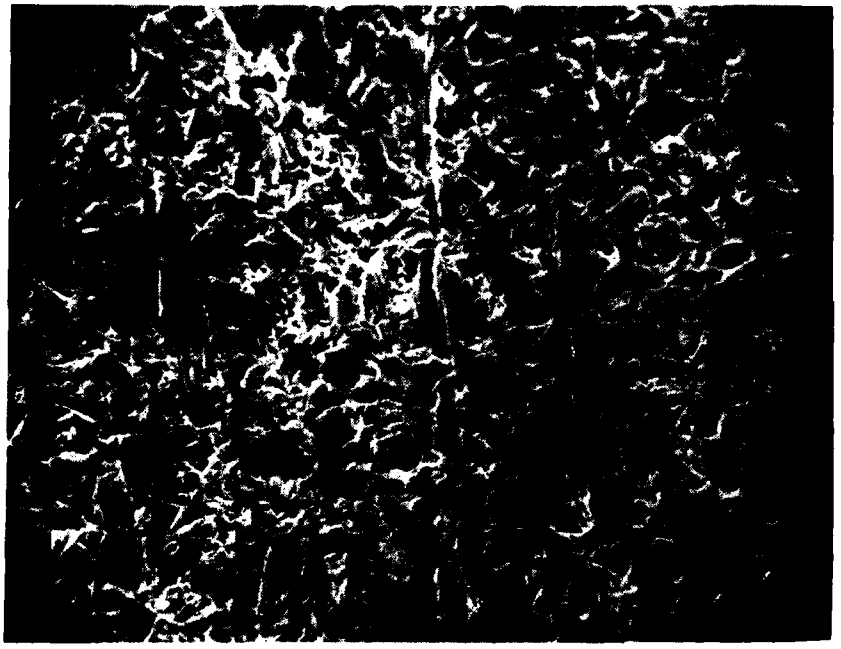


Figure 24

Copper foil surface after power scrubbing at 1200X.

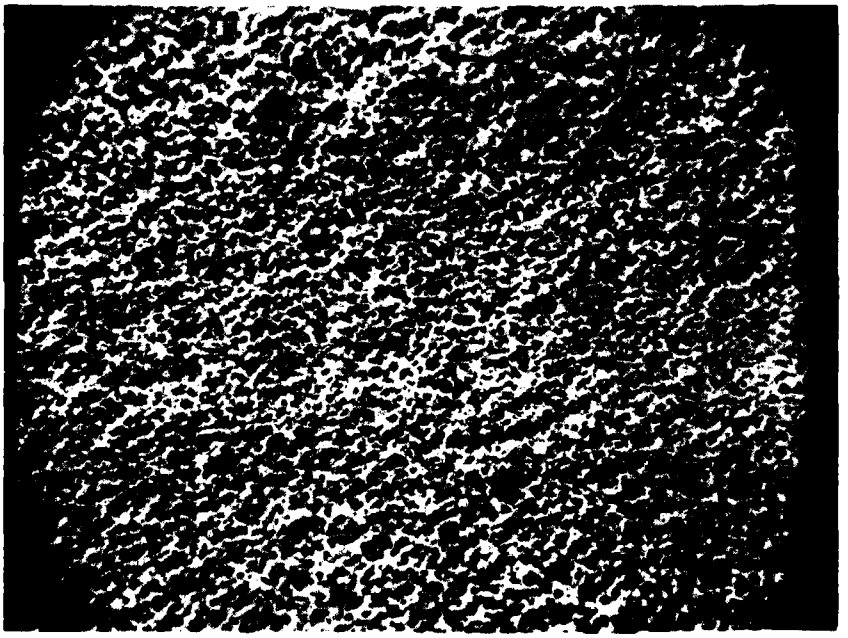


Figure 25

Copper foil surface after power scrubbing and one minute immersion in $FeCl_3$ and HCl (50-50%) followed by hot water spray rinse and one minute immersion in 25% HCl followed by final hot water spray rinse at 1200X.

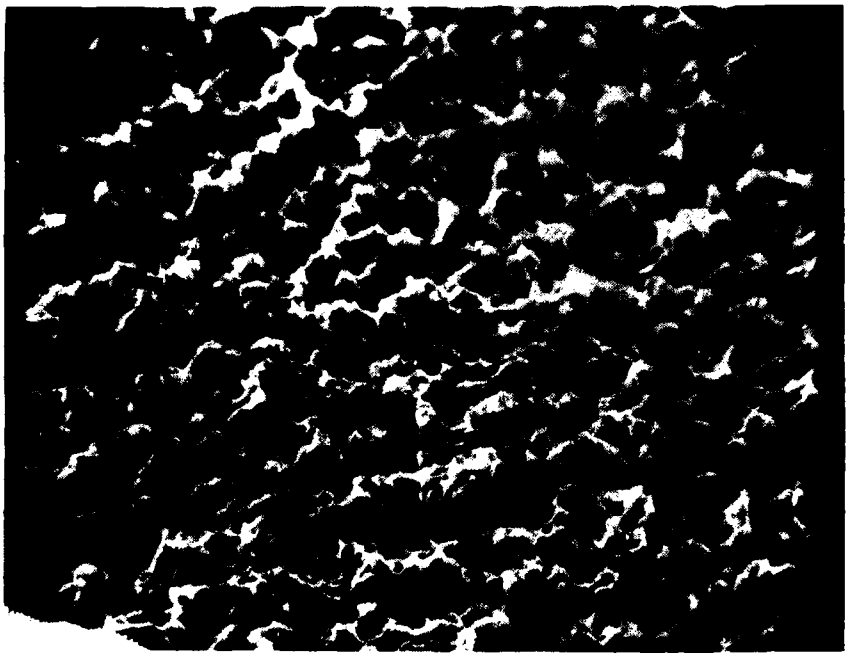


Figure 26

The same surface as Figure 25 at 5200X.

Table 18 Variation of Peel Strength as a Function of Varying Temperature of the Red Oxide Solution

Solution Temperature	Peel Strength, ppi
180°F	4.43
190°F	5.87
200°F	5.33
210°F	3.83

NOTE: Immersion Time - Two Minutes in Solution

Table 19 Variation of Peel Strength as a Function of Immersion Time in Red Oxide Solution at 195 - 200°F

Immersion Time Minutes	Peel Strength, ppi
1	3.70
3	3.27
5	5.30
10	3.73

Table 19A Comparison of Peel Strength Values Using Roller Drum Technique and Hand Held Instron Testing

Specimen	Peel Strength, ppi: ASTM D3167 Peel Tester, 1/2" Wide Sample	Peel Strength, ppi: Instron Tester, Hand Held, 1/4" Wide Sample	Comparison of ASTM D3167 Peel Tester Versus Instron Technique
Table 17 - Sol'n 9	4.67	4.47	+ 4.5%
Table 17 - Sol'n 10	3.47	3.37	+ 3%
Table 18 - 180°F	4.43	3.93	+12.7%
Table 18 - 190°F	5.87	5.33	+ 10%
Table 18 - 200°F	5.33	4.67	+ 14%
Table 18 - 210°F	3.83	3.67	+ 4.4%
Table 19 - 1 min. Immersion	3.7	4.13	- 10%
Table 19 - 3 min. Immersion	3.27	3.13	+ 4.5%
Table 19 - 5 min. Immersion	5.30	4.97	+ 6.6%
Table 19 - 10 min. Immersion	3.73	3.63	+ 2.7%

g. EFFECTS OF AGING RED OXIDE TREATED COPPER

In a normal sequence of MLPWB fabrication, copper foil surfaces after the red oxide treatment step are processed into the laminate construction usually within hours. In some instances, such treated copper might remain overnight before the next processing step. The question arose during the study on how long the treated copper could remain at ambient conditions prior to subsequent processing. Another question was raised on whether or not a baking cycle was needed to remove any absorbed moisture from treated copper that was not processed within normal times. To study this, copper foil was treated with the standard ferric chloride-red oxide treatment. Control sample laminates were made and the remaining treated copper was allowed to remain at room ambient. Laminates were then made with the treated copper "as is" and also after the treated copper was baked for one hour at 250°F. The results of peel testing these panels are shown in Table 20. There was no significant degradation of the red oxide treated copper after four weeks. Actually, a slight increase was noted, however, it was felt that this was probably attributed to the sampling base rather than any aging effects. Similarly, no significant differences between "baked" and "unbaked" specimens were noted. While we would not recommend leaving treated copper foil unprotected for any length of time. we feel that the data does signify that once copper is red oxide trated, the resultant treatment is relatively insensitive. This area should certainly be explored in more detail by those engaged in high volume MLPWB fabrication.

h. ANALYSIS OF COPPER OXIDES

Previous analyses of grown copper oxide films by ESCA/AES and diffuse reflectance IR spectroscopy raised the question of possible damage to the oxide surface by the X-ray and electron beam excitations utilized for surface analysis. Results reported by other surface analysis laboratories (1) indicate that the energy flux density at the sample surface is sufficient to cause chemical changes.

In order to determine if such chemical changes were occurring in the copper oxide surfaces of interest in this investigation, an experiment was conducted using the ESCA/AES system. Specially grown red oxide (Cu_2O) and black oxide (CuO) films on copper foil substrates were prepared, both with and without ferric chloride ($FeCl_3$) etching prior to oxide growth. These samples were then exposed to timed periods of x-ray and electron beam radiation as utilized in ESCA/AES analyses. Both ESCA and AES spectra were recorded before, during and after these irradiation periods to establish if the oxidation state of the sample was being altered.

Copper oxide (Cu_2O or CuO) surfaces when exposed to x-ray and/or electron beam excitation at energy levels and for time increments typical of ESCA/AES analyses, do not appear to undergo any measurable change in surface oxidation state. Sputter-etching of the red oxide (Cu_2O) surfaces to remove surface carbonaceous contamination (approximately 50 A removed) results in a surface which is primarily black oxide (CuO) with low levels of red oxide (Cu_2O) and elemental copper detected. Similar sputter-etching of the black oxide (CuO) surface of the sample where the copper substrate was <u>not</u> etched with ferric chloride ($FeCl_3$), results

(1) "Radiation Damage in Electron Spectroscopy", Wagner, C.D., Paper presented at the Pittsburgh Conference, Atlantic City, N.J., 1981.

Table 20 Effect of Aging Red Oxide Treated Copper Upon Peel Strength

Sample	Peel Strength, ppi	
	Not Baked	Baked[1]
Control	4.50	4.45
Aged 1 week	3.97	4.95
Aged 2 weeks	4.52	3.78
Aged 4 weeks	5.15	4.88

[1] Baked 1 hour at 250°F

in a freshly exposed surface which is primarily black oxide (CuO) with traces of red oxide (Cu_2O). No elemental copper was detected.

ESCA analysis of the "black oxide (CuO)" sample where the copper had been etched with ferric chloride ($FeCl_3$) prior to oxide growth, indicates the as-received surface is red oxide (Cu_2O). Sputter-etching of this sample results in a surface which is primarily black oxide (CuO) with traces of red oxide (Cu_2O) but no elemental copper.

Sputter etching is a collisional process which predominantly removes atomic rather than molecular species, therefore free oxygen ions would be present in the analysis chamber after sputter etching oxide samples. The mechanics of sputter-etching when performing ESCA analyses is such that these oxygen ions would have sufficient time to react with the freshly exposed surface. One of two possible reactions can then occur, the free oxygen ions will react either with elemental copper or with the red oxide (Cu_2O) to form black oxide (CuO), the more thermodynamically stable compound. The limited amount of free oxygen ions and the relatively brief time for a reaction to occur would account for the observed presence of both CuO and elemental copper after sputter-etching surfaces which were initially Cu_2O.

The observed change in the red oxide (Cu_2O) samples after sputter-etching make it impossible to determine if the red oxide (Cu_2O) is a separate surfce layer or if it is typical of the bulk "black oxide (CuO)" film. However, the absence of any detectble elemental copper after sputter-etching, as was typical of the two red oxide (Cu_2O) samples, would tend to indicate that the observed Cu_2O layer from the available surface analysis data. Utilization of alternative techniques, such as Secondary Ion Mass Spectroscopy (SIMS), might provide additional information.

Each of the four oxide film samples were exposed for the same period of time to both x-ray and electron beam excitation (Table 21). ESCA spectra were recorded both prior to and following these irradiation periods to determine the oxidation state of the copper oxide surfaces. Spectra are included in Appendix E. Significant changes in the copper 2p photoelectron binding energies (Table 22) after these irradiation periods were observed, indication that no change in the oxidation state of the copper had occurred.

Each sample was then sputter-etched with argon ions to remove the surface carbonaceous contamination layer. ESCA spectra (See Appendix) recorded after sputter etching indicate that the surface oxidation state of the samples has been altered. Table 22 also lists the binding energy values for the copper 2p photoelectron peak after sputter etching. These values indicate that grown red oxide (Cu_2O) films are altered by sputter etching such that the post-etch

Table 21 Copper Oxide Samples and Irradiation Parameters

Samples

1. Red Oxide Treatment (2 min.) on Copper Substrate.
2. Red Oxide Treatment (2 min.) on Copper Substrate Etched with Ferric Chloride.
3. Black Oxide Treatment (2 min.) on Copper Substrate.
4. Black Oxide Treatment (2 min.) on Copper Substrate Etched with Ferric Chloride.

Irradiation Parameters

1. X-ray Irradiation: Mg Kx, 1253.6 eV.
2. Electron Beam Irradiation: Ep = 5000 eV, Ip _ 76.5 uA.
3. Sputter Etching: Ar^+, Ep = 5000 eV, Ip = 25mA, Raster = 5*

*Sputter-etching parameters provide etch rate of approximately 50 Å/min. in pure copper.

Table 22 Copper 2p Photoelectron Peak Binding Energies

Sample (1)	Irradiation (1)	Cu 2p Binding Energy (2)
1	None	934.0
1	1	933.8
1	1 + 2	933.9
1	1 + 2 + 3	933.0 (3)
2	None	933.9
2	1	933.9
2	1 + 2	934.0
2	1 + 2 + 3	933.1 (3)
3	None	929.9
3	1	933.0
3	1 + 2	933.0
3	1 + 2 + 3	933.0
4	None	934.1
4	1	933.9
4	1 + 2	933.9
4	1 + 2 + 3	933.0

1. Reference Table 21 for sample description and irradiation parameters.
2. All binding energy values charge-corrected.
3. These samples also showed a very weak signal indicating the presence of elemental copper.

surface is predominantly black oxide (CuO) with low levels of Cu_2O and elemental copper present. Sputter-etching of the black oxide (CuO) film grown on the substrate which was not etched with ferric chloride ($FeCl_3$) prior to oxide growth, results in a surface composed primarily of black oxide (CuO) with traces of red oxide (Cu_2O). No elemental copper was detected on the freshly exposed surface.

The black oxide (CuO) surface grown after the substrate has been etched with ferric chloride ($FeCl_3$) initially showed a surface oxidation state indicative of red oxide (Cu_2O). The ESCA spectrum recorded for this sample after sputter etching indicates the freshly exposed surface is the same as the previous black oxide (CuO) sample. Based on this data, the possibility exists that the initially observed red oxide (Cu_2O) is a thin surface layer and the bulk oxide film is black oxide (CuO). However, the observed alteration of red oxide (Cu_2O) films by sputter etching makes it impossible to determine without doubt that this is the actual oxide film composition. Other analytical techniques, such as SIMS, could potentially resolve this anomaly. Because this technique also utilizes sputter etching, it is possible that similar changes in oxidation state may make a definitive analysis impossible.

Diffuse Reflectance Analysis - Figure 27 shows the diffuse reflectance spectra of samples 1s-4 as identified in Table 21. Red oxide samples 1 and 2 both exhibit diffuse reflectance spectra which are similar to those previously reported. These films, 1s and 2, absorb blue radiation (350-450nm) while partially reflecting red (650 - 750 nm) which results in their dark coloration. Interestingly, the black oxide sample #3, is not linearly absorptive throughout the spectrum and the black oxide sample on ferric chloride etched copper, #4, does exhibits some reflectivity of red radiation (650 - 700 nm). This may indeed, support the ESCA data which detected a red oxide (Cu_2O) layer on sample #4.

i. RED OXIDE BATH CHARACTERIZATION

The red oxide solution changes composition with repeated use. In order to determine when the red oxide solution was no longer useful for producing the desired copper oxide surface, analytical methods were chosen to evaluate the composition of the red oxide solution. Analytical techniques were developed for the red oxide bath ingredients, namely, sodium chlorite, sodium phosphate, and sodium hydroxide.

o Sodium Chlorite

An iodometric method for analysis of sodium chlorite was tested and found to work reasonably well. This method is shown in Figure 28. A sample of new unused bath solution which contained 30 g/l of sodium chlorite ($NaClO_2$) was tested by this method and concentration was measured at 28.4 g/l. It is believed that this difference between known and experimental values was due to moisture contained in the sodium reagent.

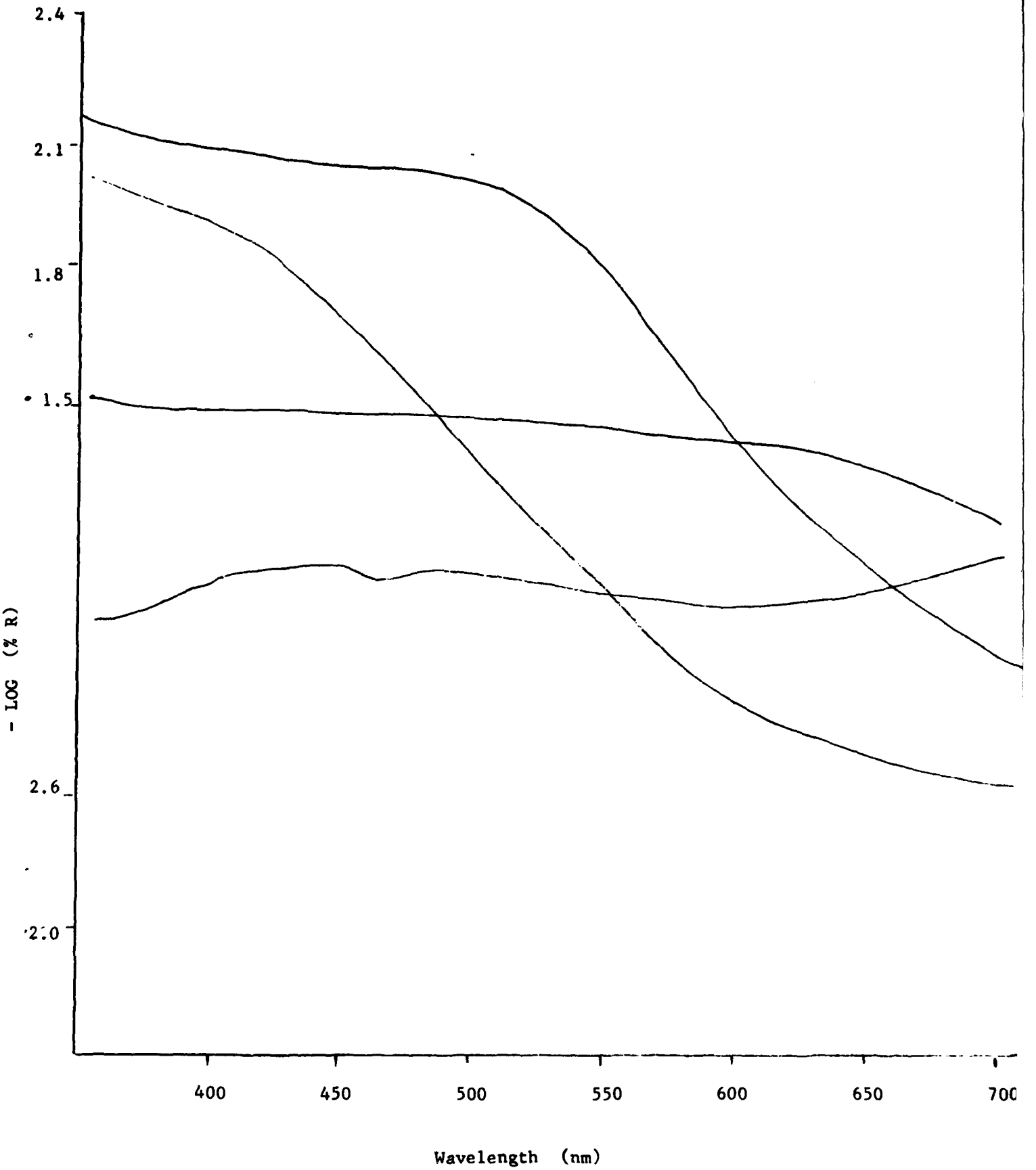


FIGURE 27 DIFFUSE REFLECTANCE SPECTRA

Reactions:

$$ClO_2^- + 4I^- + 4H^+ \rightarrow 2I_2 + Cl^- + 2H_2O$$

$$4S_2O_3^{2-} + 2I_2 \rightleftharpoons 2S_4O_6^{2-} + 2I^-$$

Pipet a 1.00 -ml sample into a 250 ml Erlenmeyer flask, dilute to 50 -ml with distilled water. Add 2-g of KI. When it is dissolved add 15-ml of 4.0 N sulfuric acid. Titrate with standard sodium thiosulfate, until the solution turns yellow. Add starch solution and continue titrating until solution is clear.

$$\frac{(\text{Normality of } Na_2S_2O_3)(\text{ml of } Na_2S_2O_3)}{4} \times 90.44 = \text{g of } NaClO_2 \text{ per liter of solution}$$

FIGURE 28 Determination of $NaClO_2$ In Red Oxide Solution

A regenerated bath solution was also tested. This bath was tested after 608 square inches of copper foil had been treated and had an additional 7.5 grams of sodium chlorite added to it. Taking into account the moisture of the reagent, the total weight of the sodium chlorite should have been 35.5 g/l. The solution was analyzed as containing 34.0 g/l indicating that 1.5 g of the sodium chlorite had been used. This works out to a use rate of 0.308 mg/l/cm^2 or 2.47 mg/l/in^2.

o Sodium Phosphate/Sodium Hydroxide

A potentiometric method for determining sodium phosphate (Na_3PO_4) in the red oxide bath solution was established. From this determination, the concentration of sodium hydroxide is then established as calculated from the difference in total basicity. Figure 29 delineates the analytical procedure for these measurements.

Using these procedures, two experimental solutions were prepared and then analyzed. The results as shown in Table 23, indicate that the values obtained for sodium chlorite, sodium hydroxide, and sodium triphosphate are determinable with a relatively small error compared to their theoretical values. The starred values were not prepared with the same accuracy as the two experimental solutions and such deviations may be expected.

j. ALTERNATE COPPER TREATMENTS

While our studies indicated that the ferric chloride-red oxide treatment produced the optimum results for improving inner layer adhesion, additional tests of alternate treatments were warranted.

In one study, Kerimid 601 polyimide, the principal resin of all polyimide prepregs qualified to military specifications, was used as a primer. The copper foil was cleaned only for one set of samples and another set was given the full ferric chloride-red oxide treatment prior to priming with Kerimid 601. As seen in Table 24, zero peel strength was found in the first set where Kerimid 601 was used on clean copper only. When used on red oxide treated copper, the Kerimid 601 produced reasonable peel strengths but still below that which is obtained with red oxide treated copper alone.

Two other commerical treatments were also evaluated, one was a cupric oxide system and our results showed very poor peel strengths. The other was said to be a mixture of cuprous and cupric oxides. Our results gave much lower values than claimed by the vendor however we did not follow his recommended instructions exactly. We used the standard ferric chloride treatment followed by the copper oxide treatment. The manufacturer recommends an alkaline soak cleaning followed by an acid neutralizer/cleaner prior to copper oxide treatment. Since the literature reports exceptionally high peel strength values for the product, it would appear the vendor process must be closely followed to achieve this. Very late in the program we sent pieces of copper foil to the vendor and asked him to copper treat them for us. The vendor graciously did so but we later found very poor peel strength results. We did not pursue this further but it is possible that the surface preparation might have been damaged in transit.

Take a known amount of sample, 5-25 ml. Dilute to 50 ml with H_2O. Measure the initial pH. Titrate with 0.2 N HCl using large increments (0.5-1.0 ml) at first and making them smaller as the change in pH becomes larger and the endpoint is approached. Measure the pH after each addition of titrant. Continue titrating until the pH of the solution is below 2.5.

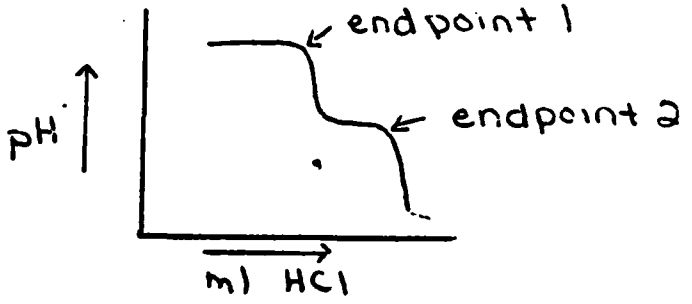
Plot the pH vs. the volume of HCl. Determine the two endpoints. the first should be located at a pH of about 10-11, and the second located at about pH 5-6. The first endpoint corresponds to the following:

$$2\ HCl + NaOH + Na_3PO_4 \rightleftharpoons 2\ NaCl + H_2O + HNa_2PO_4$$

and the second endpoint is represented by this equation:

$$2\ HCl + HNa_2PO_4 \rightleftharpoons 2\ NaCl + H_3PO_4$$

The curve should look similar to this:



Calculations

1. Endpoint 2 - endpoint 1 = ml of HCl used to titrate HNa_2PO_4

2. $$\frac{(\text{ml of HCl determined in (1)})(0.2\ N)}{\text{ml of Sample Titrated}} = N \text{ of } HNa_2PO_4$$

3. $$\frac{N \text{ of } HNa_2PO_4}{2} = \text{Molarity of } Na_3PO_4 \text{ in Bath}$$

4. $(M \text{ of } Na_3PO_4)(163.94 \text{ g } Na_3PO_4/\text{mole}) = \text{g/l } Na_3PO_4$

5. $$\frac{(\text{endpoint 1})(0.2\ N)}{\text{ml of sample titrated}} = \text{Molarity of } (NaOH + Na_3PO_4)$$

6. Molarity of mixture - Molarity of Na_3PO_4 determined in (3)
   = Molarity of NaOH

7. (Molarity of NaOH)(39.9978 g NaOH/mole) = g/l NaOH

FIGURE 29 Potentiometric Method for the Determination of Na_3PO_4 and NaOH in Red Oxide Solution

Table 23 Results of Analysis of Red Oxide Bath

	$NaClO_2$ (g/l)			NaOH (g/l)			Na_3PO_4 (g/l)		
	Theor	Exper	% Error	Theor	Exper	% Error	Theor	Exper	% Error
Standard Soln*	30	28.43	5.2	5	3.83	23	10	2.98	70
24722-25*	6	5.80	3.3	1.43	1.34	6.3	2.85	3.11	9.1
24722-26*	12	11.7	2.5	1.43	1.23	14	2.85	3.02	5.9
Exper I	59.7	61.2	3.7	20.1	19.28	3.5	10.1	9.63	3.7
Exper II	29.8	30.6	2.0	10.1	9.34	2.6	5.1	4.90	2.0
Regenerated**	37.5	34.0	9.3	12.5	11.9	6.0	6.25	8.59	37

* Process lab solution prepared to 0.1 g accuracy
** Regenerated Solution.

Table 24 Peel Strengths of Various Other Surface Treatments on Copper

Sample	Peel Strength, ppi
Kerimid 601 as primer, no red oxide treatment	0
Kerimid 601 as primer over red oxide treatment	3.57
Commercial Black Oxide with no $FeCl_3$ pre-etch	0.76
Commercial Black Oxide with $FeCl_3$ pre-etch	0.78
Commercial Mixed Oxides with no $FeCl_3$ pre-etch	0.14*
Commercial Mixed Oxides with $FeCl_3$ pre-etch	2.1*

*Vendor process not followed exactly. See text.

k. EFFECT OF FERRIC CHLORIDE ETCH ON COPPER REMOVAL

Questions were raised in regards to the amount of copper removed during the ferric chloride etch process. A brief study showed a removal rate of about 0.1 mil from a 1.4 mil thick piece of copper foil laminated to a substrate. This was after a standard one minute immersion with agitation during the etch. Further tests were then conducted. A sheet of seven mil copper approximately 6" square with alternately marked and bare areas was given the standard ferric oxide etch of 1 minute. Table 25 shows the thickness measurements made by the calibration laboratory on the alternate masked and bare areas. The micrometer was calibrated to + 0.05 mils. Because the etching was done from both sides, the average of the difference was divided by two. The values varied between 0.1 and 0.2 mils (0.0025 and 0.005 mm) with an average of 0.13 mils (0.0033mm).

Metallographic sections were also taken and the thickness reductions measured. Figure 30 is a photomicrograph of one of the sections. It can be seen that the surface is roughened and irregular with variations in the amount of reduction. The median reduction was between 0.10 mils and 0.15 mils. Subsequently, the question of agitation was also raised on the ferric chloride etch. Samples were made wherein they were etched in an agitated and non-agitated ferric chloride solution.

Two boards approximately eight mils thick with 1 oz. copper on both sides had alternate masked and bare strips, 1/2 inch wide. These were immersed for one minute in the standard hydrochloric acid/ferric chloride solution at room temperature; one with agitation and one without. Six thickness measurements were made on the masked areas and eight measurements were made on the etched areas of each board and difference of the average obtained. These measurements were made in the calibration laboratory using a micrometer calibrated to 0.05 mils. The values were divided in half because the boards were etched from both sides. The agitated board showed an average removal of 0.085 mils per surface. The unagitated board showed measured average of only 0.003 mils per surface; the board was discolored but almost no metal removed. Metallographic sections were taken through the board and measurements made optically. In this case, the unagitated board showed no measurable amount of metal removed.

l. SUMMARY/RECOMMENDATIONS

The primary cause of inner layer adhesion of MLPWB's is interfacial failure at the copper-resin interface. Improper cleaning can be a major contributor to this problem, however even with proper cleaning, interfacial failures will still occur within polyimide MLPWB's if the copper surfaces are not properly prepared. Red oxide solutions based on sodium chlorite provide an excellent surface treatment for copper particularly when a ferric chloride/hydrochloric acid pre-etch is used with the oxide coating. This surface preparation has proven to eliminate inner layer adhesion problems of polyimide MLPWB. When properly applied the adhesion to inner layer copper surfaces should exceed the shear strength of the cured polyimide. It would appear that wide variations in the sodium chlorite solution formula will still provide an adequate surface treatment for copper. Analytical characterization of the red oxide coating shows that it is

Table 25
Thickness Measurements of Etched Copper Foil ($FeCl_3$ etchant)

Position	Unetched	Etched	Difference	Difference/2
1	6.7 mils	6.4 mils	0.3 mils	0.15 mils
2	6.9	6.5	0.4	0.2
3	7.4	7.2	0.2	0.1
4	7.5	7.3	0.2	0.1
5	7.3	7.1	0.2	0.1
6	7.1	6.9	0.2	0.1
7	6.9	6.6	0.3	0.15
8	6.9	6.6	0.3	0.15
		AVG.	.13 mils	

Reduction of seven mil copper sheet by ferric chloride etch as measured by difference between masked and unmasked areas.

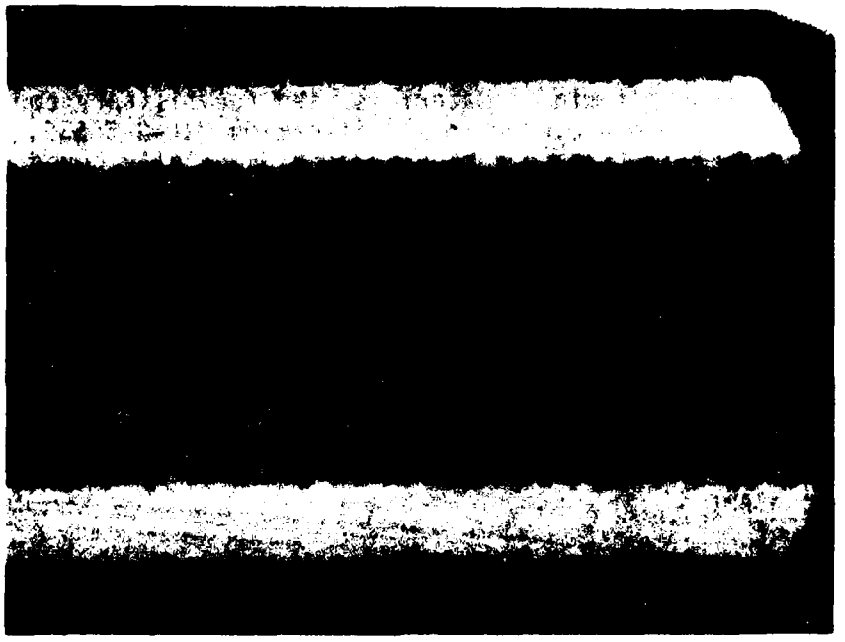


FIGURE 30

Metallographic cross section through etched area of agitated board.

NOTE: Roughened surface.

Magnification = 340X

a mixture of cuprous (red) oxide and cupric (black) oxide. The red oxide nomenclature applied to the sodium chlorite formulations might best be called a brown oxide to eliminate some of the confusion concerning their nature.

It is recommended that further evaluation of this oxide formulation be conducted. In addition, the effect of other pre-etchants other than ferric chloride/hydrochloric acid should also be evaluated. Most likely this effort would be undertaken by some of the companies that supply such materials to the printed circuit industry. As a matter of convenience and reproducibility, it would seem advantageous to purchase such solutions already mixed to the proper concentrations. It is recommended that the number of baths or solutions be kept to a minimum and as simple as possible.

5. CHARACTERIZATION OF PREPREG MATERIALS

a. CURRENT INDUSTRY PROCEDURES FOR QUALIFICATION AND QUALITY CONTROL

Polyimide and epoxy prepreg laminate materials used for military equipment applications have normally been procured to specification MIL-G-55636. Recently the major military specifications covering prepregs and fully cured laminates have been incorporated into one specification, namely, MIL-P-13949. Qualification inspection includes the following tests for prepreg materials per MIL-P-13949:

- Visual and dimensional inspection
- Presence of dicyandiamide crystals
- Thread count
- Glass cloth thickness
- Fabric weight
- Gel time
- Volatile content
- Resin content
- Resin flow
- Cured thickness
- Electrical strength
- Dielectric constant and dissipation factor
- Flammability (where applicable)

Quality conformance inspection consists of a Group A and Group B inspection. Group A inspection tests for:

- Visual and dimesional inspection
- Presence of discyandiamide crystals
- Gel time
- Resin content
- Resin flow
- Cured thickness

Group B inspection consists of inspecting sheets that have passed the Group A inspection according to a specific sampling plan. The primary inspections include:

- o Thread count
- o Glass cloth thickness
- o Fabric weight
- o Volatile content

There are also periodic inspections on a Group C basis for prepregs.

It has been seen that while most of the required tests are not sophisticated, they are thorough and repeatable. One of the major efforts of this study was to analytically characterize prepreg materials to determine if even better test methods were possible.

b. INITIAL CHARACTERIZATION OF PREPREG MATERIALS

The initial characterizations of the prepregs used in the first part of this study are shown in Tables 26-28.

Liquid Chromatography - Although tetrahydrofuran (THF) is not an ideal solvent for the Kerimid resin system, samples of Mica and Atlantic polyimide B-stage were prepared for gel permeation liquid chromatography (GPC) analysis using THF to remove the free methylene dianiline (MDA) and n-methyl-pyrrolidone (NMP). Since both MDA and NMP are readily soluble in THF it was speculated that GPC might be employed to quantify these constituents for the B-stage resins. For comparison and a baseline, Kerimid 601 resin powder was also analyzed. A substantial quantity of the imide resin was also found to be soluble in the THF.

The GPC chromatograms of Kerimid 601, Mica and Atlantic polyimide B-stage resins are shown in Figures 31, 32, and 33, respectively. Quite surprisingly, the three chromatograms are quite similar. The high molar absorbtivity of MDA at 254 nm makes it easy to detect. No attempt was made to quantify the amount of free MDA in any sample at the time. The Atlantic samples exhibited a comparable quantity of MDA to that found in the Kerimid 601 resin. By comparison, the Mica sample had approximately 10% less free MDA. The other weight fractions of the polyimide resins were identical.

Unfortunately, NMP does not exhibit a significant molar absorptivity at 254 nm and it is not easily detected. The refractive index detector, however, does indicate the presence of solvent weight fractions in both the B-stage materials. By comparison, no solvent weight fractions were detected in the Kerimid 601 resin. To better quantify the amount and types of solvents contained in each of the B-stage resins, we later continued examination of the polyimide volatiles.

Infrared Spectroscopy - The infrared spectra of Kerimid 601 and the Mica and Oak-Atlantic B-stage resins are shown as Figure 34, 35, and 36, respectively. The spectra are exceedingly similar and even instrumental subtraction of spectra could not elucidate differences. Some absorptions worth noting are

TABLE 26 - CHARACTERIZATION OF FORTIN 1039 EPOXY PREPREG

B-Stage	
Thickness	4.5 mils
Range	4.0 - 5.4 mils
Resin Content	66.7% by weight
Glass/Resin (g/r)	0.50
DSC	Melt Endotherm @ 62°C
	Cure Initiation @ 140°C
Cured B-Stage	
Resin Content	48.9%
g/r	1.04
T_g	128°C
% Extractables	0.43% (as resin only, 0.88%)
C-Stage	
Resin Content	41.5%
g/r	1.41
T_g	135°C
% Extractables	0.49% (as resin only, 1.18%)

TABLE 27 - CHARACTERIZATION OF POLYCLAD 1226F AND 1225 (C-STAGE) EPOXY MATERIAL

B-Stage (1226F)

Thickness	4.3 mils
Range	3.8 ----> 5.3 mils
Resin Content	63.5%
g/r (glass/resin)	0.575
DSC -	
Melt endotherm @	64°C
Cure initiation @	148°C

Cured B-Stage (1226F)

Resin Content	48.06%
g/r	1.08
T_g	116°C
% Extractables	4.5

C-Stage (1225)

Resin Content	61.8%
g/r	0.616
T_g	135°C
% Extractables	1.6

TABLE 28 - POLYIMIDE MATERIALS CHARACTERIZATION

Oak - Atlantic Polyimide B-Stage

Resin Content	62.1%
Average Thickness	0.0047"
DSC Data :	
Cure Initiation	177°C
Peak Exotherm	235°C
Endo/Exo Inflection @	80°C

Mica Polyimide B-Stage

Resin Content	64.1%
Average Thicknesses	0.0046"
DSC Data:	
Cure Initiation	187°C
Peak Exotherm	241°C
Endothermic melt @	82°C

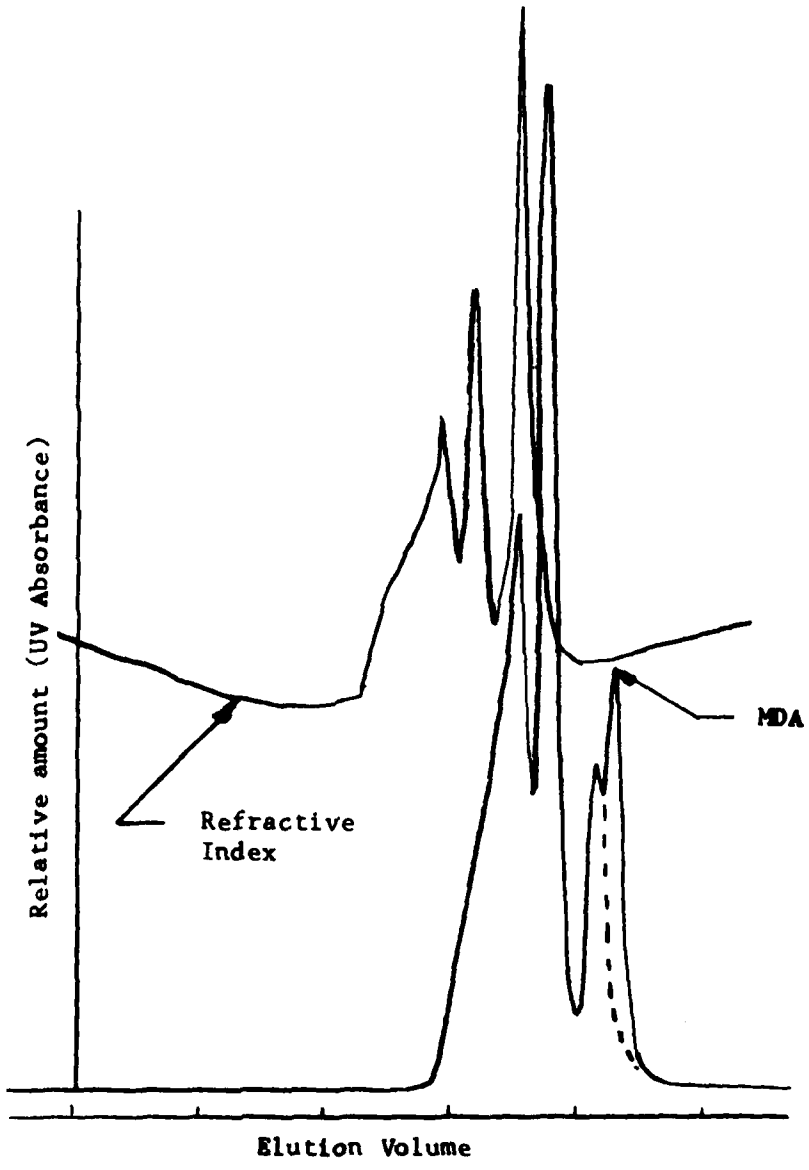


FIGURE 31 GPC OF KERIMID 601 RESIN POWDER

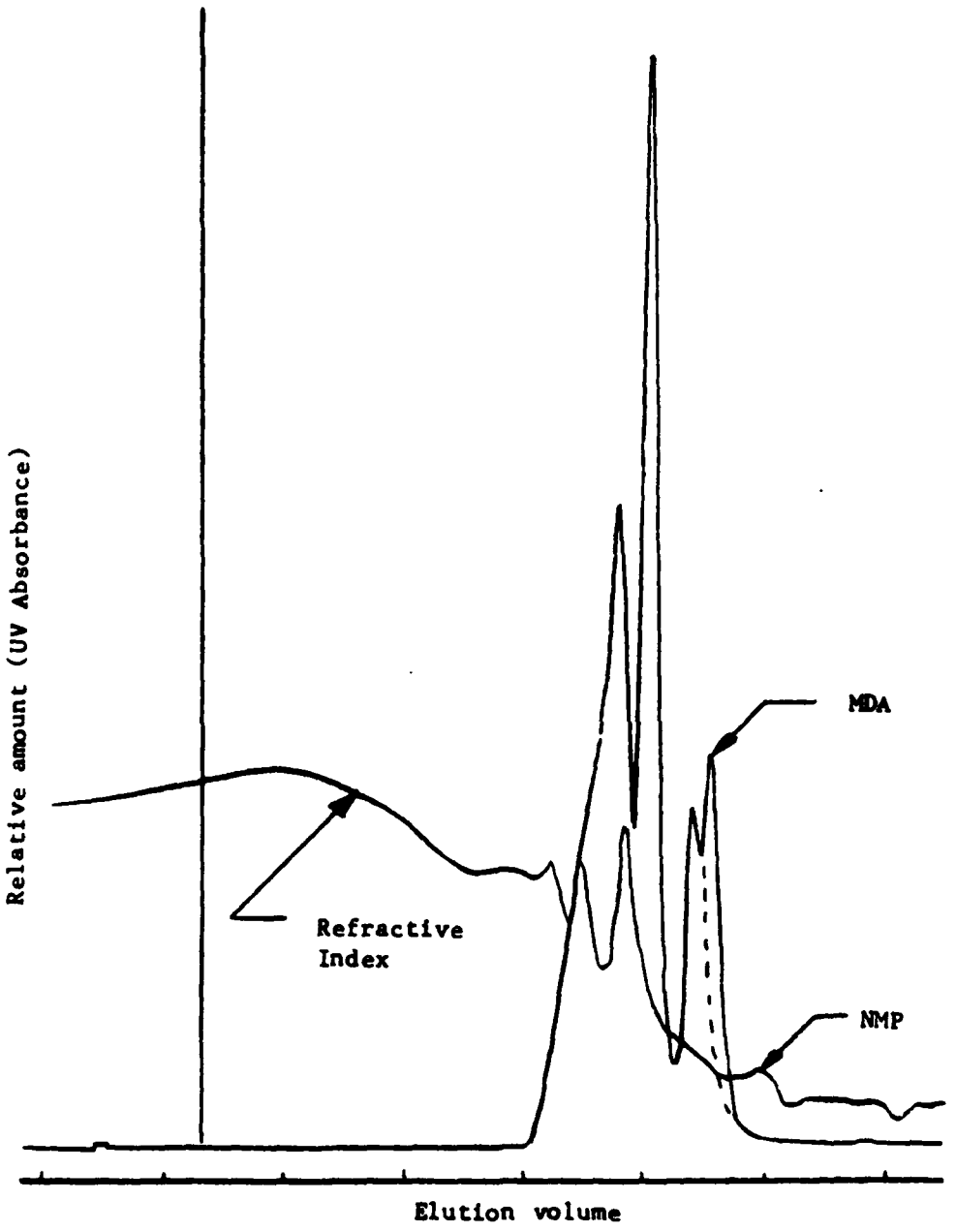


FIGURE 32 GPC of Mica Prepreg

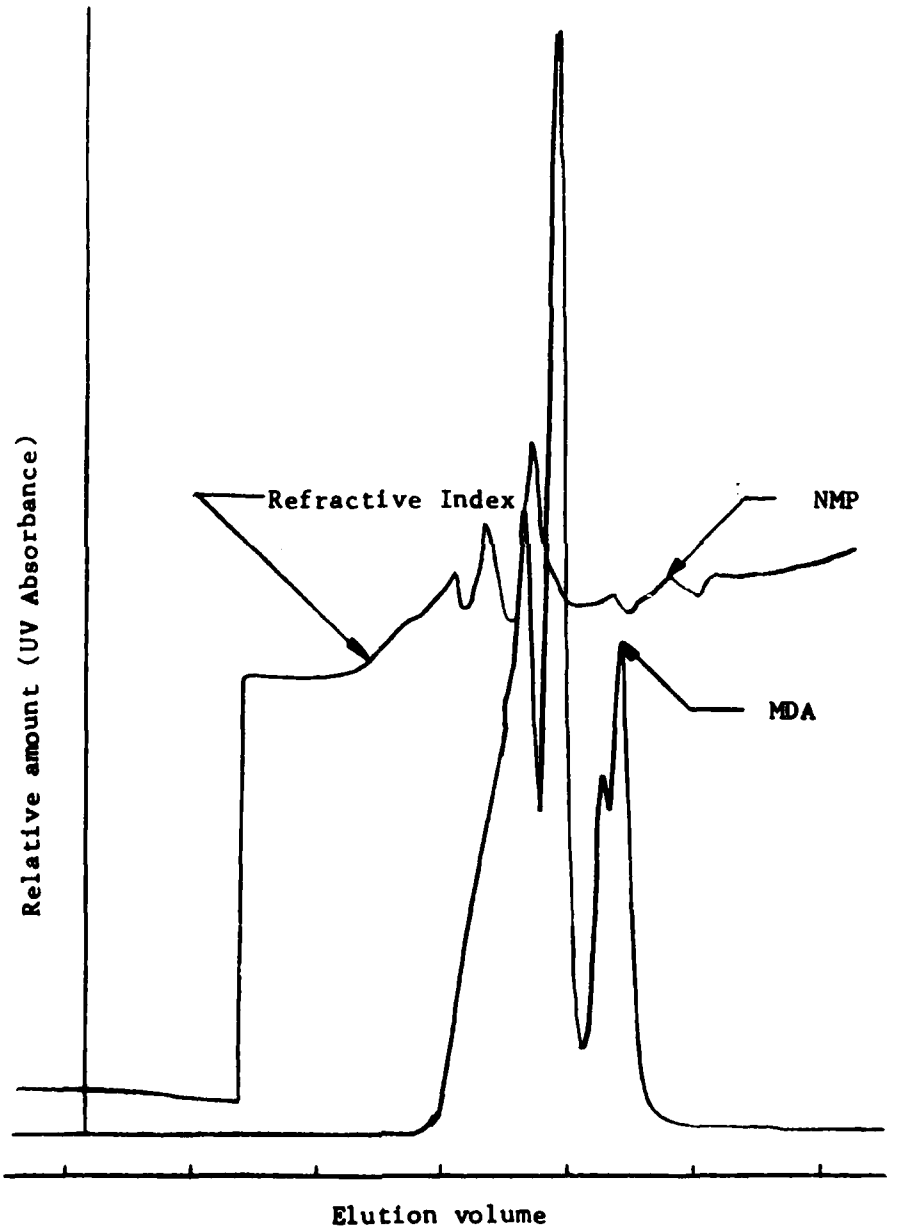


FIGURE 33 GPC OF ATLANTIC PREPREG

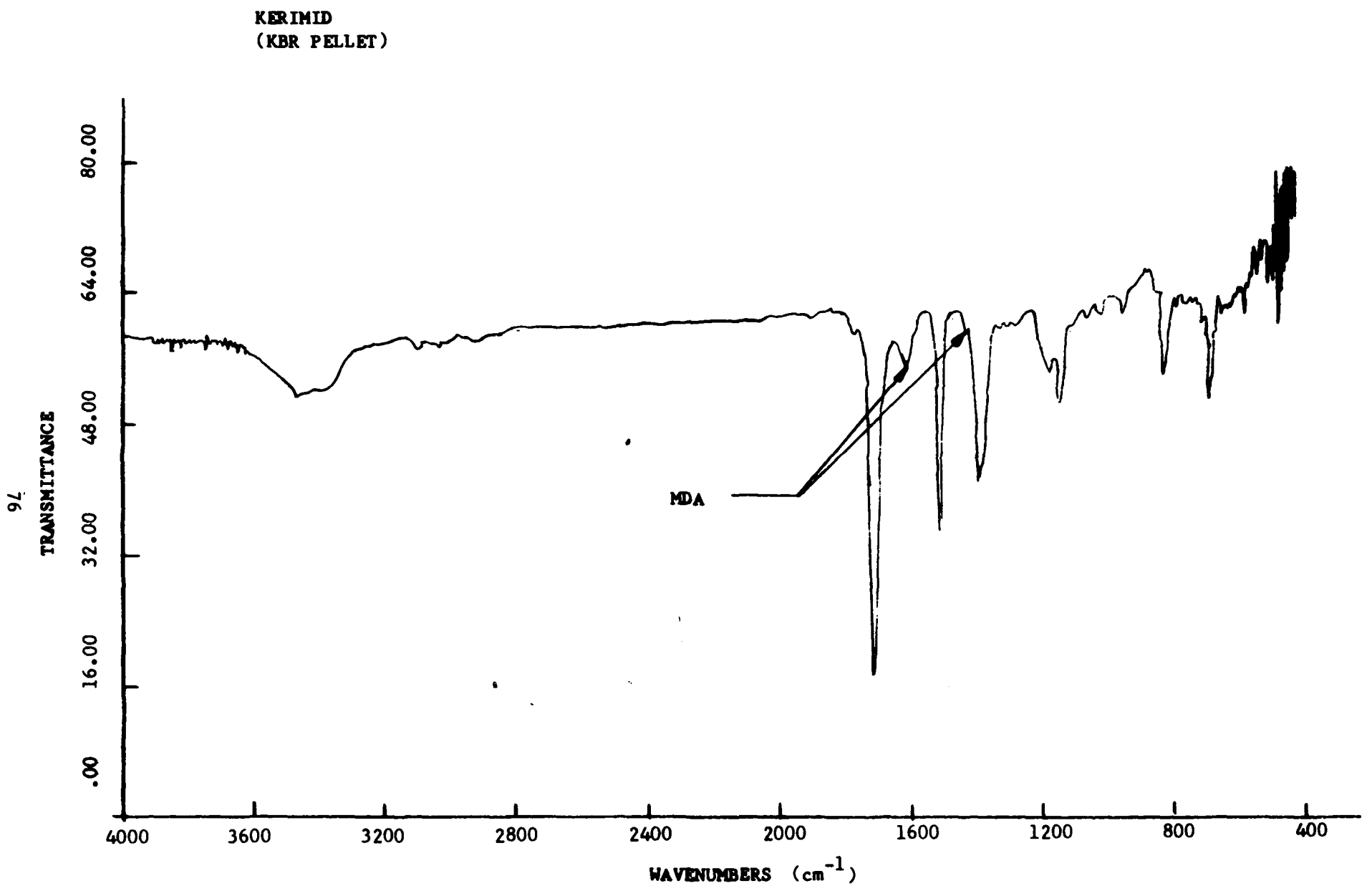


FIGURE 34 FTIR SPECTRUM OF KERIMID 601 RESIN

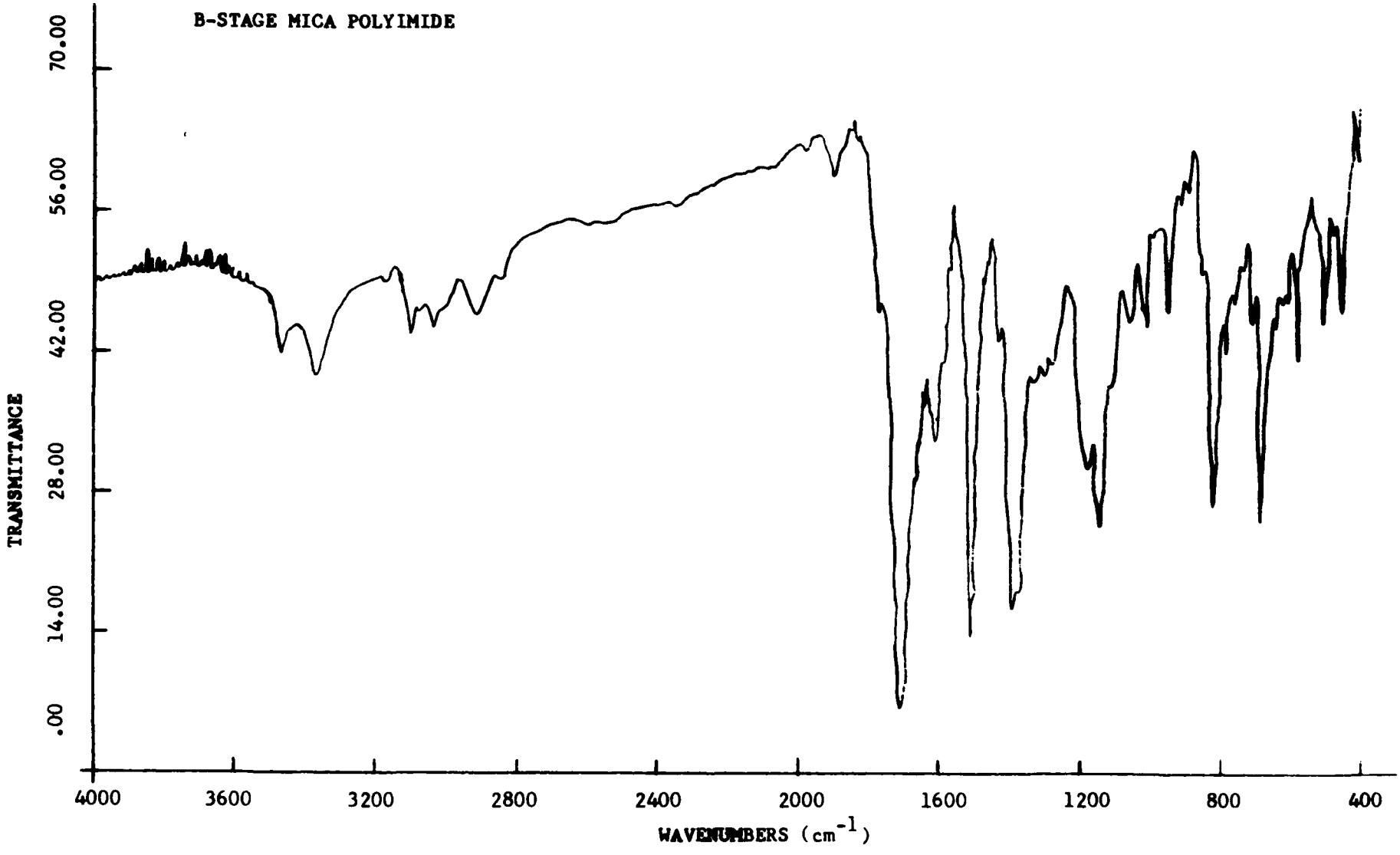


FIGURE 35 FTIR SPECTRUM OF MICA POLYIMIDE PREPREG

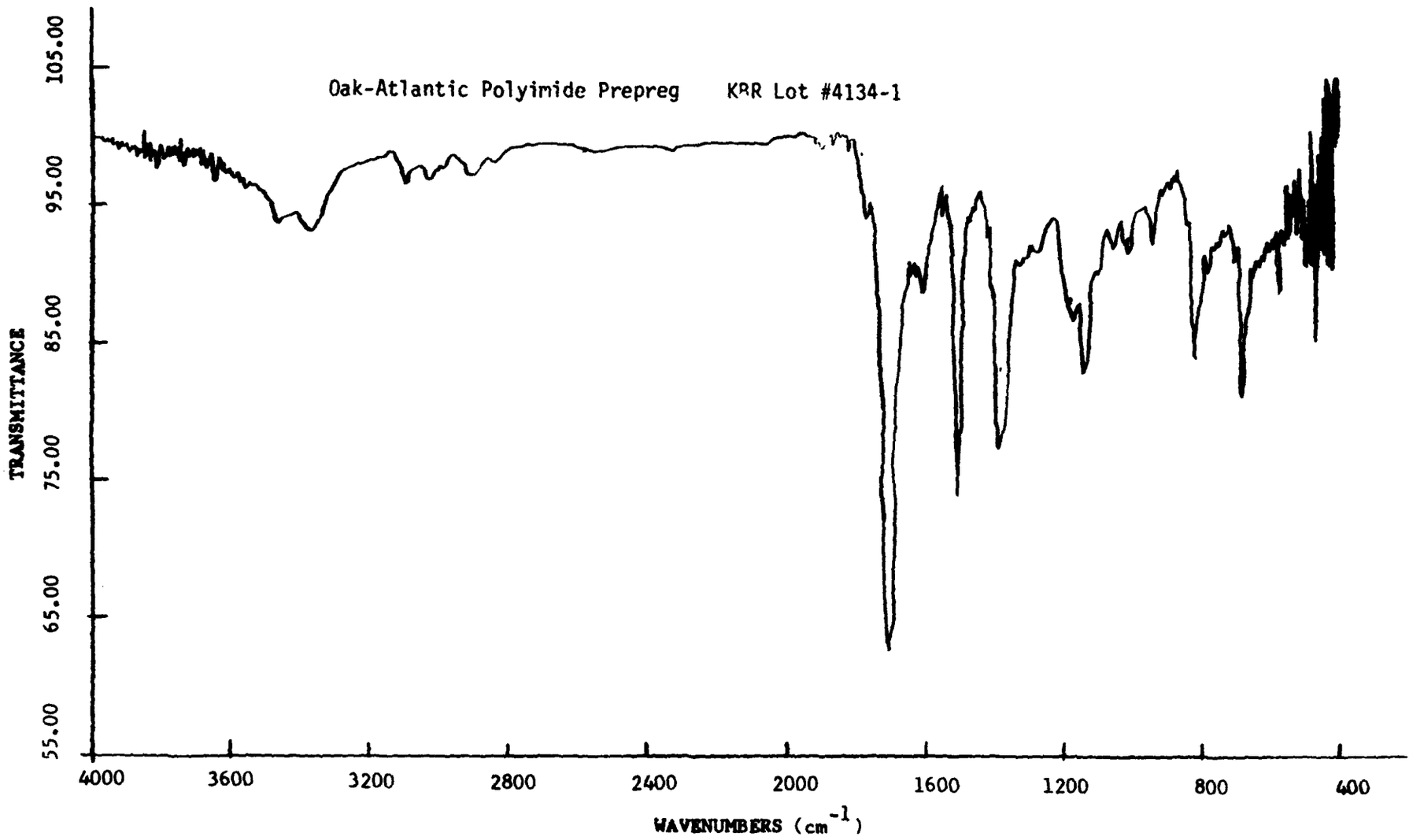


FIGURE 36 FTIR SPECTRUM OF OAK-ATLANTIC POLYIMIDE PREPREG

the amine stretch near 3400 cm^{-1}, the imide carbonyl stretch at about 1700 cm^{-1}, and the substituted aromatic deformation at about 820 cm^{-1}. The infrared spectra of the cured Mica and Atlantic resins are shown in Figure 37 and 38 respectively.

Like the starting resins, the spectra of the cured Mica and Atlantic polyimides are virtually identical and no differences were identified by computer subtraction of the spectra. Comparing these spectra to those of the B-stage resins, a number of changes in the spectra have occurred. A new absorption occurs near 1640 cm^{-1} and the absorption at about 1180 cm^{11} is significantly more intense. By comparison, the absorption near 820 cm^{-1} is not as discrete and of reduced intensity. Absorptions occurring at about 1140 and 1060 cm^{-1} in the B-stage resins are not found in the spectra of the cured materials.

The assumption that the 1140 and 1180 cm^{-1} absorptions originate from the same carbonyl unit is consistent with the spectroscopic data of the resins and the cured laminates. The fact that curing the resin intensifies the 1180 cm^{-1} absorption while eliminating the 1140 cm^{-1} absorption makes the relative intensity of these absorptions a good candidate for a "quality indicator" of the condition of the base resin.

The following Table lists the 1180 and 1140 cm^{-1} absorbance values and ratio for Kerimid 601, Mica and Atlantic resins.

	$A_{1140\ cm^{-1}}$	$A_{1180\ cm^{-1}}$	R*
Kerimid 601	0.312	0.257	1.21
Mica	0.336	0.292	1.15
Atlantic	0.285	0.255	1.12

R* = Ratio of $A_{1140\ cm^{-1}}$ to $A_{1180\ cm^{-1}}$.

Thermal Analysis - The Differential Scanning Calorimeter (DSC) data for Kerimid 601, Mica and Oak-Atlantic B-stage resins are shown in Figures 41, 42, and 43, respectively. The DSC data indicated some significant differences among the resins. All three materials exhibited an endothermic transition around 80°C. As can be seen from the figures, the shape and intensity of these transitions vary considerably with each sample. The fact that these transitions occur near the melting point (92°C) of methylenedianiline (MDA) lead us to speculate that the DSC was actually recording the melt endotherm of the free

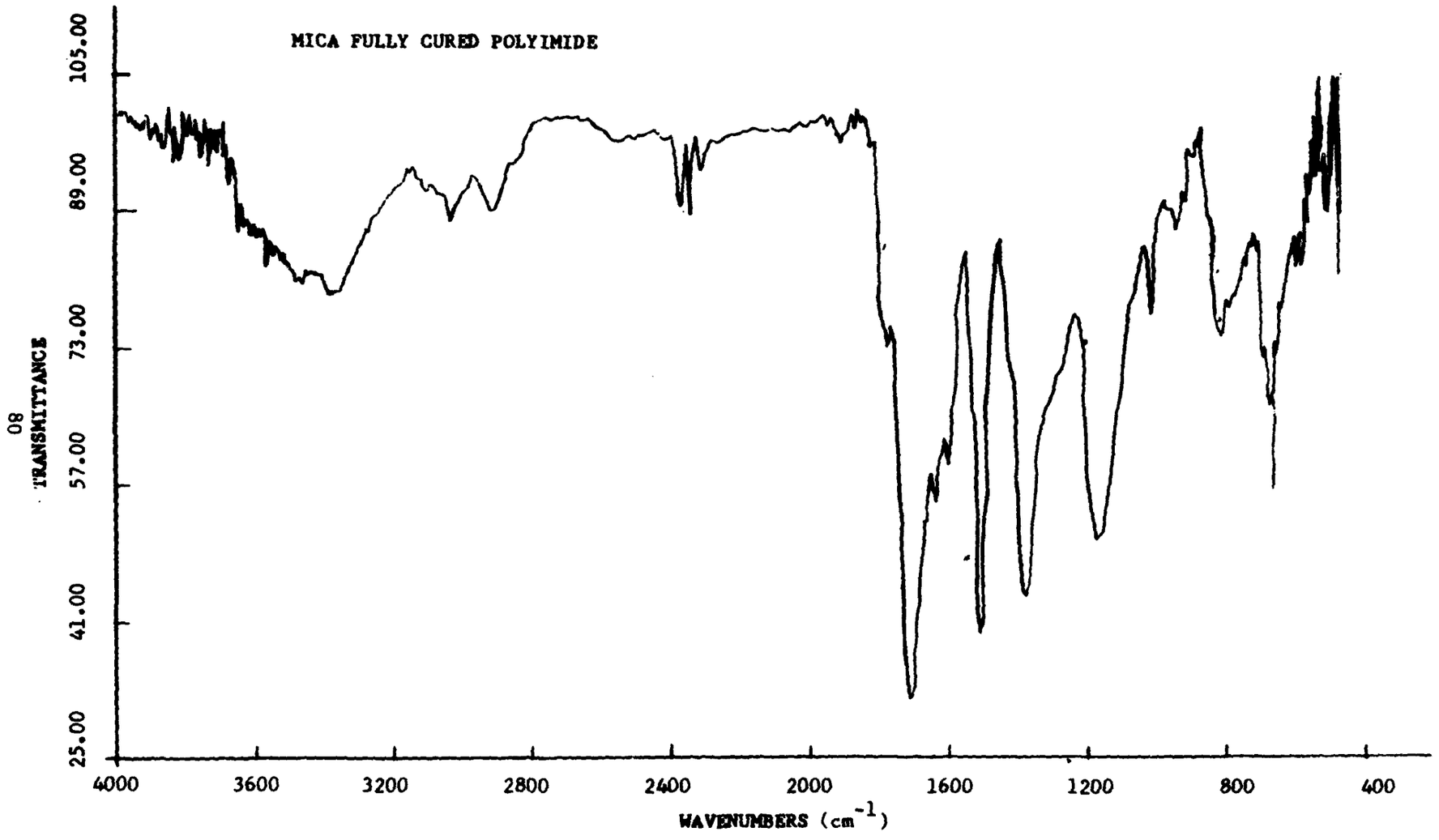


FIGURE 37 FTIR SPECTRUM OF CURED MICA PREPREG

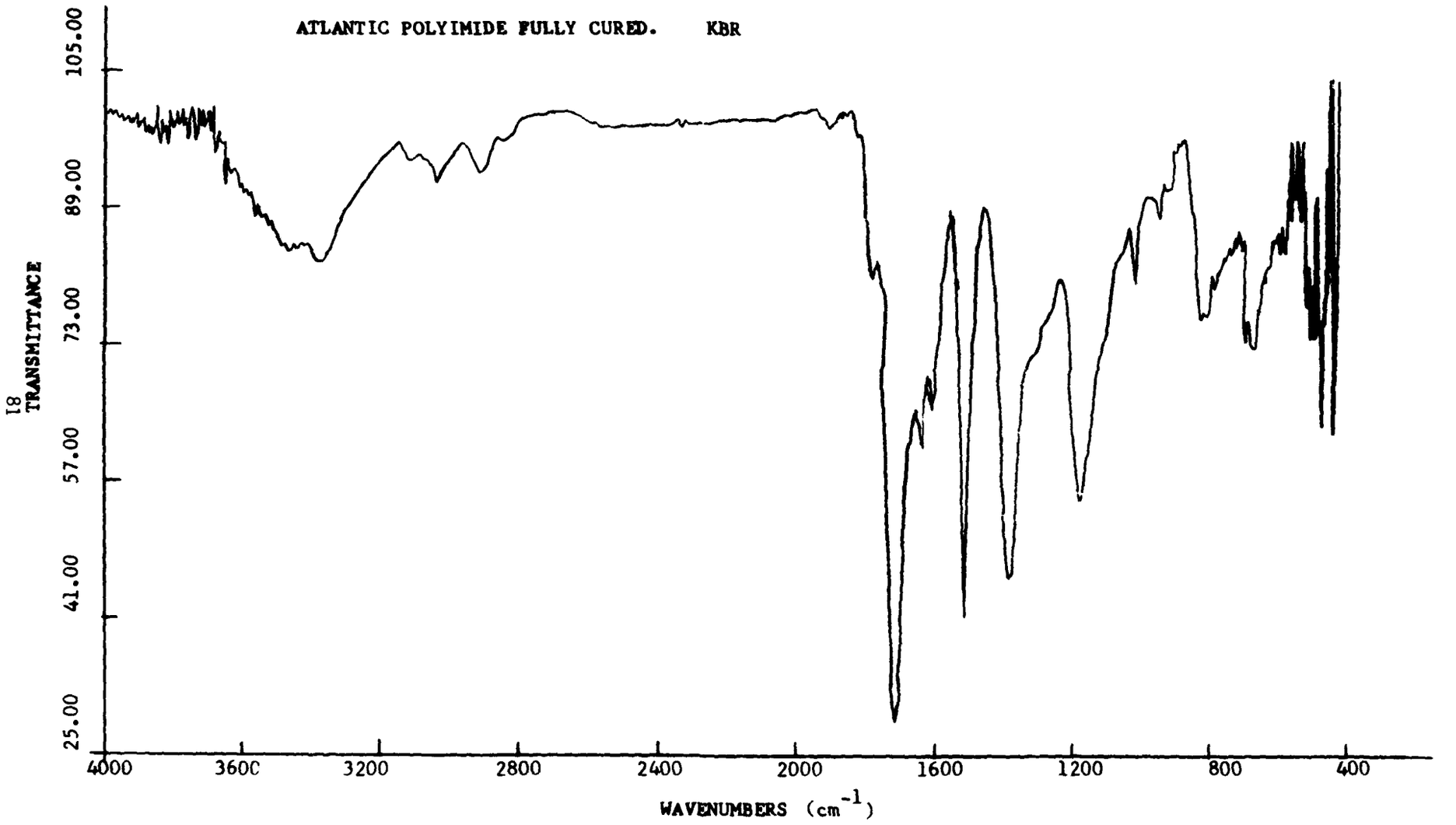


FIGURE 38 FTIR SPECTRUM OF CURED OAK-ATLANTIC PREPREG

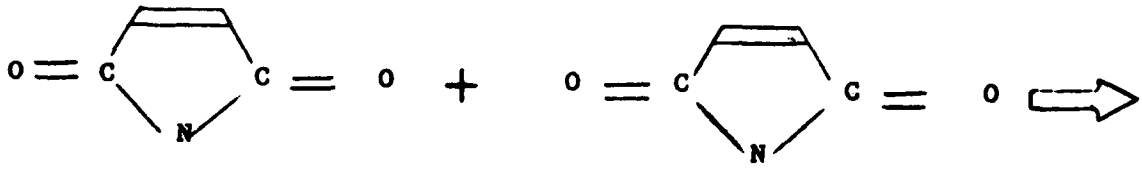


FIGURE 39 THE REACTIVE MALEIMIDE END GROUPS OF KERIMID 601

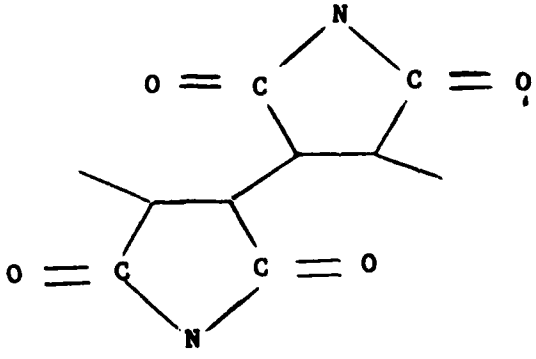


FIGURE 40 THE 1, 4-DIONE STRUCTURE OF CURED MALEIMIDE RESIN

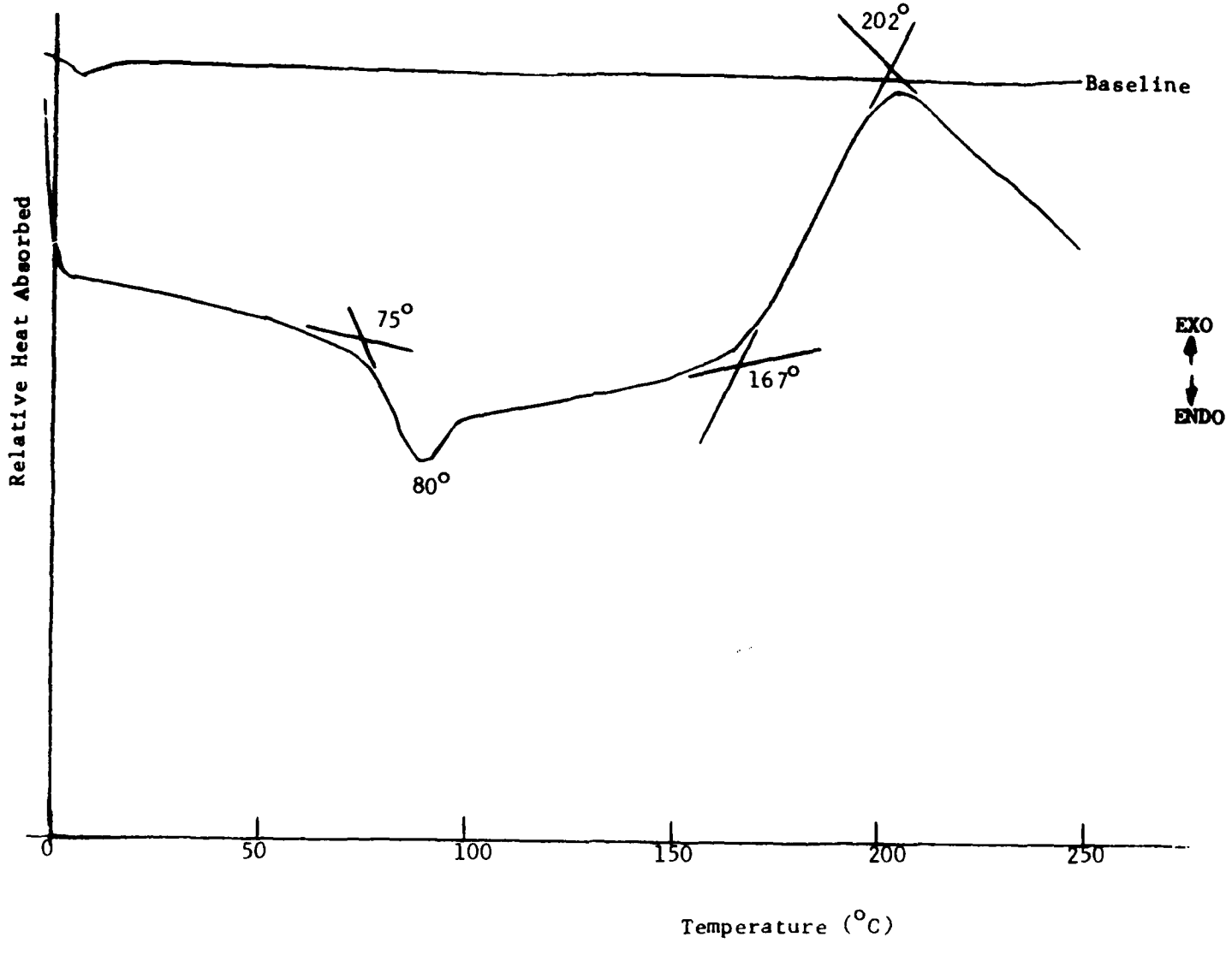


FIGURE 41 DSC OF KERIMID 601

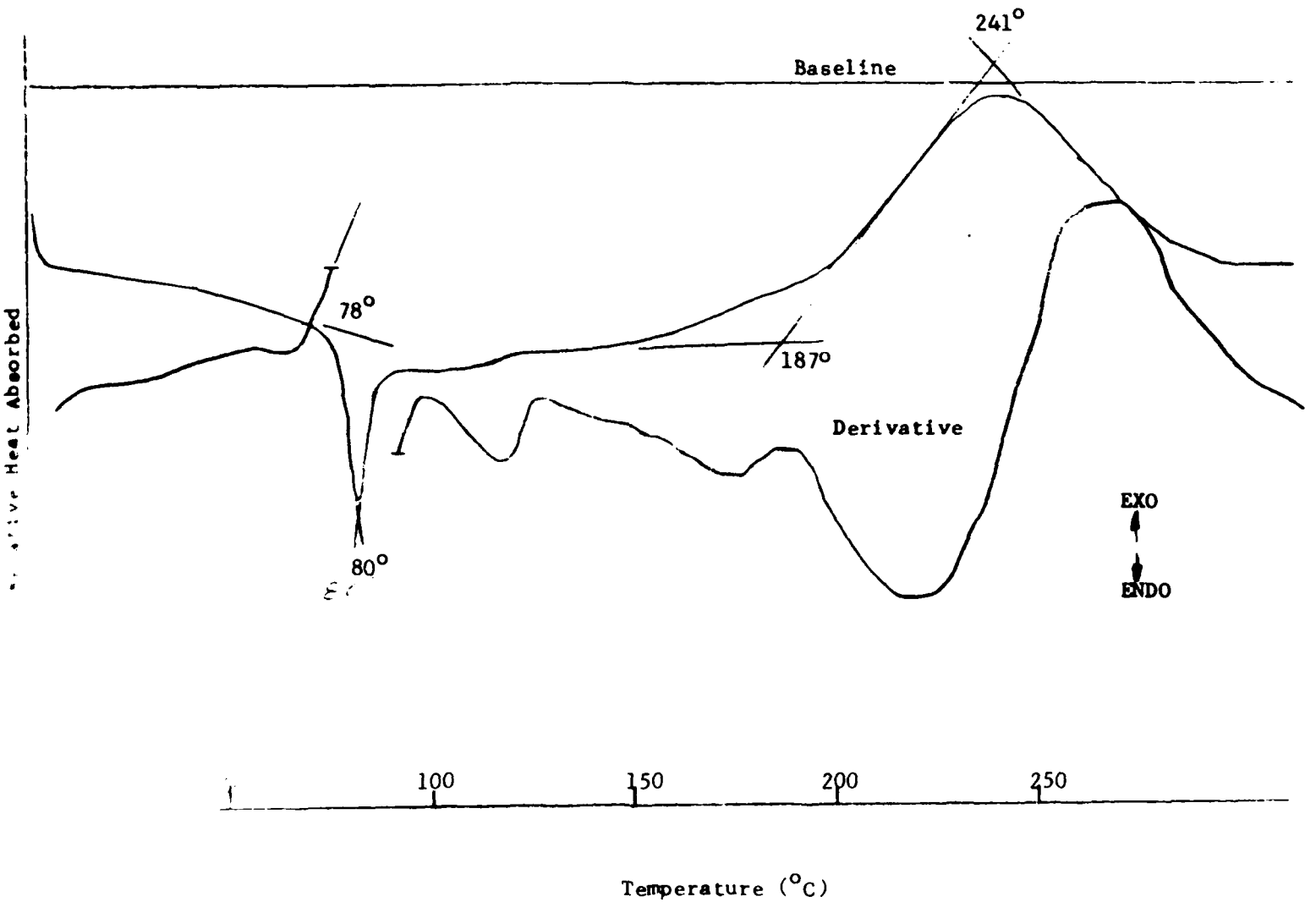
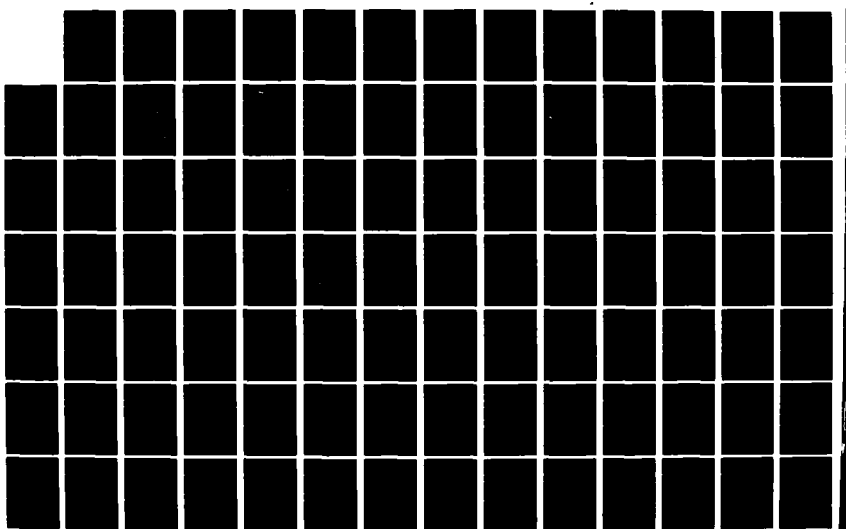
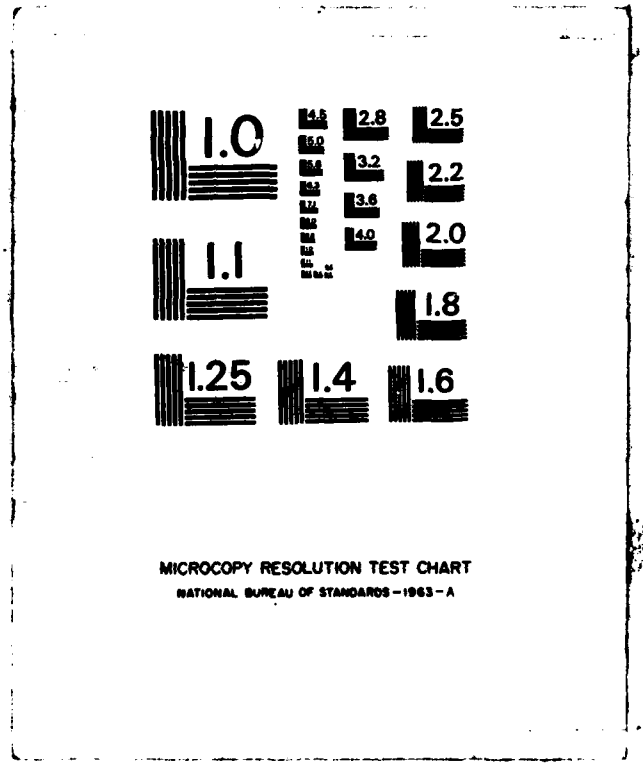


FIGURE 42 DSC OF MICA PREPRE.

AD-A122 067 DEVELOPMENT OF IMPROVED PRINTED WIRING BOARD INNER LAYER ADHESION(U) RAYTHEON CO SUDBURY MA EQUIPMENT DIV T E BAKER JUN 82 AFWAL-TR-82-4054 F33615-79-C-5131 2/3

UNCLASSIFIED F/G 11/1 NL




1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
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5.0
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS - 1963 - A

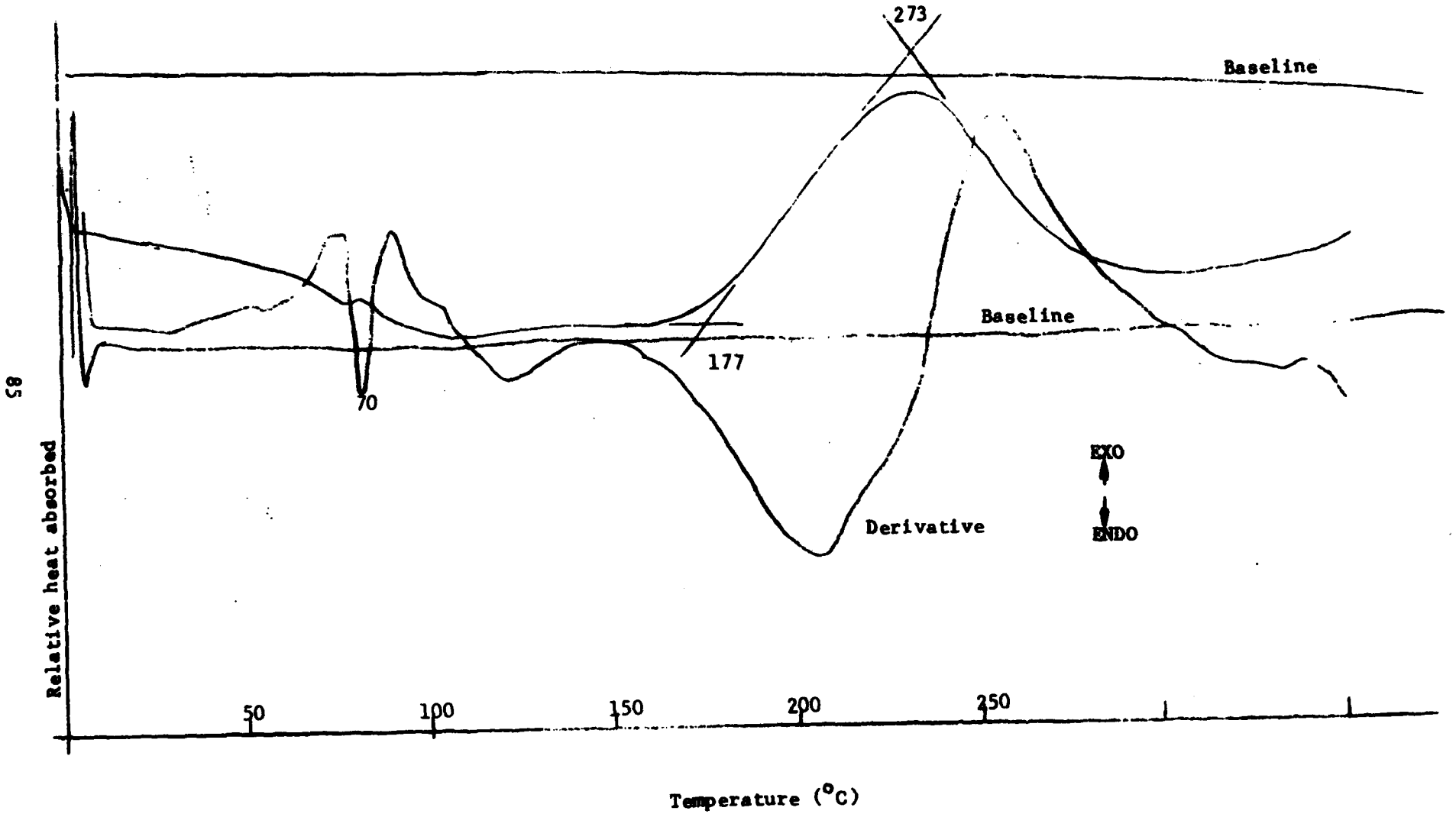


FIGURE 43 DSC OF OAK-ATLANTIC PREPREG

MDA and may be useful to quantify MDA in the laminates. If this were true, then the Mica sample would obviously contain more free MDA than either the Atlantic or Kerimid 601 resins. This is not the case, however, for GPC analysis shows Mica resin to actually contain slightly less free MDA than the other resins. The presence of a low boiling point solvent was another consideration and, indeed the strong endothermic transition of the Mica resin was found to be significantly less intense after heating the resin to 100°C and rerunning the DSC of the same sample (Figures 44A and 45B). At 100°C the polyimide resins begin to melt and will flow under pressure. Presumably, the MDA will also begin to react. Believing that the endothermic transition of the Mica sample was attributable to a low boiling point solvent and recognizing that 90° or 100°C is not an acceptable "drying" temperature, we exposed Mica B-stage laminate to 48 hours at 65°C in an attempt to remove what we thought was solvent. Surprisingly, this thermal conditioning resulted in a new endotherm maximum near 98°C (Figure 44C). Similar thermal conditioning of Atlantic resin developed a peak endotherm at about 94°C (Figure 45B). Rerunning the DSC of this sample (Figure 45C) showed no peak endotherm but just a Tg of 78°C, similar to the rerun Mica sample (Figure 44B). Our ability to make the peak endothermic transition appear or disappear as a function of the thermal conditioning of the sample lead us to believe that the transition was actually attributable to the degree of crystallinity of the base resin. It is difficult to explain why the peak endotherm can occur over such a wide range of temperatures (80-100°C) if, indeed, its origin is crystalline structure. One possibility, is that more than one crystalline structure exists for the resin. As such, the particular crystalline structures formed (e.g., α or β) would be a function of the thermal conditioning temperature.

Additional differences among the DSC's of the samples can be noted in the location and shape of the broad exothermic transitions which occur above 150°C. The following table lists the differences in the initiation and peak temperatures of the exotherm for the three samples. The specific temperatures were obtained by using the graphic tangent method of determining an inflection.

	Initiation (°C)	Peak (°C)
Kerimid 601	167	202
Mica	187	241
Atlantic	177	233

The tabular data does not show the exothermic activity which occurs with the Mica material below 187°C. It is possible that the high initiation temperature obtained for the Mica material by this method is actually a result of an overlapping endotherm at about 200°C due to the evaporation of NMP solvent at this temperature. It is known from thermogravimetric analysis (TGA) which is discussed in the following paragraph, that the Mica laminate exhibits a substantial weight loss between 150 and 200°C. As such, the graphic method for determining the exotherm initiation may possibly be a revealing inspection criteria for quality control.

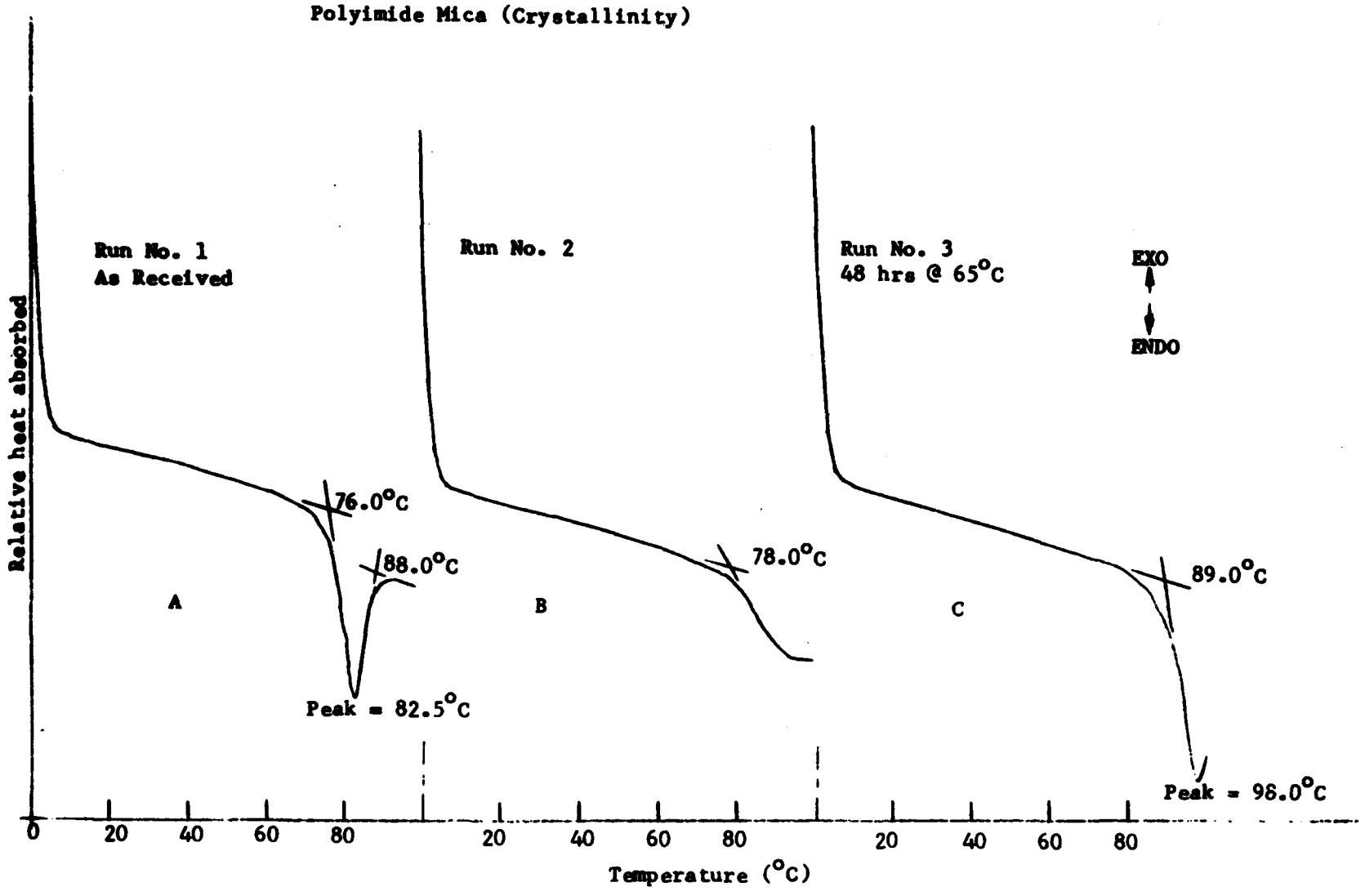


FIGURE 44 AGING EFFECTS ON THE LOW TEMPERATURE DSC PEAKS FOR MICA PREPREG

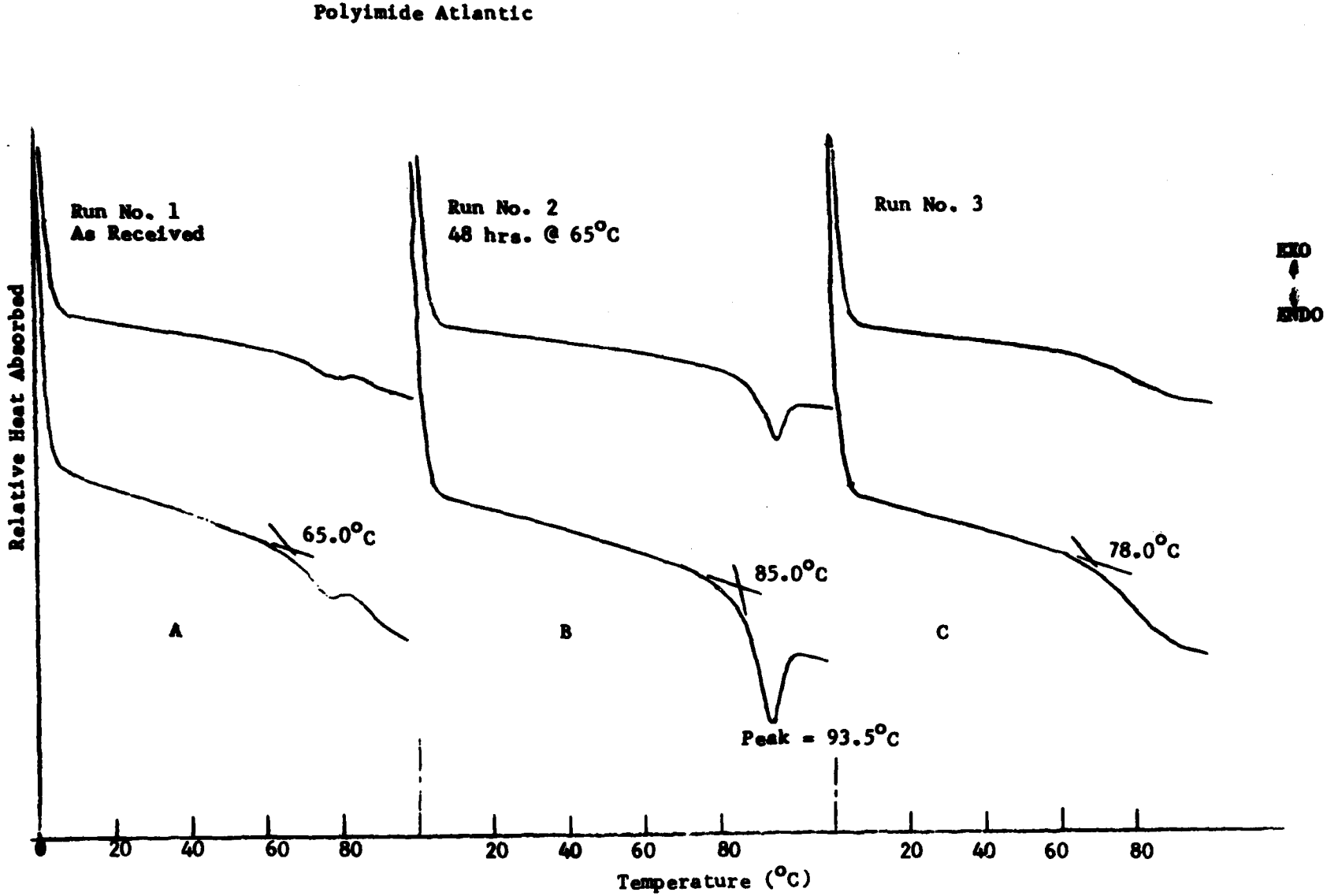


FIGURE 45 AGING EFFECTS ON LOW TEMPERATURE DSC PEAKS FOR OAK-ATLANTIC PREPREG

Thermogravimetric Analysis - Thermogravimetric analysis (TGA) of the resins revealed a significant difference in their volatile content. This data is shown in Figure 46. Storing Mica laminate at room temperature under 1 torr vacuum was evaluated as a possible means of removing the volatiles, but as can be seen from this figure, the vacuum storage has little effect on the volatiles. The Kerimid material was found to contain a total volatile content comparable to the Atlantic resin, but the volatiles are evolved at a substantially lower temperature, i.e., 100°C, as opposed to 200°C.

Thermomechanical Analysis - A modified thermal mechanical analysis (TMA) was performed on the Mica and Oak-Atlantic prepregs. The test performed utilized the Dupont parallel plate rheometry cage which contained six plies of the 0.004 inch laminate. The TMA probe was loaded with a two pound weight and the sample's compression was monitored as the cell temperature increased at a rate of 10°C/min. The design of this test was developed to parallel actual laminating conditions as closely as possible. The data is shown in Figure 47. The flow properties of the two resins are seen to be very similar. Interestingly, the vicosity of the two resins does not fall off sharply at a single temperature but steps down, first at 100°C and second at about 150°C. An obvious problem could occur with laminates made from resins which exhibit this two step viscosity reduction. The high pressures utilized in laminate manufacturing (~200 psi) could successfully deform the resin to the required thickness at a laminate temperature of only 130°C. Proper viscosity reduction and maximum inter-laminate flow requires a laminate temperature of at least 170°C, however.

c. FURTHER CHARACTERIZATION OF PREPREGS

New Lot of Mica Prepreg - A new lot of Mica prepreg polyimide, No. 8254-12, was received and characterized for comparison to the previously used Mica Lot No. 7996-5.

In general, the new lot is comparable to the previous lot, however slight differences can be noted. The DSC data indicates a difference of 11°C at the temperature at which the first endothermic transition occurs. Also, the percent weight loss is significantly less for the new lot using thermogravimetric analysis (TGA). An additional difference was also noted from Thermal Mechanical Analysis (TMA) in determining the temperature a which viscosity reduction occurs. This temperature was noticeably lower for the newer lot.

A comparison of this data is shown in Table 29. As will be seen, the data indicates there is no basic difference in laminates produced from either material, once the adhesion to copper is optimized by surface treatment.

Analytical Characterization of Norplex Polyimide B-Stage - A third B-stage polyimide from Norplex was also obtained for this study. Characterization studies and adhesion testing were performed on the Norplex material so that it could be compared to the Mica and Oak-Atlantic prepregs. The results of the analytical charcterization on the Norplex material are as follows:

o Resin Content

The resin content of the B-stage laminate was determined by extracting the resin

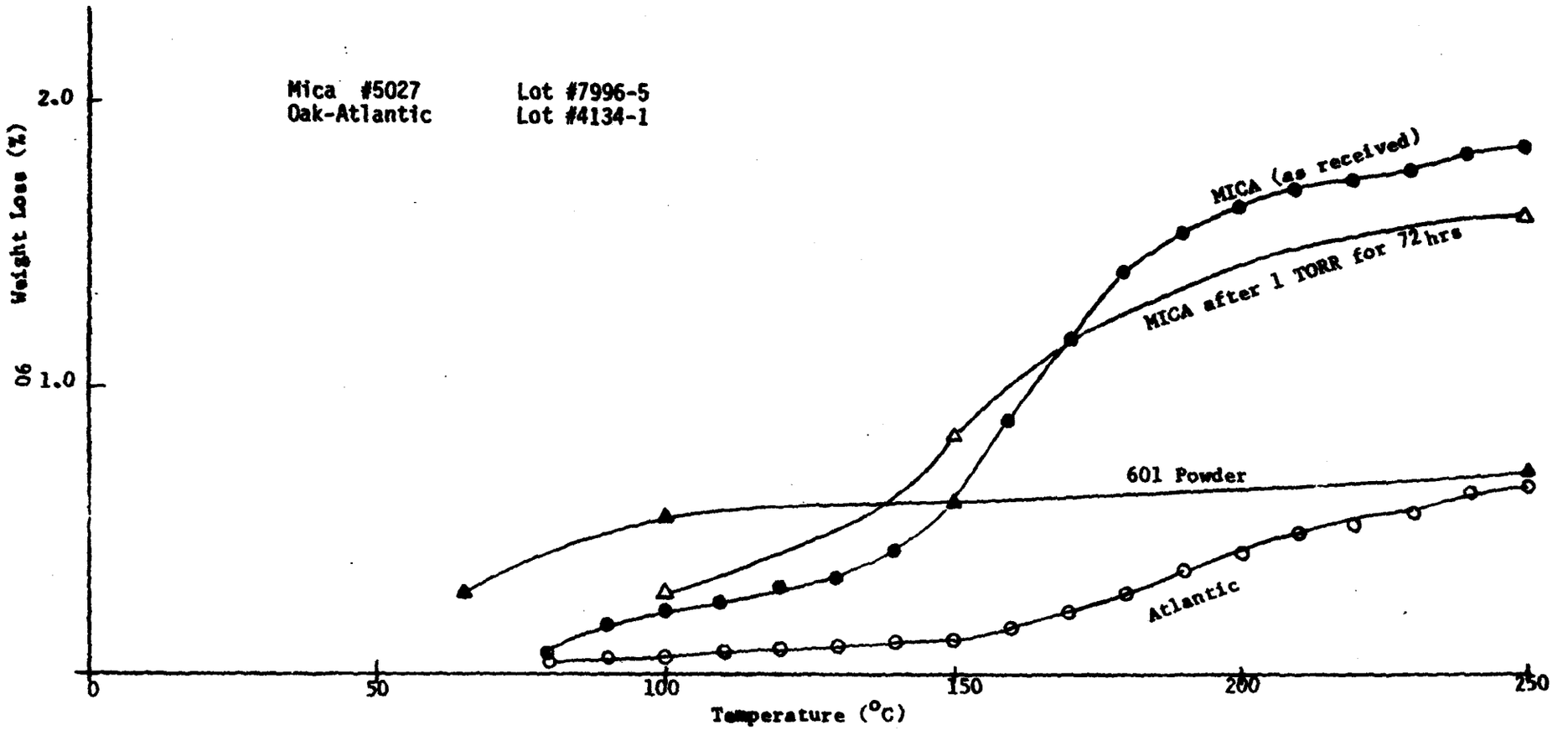


FIGURE 46 WEIGHT LOSS VERSUS TEMPERATURE FOR VARIOUS POLYIMIDE SAMPLES

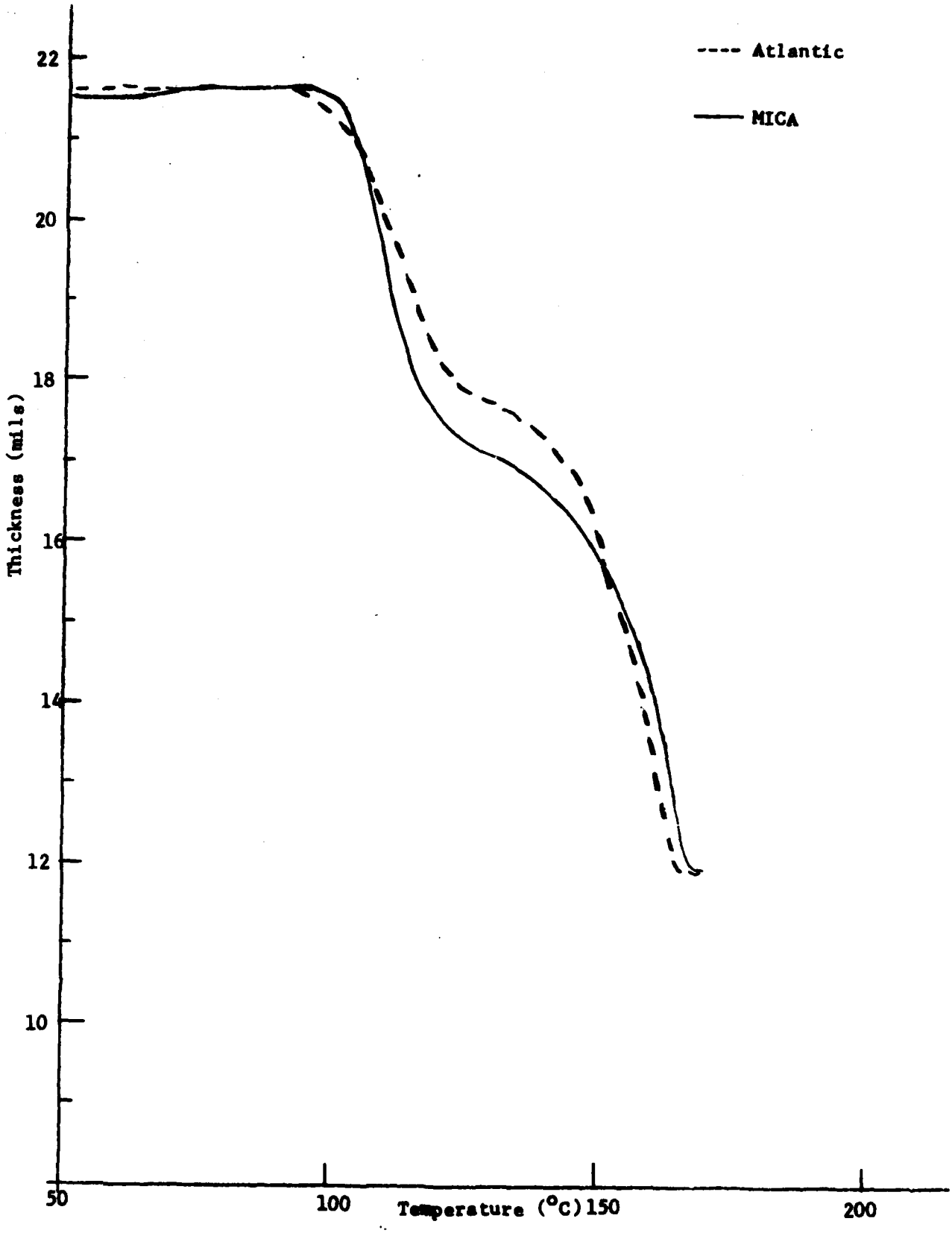


FIGURE 47 FLOW AS EFFECTED BY TEMPERATURE FOR MICA AND ATLANTIC PREPREG

TABLE 29 - COMPARISON OF ANALYTICAL CHARACTERIZATION OF MICA PREPREG LOTS 7996-5 AND 8254-12

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Lot #	A 1140 cm-1 / A 1180 cm-1
7996-5	1.15
8254-12	1.13

LIQUID CHROMATOGRAPHY

Ultraviolet Absorption Detection

Location from Injection		1/2 Height/Width (1/2hw)
3.70"	Lot #7996-5	0.14"
	Lot #8254-12	0.14"

REFRACTIVE INDEX DETECTOR

Lot #	Loc.	1/2 hw
7996-5	3.70"	0.15"
	4.08"	0.14"
8254-12	3.70"	0.14"
	4.08"	0.14"

THERMAL ANALYSIS

Differential Scanning Calorimetry (DSC)

Endothermic Transition		Exothermic Transition	
Lot #	Peak °C	Initiation °C	Peak °C
7996-5	80	187	241
8254-12	69	185	242

TABLE 29 - COMPARISON OF ANALYTICAL CHARACTERIZATION OF MICA PREPREG LOTS 7996-5 AND 8254-12 (Cont'd)

THERMAL GRAVIMETRIC ANALYSIS (TGA)

Lot #	TWL (%)
7996-5	1.85
8254-12	1.10

8254-12 - After 3 days in desiccator 0.90 (over $CaSO_4$)

THERMAL-MECHANICAL ANALYSIS (TMA)

	Viscosity Reduction T (°C) (Compression T)	
Lot #	First	Second
7996-5	100	150
8254-12	94	138

from the glass using dimethyl formamide. The resin content is calculated from the weight of the glass and the weight of the starting material. The resin content of the Norplex, Atlantic and Mica are similar; results are summarized in Table 30.

o FT-IR

The infrared spectra of the Norplex B-stage resin is shown in Figure 48. The absorptions at 1140 cm^{-1} were ratioed, and found to be equal to 1.11; this compares to 1.36 for Atlantic and 1.15 for Mica. The absorption at 1140 cm^{-1} is attributed to the imide stretch of the maleimide resin and the absorption at 1180 cm^{-1} attributed to the 1,4 dione structure in the polymerized material. The data indicates that the Norplex is more polymerized than the Atlantic B-stage but similar to the Mica.

o Thermal Analysis

The Differential Scanning Calorimeter (DSC) data is also reported in Table 30. The Tg of the Norplex is approximately 22°C lower than that of Atlantic and Mica B-stage. The position of the Tg increases with staging; this was seen in the advance staging study using Atlantic B-stage. Evaluation of this data seemed to indicate that the Norplex was less polymerized than Mica and Atlantic B-stage.

Substantial differences were also seen in the cure initiations and peak exotherm temperatures among the Norplex and the Atlantic and Mica B-stage. The Norplex DSC is shown in Figure 49.

o TMA

The test performed was a modified thermomechanical analysis (TMA) utilizing the Dupont parallel plate rheometry cage containing one ply of 0.004 inch laminate with the TMA probe loaded with a 100 g weight. The sample's compression was monitored as the cell temperature increased at a rate of 10°C per minute. This test was used to determine the softening temperature of the laminate; the data is shown in Figure 50. The Norplex B-stage tested had the same softening temperature as the Mica, 92°C; this was only slightly above the softening temperature of the Atlantic, 90°C.

o TGA

Thermogravimetric analysis (TGA) of the Norplex resin revealed a total volatile content of 2.12%. The data is shown in Figure 51. The volatiles appear to be due to the evaporation of NMP solvent rather than moisture.

o Liquid Chromatography

The chromatograms of the Norplex, Atlantic and Mica B-stage revealed differences in the amount of free methylene dianiline (MDA) detected. The Norplex B-stage tested has about 30% more free MDA than the Mica and 20% more MDA than the Atlantic.

TABLE 30 - COMPARISON OF NORPLEX, ATLANTIC, AND MICA PREPREGS

	Norplex	Atlantic	Mica
% Resin Content	61	62	64
Ave. Thickness (in.)	0.0047	0.0047	0.0046
FTIR $\frac{1140\ cm^{-1}}{1180\ cm^{-1}}$	1.11	1.36	1.15
DSC			
Tg (°C)	61	83	82
Cure Initiation (°C)	149	177	187
Peak (°C)	248	233	241
TMA			
Softening T, °C	92	90	92
TGA			
Volatile Content (percent)	2.12	0.65	1.85

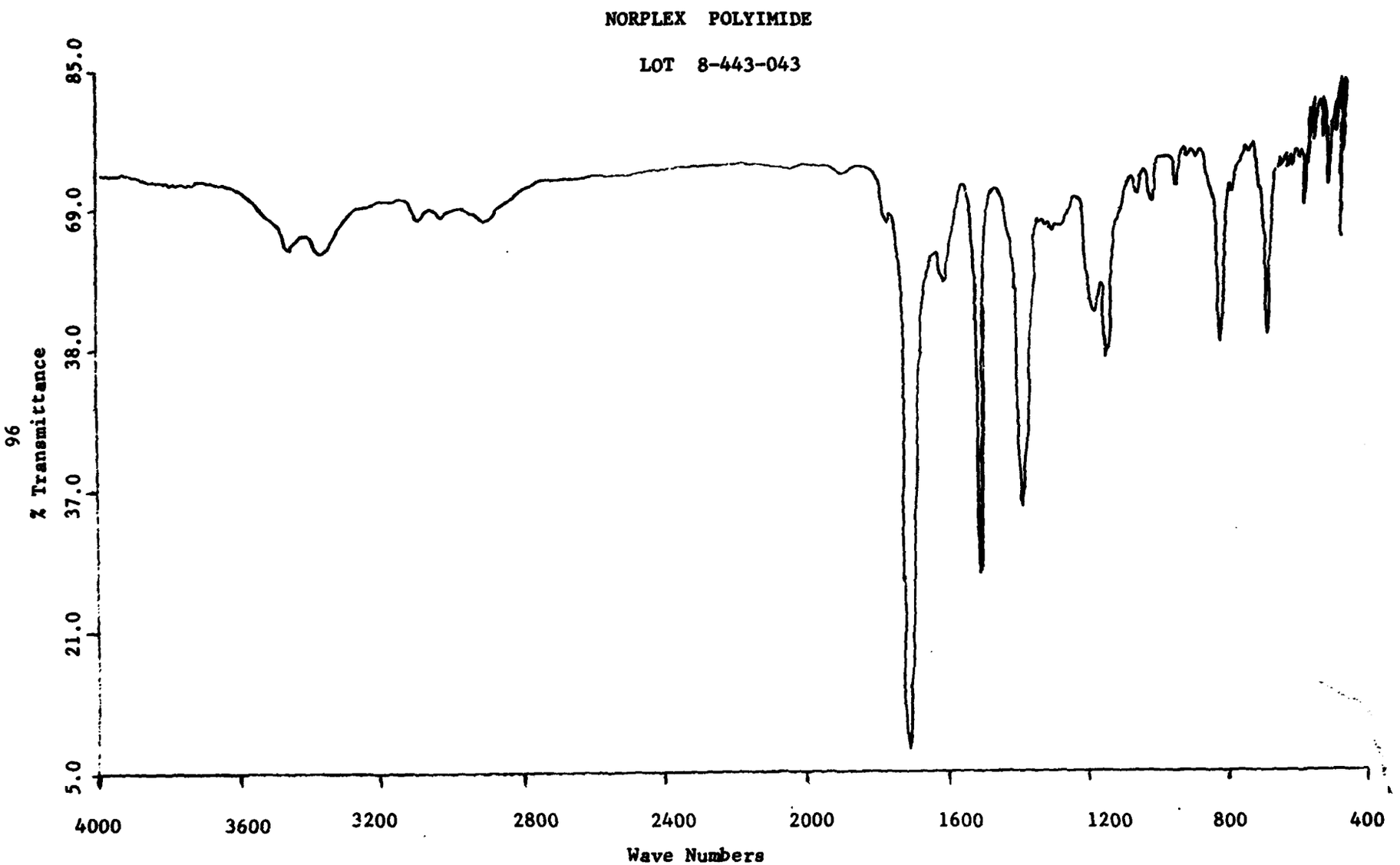


FIGURE 48 INFRARED SPECTRUM OF NOPLEX POLYIMIDE

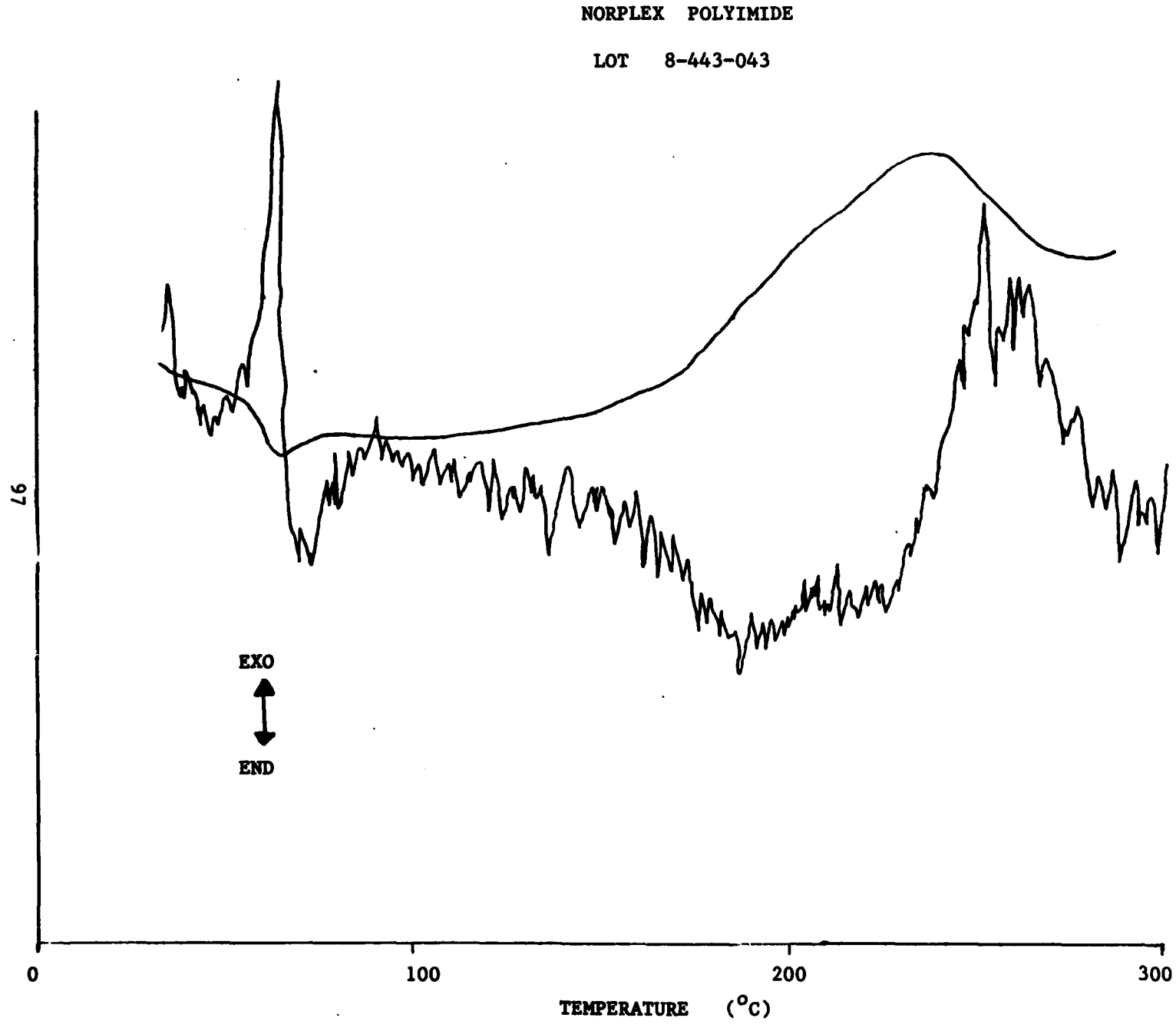


FIGURE 49 DSC PROFILE OF NORPLEX POLYIMIDE

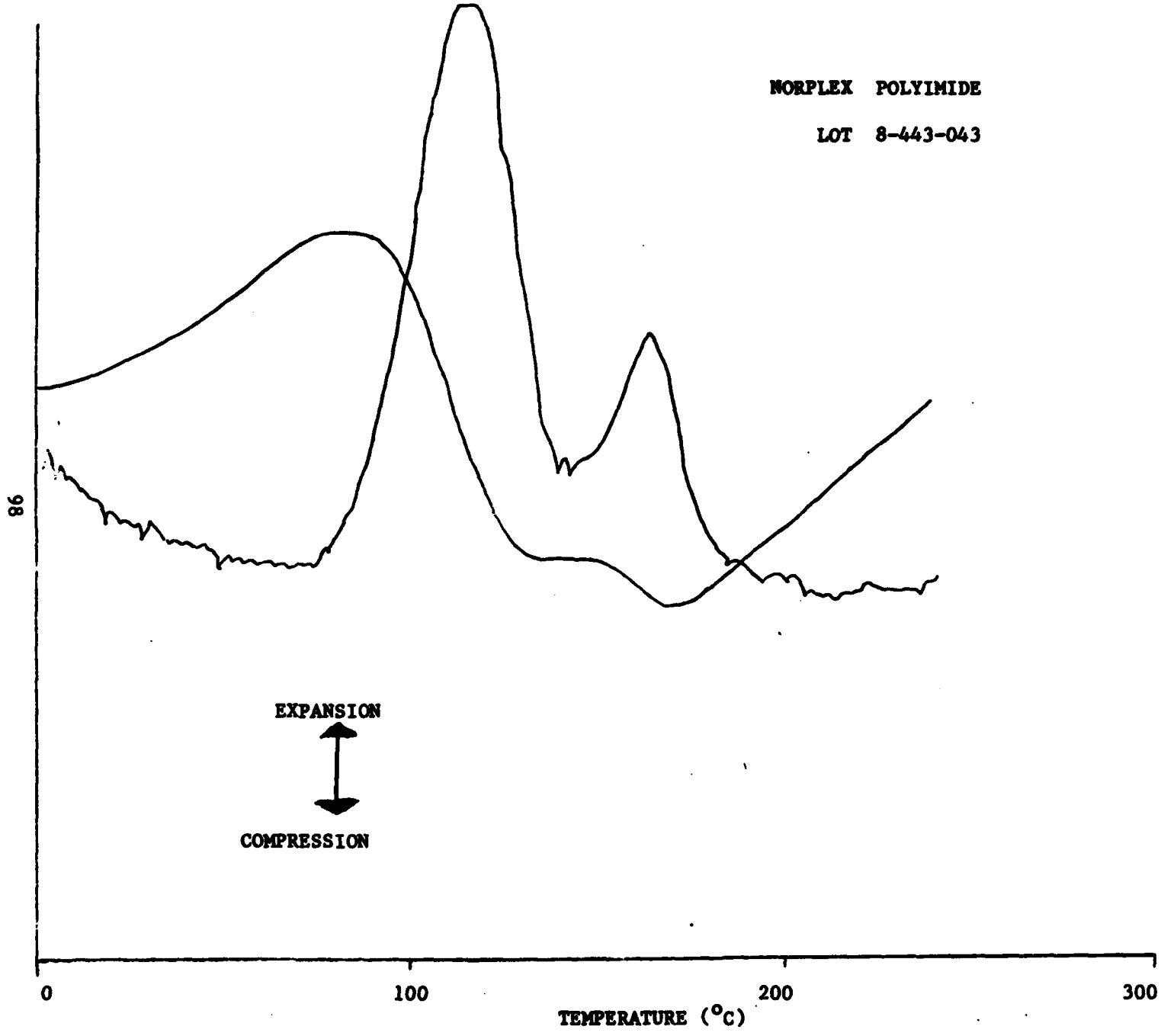


FIGURE 50 TMA PROFILE OF NORPLEX POLYIMIDE

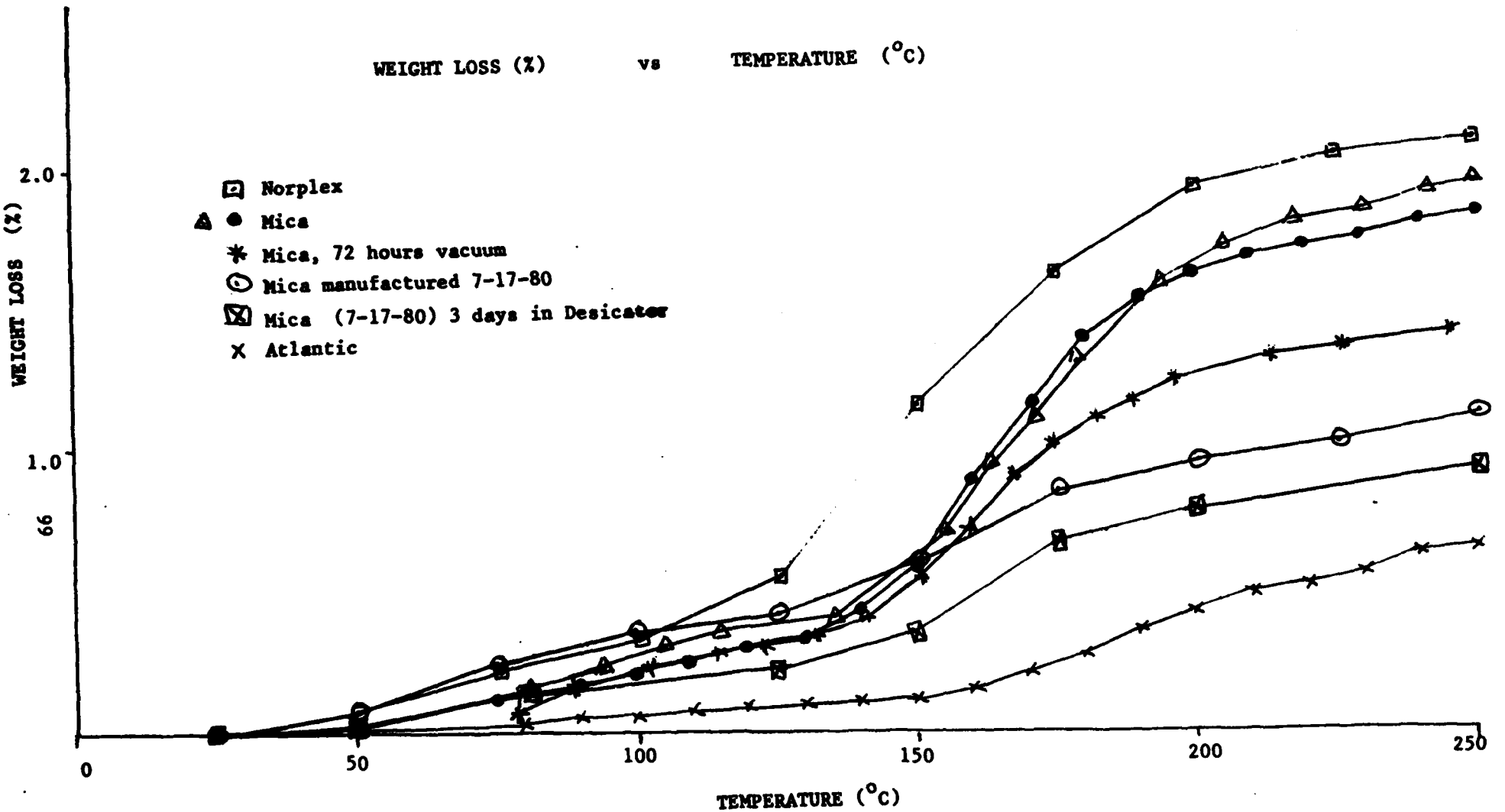


FIGURE 51 TGA PROFILE OF NORPLEX MICA AND ATLANTIC POLYIMIDES

o Summary of Norplex Prepreg

The IR data indicated the Norplex was more polymerized than the Atlantic B-stage, the DSC indicated it is less polymerized and the TMA data indicated that the two are approximately the same.

Baseline Characterization of Polyimide Resin (Kerimid 601) - In order to effectively establish the baseline data determined analytically for the various prepregs, it is necessary to fully characterize the starting resin system. Therefore, a new sample of Kerimid 601 polyimide resin was obtained from Rhone-Poulenc for this purpose. FTIR, Thermal Analysis, and Liquid Chromatography Analysis were then performed.

o FT-IR

The infrared spectra of the Kerimid 601 resin (Lot #80289) is shown in Figure 52 and the ratio of the absorptions at 1140 cm-1 to 1180 cm -1 was determined to be 1.29.

A comparison of the ratio of the Kerimid resin to the Atlantic, Mica and Norplex B-stage is shown in Table 31. It has already been shown that the ratio usually decreases with staging therefore, it was expected that the Kerimid resin would have a higher ratio than the B-stage material. But the Atlantic B-stage (R = 1.36) had a higher ratio than the Kerimid resin. It may be that the Atlantic B-stage was prepared from a lot of Kerimid with a higher ratio than this lot (#80289) had.

o Thermal Aging

The Tg of the Kerimid was determined to be 73°C. This is lower than the Tg of the Atlantic and Mica B-stage but higher than the Norplex (Tg = 61). The position of the Tg increases with staging and it was expected that the Tg of the Kerimid would be lower than the Tg of all the B-stage materials. The low Tg value of the Norplex may be attributed to two things: the Norplex was probably made from a lot of Kerimid different than the one tested or the Norplex B-stage contained a high amount of solvent, which could lower the Tg.

o TGA

The thermogravimetric analysis of the Kerimid resin revealed a total weight loss of 0.73%. The loss appears to be due to moisture. This is shown in Figure 53.

o Liquid Chromatography

The amount of free methylene diamiline (MDA) was determined to be 8% for Kerimid 601 resin. A comparison between the amount of free MDA in the different prepreg materials also shown in Table 31. As expected, the Kerimid contains more MDA than the prepregs.

The free MDA was measured using a technique based on the gel permeation chromatography (GPC) mode of liquid chromatogrqphy. This technique had pre-

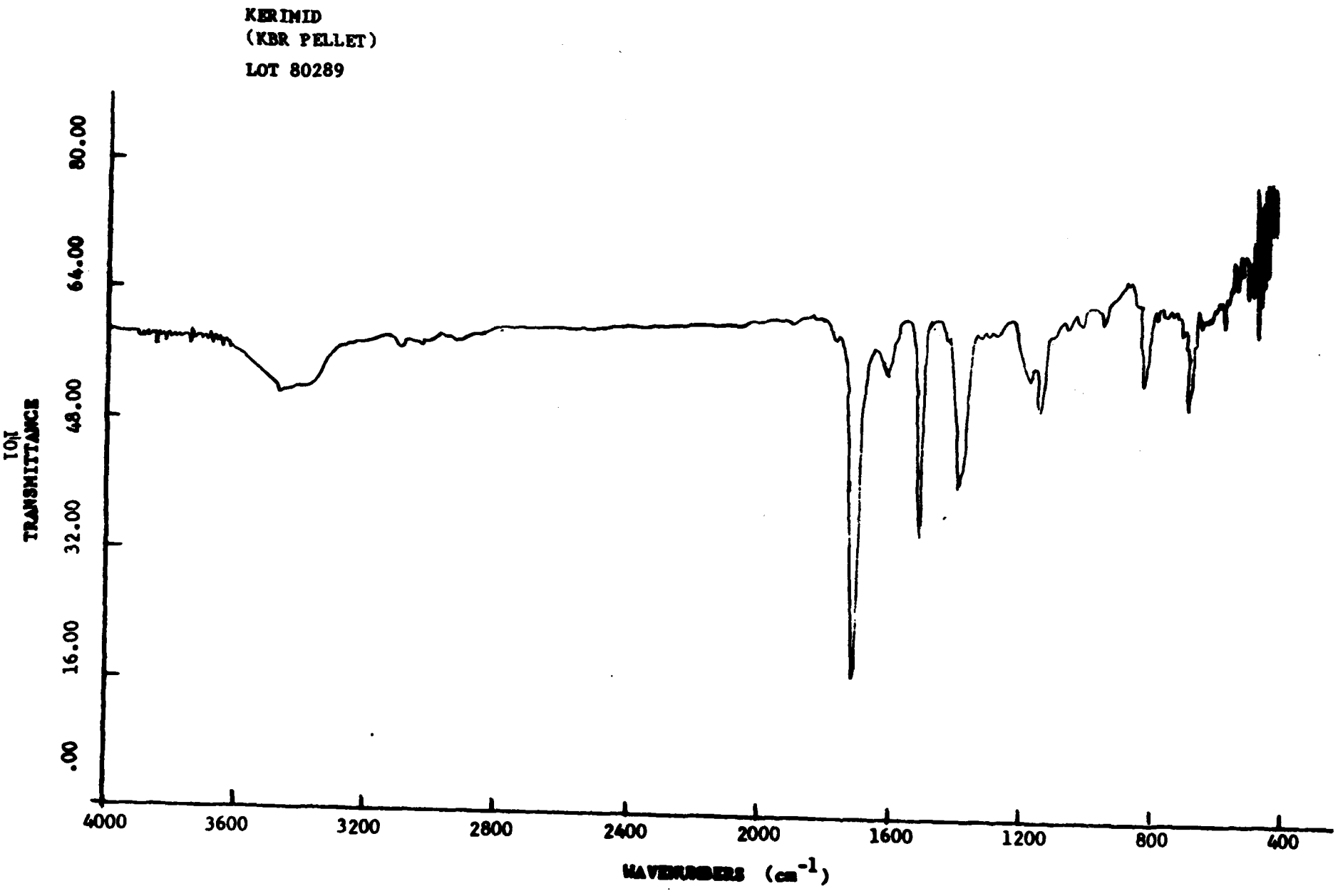


FIGURE 52 FTIR SPECTRUM OF KERIMID 601 RESIN

TABLE 31 - COMPARISON OF ANALYTICAL DATA OF KERIMID 601 TO THREE PREPREG LAMINATE MATERIALS

	Kerimid 601 Lot #80289	Norplex Lot #8-443-048	Atlantic Lot #4080-1	Lot #8254-12
FTIR				
$\frac{1140\ cm^{-1}}{1180\ cm^{-1}}$	1.29	1.11	1.36	1.15
DSC				
Tg (°C)	73	61	83	82
Cure Initiation (°C)	159	149	177	187
Peak (°C)	225	248	233	241
TGA				
Volatile Content (percent)	0.73	2.12	0.65	1.85
Free MDA	8%	6%	4%	6%

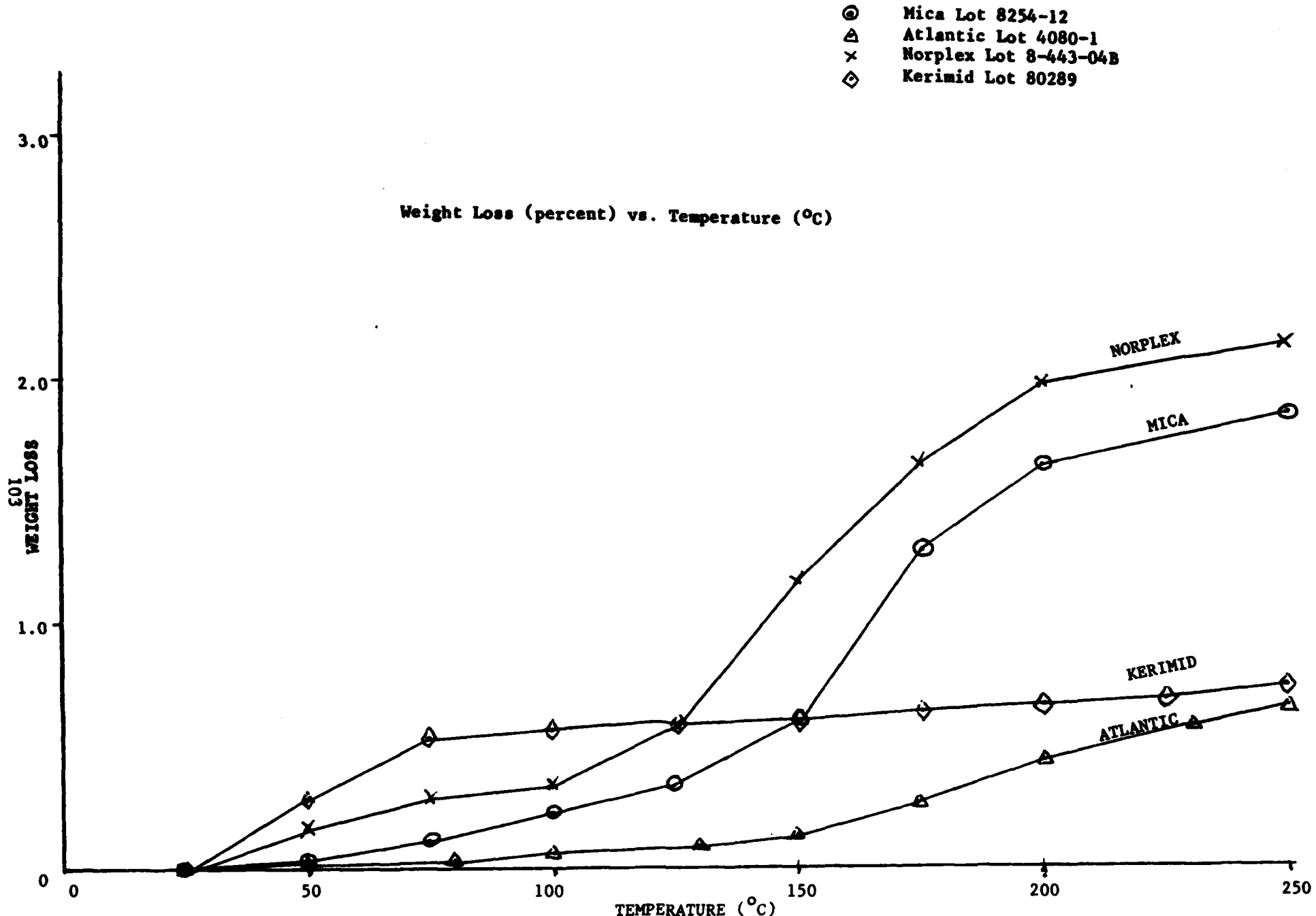


FIGURE 53 TGA PROFILE OF KERIMID 601 AND THREE PREPREG LAMINATES

viously been developed for determining the dimer content of paraxylylene. It worked quite well and appears to be a viable method for determining the free MDA in Kerimid 601 resin.

We had received a copy of a technique for the colorimetric determination of free 4,4' -methylenedianiline (MDA) in Kerimid 601 (See Appendix). We understand that this test was developed by Prolabo of Paris, France for Rhone-Poulenc, the suppliers of Kerimid 601. We explored the possibility of using this technique but found that some of the required chemicals are only available from France. Because of the time constraints of the program, we therefore felt that further investigation of this technique was not feasible.

d. CHARACTERIZATION OF FINAL LOTS OF POLYIMIDE PREPREG

A new lot of polyimide prepreg from Oak-Atlantic (Lot #6045-2) and from Mica (Lot #9009-6) were obtained for use in making the specimens to be used for evaluating the improved materials and processes in fabricated MLPWB's. A third sample, Nelco (Lot #N-7305-104), was received from the vendor to establish its analytical characterizations and compare it to the Mica and Oak materials.

The results of these baseline characterizations are summarized in Table 32. The thermogravimetric data is shown in Figure 54.

While all three prepregs had less than 2% volatile content, the Nelco material was significantly less than the other two. Nelco also had less free MDA than Oak and Mica.

e. ADVANCED STAGING OF PREPREG POLYIMIDES

Atlantic Material - Atlantic B-stage poyimide, Lot #4808-1, was evaluated with respect to the point at which staging advancement significantly affects the production and performance of the printed circuit board.

B-stage samples were advanced staged at 284°F (140°C) for periods of 1/2, 1, 2, and 4 hours. Samples of the advanced staged material were then analyzed by Fourier-Transform Infrared Spectroscopy (FT-IR) and the ratio of absorptions at 1140 cm-1 to 1180 cm-1 measured. Thermal mechanical analysis (TMA) and differential scanning calorimetry were also conducted to establish softening temperature and glass transition temperature (Tg) of the advanced staged samples. Inner laminar adhesion strengths were also measured on circuit boards made using the advance staged B-stage materials. Table 33 is a summary of the initial results on advanced staging. As can be seen, the inner laminar shear strength appeared to be inversely proportional to the amount of advance staging. There also appears to be direct correlation to the softening temperature, glass transition temperature, and ratio of the infrared absorptions (1140 cm^{-1} to 1180 cm^{-1}).

The advanced staged B-stage polyimide materials were tested for inner laminar adhesive shear strength per ASTM D2733. Samples were made using the standard

TABLE 32 - BASELINE CHARACTERIZATION OF NELCO, ATLANTIC AND MICA PREPREG

	Nelco Lot N-7305-108	Atlantic Lot 6045-2	Mica 9009-6
% Resin	63.7	63.3	60.6
FTIR $\frac{1140\ cm^{-1}}{1180\ cm^{-1}}$	1.16	1.24	1.23
DSC Tg °C	81	73	84
Cure Initiation	164	168	163
Peak (°C)	239	228	232
TMA			
Softening T (°C)	93	95	95
TGA			
% Volatile Content	0.84	1.17	1.70
Free MDA	6.8	12.4	7.6
Ave. Thickness, in.	0.0056	0.0048	.0054

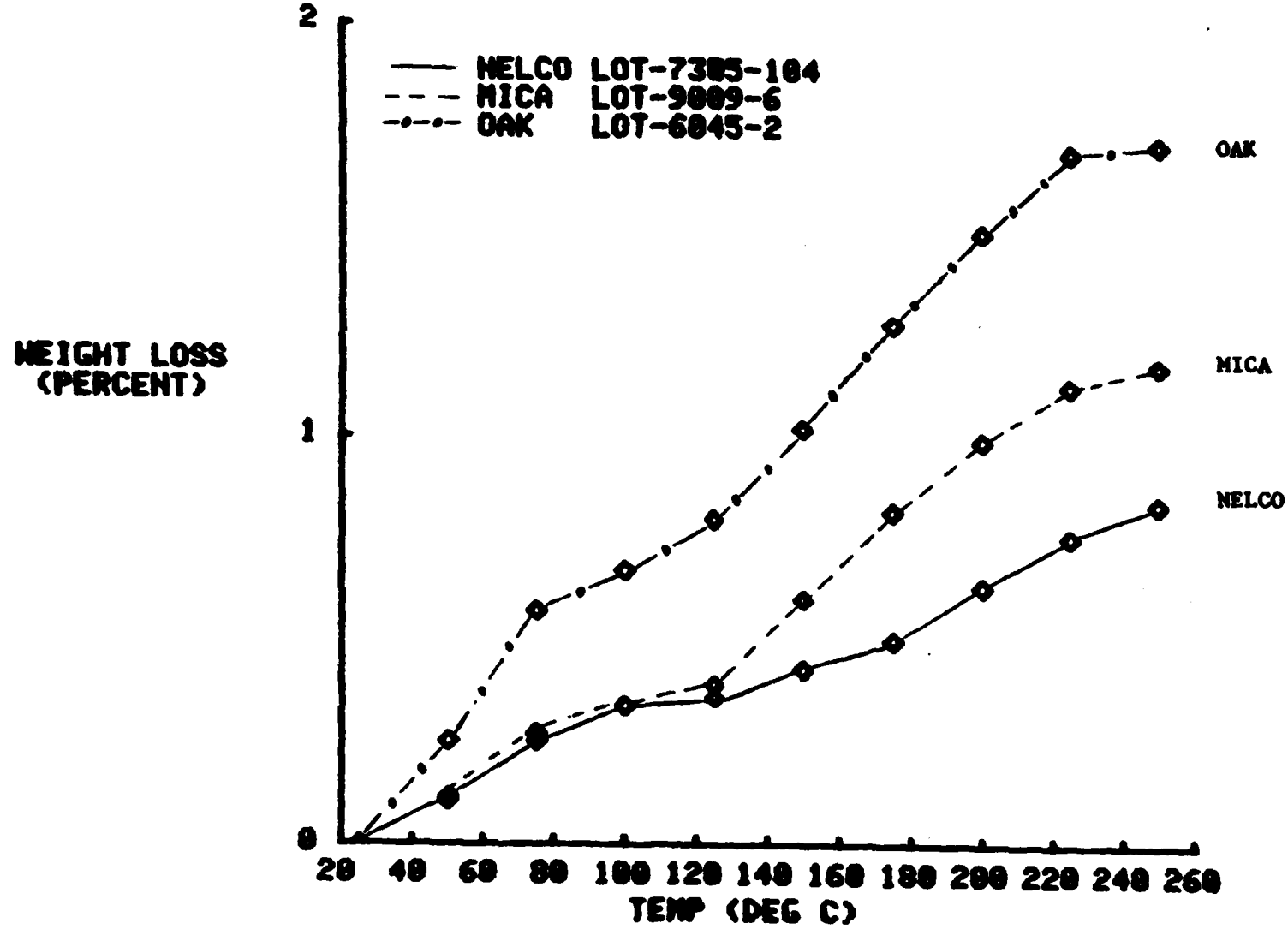


FIGURE 54 WEIGHT LOSS BY TGA (PERCENT) VS TEMP. (DEG C)

Table 33 Results of Advanced Staging Polyimide (Atlantic)

Time (at 140°C) Adv. Staged (hrs)	Shear Strength (psi)	TMA (Softening T, °C)	DSC (Tg, °C)	FTIR 1140 cm-1 / 1180 cm-1
0	2050	90	83	1.36
1/2	*	110	95	*
1	1552	112	95	1.17
2	1334	127	106	1.14
4	Sample Broke Apart While Preparing for Testing	129	108	1.04

*Under test at the time

ferric chloride etch, red oxide treatment, hot press laminating cycle, and four hours post cure at 425°F (218°C). Table 34 shows the results of 1, 2 and 4 hours advance staging at 140°C. Aging for one hour showed a loss of strength (from a 2050 psi control) however the fracture mode was still cohesive. Two hour staging not only showed a significant decrease in adhesive shear strength but also a change in fracture mode to partially adhesive failure. Four hour staging showed essentially no strength and the panels delaminated upon handling.

It should be noted that a 1/2 hour staged sample had not been tested for lap shear strength at this time in the study. Subsesquent testing gave a value of 1328 psi which was much lower than expected. Additional tests were then performed. B-stage material (Atlantic) was then cured at 185°C and analyzed by FT-IR and the ratio at 1140 cm-1 to 1180 cm-1 measured. Figure 55 shows the change in the intensities of absorptions as a function of staging advancement at 185°C. The curves are normalized to the intensity of the absorption at 1140 but this intensity does in fact change. The 1140 absorption decreases in intensity while the 1180 absorption increases. Figure 56 shows the relationship between change in absorption as a function of time. This data was collected on material cured two hours at 185°C and post cured at 233°C for four hours.

Figure 57 is the percentage of extractable material, using dimethyl formamide as a solvent, with time. Table 35 shows the relationship of time with percent reacted and with percent extractable. The prepreg has been assigned an arbitrary value of zero percent reacted and the post-baked for 4 hours sample as 100%. Figure 58 shows the relationship of percent reacted versus time for six different temperatures. At 79°C, 93°C, and 139°C the prepreg appears to react to a certain extent and then "unreact". This is not exhibited in the material cured at or above 150°C. A possible explanation could be the existence of a side reaction taking place which has functional groups which absorb at or near 1140 cm-1 and/or 1180 cm-1; at temperatures at or above 150°C this reaction may take place too quickly to observe. The fact that the "unreaction" was not observed in the material cured at 107°C, may be attributed to the B-stage, cured at this temperature, standing at room temperature (it is normally refrigerated) for an extended period of time before use. An Arrhenius plot of the material is shown in Figure 59. The Arrhenius plot make it possible to determine the storage life of the B-stage at a particular temperature.

As previously mentioned, the shear strength for the 1/2 hour staged sample did not seem to correlate. It was also found that the FTIR data did also not seem to correlate. Table 36 summarizes the completed data missing from Table 33. Both the shear strength and FTIR data were lower than expected. The 1/2 hour sample may have been incorrectly staged, but if this were true, the TMA and DSC data would be expected to also reflect this, and they did not. It was noted before that at temperatures below 150°C, the material would appear to react to a certain point and then "unreact". If so, the 1/2 hour sample could be at the point just before it "unreacts".

Table 34 Shear Strength of Laminates

Made with Advance Staged B-stage Polyimide (Atlantic)

Specimen ID	Test Temp	Shear Stress	Fracture Mode
24722-33 Aged 1 hr/140°C			
-1	23°C	1360 psi	Cohesive Thru "C" Stage
-2	23°C	1744	Cohesive Thru "C" Stage
-3	200°C	1680	Cohesive Thru "B" Stage
-4	200°C	1512	Cohesive Thru "C" Stage
24722-32 Aged 2 hr/140°C			
-1	23°C	1188 psi	Partly Adhesive/Cohesive
-2	23°C	1480	Partly Adhesive/Cohesive
-3	200°C	1256	Partly Adhesive/Cohesive
-4	200°C	1192	Partly Adhesive/Cohesive
24722-34 Aged 4 hr/140°C			
-1			
-2		All specimens broke on handling indicating very low adhesion strength.	
-3			
-4			

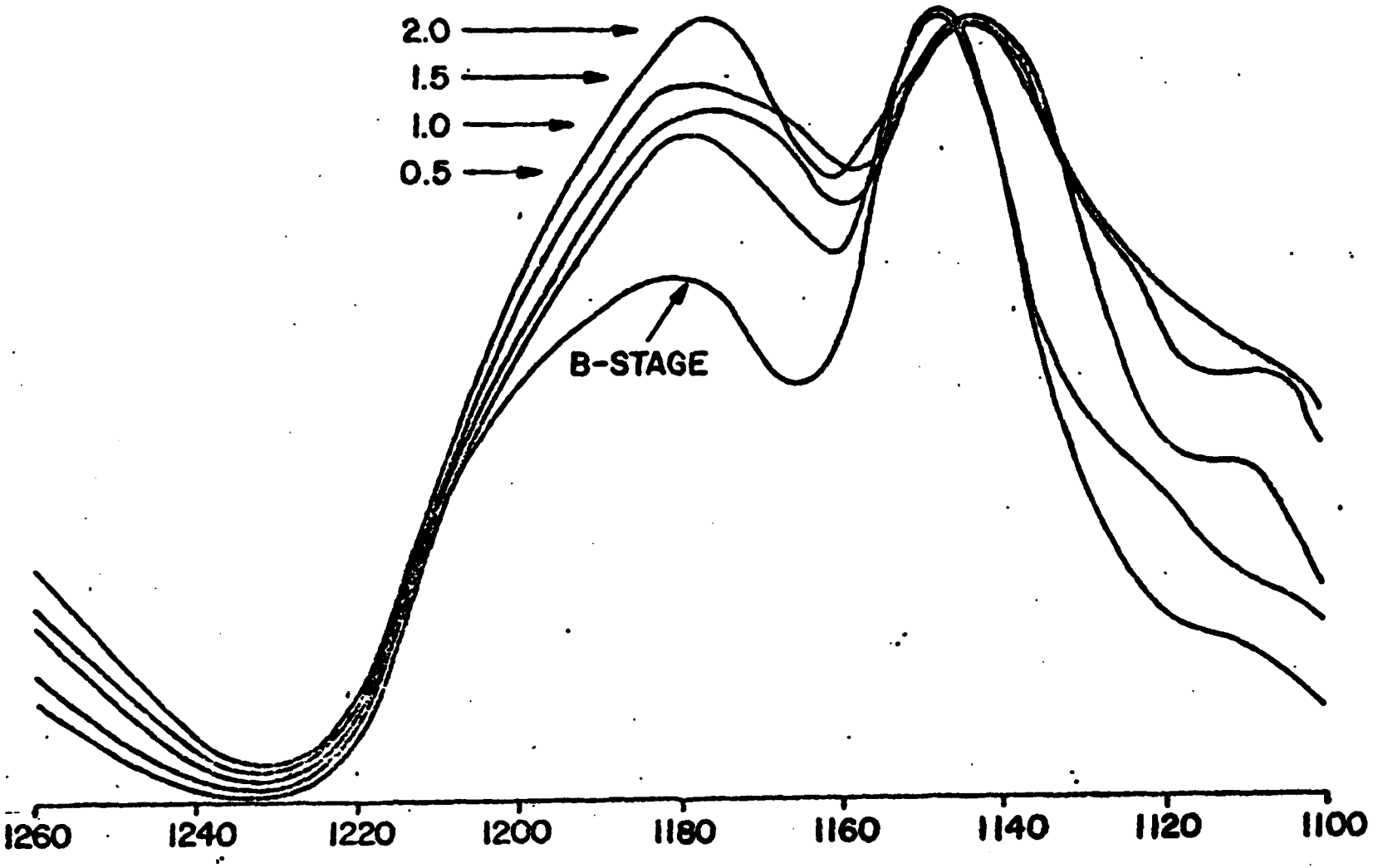


FIGURE 55 CHANGE IN ABSORPTION AS A FUNCTION OF ADVANCEMENT AT 185°C

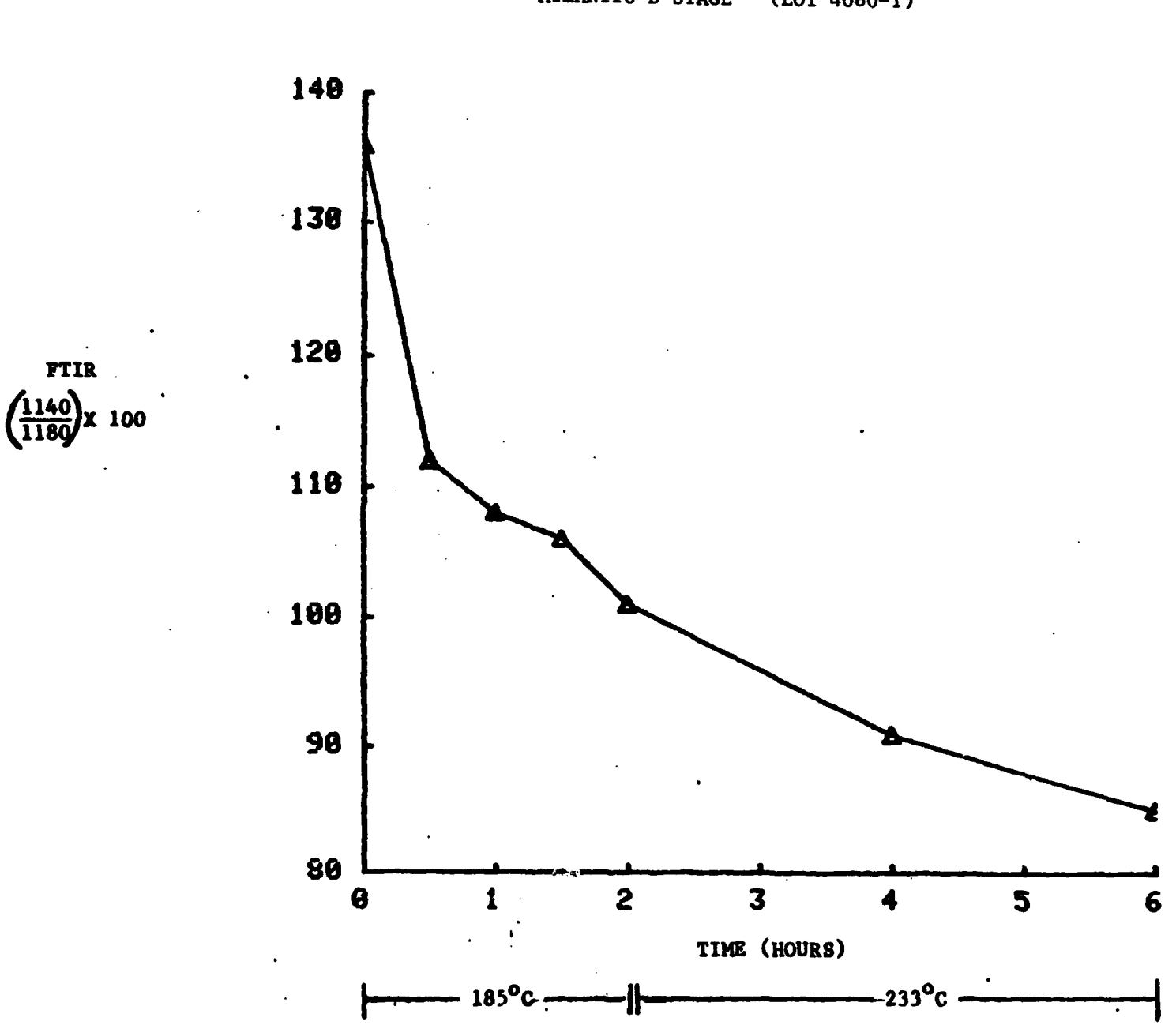


FIGURE 56 FTIR (1140/1180) *100 VS TIME (HOURS)

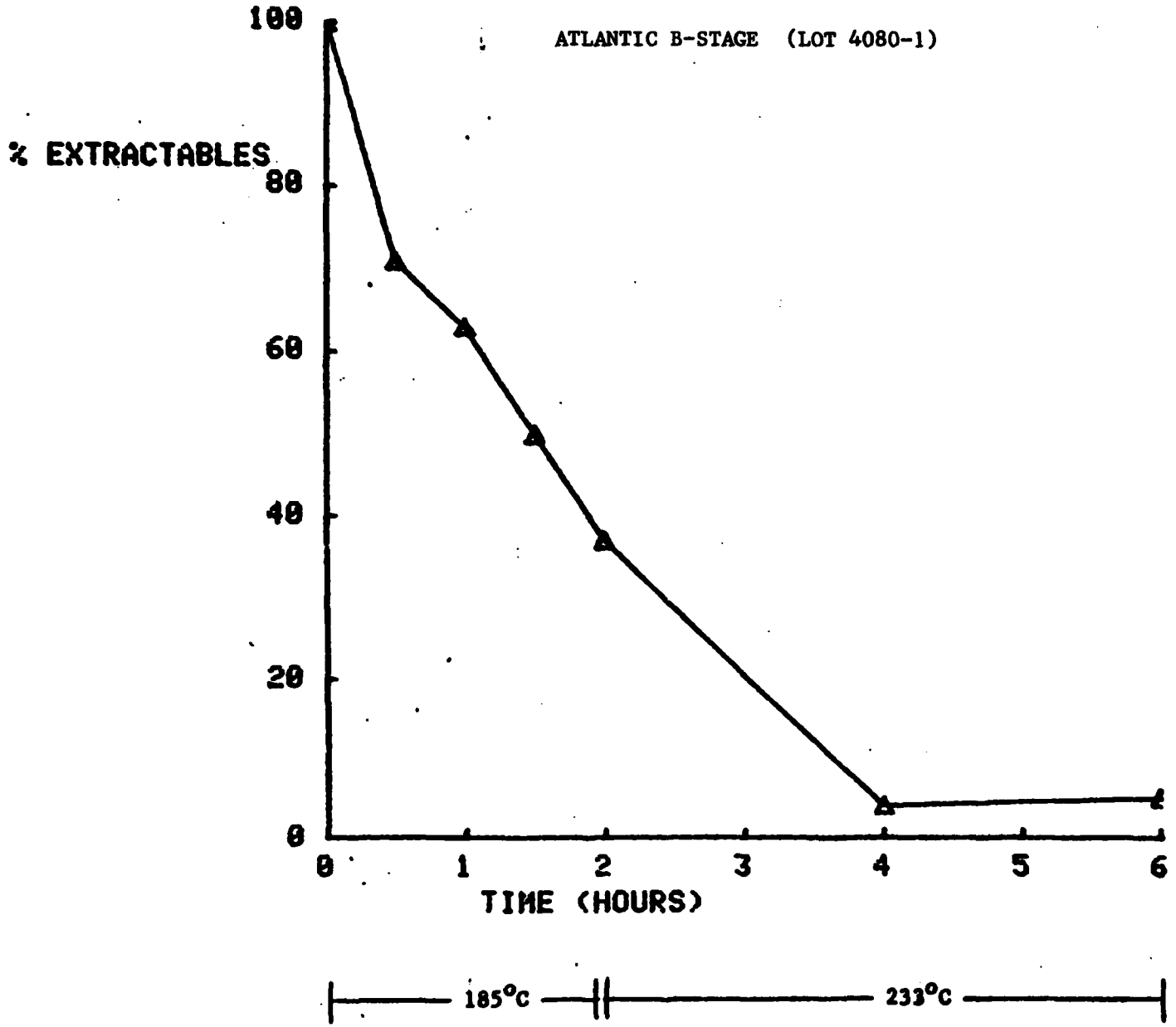


FIGURE 57 % EXTRACTABLES VS TIME (HOURS)

Table 35 Relationship Between Percent Extractable and Percent Reacted of Advanced Staged Polyimide (Atlantic)

	Time (hrs.)	FTIR 1140 cm-1 / 1180 cm-1	Percent Extractable	Percent Reacted
	0	1.36	100	0
Cured at 185°C	1/2	1.12	71	46
	1	1.08	63	54
	1 1/2	1.06	50	56
	2	1.01	37	68
Post Baked at 233°C	4	0.91	4	88
	6	0.85	5	100

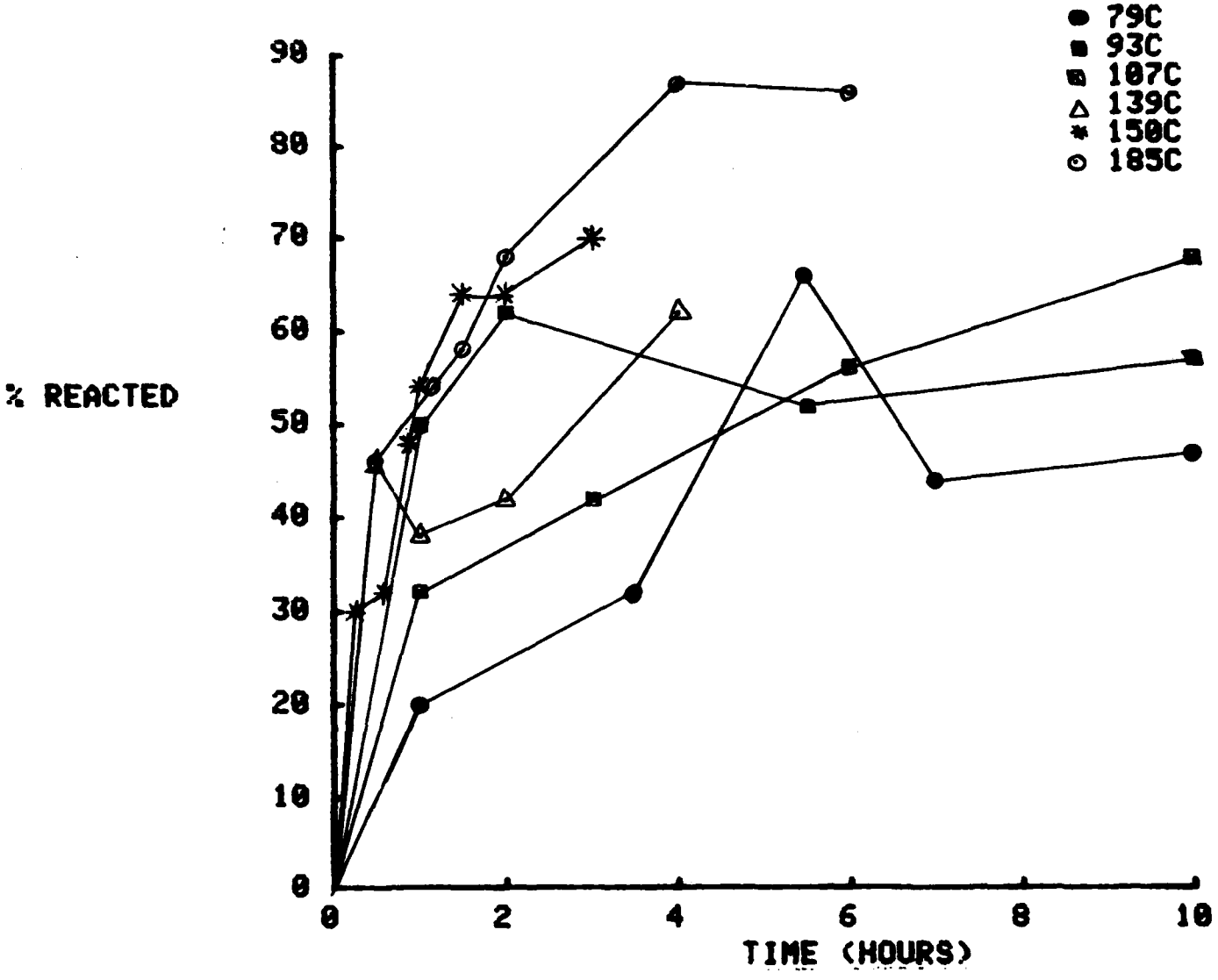


FIGURE 58 % REACTED VS TIME (HOURS)

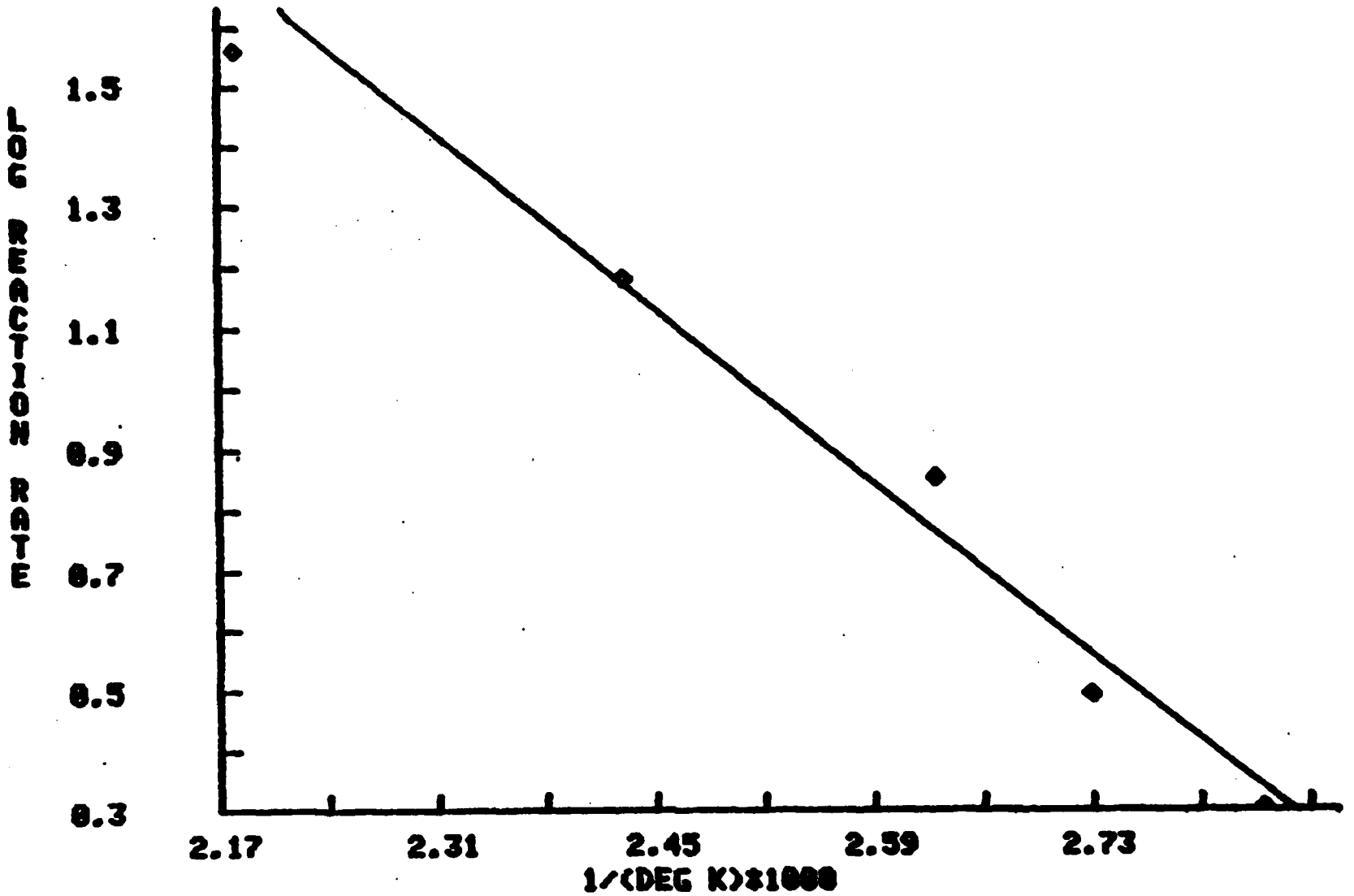


FIGURE 59 ARRHENIUS PLOT OF ATLANTIC POLYIMIDE

Table 36 Results of Advanced Staging Polyimide

Time (at 140°C) Adv. Staged (hrs)	Shear Strength (psi)	TMA (softening T, °C)	DSC (Tg, °C)	FTIR 1140 cm-1 / 1180 cm-1
0	2050	90	83	1.36
1/2	1328	110	95	1.12
1	1552	112	95	1.17
2	1334	127	106	1.14
4	Sample Broke Apart While Preparing for Testing	129	108	1.04

The shear strength of the 1/2 hour sample is slightly lower than the shear strength of the two hour sample, but the failure mode of the 1/2 hour sample is cohesive while the failure mode of the 2 hour sample is partially adhesive. Another sample of B-stage was later advanced staged for a 1/2 hour to resolve any conflicts existing in the data. The relationship between inner laminar shear strength and the length of advanced staging is shown in Figure 60. The relationship is approximately inversely proportional if the 1/2 hour sample is ignored. However, ignoring the 1/2 hour data may not be valid.

The next three figures (Figures 61, 62, and 63) show the relationship between shear strength and TMA, DSC, and FTIR. There is almost a linear relationship between TMA, DSC, and the shear strength, if the 1/2 hour sample is again ignored. Figures 64, 65, and 66 are TMA, DSC and FTIR vs. time. Each exhibits a dramatic change for 1 - 2 hours which then levels off.

At this point of the study, only the FTIR indicated that the shear strength of the 1/2 hour sample may be low. It was believed that if after testing another 1/2 hour sample, similar values were obtained, this would indicate that the DSC and TMA are not valid methods for predicting processibility of the B-stage.

A new set of samples were made. The results of testing these new samples did not confirm the previous low shear strength results and actually gave values significantly higher than the initial unstaged central samples. Table 37 summarizes the data on lap shear strengths as a function of staging time.

Because of these surprising results, another duplicate set of 1/2 staged samples were made and tested. Table 38 shows a comparison of the original data at 1/2 hour and the duplicate tests. All these data could fall within the normal scatter for shear test data; the duplicate room temperature values being slightly higher and the 200°C values being slightly lower. It can be stated that advanced staging for 1/2 hour definitely does not lower the shear strength.

Norplex Material - To verify results obtained on the advanced staging of the Oak-Atlantic polyimide prepreg, similar testing was performed on the Norplex polyimide. Norplex B-stage polyimide was advanced at 140°C and samples tested at discrete time intervals. The softening temperature vs. time is shown in Figure 67. A comparison of this curve, with the curve previously reported for the Atlantic indicates a similar change in the softening temperature with time for the two B-stage materials.

The FTIR data is shown in Figure 68. It was shown that the Atlantic polyimide reacts to a certain extent and then "unreacts" at staging temperatures below 150°C. Analysis of the Norplex revealed a similar phenomenon, only the Norplex B-stage appears to be at the point just before it "unreacts", i.e., similar to the 1/2 hour staged samples of Atlantic. The ratio of Norplex B-stage is 1.13 and the ratio of the Atlantic sample cured 1/2 hour at 140°C is 1.12. A comparison of the change in the ratio with time at 140°C starting with the one hour sample and going to four hours revealed that the Norplex ratio changed slightly faster than the Atlantic but not significantly.

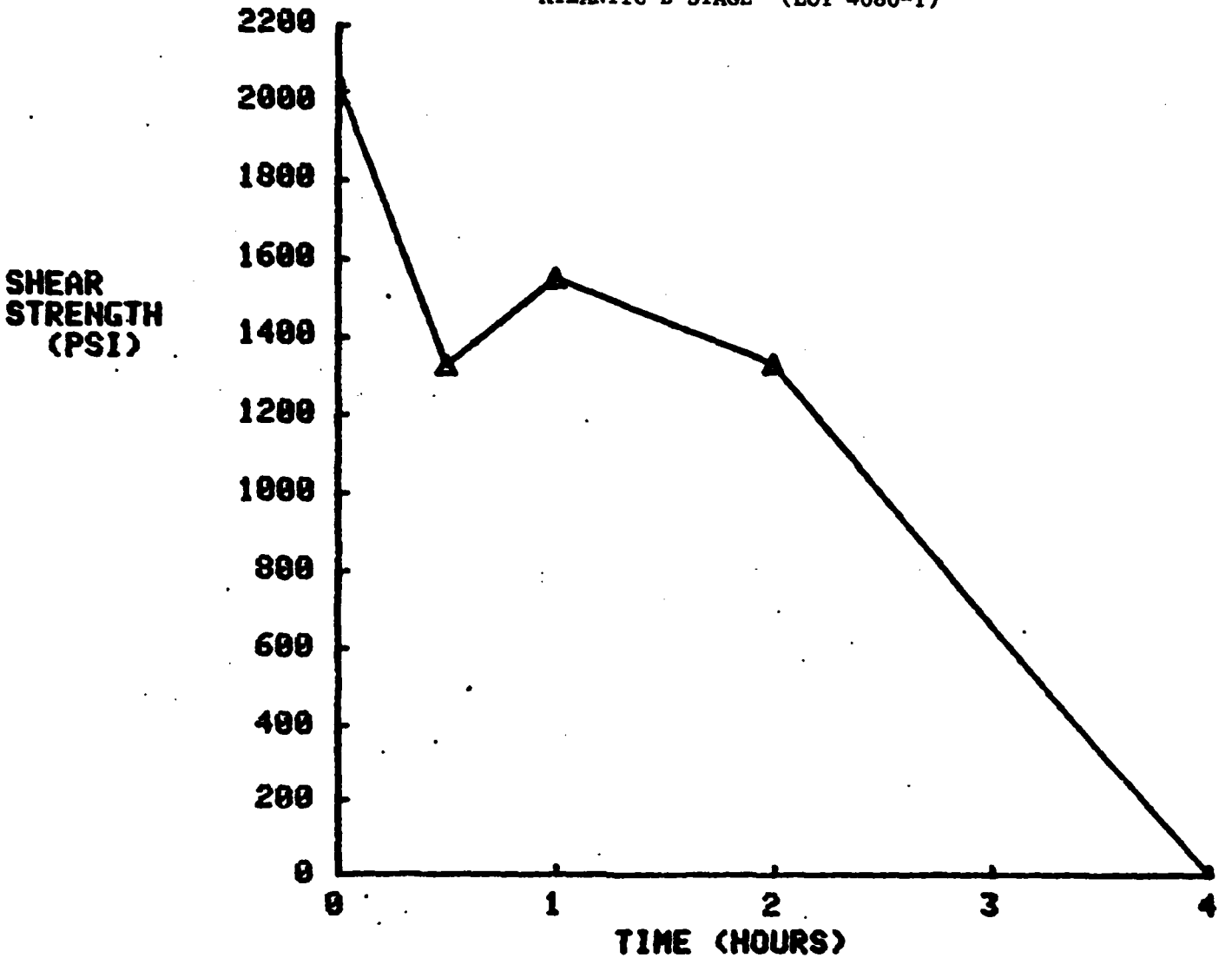


FIGURE 60 SHEAR STRENGTH (PSI) VS TIME (HOURS)

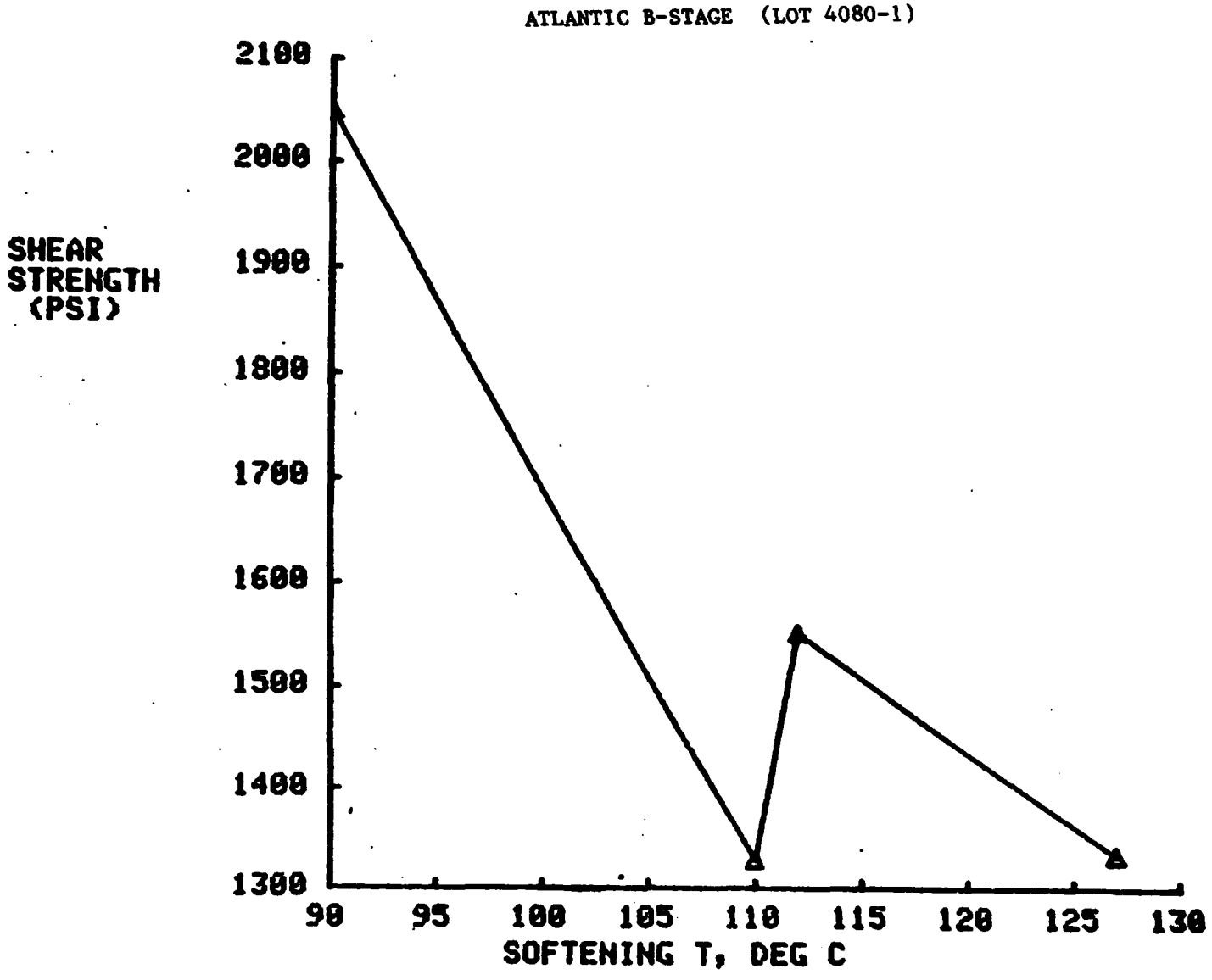


FIGURE 61 SHEAR STRENGTH (PSI) VS SOFTENING T, DEG C

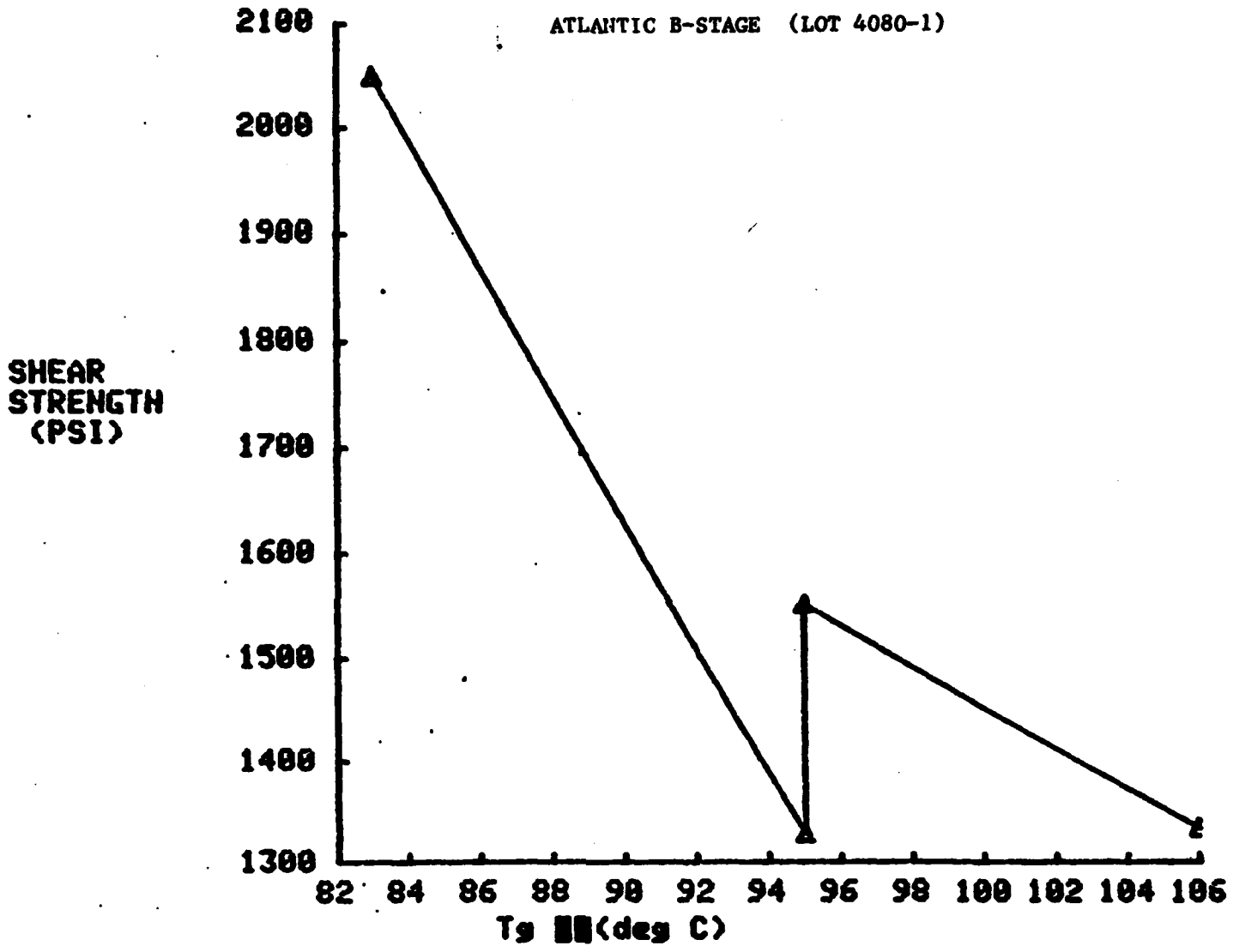


FIGURE 62 SHEAR STRENGTH (PSI) VS T_G (DEG C)

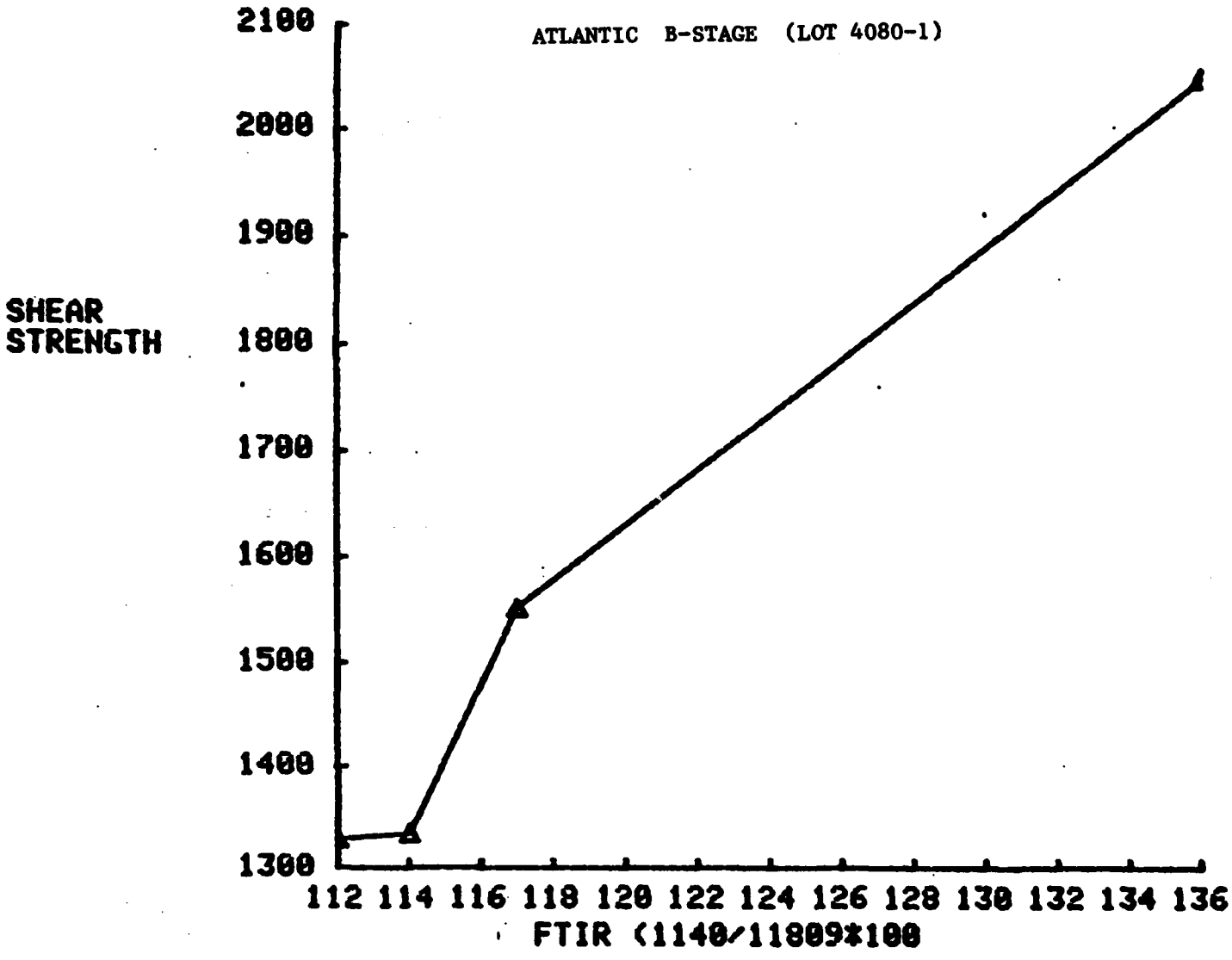


FIGURE 63 SHEAR STRENGTH (PSI) VS FTIR (1140/1180)*100

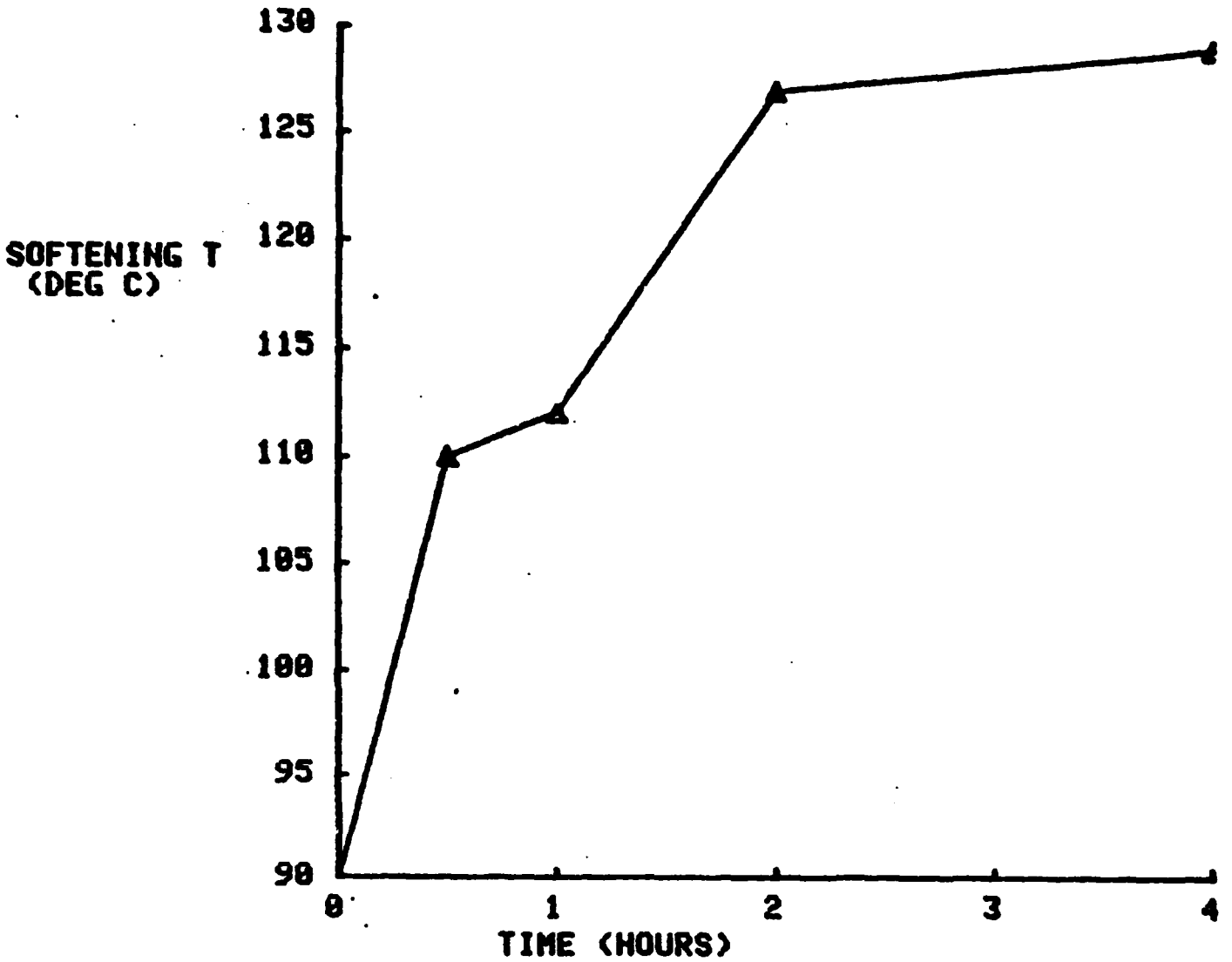


FIGURE 64 SOFTENING T (DEG C) VS TIME (HOURS)

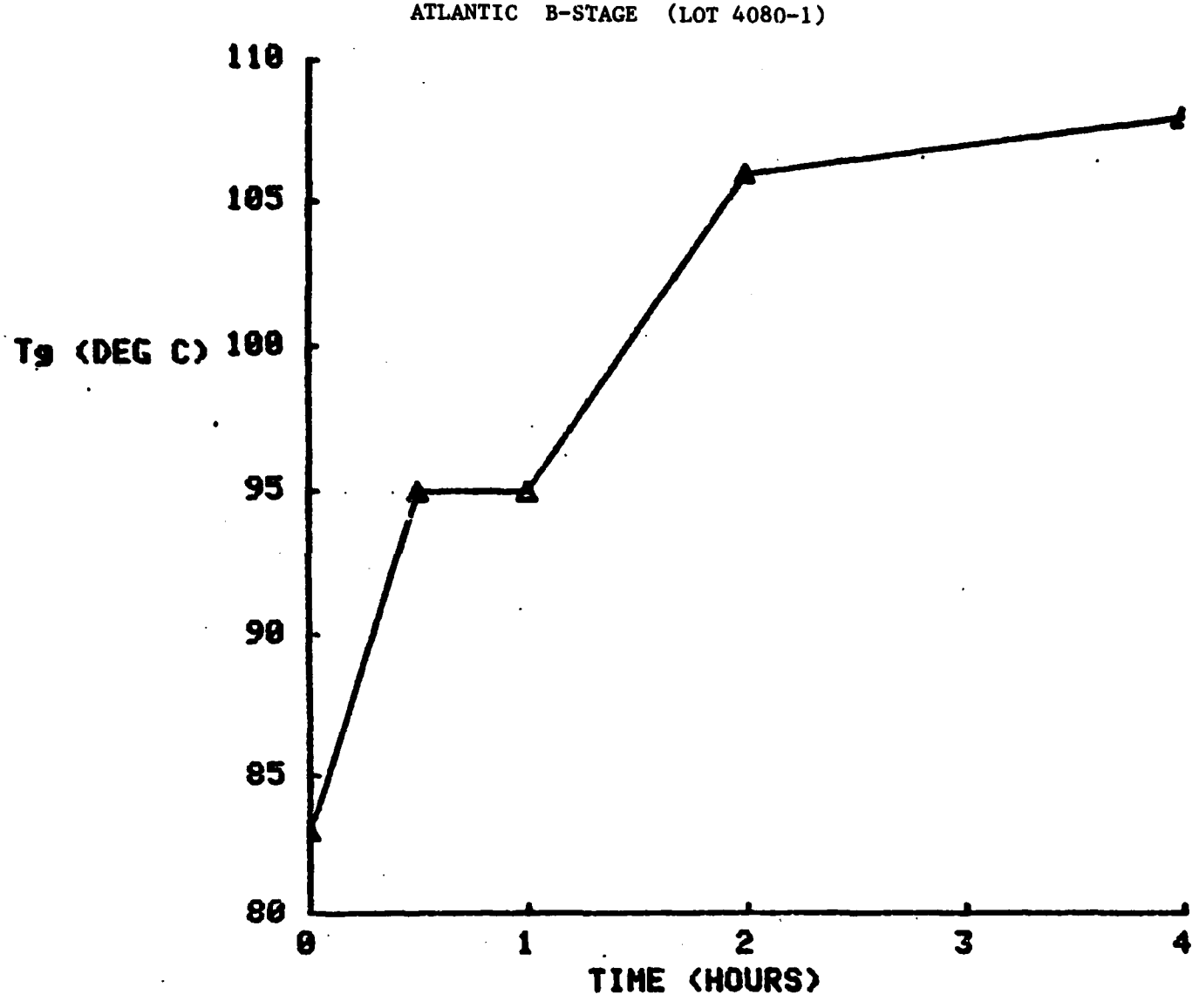


FIGURE 65 T_G (DEG C) VS TIME (HOURS)

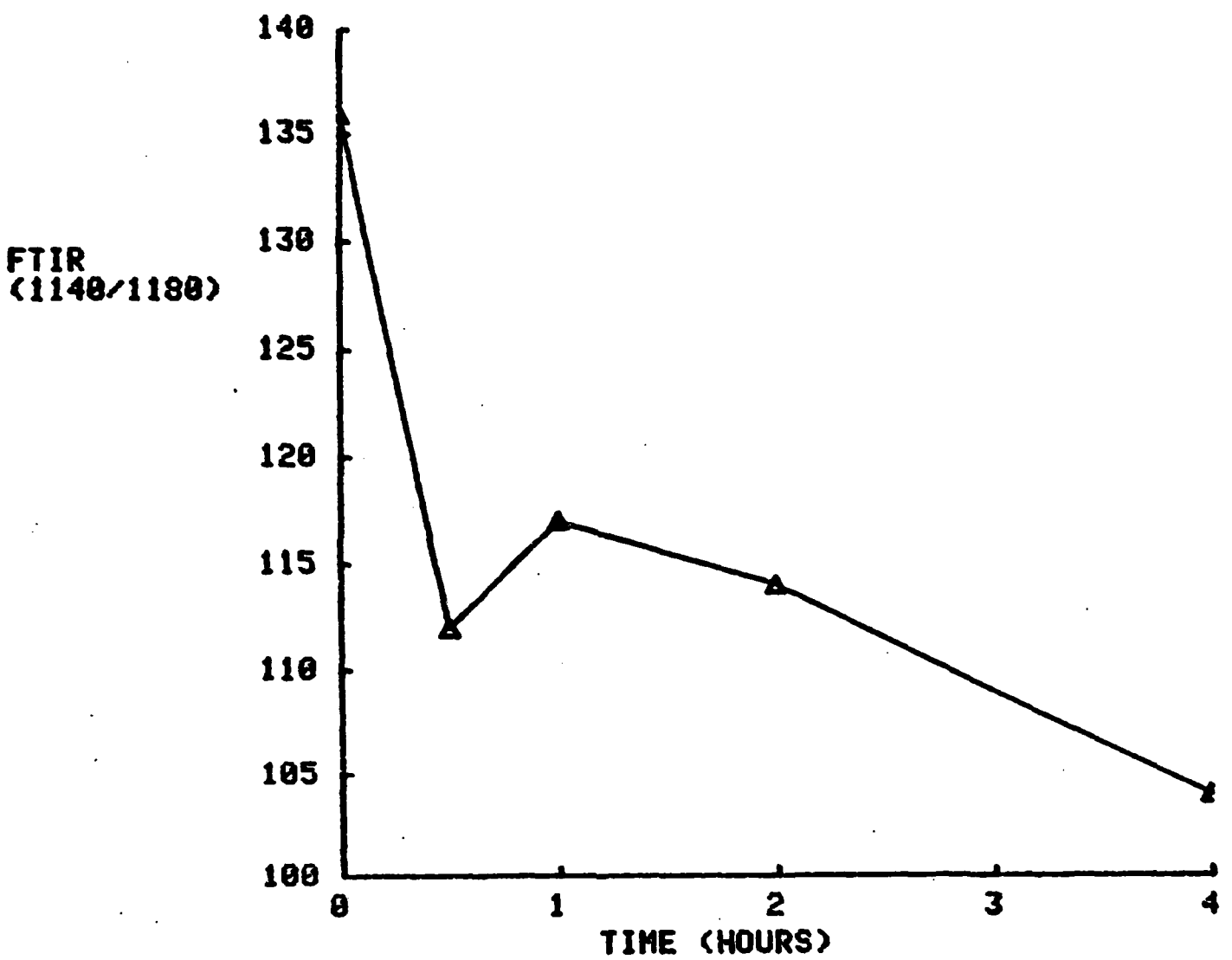


FIGURE 66 FTIR (1140/1180)*100 VS TIME (HOURS)

Table 37 Shear Strength of Laminates Made with Advanced Staged B-Stage Polyimide (Atlantic)

Specimen ID	Test Temp	Shear Stress	Fracture Mode
24722-40 Aged 1/2 hr/140°C			
-1	23°C	2520 psi	Cohesive thru "B" Stage
-2	200°C	2720 psi	Cohesive thru "B" Stage
24722-33 Aged 1 hrs/140°C			
-1	23°C	1360 psi	Cohesive thru "C" Stage
-2	23°C	1744 psi	Cohesive thru "C" Stage
-3	200°C	1680 psi	Cohesive thru "C" Stage
-4	200°C	1512 psi	Cohesive thru "C" Stage
24722-32 Aged 2 hrs/140°C			
-1	23°C	1188 psi	Partly Adhesive/Cohesive
-2	23°C	1480 psi	Partly Adhesive/Cohesive
-3	200°C	1256 psi	Partly Adhesive/Cohesive
-4	200°C	1192 psi	Partly Adhesive/Cohesive
24722-34 Aged 4 hrs/140°C			
-1			
-2	All specimens broke on handling indicating very low adhesion strength.		
-3			
-4			

Table 38 Shear Strength of Duplicate Specimens with Advanced Staged "B" Staged Polyimide (Atlantic)

Specimen* ID		Test Temp	Shear Strength	Fracture Mode
24722-40A++				
Aged 1/2 hr/140°C				
	-1	23°C	3280	Mostly Cohesive Thru C
	-2	23°C	2720	Mixed Cohesive/Adhesive
	-3	200°C	2400	Mostly Cohesive Thru C Partially Adhesive, Partially Tensile
	-4	200°C	2540	Mostly Cohesive Thru C
24722-40				
Aged 1/2 hr/140°C				
	-1	23°C	2520	Cohesive Thru B
	-2	200°C	2720	Cohesive Thru B

* All test panels given standard red oxide, standard ferric chloride treatment, hot press, post cure 4 hours/218°C.

++ Duplicate specimens.

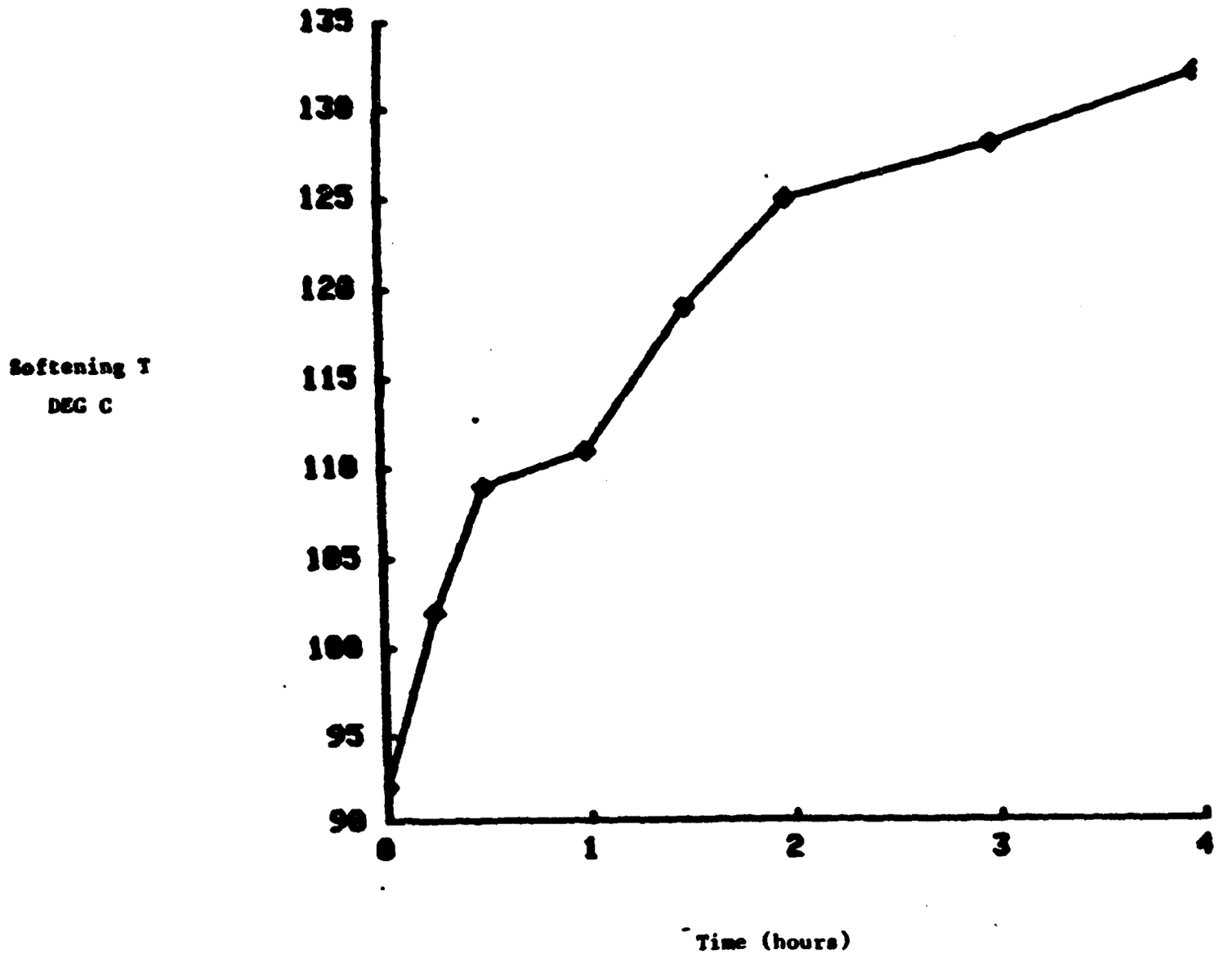


FIGURE 67 NORPLEX POLYIMIDE
SOFTENING T (DEG C) VS TIME (HOURS) CURED AT 140°C

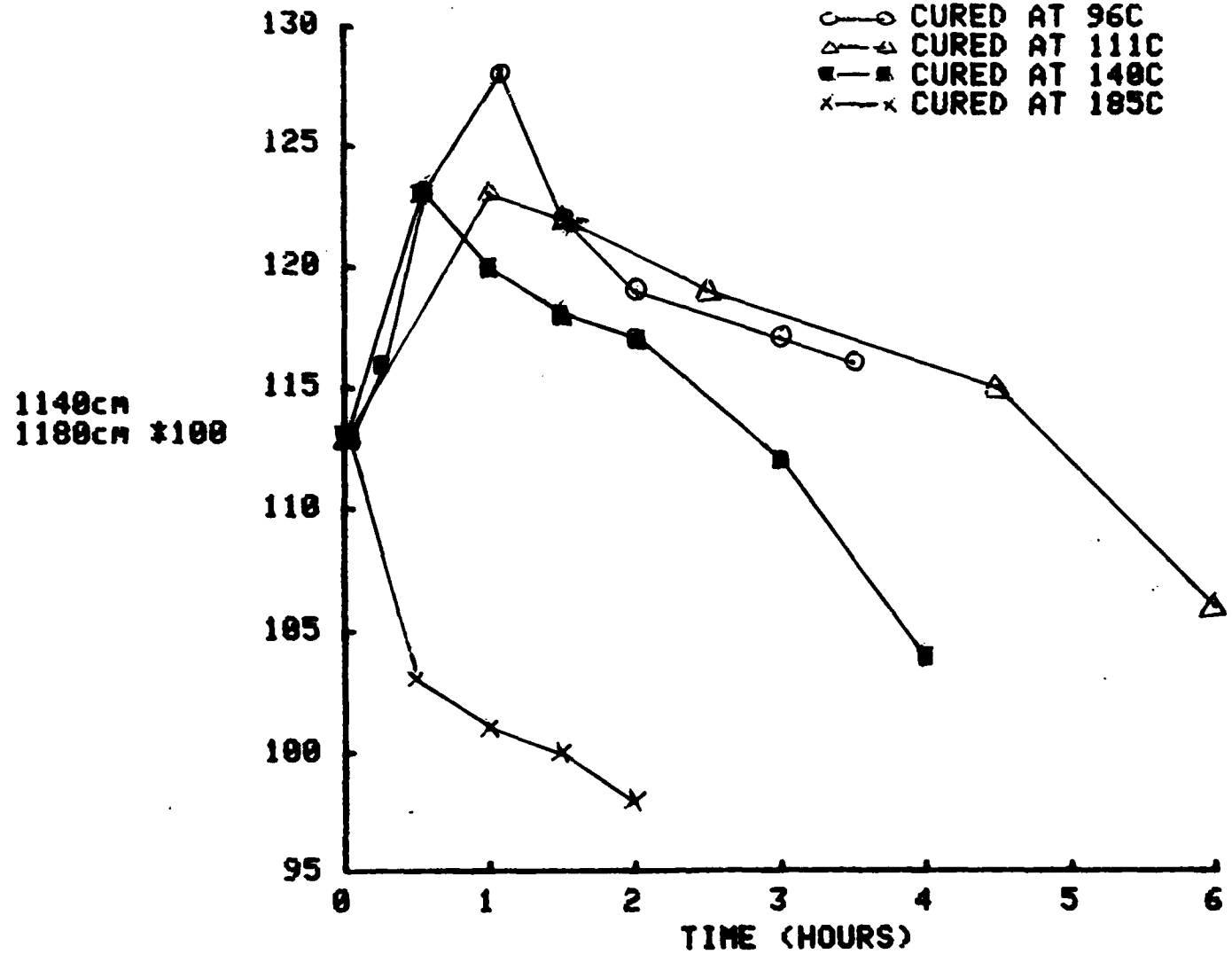


FIGURE 68 FTIR (1140cm/1180cm) *100 VS TIME (HOURS)
NORPLEX B-STAGE (LOT:8-443-04B)

The curve of the Tg vs. time is shown in Figure 69. It was reported that the portion of the Tg of the Norplex B-stage, Tg = 61°C, was lower than the Tg of the Atlantic B-stage, Tg = 23°C, and the cure initiation temperature of the Norplex was also lower than that of the Atlantic. It was thought that the low Tg and initiation temperature may be due to solvent effects. In order to determine if these low values were in fact due to solvent, a sample of B-stage was cured for 1/2 hour at 185°C. The cure initiation changed from 149°C to 198°C probably due to loss of solvent, indicating that the solvent is a possible explanation for the low values.

The percent reacted vs. time is shown in Figure 70; this was determined the same way it was for the Atlantic polyimide. An Arrhenius plot of the material is shown in Figure 71. The reaction rate was determined after the sample had reacted sixty percent.

In addition to analytical characterization of advanced staged Norplex, the effects of advanced staging on interlaminar shear strength were studied and is shown in Table 39. The results were similar to previous studies on (2) hours, there was a definite loss of strength, and at four (4) hours, there was almost no adhesion strength. Figure 72 represents this data graphically. Figures 73 through 75 represent the relationship between these shear strengths and the analytical characterizations of FTIR, softening temperature, and DSC.

Final Lots of Prepregs (Atlantic and Mica) - The final lots of polyimide prepreg (Oak-Atlantic Lot #6045-2 and Mica Lot #9009-6) which were characterized and previously described were also studied for the effects of advanced aging. Prepreg material was advance staged at 140°C for periods of 1/2, 1, 2, and 4 hours. The results are summarized in Tables 40 and 41 and Figures 76 - 79.

The "free" MDA content of the staged prepreg was tested and found to decrease with the amount of staging as expected. The testing indicates that the material behaved as expected, i.e., the Tg increased with staging.

f. STAGING OF KERIMID 601 POLYIMIDE RESIN

Kerimid resin was staged at 140°C for four hours with samples being tested at discrete time intervals by FTIR ratio vs. time and the Tg vs. time and is shown in Figures 78 and 79 and Table 42. The Kerimid seems to behave simlarly to the Atlantic prepreg and also to the Norplex material.

g. EFFECTS OF HUMIDITY ON POLYIMIDE PREPREG MATERIAL

It has been fairly well established that humidity has a dramatic effect on epoxy prepregs used in MLPWB construction. A recent article (1) by J.W. Lula of Bendix Corporation clearly shows the direct relationship between delamination resistance of an epoxy MLPWB and the amount of moisture absorbed by the epoxy prepreg. Our previous testing of polyimide MLPWB's indicated that polyimides are superior to epoxies under electrical bias-humidity tests. Exposure to humidity upon polyimide prepregs and the resultant effects upon inner layer strength were never previously studied however. As part of this study, it was decided to determine if humidity was as important a factor on polyimide prepregs as it is on epoxy prepregs.

(1) "Process to Maximize the Delamination Resistance of Multilayer Printed Wiring Boards", Insulation/Circuits, Sept. 1981, pgs. 114-118, J.W. Lula, Bendix Corporation.

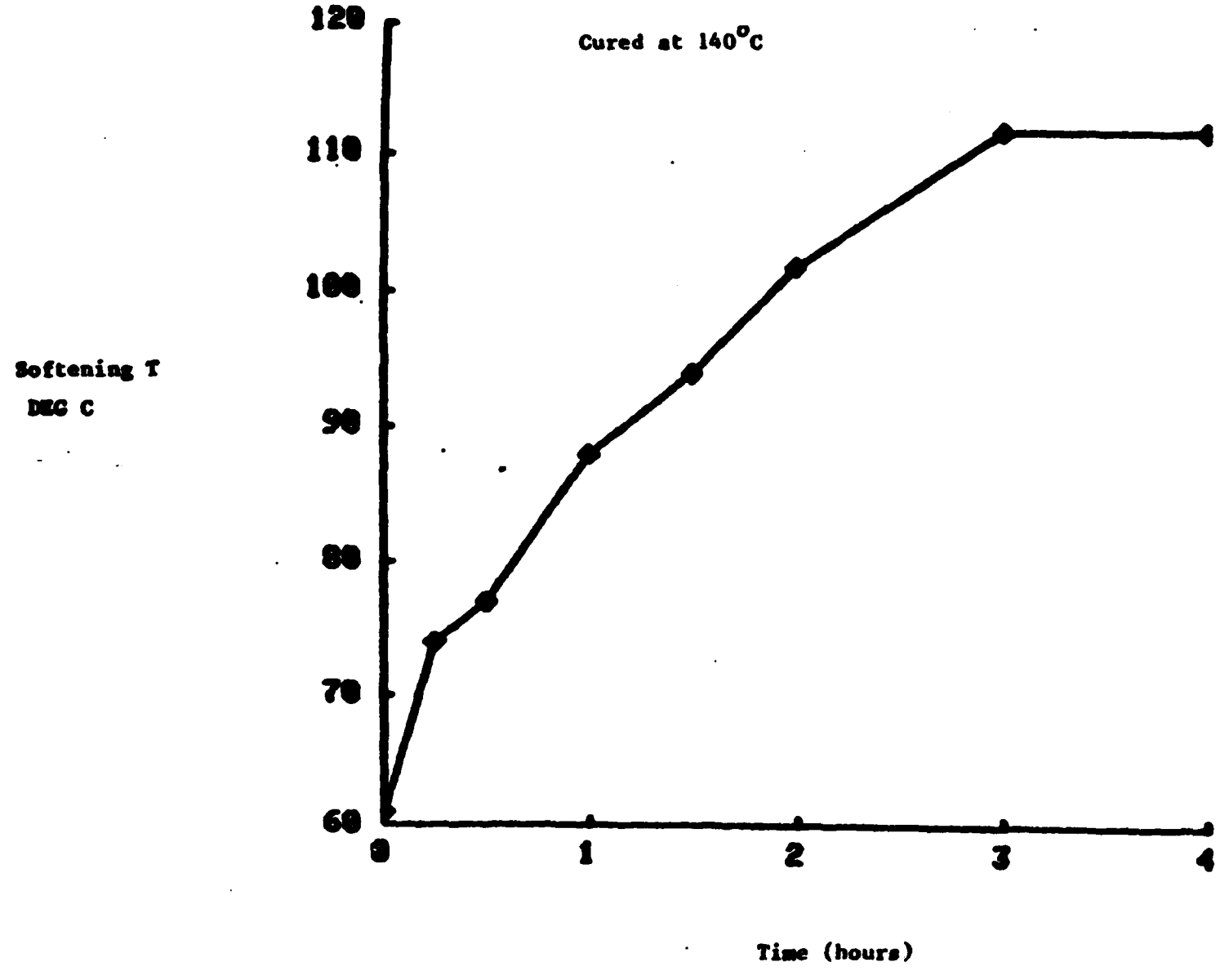


FIGURE 69 NORPLEX POLYIMIDE
DSC (T_G) VS TIME (HOURS)

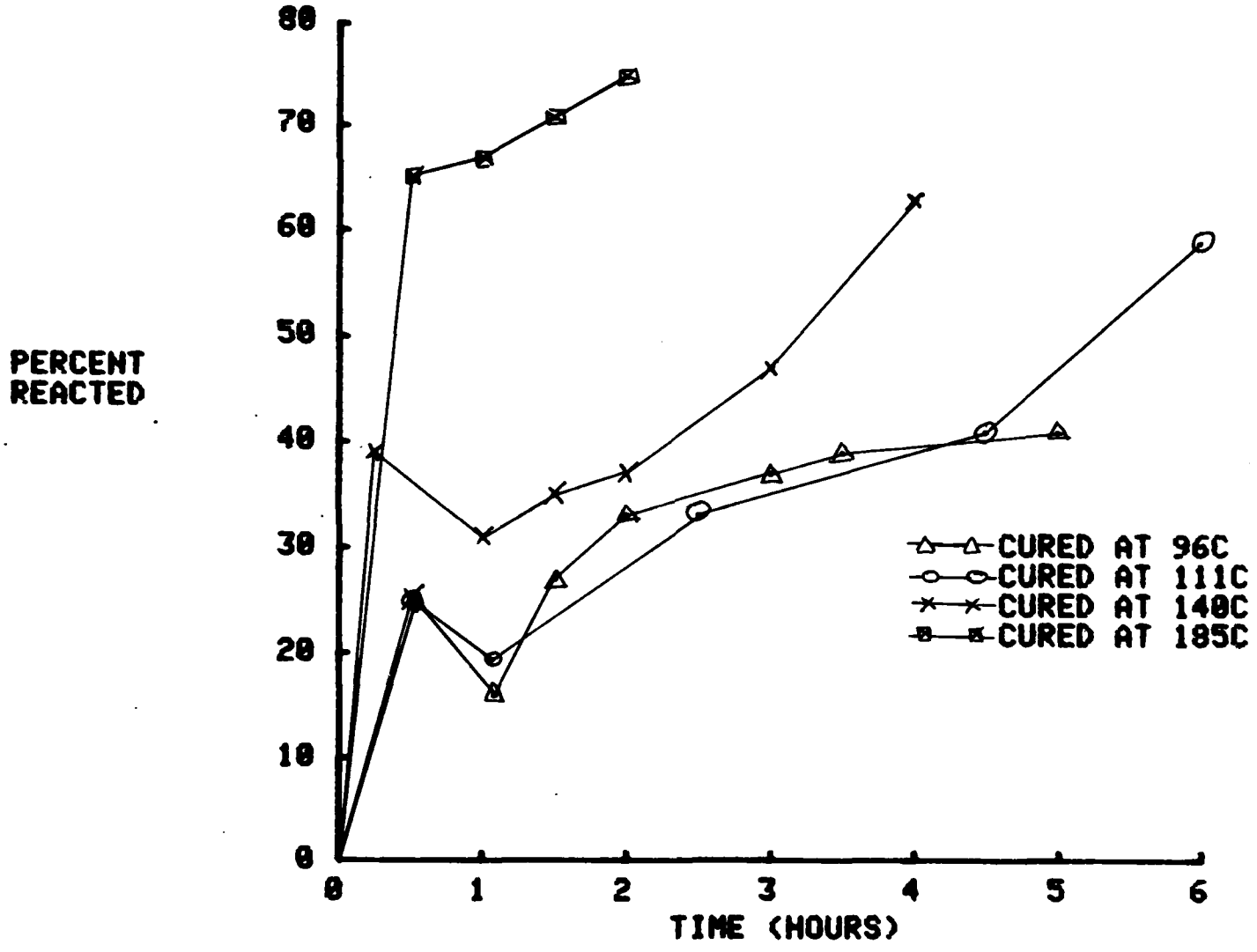


FIGURE 70 PERCENT REACTED VS TIME (HOURS) NORPLEX B-STAGE (LOT-8-443-04B)

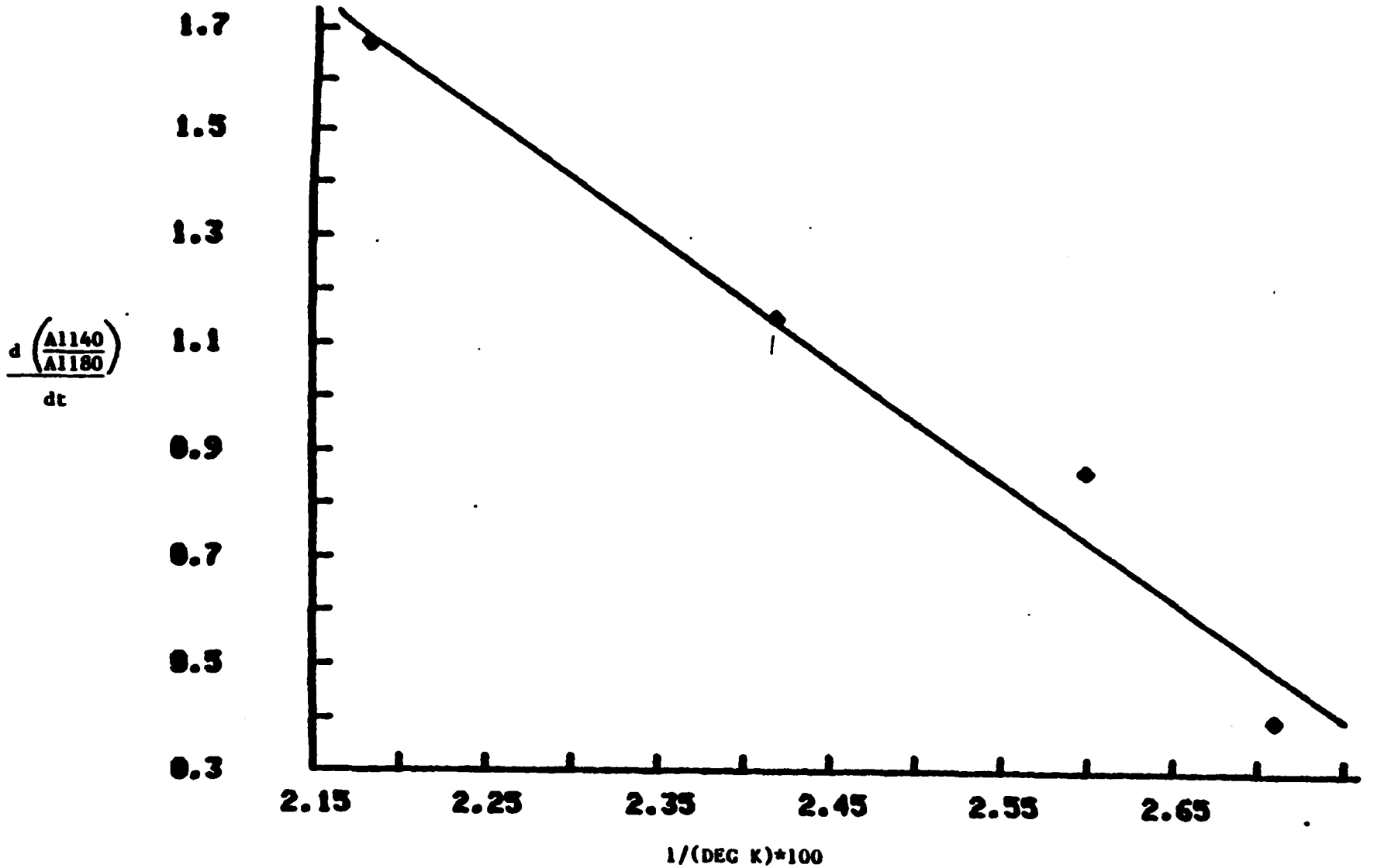


FIGURE 71 ARRHENIUS PLOT OF NORPLEX POLYIMIDE
LOG REACTION RATE VS 1/(DEG K)*1000

Table 39 Effects of Advanced Staging on Shear Strength of Norplex Polyimide

Specimen ID	Test Temp	Shear Strength	Fracture Mode
24722-44A (Advanced Staged 1/2 Hr)	23°C	3584 psi	Cohesive "C" Stage
	23°C	3500 psi	Cohesive "C" Stage
	200°C	2020 psi	Tensile Fracture
	200°C	2740 psi	Cohesive "C" Stage
24722-44B (Advanced Staged 1.0 Hr)	23°C	2480 psi	Adhesive "B" to Cu
	23°C	2872 psi	Cohesive "C" Stage
	200°C	3072 psi	Mostly Adhesive
	200°C	2928 psi	Mostly Adhesive
24722-44C (Advanced Staged 2.0 Hr)	23°C	1464 psi	Cohesive "B" Stage
	23°C	1864 psi	Cohesive "B" Stage
	200°C	1528 psi	Adhesive
	200°C	1600 psi	Adhesive
24722-44D (Advanced Staged 4.0 Hr)	Panel Delaminated When Cut for Shear Specimens		

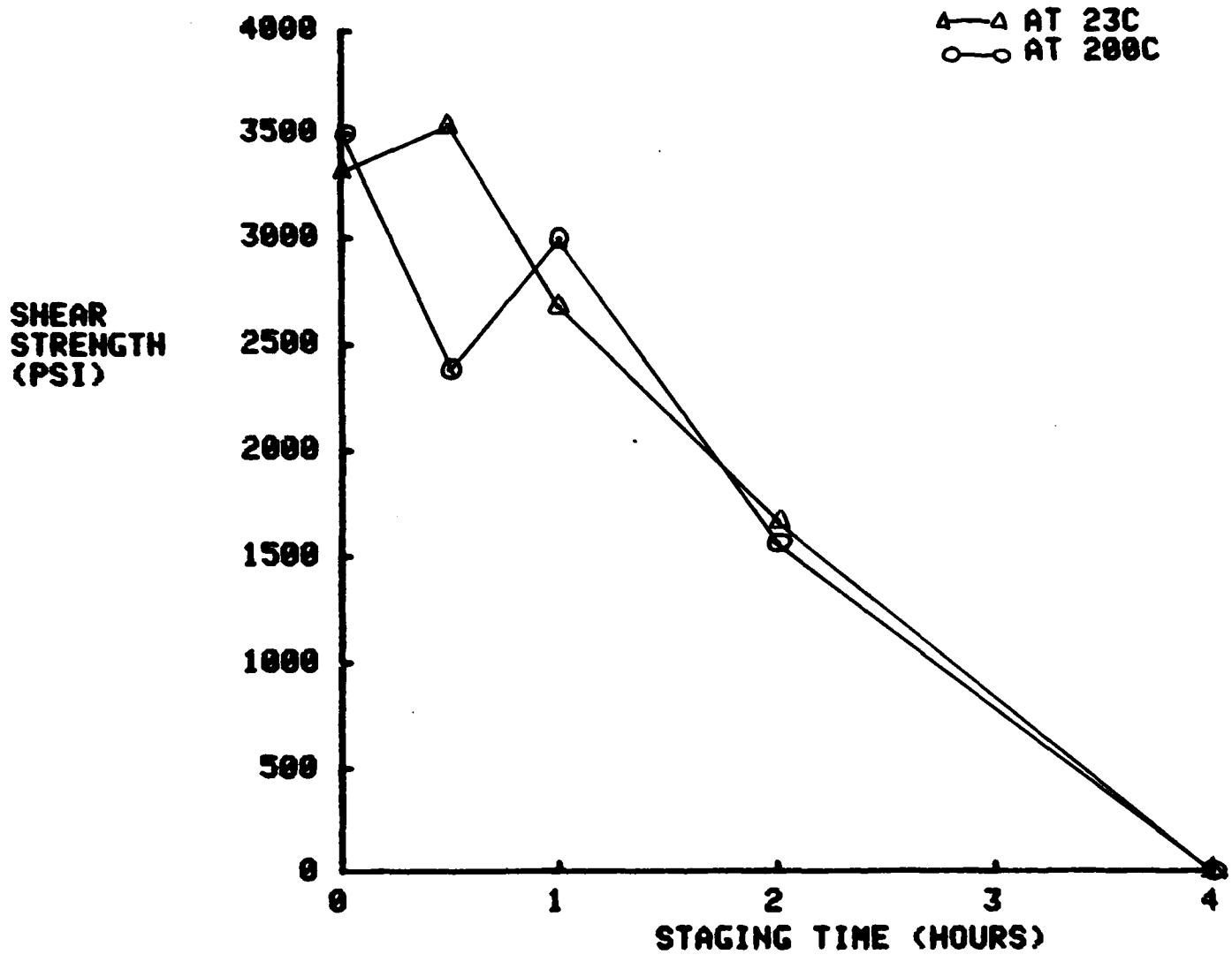


FIGURE 72 SHEAR STRENGTH (PSI) VS STAGING TIME (HOURS) AT 140°C
NORPLEX B-STAGE (LOT-8-443-04B)

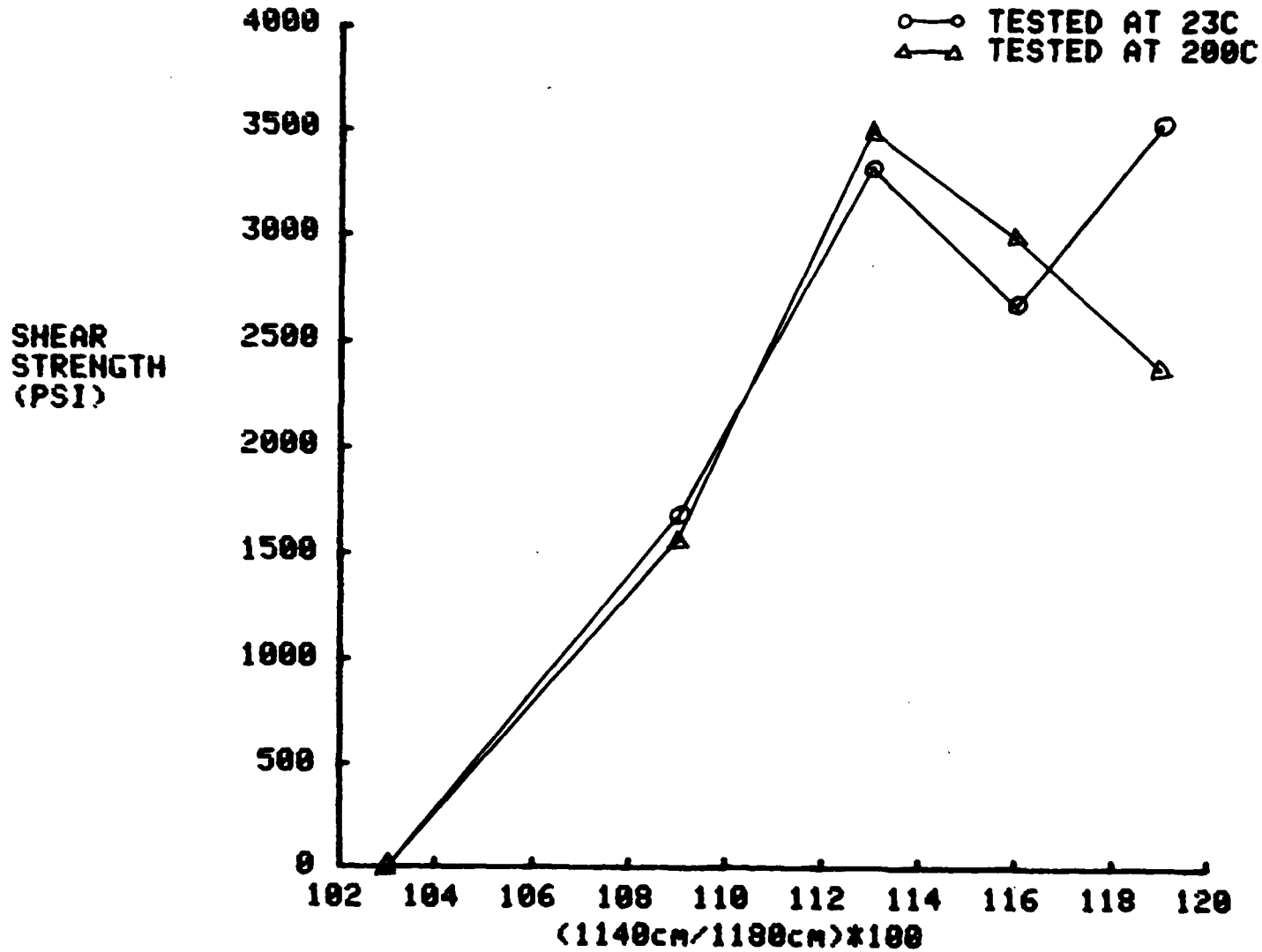


FIGURE 73 SHEAR STRENGTH (PSI) VS FTIR (1140/1180)*100
NORPLEX B-STAGE (LOT-8-443-04B)

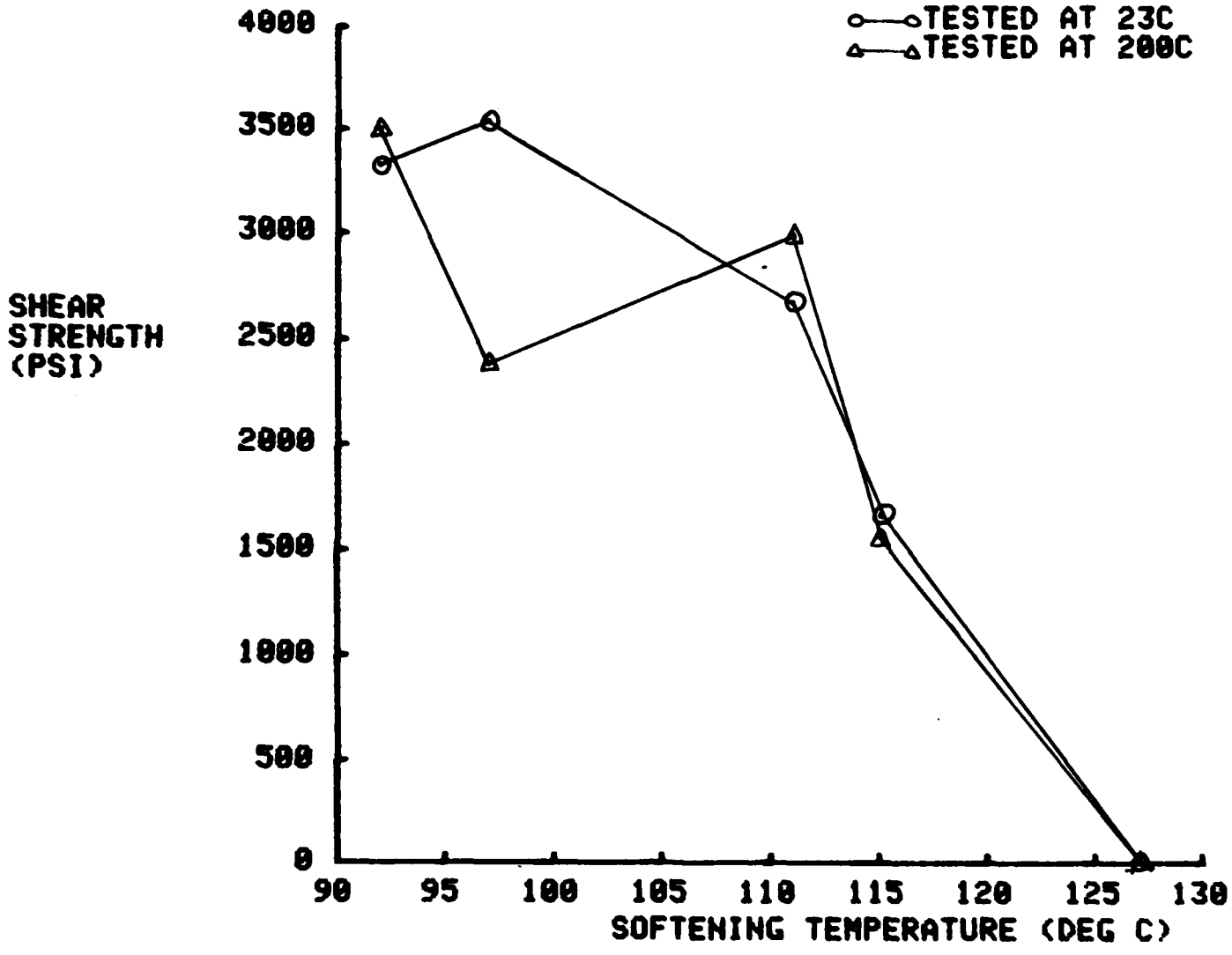


FIGURE 74 SHEAR STRENGTH (PSI) VS SOFTENING TEMPERATURE (DEG C)
NORPLEX B-STAGE (LOT-8-443-04B)

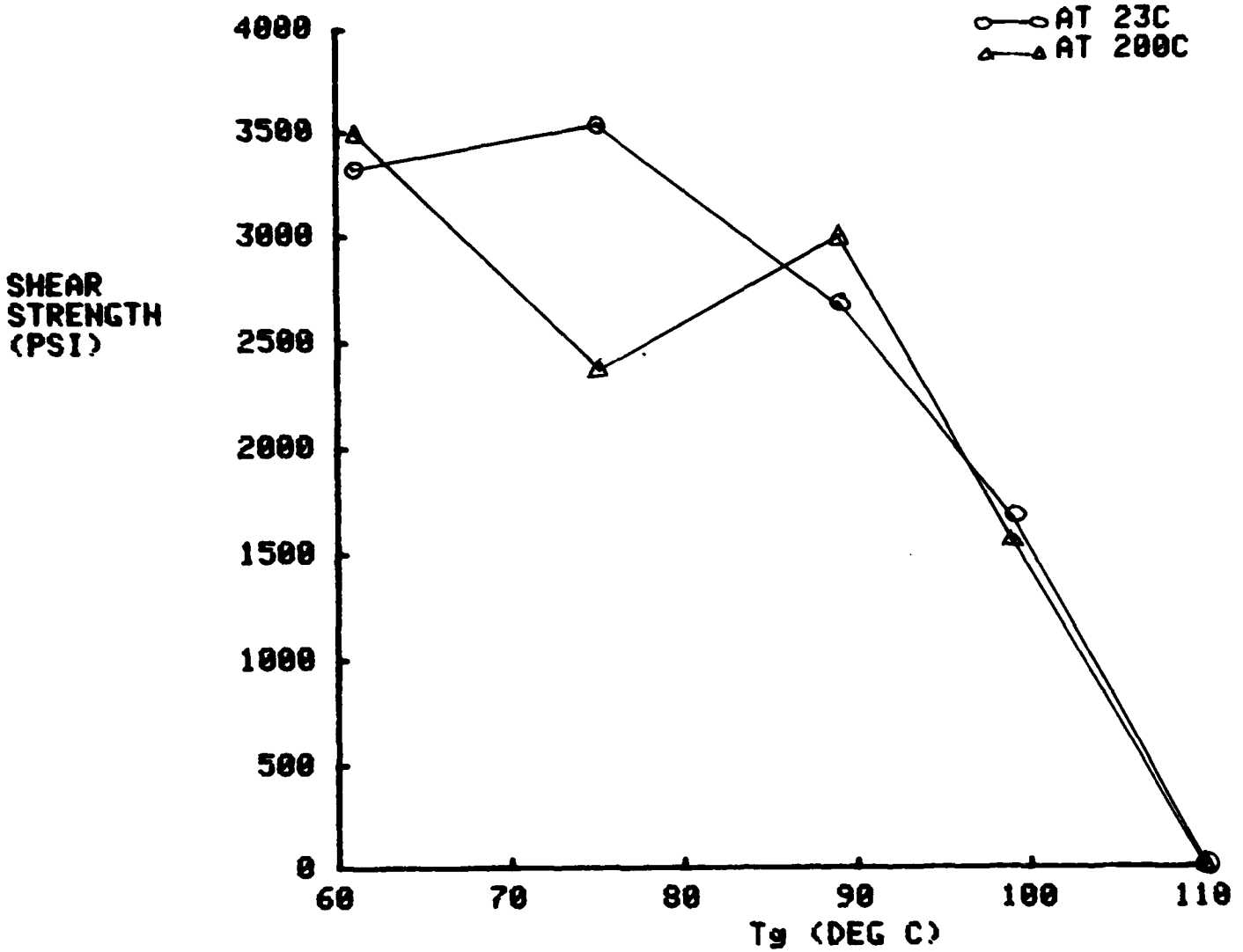


FIGURE 75 SHEAR STRENGTH (PSI) VS Tg (DEG C)
NORPLEX B-STAGE (LOT-8-443-04B)

Table 40 Advance Staging at 140°C Oak-Atlantic (Lot 6045-2)

	0 hr	1/2 hr	1 hrs	2 hrs	4 hrs
FTIR $\frac{1140\ cm^{-1}}{1180\ cm^{-1}}$	1.24	1.14	1.18	1.06	1.03
DSC					
Tg, °C	73	97	103	106	121
Cure Initiation, °C	168	162	175	176	167
Peak, °C	228	213	231	229	209
TMA					
Softening T, °C	95	100	113	119	127
Free MDA	12.4	5.2	3.6	2.0	0.9

Table 41 Advance Staging at 140°C Mica (Lot 9009-6)

	0 hr	1/2 hr	1 hrs	2 hrs	4 hrs
FTIR $\frac{1140\ cm^{-1}}{1180\ cm^{-1}}$	1.23	1.14	1.17	1.04	1.01
DSC					
Tg, °C	84	96	101	107	120
Cure Initiation, °C	163	166	173	173	173
Peak, °C	232	230	231	230	230
TMA					
Softening T, °C	95	106	109	118	122
Free MDA	7.6	5.2	3.3	2.4	1.0

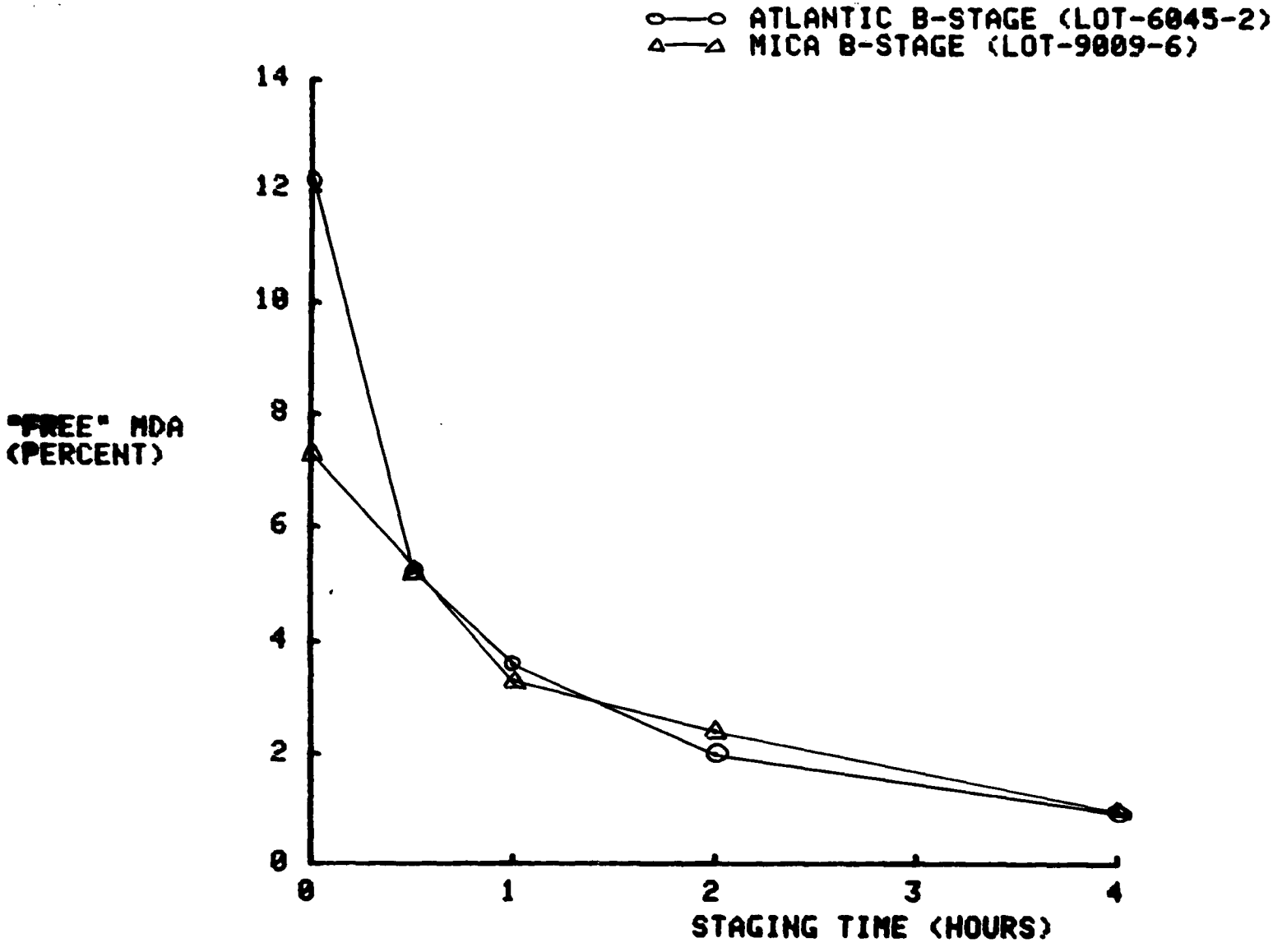


FIGURE 76 "FREE" MDA (PERCENT) VS STAGING TIME (HOURS) AT 140°C

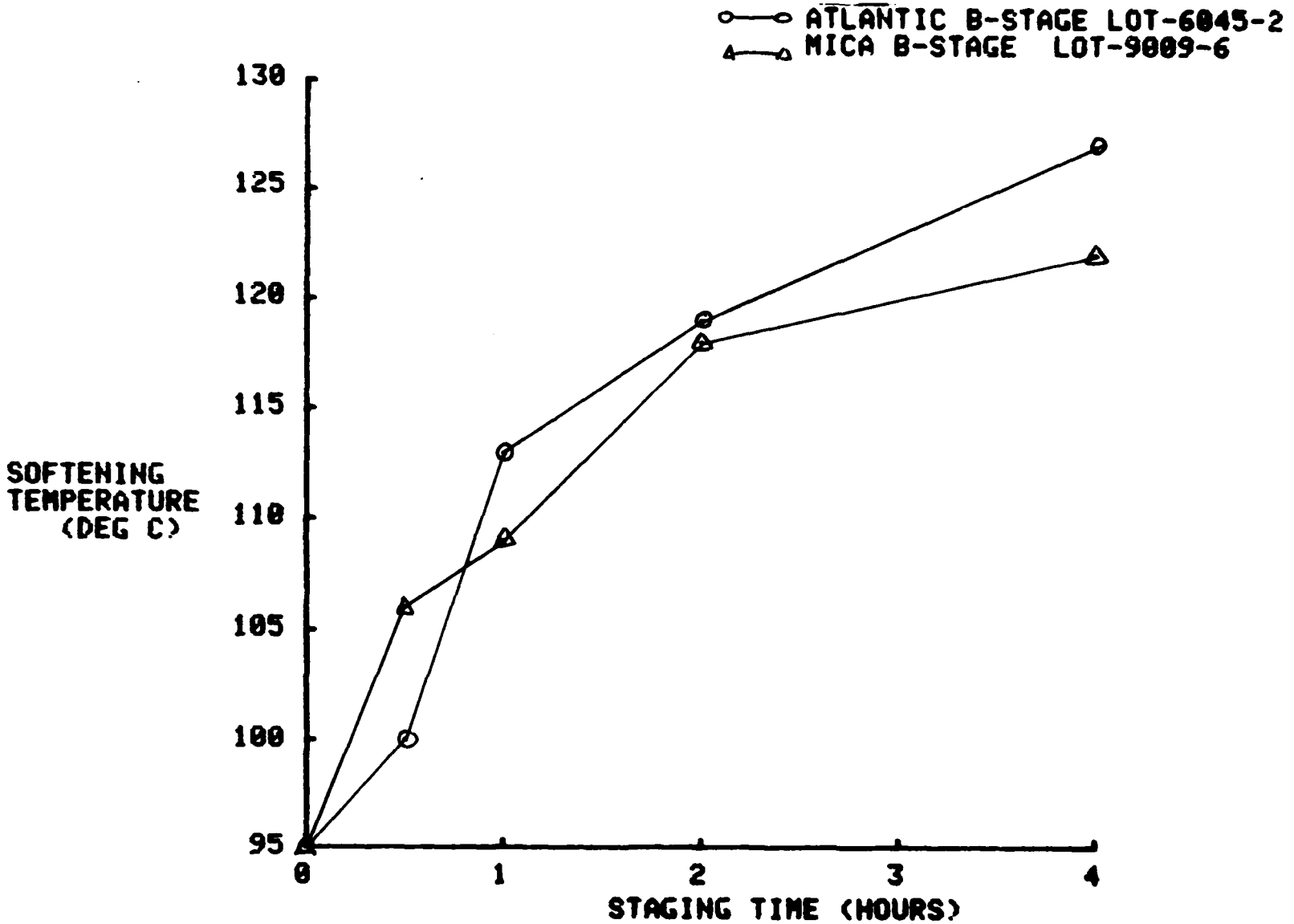


FIGURE 77 TMA-SOFTENING TEMP (DEG C) VS STAGING TIME (HOURS) AT 140°C

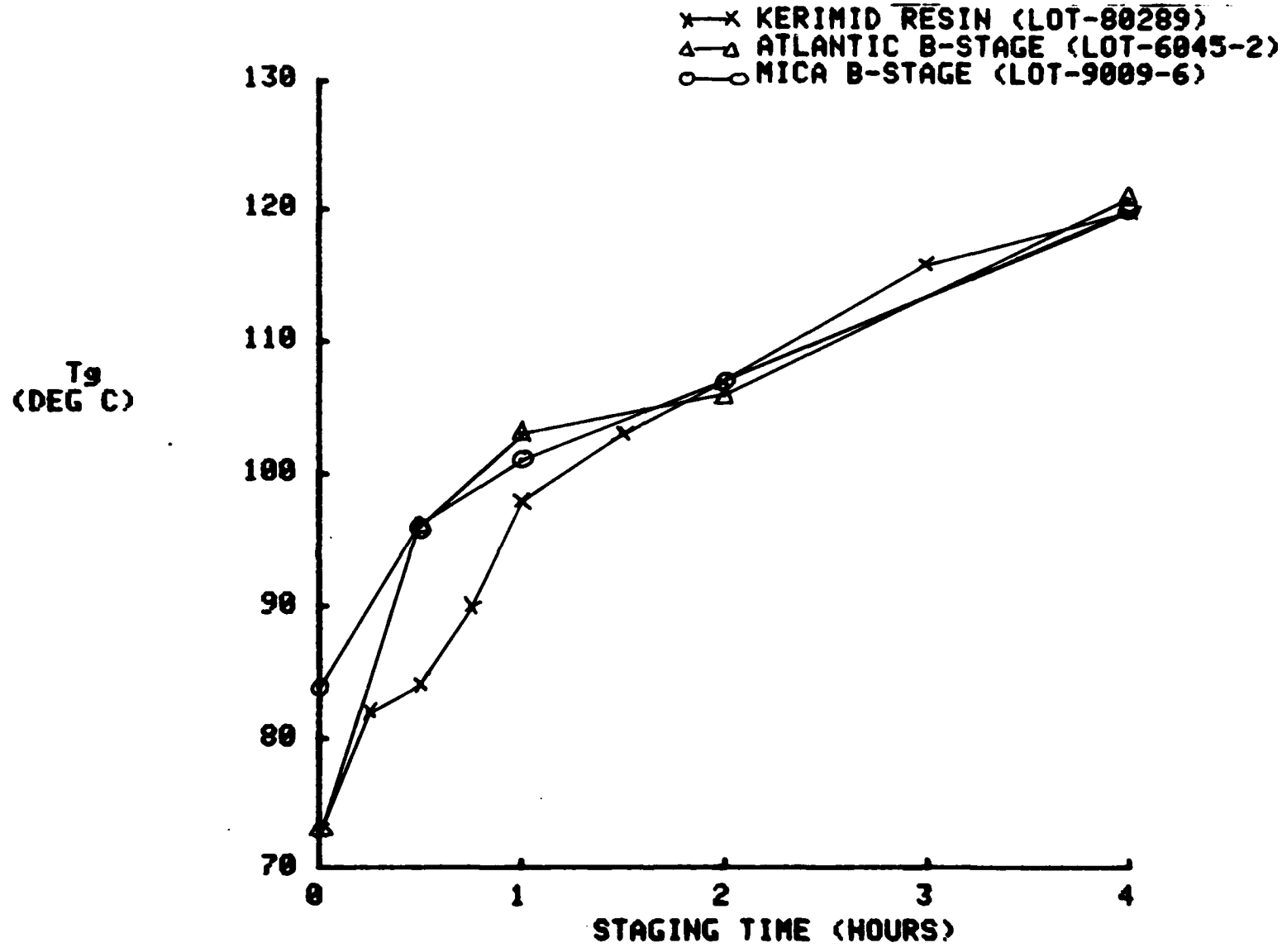


FIGURE 78 DSC, T_G (DEG C) VS STAGING TIME (HOURS) AT 140°C

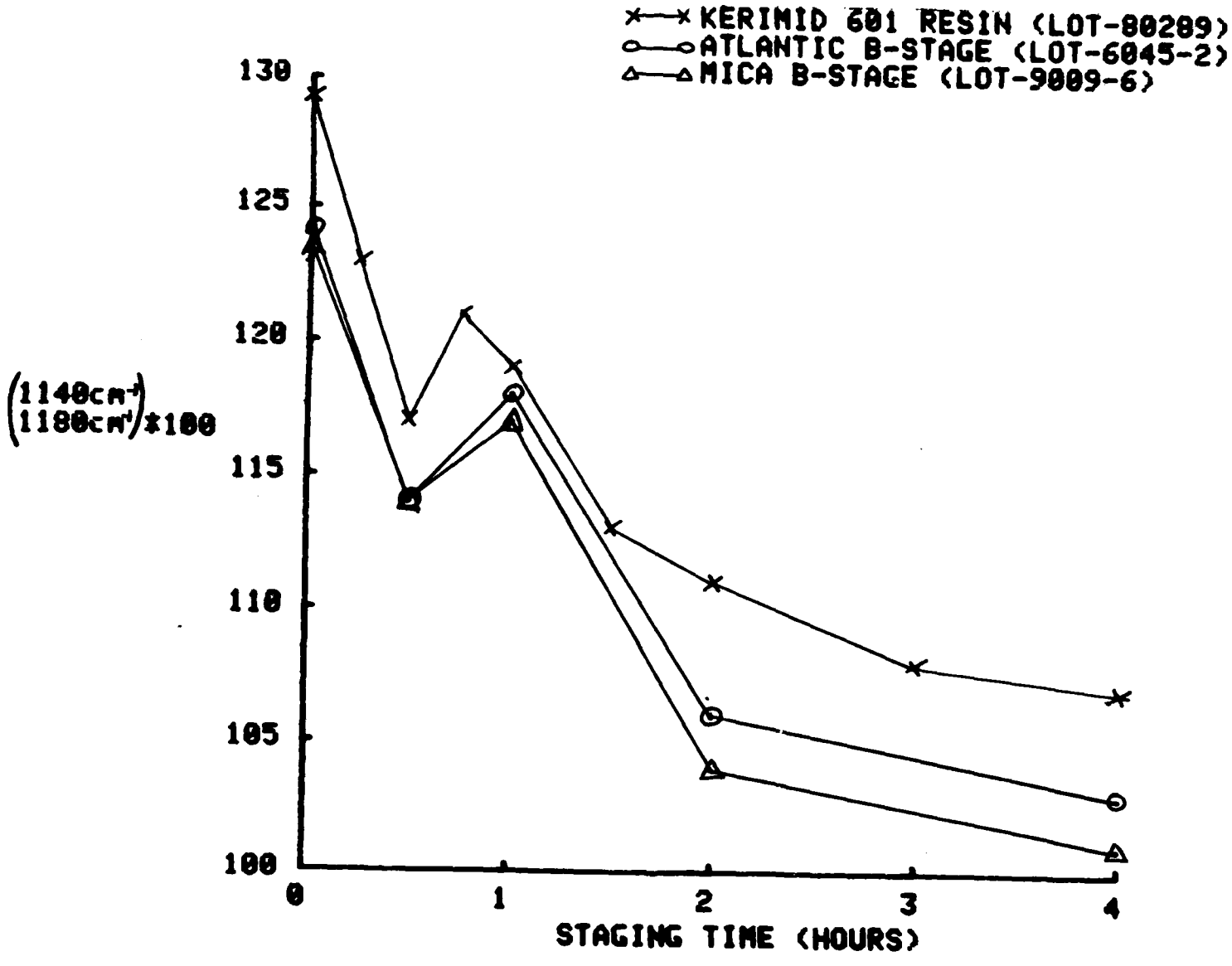


FIGURE 79 FTIR (1140/1180)*100 VS STAGING TIME (HOURS) AT 140°C

Table 42 FTIR and Tg for Kerimid 601 Staged at 140°C

Time (hours)	DSC, Tg (°C)	FTIR 1140 cm-1 / 1180 cm-1
0.00	73	1.29
0.25	82	1.23
0.50	84	1.17
0.75	90	1.21
1.00	98	1.19
1.50	103	1.13
2.00	107	1.11
3.00	116	1.08
4.00	120	1.07

Samples of polyimide prepreg were exposed to four different environments, namely, dessication, 31%, 52%, and 79% relative humidity. The humidity environments were achieved through the use of various salt solutions. The prepregs were monitored gravimetrically in their environments and reached equilibrium after about 48 hours. They were allowed to remain in environment for 15 days however prior to processing into multilayer lap shear panels. The results of lap shear testing as seen in Table 43 show no significant degradation of strength as a function of the humidity to which the prepregs were exposed.

It would appear that the chemistry of polyimides is such that they are much less sensitive than epoxy resins to moisture. The analytical characterization of the humidity exposed prepreg is summarized in Table 44. Exposure to humidity has some slight effect on peak DSC temperature and softening temperature, however the other parameters are for the most part, unaffected by humidity.

h. SUMMARY/RECOMMENDATIONS

Polyimide prepreg materials supplied to MIL-P-13949 show a remarkable consistency of high quality and uniformity. Variations among different prepreg suppliers and variations within different lots from a supplier are quite slight. At the start of this program, variations in the quality of prepregs were suspected as one possible source of inner layer delamination problems within MLPWB's. Not only was this found not to be the case, but in fact, the prepregs were of exceptionaly high consistency.

Analytical characterizations of these prepregs appear to be quite viable as a means of establishing and monitoring quality control. The techniques of differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA) provide the most reproducible techniques for characterization. Gel permeation chromatography also offers a good technique, however it is more time-consuming compared to the first two techniques. Analysis by Fourier Transform Infrared spectroscopy would require more study to establish its effectiveness as a quality control technique.

At this time we would recommend that the results of this study be evaluated by IPC. In particular, DSC and TMA techniques could emerge as possible tests methods for eventual inclusion into MIL-P-13949.

6. ENVIRONMENTAL EVALUATION OF POLYIMIDE LAMINATES AND MLPWB's

a. THERMAL AGING OF POLYIMIDE LAMINATES

Two panels that had been previously sampled and tested, 24722-14A (Atlantic) and 24722-15A (Mica), were thermally aged to determine the effect on adhesion as measured by shear strength. Table 9 lists the process history and original test results. Table 45 shows the aging profiles and the resultant shear strengths. Aging 96 hours at 156°C had no effect on either sample. Additional aging for 144 hours at 185°C had no effect on the Atlantic panel but the Mica panel delaminated on handling. The Atlantic panel was further aged for 192 hours at 185°C (336 hours total at 185°C) with no effect on shear strength. As can be seen in Table 45, the Mica panel was weaker initially, showing adhesive failure prior to aging. These tests indicate that thermal aging at this temperature range has little effect on a good panel but may accelerate deterioration on a laminate which is not initially optimized.

Table 43 Lap Shear Strength of Panels Fabricated from Humidity Exposed Polyimide Prepreg

Specimen	Prepreg Conditioning	Lap Shear @ 23°C (psi)	Fracture Mode	Lap Shear @ 200°C (psi)	Fracture Mode
24722-62A					
1	(Dessicated)	1918	70% Adhesive "B" to Cu, 30% Cohesive "C"	2395	Cohesive Thru "B"
2		1632	5% Adhesive "B" to Cu, 95% Cohesive "C"	1835	Cohesive Thru "B"
24722-61A					
1	(31% R.H.)	245	Adhesive "B" to Cu	970	Adhesive "B" to Cu
2		1198	10% Adhesive "B" to Cu, 90% Cohesive "C"	1942	50% Adhesive "B" to Cu 50% Cohesive "B"
24722-62B					
1	(52% R.H.)	1706	5% Adhesive "B" to Cu, 95% Cohesive "C"	1756	Cohesive Thru "B"
2		1364	5% Adhesive "B" to Cu, 95% Cohesive "C"	1970	Cohesive Thru "B"
24722-61B					
1	(79% R.H.)	1595	10% Adhesive "B" to Cu, 90% Cohesive "C"	1725	Cohesive Thru "C"
2		1540	20% Adhesive "B" to Cu, 80% Cohesive "C"	2015	Mostly Cohesive "C"

Table 44 Analytical Characterization of Humidity Exposure "B" Stage Prepreg

	Humidity Exposure				
	B-Stage	Dessicant	31%	52%	79%
% Weight Gain (Resin Only)	--	-0.362	0.069	0.226	0.571
FTIR $\frac{1140\ cm^{-1}}{1180\ cm^{-1}}$	1.24	1.26	1.25	1.25	1.25
DSC Tg (°C)	73	83	76	80	75
Cure Initiation (°C)	168	175	175	173	174
Peak (°C)	228	237	240	244	240
TMA Softening T (°C)	95	92	98	102	99
TGA % Volatiles	1.17	0.95	0.95	0.99	1.19
GPC Free MDA	12.4	6.6	6.0	6.4	5.9

Table 45 Effect of Thermal Aging on Shear Strength

Specimen ID	Aging Profile	Test Temp	Shear Strength	Fracture Mode
24722-14A*				
-1	0	23°C	1608 psi	Cohesive thru "B"
-2	0	23°C	1572 psi	Mixed
-3	0	200°C	1752 psi	Tensile fracture
-4	0	200°C	1976 psi	Cohesive thru "B" & "C"
-5	96 hrs/156°C	23°C	1580 psi	Cohesive
-6	96 hrs/156°C	200°C	1648 psi	Cohesive
-7	96 hrs/156°C + 144 hrs/185°C	23°C	1576 psi	Cohesive
-8	96 hrs/156°C + 144 hrs/185°C	200°C	1096 psi	Adhesive
-9	96 hrs/156°C + 336 hrs/185°C	23°C	2104 psi	Cohesive thru "C"
-10	96 hrs/156°C + 336 hrs/185°C	200°C	1668 psi	Cohesive thru "B"
24722-15A				
-1	0	23°C	1288 psi	Adhesive "B" to "C"
-2	0	23°C	1200 psi	Adhesive "B" to "C"
-3	0	200°C	1124 psi	Mixed adhesive/cohesive
-4	0	200°C	1340 psi	Cohesive
-5	96 hrs/156°C	23°C	1372 psi	Adhesive
-6	96 hrs/156°C	200°C	1040 psi	Cohesive
-7	96 hrs/156°C + 144 hrs/185°C	Delaminated on Handling		
-8				

*24722-14A - Atlantic, Cold Press, Cure 177°C/5 hrs., Post Bake 218°C/4 hrs.
**24722-15A - Mica, Cold Press, Cure 177°C/5 hrs., Post Bake 218°C/4 hrs.

Thermal aging studies were also performed on lap shear laminates made with Norplex prepreg. The panels were made similarly to previous Mica and Atlantic panels using the standard ferric chloride/red oxide surface treatment, and the standard hot press/post cure bake. Table 46 shows the test results at 23°C and 200°C on both. The shear strength was unusually high with fracture occurring through the "C" stage. Two duplicate panels were subsequently made and tested. Table 47 shows the results of the shear tests on the duplicate and original panels. The values from the duplicate panels are slightly lower but would fall within the expected scatter for shear testing. Two Norplex panels (24722-41A, and 41B) were subjected to thermal aging similar to the aging to which the Mica and Atlantic material had been subjected to determine if these panels did deteriorate with time at temperature. Table 48 shows the initial results. There was no indication of any deterioration of shear strength at the time/temperature profiles as shown. Continued aging of these panels was performed at 185°C. Figure 80 represents the shear strengths as a function of thermal aging of one Norplex panel tested at 23°C and 200°C. In each case, the first 96 hours of thermal aging was at 156°C with the remainder of aging at 185°C. Figure 81 shows data for another Norplex panel similarly processed and aged. Their curves were quite similar to previously tested Mica and Atlantic materials.

Eight new panels were then made; four each with the new lots of Mica and Oak-Atlantic prepregs and C-stage materials for thermal aging studies. Lap shear samples were tested from each panel for control purposes. The average values for each panel are reported in Table 49. The values obtsained after exposing samples for 99 hours at 160°C and 220°C respectively are shown in Table 50. It is seen that fracture mode failures have shifted from essentially all "C" stage failures (for the controls) to a mixed mode of adhesive and cohesive failures.

Samples of these panels were further aged for 450 hours and 720 hours at 160°C and 220°C. Table 51 is a summary of these results.

The analysis of these results indicate that the data is not as straight forward as one would hope. For example, the Oak-Atlantic samples tested at 160°C showed reasonable and expected degradation after 720 hours. The same material exposed to 220°C for 720 hours showed on the average the same strength as the control samples with no degradation whatsoever. The Mica samples showed a wide scatter of values after 99 hours (at 160°C and 220°C) and only slight degradation after 450 hours at 160°C and significant degradation after this time at 220°C.

The wide scatter in results did not allow for a meaningful treatment of the data to determine if it met an Arrhenius correlation. It appears that a much larger sampling base is needed to perform this type of study. It has been demonstrated however, that when properly fabricated, the polyimides are extremely stable at high temperatures.

b. INITIAL ENVIRONMENTAL EVALUATION OF POLYIMIDE MLPWB's

Approximately midway through the program, MLPWB's were fabricated in accordance with MIL-STD-275 using the apparently optimized process of ferric chloride/red oxide treatment for the copper, cold press lamination, and 425°F post cure conditioning. Mica material was used for these environmental tests and gave

Table 46 Shear Strength of Laminates Using "B" Stage Norplex 108

Specimen ID	Test Temp	Shear Strength	Fracture Mode
24722-41A	23°C	3700 psi	Cohesive thru "C"
	200°C	2960 psi	Cohesive thru "C"
24722-41A	23°C	3900 psi	Cohesive thru "C"
	200°C	3100 psi	Cohesive thru "C"

Table 47 Shear Strength of Laminates Using "B" Stage Norplex 108

Duplicate Specimens

Specimen ** ID	Test Temp	Shear Strength	Fracture Mode
24722-42A-1*	23°C	3696	Mostly Cohesive Thru B
-2	200°C	2668	Tensile
24722-42B-1*	23°C	2996	Mostly Cohesive Thru B
-2	200°C	2416	Tensile
24722-41A-1	23°C	3700	Cohesive Thru C
-2	200°C	2960	Cohesive Thru C
24722-41B-1	23°C	3900	Cohesive Thru C
-2	200°C	3100	Cohesive Thru C

** All specimen panels had standard red oxide and ferric chloride treatment - hot press cycle - post cure 4 hrs/218°C.

* Duplicate test panels.

Table 48 Effects of Thermal Aging on Shear Strength of Norplex Polyimide

Specimen ID	Aging Profile	Test Temp	Shear Strength	Fracture Mode
24722-41A	0	23°C	3700 psi	Cohesive Thru C
-41B	0	23°C	3900 psi	Cohesive Thru C
-41A	0	200°C	2900 psi	Cohesive Thru C
-41B	0	200°C	3100 psi	Cohesive Thru C
27722-41A	96 hrs/156°C + 48 hrs/185°C	23°C	3750 psi	Mostly Cohesive Thru B
-41B	96 hrs/156°C + 48 hrs/185°C	23°C	3470 psi	Cohesive Thru B
-41A	96 hrs/156°C + 48 hrs/185°C	200°C	3052 psi	Cohesive Thru B
-41B	96 hrs/156°C + 48 hrs/185°C	200°C	3220 psi	Cohesive Thru B

*All test panels were given the standard red oxide and standard ferric chloride treatment - hot press cycle, post cure 4 hrs/218°C.

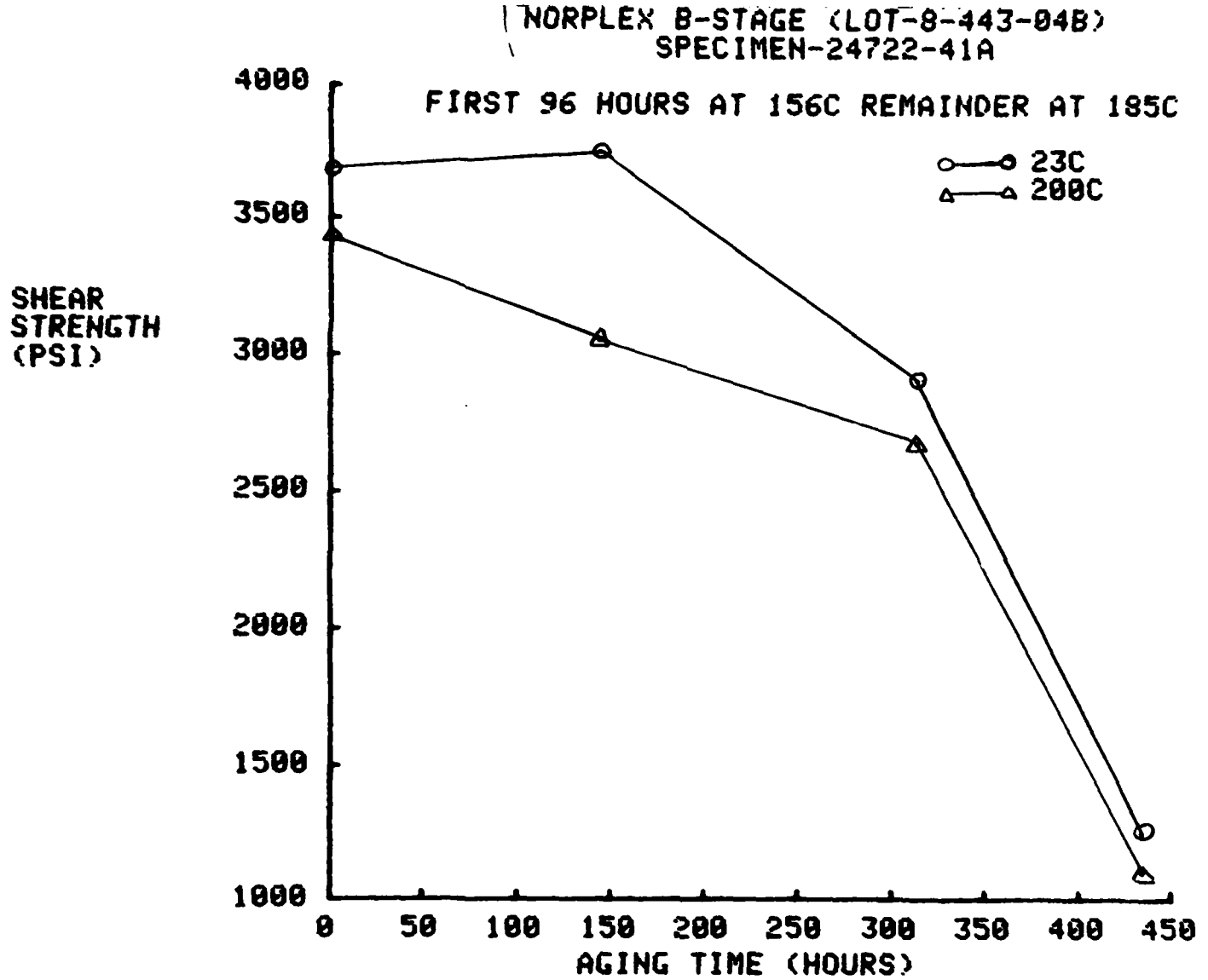


FIGURE 80 SHEAR STRENGTH (PSI) VS AGING TIME (HOURS)

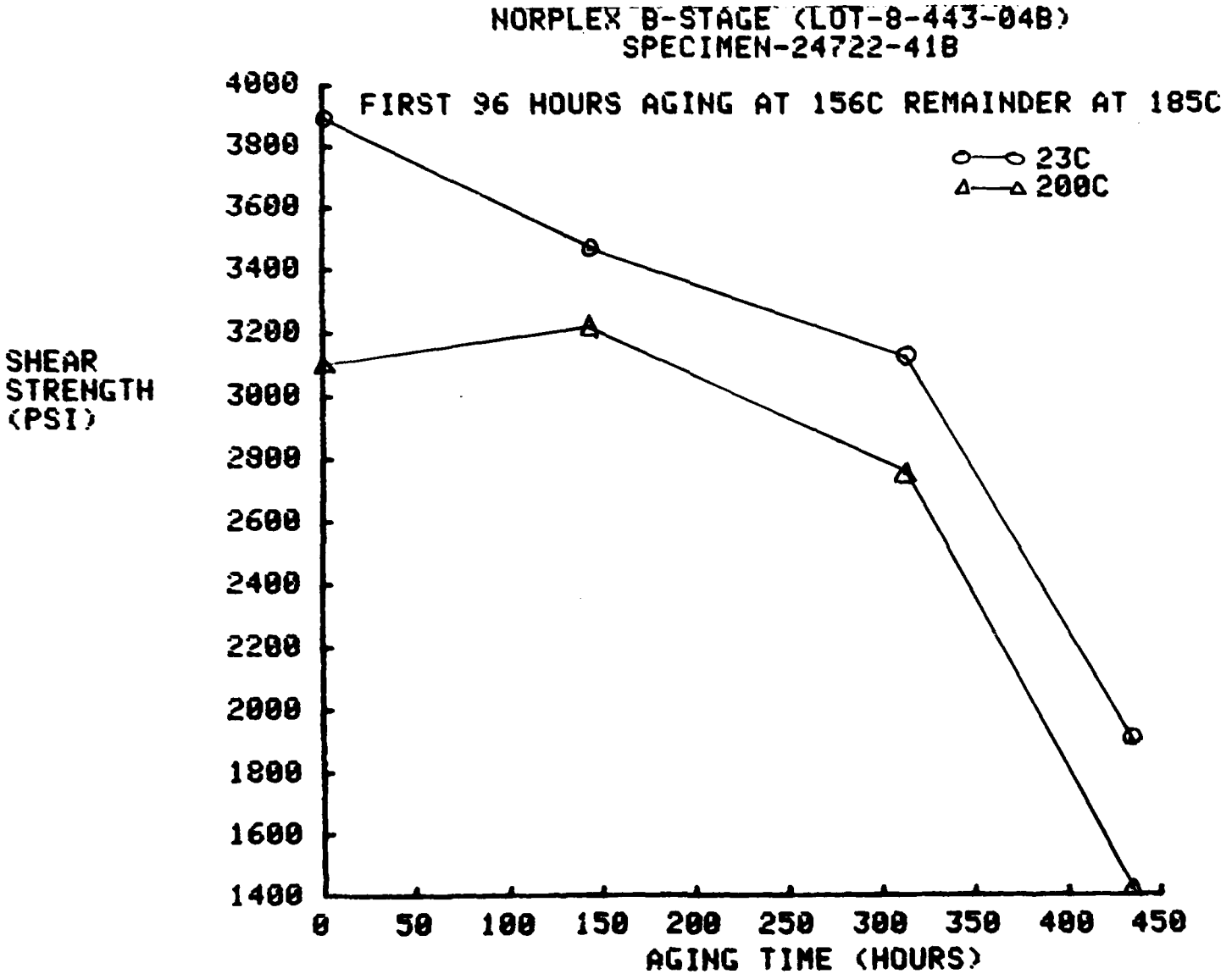


FIGURE 81 SHEAR STRENGTH (PSI) VS AGING TIME (HOURS)

Table 49 Lap Shear Values for Control Specimens Used in Thermal Aging Study

Specimen ID	Material Used	Lap Shear at 23°C psi, (Avg. of Three Specimens)	Fracture Mode (Typical)
24722-47			
A	Oak-Atlantic	2160	Cohesive Failure in "C" Stage
B	Oak-Atlantic	[illegible]	Cohesive Failure in "C" Stage
C	Mica	[illegible]	Cohesive Failure in "C" Stage
D	Mica	1975	Cohesive Failure in "C" Stage
24722-49			
A	Oak-Atlantic	2048	Cohesive Failure in "C" Stage
B	Oak-Atlantic	1990	Cohesive Failure in "C" Stage
C	Mica	2018	Cohesive Failure in "C" Stage
D	Mica	1770	Cohesive Failure in "C" Stage

Table 50 Lap Shear Values of Thermally Aged Panels (Initial)

Specimen ID	Aging Profile	Shear Strength at 23°C (psi)	Fracture Mode
24722-47			
A	99 hrs. at 220°C	2040	100% Adhesive - Copper to B Stage
B	99 hrs. at 220°C	1752	40% Adhesive (Copper/B) 60% Cohesive Thru C
C	99 hrs. at 220°C	1824	100% Adhesive - Copper/B
D	99 hrs. at 220°C	---*	100% Adhesive - Copper to B
24722-49			
A	99 hrs. at 220°C	1888	40% Adhesive (Copper/B) 60% Cohesive Thru C
B	99 hrs. at 220°C	1904	20% Adhesive (Copper/B) 80% Cohesive Thru C
C	99 hrs. at 220°C	1896	20% Adhesive (Copper/B) 80% Cohesive Thru C
D	99 hrs. at 220°C	1776	10% Adhesive (Copper/B) 90% Cohesive Thru C
24722-47			
A	99 hrs. at 160°C	2028	80% Adhesive - 20% Cohesive Thru C
B	99 hrs. at 160°C	1784	100% Adhesive
C	99 hrs. at 160°C	1920	90% Adhesive - 10% Cohesive Thru B
D	99 hrs. at 160°C	540	100% Adhesive
24722-49			
A	99 hrs. at 160°C	2248	25% Adhesive - 75% Cohesive Thru C
B	99 hrs. at 160°C	2216	100% Cohesive Thru C
C	99 hrs. at 160°C	1896	10% Adhesive - 90% Cohesive Thru C
D	99 hrs. at 160°C	2830	70% Adhesive - 30% Cohesive Thru B

All adhesion failures were Copper to B Stage interfaces.
Most, but not all, cohesive failures were thru the C Stage.

*Specimen delaminated when notched after aging.

Table 51 Lap Shear Values of Thermally Aged Panels

Specimen ID	Aging Profile	Shear Strength at 23°C (psi)	Fracture Mode
24722-47			
C	450 hrs at 220°C	1230	Adhesive "B" Stage to Copper
D	450 hrs at 220°C	---*	
24722-49			
C	450 hrs at 220°C	818	Adhesive "B" Stage to Copper
D	450 hrs at 220°C	816	Adhesive "B" Stage to Copper
24722-47			
C	450 hrs at 160°C	---*	
D	450 hrs at 160°C	1803	75% Adhesive "B" Stage to Copper, 25% Cohesive "B" Stage
24722-49			
C	450 hrs at 160°C	2118	Cohesive Thru "C" Stage
D	450 hrs at 160°C	2279	10% Adhesive "B" Stage to Copper 90% Cohesive "C" Stage
24722-47			
A	720 hrs at 220°C	2071	60% Adhesive "B" Stage to Copper, 40% Cohesive "B" Stage
B	720 hrs at 220°C	1660	80% Adhesive "B" Stage to Copper, 20% Cohesive "B" Stage
24722-49			
A	720 hrs at 220°C	2337	40% Adhesive "B" Stage to Copper, 60% Cohesive "C" Stage
B	720 hrs at 220°C	2054	10% Adhesive "B" Stage to Copper, 90% Cohesive "C" Stage
24722-47			
A	720 hrs at 160°C	1113	Adhesive "B" Stage to Copper
B	720 hrs at 160°C	1233	Adhesive "B" Stage to Copper
24722-49			
A	720 hrs at 160°C	1025	Adhesive "B" Stage to Copper
B	720 hrs at 160°C	1017	Adhesive "B" Stage to Copper

an indication on how effective the optimized process was. Tests performed were humidity exposure with and without bias electrical voltage, temperature cycling, and thermal shocks. The procedures used and the results were as follows:

o Humidity Exposure

Five (5) coupons, pattern E, were subjected to humidity per MIL-STD-202, Method 106. Three (3) coupons were biased with 100 VDC potential, both between and across layers, and the remaining coupons were not biased. The two unbiased samples were used as controls. The samples were subjected to ten continuous cycles (240 hours). Insulation resistance (I.R.) measurements at 100 VDC were recorded initially, periodically during humidity, and after humidity.

The average results of insulation resistance testing at humidity are shown in Table 52. The detailed data sheets on these tests are also included in the Appendix.

As can be seen from the results, the polyimide MLPWB's performed exceptionally well.

o Temperature Cycling

MLPWB's were temperature cycled in accordance with MIL-STD-202, Method 102, test condition C. Five coupons, pattern D, were subjected to 100 cycles of temperature cycling with one cycle consisting of -65°C for 30 minutes, 25°C for 10 minutes, 125°C for 30 minutes and 25°C for 10 minutes. Visual examinations were performed every tenth cycle. The results of examination showed no evidence of delamination or degradation of any sample.

o Thermal Shock

MLPWB's were thermal shocked in accordance with MIL-STD-202, Method 107, test condition B-3. Five coupons, pattern G, were subjected to 100 cycles of thermal shock with one cycle consisting of -65°C for 15 minutes, transferred immediately into 125°C for 15 minutes, then immediately back to -65°C. Visual examination was performed every tenth cycle. The results of examination showed no evidence of delamination or degradation of any sample.

o Thermal Shock - Solder Float

Samples of the MLPWB's were also shocked by floating on top of a molten solder bath at 250°C for ten seconds. Also, two previously made panels (24722-3 and 24722-4, one Atlantic, one Mica) were also thermally shocked by floating in a molten solder bath. There was no evidence of any delamination or other deleterious effects in any of the MLPWB's or polyimide panels.

c. EVALUATION OF IMPROVED MATERIALS AND PROCESSES IN FABRICATED MLPWB

Sixty specimens of coupons per MIL-STD-275 were fabricated using both Mica and Oak-Atlantic polyimide prepregs and "C" stage materials. These specimens were fabricated using the technology developed during this investigation that gave the most improvement for inner layer adhesion. A portion of these samples were

TABLE 52 - HUMIDITY INSULATION RESISTANCE TESTS

	Average Insulation Resistance Across Layers	Average Insulation Resistance Between Layers
	OHMS	OHMS
Biased Coupons S/N 1, 2, 3	5.6×10^{12}	9.2×10^{11}
Control Coupons S/N 4, 5	7.2×10^{10}	5.5×10^{13}

NOTE: The initial and final I.R. measurements all read $>5.0 \times 10^{13}$ ohms (limit of the megohmeter). The physical appearance of the coupons was unchanged after humidity.

Material: Mica

retained for delivery to AFWAL as part of the contractual requirements. The other portion of these specimens were environmentally tested as follows:

o Humidity Exposure

Pattern E coupons were subjected to humidity per MIL-STD-202, Method 106. The

coupons were biased with 100 VDC potential both between and across layers with the remaining layers unbiased. Unbiased samples were used as controls. The samples were subjected to ten continuous cycles (240 hours). Insulation resistance (IR) at 100 VDC was recorded initially, periodically during humidity, and after humidity. The minimum allowable resistance between test points for all IR measurements was 500 megohms.

The results showed no blistering, measling, crazing or delaminatin due to humidity. All of the IR measurements were greater than 500 megohms except for one post humidity reading on one point in layer four of one sample which read 150 megohms. The other measurements on this specimen within and betweeen layers were above specification. It appears that this anomaly was possibly attributed to an instrumentation problem.

o Temperature Cycling

MLPWB's were temperature cycled in accordance with MIL-STD-202, Method 102, test condition C. Pattern D coupons were subjected to 100 cycles of temperature cycling with one cycle consisting of -65°C for 30 minutes, 25°C for 10 minutes, 125°C for 30 minutes, and 25°C for 10 minutes. Visual examination was made every tenth cycle.

All test samples passed temperature cycling.

o Thermal Shock

MLPWB's were thermal shocked in accordance with MIL-STD-202, Method 107, test condition B-3. Pattern G coupons were subjected to 100 cycles of thermal shock with one cycle consisting of -65°C for 15 minutes, transferred immediately into 125°C for 15 minutes, then immediately back to -65°C. Visual examination was performed every tenth cycle.

All test samples passed thermal shock.

o Thermal Shock - Solder Float

Various coupon samples were floated on top of a molten solder bath at 250°C for various lengths of time and then examined for evidence of delamination or other deleterious effects.

All test samples passed solder float with no indication of delamination or separation.

SECTION III
CONCLUSIONS

Based on the exploratory development studies completed in this investigation, the following summary statements and conclusions are presented:

- The primary failure mechanism of polyimide MLPWB inner layer adhesion is adhesive failure to inner copper surfaces.
- Optimization of inner layer adhesion can be achieved using a ferric chloride/red oxide surface treatment on copper surfaces.
- Polyimide prepreg materials qualified to MIL-P-13949 demonstrate high quality and consistency.
- Polyimide prepreg materials have less sensititivty to moisture than epoxies.
- Polyimide MLPWB have excellent moisture resistance, and thermal cycle/shock resistance when properly fabricated.
- The ASTM D2733 method for determining lap shear provides an excellent technique for measuring inner layer lap shear of MLPWB.
- The ASTM D3167 floating roller technique for peel testing shows possibilities for further exploration for use on MLPWB.
- Analytical techniques are available for sophisticated characterization of prepreg materials.

SECTION IV

SUGGESTED TEST CHANGES AND ACCEPTANCE CRITERIA FOR POLYIMIDE MLPWB

1. PREPREG CRITERIA

Recent changes in military specifications have resulted in the latest revision (F) of MIL-P-13949 now specifying the requirements for both fully cured ("C"-stage) metal clad laminates for printed wiring boards and also for preimpregnated ("B"-stage) laminate materials. The results of this study indicate that the quality and consistency of polyimide prepregs are excellent. The requirements for controlling prepreg quality per MIL-P-13949 include the primary tests for gel time, volatile content, and resin content and resin flow. While some of these tests may appear to be a little crude, they are for the most part quite effective in controlling prepreg quality.

Analytical tecniques such as those demonstrated in this study could be incorporated as auxiliary tests; however, at this time, it certainly does not seem necessary. Of these, the technique of thermogravimetric analysis could readily be substituted for the existing method for determining volatile content. While differential scanning calorimetry and thermal mechanical anaylsis are powerful analytical characterization techniques, extended studies would definately be needed to closely establish correlations with gel time and resin flow. Therefore it is recommended at this time that the test criteria established for prepreg materials per MIL-P-13949F remain as is.

2. "C"-STAGE CRITERIA

It is recommended that the procedure for measuring the peel strength of metal foil on "C" stage laminates be tightened and a specific technique become standardized. The existing technique per MIL-P-13949 is lacking in defining a specific test fixture. The peel strength testing in this study showed the potential of the floating roller technique for this application. We feel that additional effort is needed to fully establish its effectiveness for use in peel testing of PCB materials however the initial testing has been most encouraging.

3. COPPER SURFACE TREATMENT

The use of a copper surface treatment for inner layers of a MLPWB is without doubt a necessity. The red oxide treatment described in this study when used with the ferric chloride/hydrochloride and pre-etch definitely warrants consideration. The incorporation of this copper surface treatment into military specifications at this time would be premature. The materials and processes and techniques developed in this exploratory development program should be demonstrated on a prototype/production basis first prior to any consideration of making it mandatory.

4. LAP SHEAR TEST SPECIMEN

The ASTM D2733 method developed for measuring the inner layer lap shear strength of MLPWB configurations also requires further consideration. It is suggested that this technique, or an acceptable modification, should be incorporated into preproduction qualification testing requirements particularly for polyimide MLPWB. This technique would demonstrate the effectiveness and quality of the materials and processes used for MPLWB fabrication.

SECTION V

ENVIRONMENTAL IMPACT

The technology developed in this study should have no adverse environmental consequences even on a full scale production basis. The chemical solutions used for treatment of copper inner layer surfaces are standard materials used within the printed wiring board industry. These chemicals, particularly ferric chloride, hydrochloric acid, sodium chlorite, sodium hydroxide, and sodium phosphate must of course be used and disposed of in accordance with existing state and federal regulations.

APPENDIX A
CONTEMPORARY PROCESSES FOR POLYIMIDE MULTILAYER FABRICATION

POLYIMIDE MULTILAYERS — FABRICATION PROCESS

Outline

Process No.	Title
100	Material Preparation
200	Clean Laminate Material
300	Image Application — Inner Layers
400	Etch Material/Inspect
500	Strip Resist/Bake
600	Apply Surface Treatment
700	Laminate and Post Bake
800	Drill/X-Ray Inspect
900	Clean Drilled Holes
1000	Comments on Completion of Multilayer Board

Process 100: Material Preparation

Procedure: Determine the required panel size of the multilayer board from the "X" and "Y" dimension of the supplied artwork. Allow at least a two inch border all around the artwork including the coupon. Remember that laminate is fabricated in multiples of feet (i.e., 3' x 4', 3' x 3', 3' x 2', etc.). Therefore, the optimum flat size is evenly divisible into these dimensions (e.g., 6" x 9", 9" x 12", 12" x 12", 18" x 12", 18" x 9", etc.). Shear the material and prepreg into the required panel size and designate the orientation of the direction of the weave on each panel and piece of prepreg. Note: The 3' (36") dimension is always perpendicular to the direction of the cloth when being treated. A method of designation can be cutting the corner off the lower right hand corner of all the material. Pierce the tooling holes congruent with the laminating fixture and artwork tooling holes.

Equipment: Di-Acro shears ser. no. 1331

Paper cutter — 24" wide

Two (2) hole air driven punch

Comments: As with epoxy prepreg, polyimide prepreg should be handled with care. Use white gloves and avoid any material contamination from shearing.

Process 200: Clean Laminate Material

Procedure: Using white dot pumice sparingly, power scrub the laminate material until the copper surface is shiny and clean. Use the water break test to insure the cleanliness of the material. That is, water should not bead or form droplets over a clean copper surface. Air dry using the pressurized air gun. Bake the material at 200°F for 10-15 minutes.

Equipment: Motor driven power scrub brush

Pressurized, oil free, air-air gun

Oven. Air circulating - 200°F

Comments: This process is impossible with double sided treated copper laminate. A three minute degrease in trichloroethane-1,1,1 is recommended for cleaning double sided treated copper.

Process 300: Image Application

Apply Riston after the Riston laminator has reached the thermostatically set temperature (about 200°F). Remember to let the Riston photopolymer advance about 6" before entering the panel in between the laminating rollers. Cut the Riston from the trailing edge of the panel and trim the edges of Riston. Cut away Resist around the tooling holes.

Pin the corresponding artwork to the material, making sure the emulsion side is against the Resist, and place the package in the exposure table frame. Close top frame cover, switch vacuum pump on, and expose the Resist for two minutes (Riston 211R Resist — other Resists might have different settings). Remove panel and dismantle film.

Remove the Mylar coverlay from the exposed panel and develop the film in the Dupont Conveyorized Developer. Use a conveyor speed of 2.5 for the 1 mil Resist. Use the provided carrier for the thin laminates in order to eliminate the problem of material wrapping itself around the conveyor rolls. Remove the developed panel and touch-up the image with an alkali soluble ink Resist.

Equipment: Riston Laminator, Dupont type "A"

Colight DMVL exposure unit

Riston II — Conveyorized Aqueous Processor CAP-24

Materials: Riston 211R Aqueous soluble, alkali

Riston 218 Strippable photopolymer — dry film

Artwork: Polyester base film

Developer: Riston Developer 2000 — sodium borate or sodium carbonate solution with butyl cellosolve acetate added.

Comments: None

Process 400: Etch Material/Inspect

Procedure: Tape the imaged inner layer material to the provided epoxy leader. Set all valves and switches for the conveyorized etcher. Temperature of the chromic-sulfuric acid is 130°F. Etch at a conveyor speed of 2.5'/min.

Inspect circuitry for shorts, open circuitry. Spurious foil, nicks, etc., repair where feasible.

Equipment: Chemcut Conveyorized Etcher

3x magnification glass eye lamp

Exacto knife

Materials: Shipley CR10 etchant or equivalent

Hydrazine (N_2H_4) neutralizer

Comments: None

Process 500: Strip Resist-Bake

Immerse etched panel into stainless steel tank filled with Resist stripper. Hang them on the provided hooks. Strip for approximately three (3) minutes. Rinse thoroughly with running warm water Rinse again with cold water and then hand pumice scrub. Rinse thoroughly again, air dry, and bake the panels for 10 min at 200°F.

Equipment: Scrub brush, nylon

Stainless steel tank, 6" x 24" x 24"

Pressurized air gun

Materials: White dot pumice

Dupont 3030 stripper for Riston

Comments: Stripper 3030 is comprised of butyl cellosolve acetate and a sodium hydroxide solution — could have detrimental effects on polyimide material since the material is exposed to the stripper at this point (i.e., the copper is etched). Most probably it would require a long exposure time, however.

Process 600: Apply Surface Treatment

A. "Red" Oxide Surfaces

Make up an alkaline solution using the following formulation:

5 g/l — sodium hydroxide (pellets or flake)

10 g/l — trisodium phosphate ($Na_3PO_4 12H_2O$)

30 g/l — sodium chlorite ($NaClO_2$)

Do not substitute commercial products for the above mentioned reagent grade chemicals (i.e., Cascade, Drano, and/or Chlorox). Use D.I. water for the makeup. Power scrub, rinse and dry the inner layers as per process #200. Heat the "red" oxide solution to 180°F. Immerse the panels for 4 min in the hot alkaline solution. A red-black surface will appear on all the exposed copper surface areas. Spray rinse with tepid water for at least 1 min. Immersion rinse for 1 min in cold water and air dry. Bake the panels at 200°F for ½ hr.

B. 50%, 50%, ferric chloride/hydrochloric acid solution

Make up the solution as follows:

- ½ by volume ready circuit etch, Hunt Chemical, 42°BE'
- ½ by volume hydrochloric acid reagent grade, 37% by volume HCl

Power scrub, rinse and dry the inner layers as per process #200. Immerse etched panel in the above etchant solution for 1 min at room temperature. A white chloride residue quickly appears. It is mandatory that a strong, hot water spray be applied quickly in order to remove this precipitate. Spray rinse for at least 45 seconds. Then, immerse the panel in a 25% solution of hydrochloric acid for 1 min. Remove the panel, hot water spray rinse, cold water spray rinse and air dry. Oven dry for 15 min at 200°F.

Equipment: Stainless steel tank, 316SS, heater

Thermostat — stainless heaters

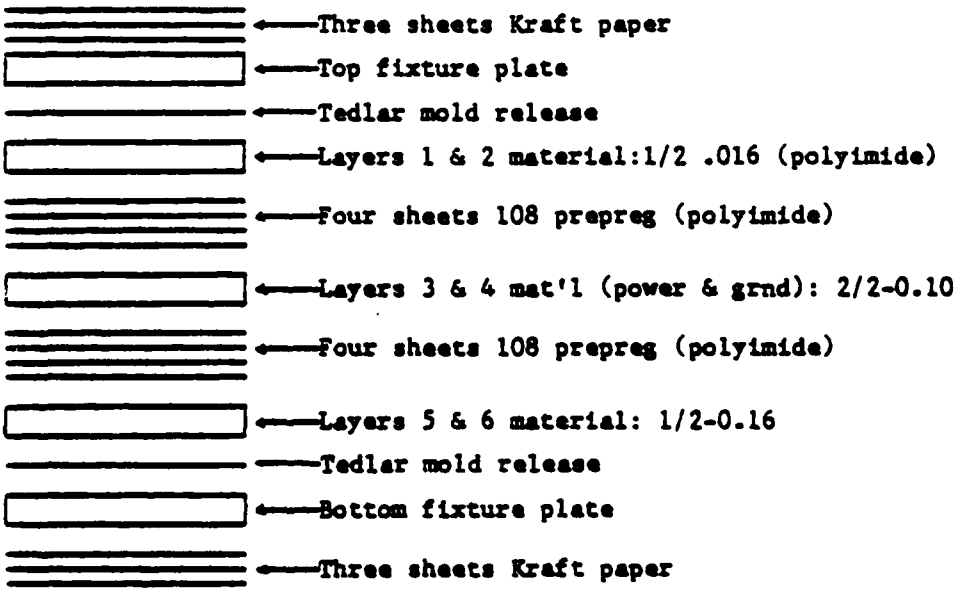
Materials: Ready circuit etch, Hunt Chemical Co.

Hydrochloric acid, 37% by volume, reagent.

Comments: The uniformity and consistency of both the red oxide treatment and ferric chloride etch surface treatment are difficult to obtain with the present laboratory set up. The dormant copper surface becomes active after the FeCl/HCl etch and easily oxidizes. Also, as stated in the report, a mixture of cuprous and cupric oxide crystals are grown with the controlled "red" oxide method, thereby speculating as to the homogeneous nature of the surface. The removal of the white chloride (?) precipitate in the FeCl/HCl etch is difficult also.

Process 700: Laminate and Post Bake

Procedure: Lay-up the package to be laminated per the attached lay-up sheet for the particular MLB in question. For example, a six (6) layer MLB with four (4) signal layers and power and ground layers will look as follows:



Desired thickness: .062 ± .005

Note: only layers 2 & 5 would be printed and etched at this point; layers 1 & 6 would be solid copper for completion of these outside layers.

There are two (2) laminating cycles that are presently being used depending on the properties of the received polyimide prepreg.

A. Hot Cycle-Manual Cycle

- Set platens to 375°F
- Set high/low pressure switch to "high"
- Set auto/manual switch to "manual"
- Adjust pressure gauge to 350 psi for the particular panel size after closing the press

Once the indicators show that 375°F has been reached, open the press and insert the laid-up package with Kraft paper on either side. Close the press quickly and laminate for 2½ hrs. Cool down with water for 15 min under pressure. Remove the package and dismantle it. Shear the excess polyimide resin from the edges of the panel. Be sure to leave the tooling holes intact. Using a calibrated air circulating oven, further cure the panel at 450°F for 4 hrs.

B. Modified Hot Press Cycle — Manual

- Set platens to 200°F
- Set high/low pressure switch to "high"
- Set auto/manual switch to "manual"
- Adjust pressure gauge to 350 psi for the particular panel size after closing the press

Once the indicators show that 200°F has been reached, open the press and insert the laid-up package with Kraft paper on either side. Close the press and reset the digital temperature dials to 375°F. Laminate under high pressure for 2½ hrs. Cool down with water for 15 minutes under pressure. Remove the package and dismantle it. Shear the excess polyimide resin from the edges of the panel. Be sure to leave the tooling

holes intact. Using a calibrated air circulating oven, further cure the panel at 450°F for 4 hrs.

Equipment: PHI, electric heated, 2 opening 100T hydraulic press
Laminating fixtures
Air circulating oven

Comments: The laminating cycle effects on adhesion between copper and polyimide has been described in the interim report polyimide study prepared by Joe Geraghty 9 January 1980.

Process 800: Drill/X-Ray Inspect for Registration

Procedure: Load and wind the provided drill tape onto the reel of the W/C Controller. Drill the provided coupon hole array on the first panel of a given order. Overlay the A/W of any inner layer negative to establish an offset if required. Drill speeds and feeds for any given drill diameter are provided on the attached sheet. Use only new, standard 1/8" shank, carbide drills. Change drills after 500 holes are drilled. After completion of the coupon array, drill the remainder of the board and x-ray the panel. Expose and develop the x-ray film (Polaroid 108). Continue drilling the remainder of the order if the x-ray is positive (i.e., the holes are centrally registered in the pad areas). Call the production supervisor if they are not registered properly.

Equipment: Excellon XL-2 N/C controlled
Three station, Westlund ball bearing spindles
Faxitron x-ray unit
Carbide drills, 1/8" std. shk.

Comments: Particulars about back-up material, operation of the drill, and loading and operating the N/C controller were not covered since they are the same as for epoxy MLB's.

Diameter	Feed (in/min)	Speed (rev/min x 10^3)
.014 - .032	60	60
.032 - .062	90	60
greater than .062	70	60

Process 900: Clean Drilled Holes

Procedure: Using a motorized orbital sander, sand both sides of the drilled panel to remove any burrs. Power scrub clean, rinse, and dry the panels per process #200. Then, plasma etch as follows:

LFE Model PSM-1224

1000 watt RF output

time: 10 min

Make up of gas: 30% CF_4

70% O_2

Chamber pressure: 400 mμ

Care should be taken when removing the panels from the chamber since they will be hot.

Equipment: LFE model PSM-1224 plasma etcher

holding fixture for panels

orbital sander

motorized scrub brush

Pressurized air gun

Comments: This process is based on limited production quantities. Further studies are anticipated.

Process 1000: Completion of MLB Board

Procedure: The remaining process is as follows:

- Electroless copper plate
- Electrolytic copper plate — acid copper
- Sand, clean panel, bake at 200°F for ½ hr.

- Photo outside layers (H6 in example)
- Touch-up
- Solder plate
- Strip Resist
- Etch
- Reflow solder
- Rout to size

Equipment: General PCB shop equipment: plating, etching, etc.

Comments: Only one operation is different for polyimide materials than for epoxy PCB's. Routing might require special router bits because of the brittle nature of the polyimide/glass material. Thus far, standard carbide end mill router bits have been used satisfactorily. Occurrences of total delamination during the routing operation is a possibility when the internal adhesion is poor.

AMERICAN NATIONAL STANDARD ANSI/ASTM D 2733 - 70 (Reapproved 1976)

Standard Test Methods for INTERLAMINAR SHEAR STRENGTH OF STRUCTURAL REINFORCED PLASTICS AT ELEVATED TEMPERATURES[1]

This Standard is issued under the fixed designation D 2733; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 These methods cover the determination of interlaminar shear strength of structural reinforced plastics at temperatures above the Standard Laboratory Temperature of 23 C (73.4 F).

NOTE 1—The values stated in SI units are to be regarded as the standard.

NOTE 2—Safeguards against the effects of extremely high temperatures should be utilized to protect the operator.

1.2 These methods are not intended specifically for use in determining the effect of long continued exposure at elevated temperatures or of a cyclic exposure range of temperature, although they may be used for such special tests if desired.

2. Summary of Methods

2.1 These methods consist of preparing specimens as described in 6.2 and inserting the specimens in the testing machine, with or without attachments as required. The specimens are then stressed until rupture occurs, in accordance with either of the methods outlined below:

2.1.1 *Method A* requires the use of side-supporting steel plates, tightened evenly and firmly (to the extent necessary to prevent peeling of the specimen during the test, but not to the point where the specimen is crushed) against the faces of the test specimen by means of two small clamps, located 6.5 cm (2 1/4 in.) apart. With the steel plates in place, the specimen shall be inserted in the grips of the testing machine and stressed until rupture occurs. A shear-type failure should result.

2.1.2 *Method B* does not require the use of side-supporting steel plates; hence peel effects are promoted. A shear-type failure with some peeling at the interlaminar bond should result.

3. Significance

3.1 Interlaminar shear strength properties of reinforced plastic structures at elevated temperatures are of considerable importance in predicting the strength of materials for characterization of materials for control and specification purposes, and to provide useful data for research and development studies.

4. Definition

4.1 *interlaminar shear strength*—the shear strength at rupture in which the plane of fracture is located between the layers of reinforcement of a plastic reinforced structure. It is expressed in pounds per square inch based on the distance between saw cuts.

5. Apparatus

5.1 *Testing Machine*—The tension testing machine and its accessory equipment shall conform to the requirements specified in ASTM Method D 638, Test for Tensile Properties of Plastics.[2] All mechanical parts of the apparatus that are exposed to elevated temperatures during the test shall be adjusted to

[1] These methods are under the jurisdiction of ASTM Committee D-20 on Plastics and are the direct responsibility of Subcommittee D-20.18 on Reinforced Thermosetting Plastics.

Current edition effective Dec. 24, 1970. Originally issued 1968. Replaces D 2733 - 68 T.

[2] *Annual Book of ASTM Standards*, Part 35.

function normally at these temperatures, and their accuracy shall be verified by calibration tests at the specified test temperatures. Verification shall be repeated as often as necessary to ensure correct test readings.

5.2 *Insulated Test Chamber*, through which air is circulated at the required temperature, to enclose the specimen during the actual test (Note 3). This chamber shall also enclose at least enough of the test machine components to ensure that conduction of heat through these components will not materially change the temperature of the specimen from that of the test temperature. The temperature of the air in the test chamber may be regulated by any convenient means. For high-temperature testing of plastics that are readily attacked by oxygen, the specimen may be enclosed in a capsule so that it can be tested in an inert gas atmosphere (Note 4).

NOTE 3—For detailed requirements covering enclosures for testing machines and servicing units for maintaining the desired temperatures and conditions, reference should be made to ASTM Specification E 197, for Enclosures and Servicing Units for Tests Above and Below Room Temperature.[1]

NOTE 4—Vacuum testing is generally not recommended except where a space environment is to be simulated because of the outgassing problem and because of the difficulty in heating the specimen uniformly by radiant means. When tests are made in vacuum, the necessary corrections to obtain true specimen loads must be made; for instance, any load variation due to sealing-ring friction or other features.

5.3 *Thermocouples or Thermometers*, placed in intimate contact with the test specimens in the test and conditioning chambers.

5.4 *Preconditioning Oven*—A circulating-air oven, adjusted at 50 ± 3 C (122 ± 5 F), for preconditioning test specimens when required.

NOTE 5—A test chamber should be utilized for preconditioning specimens when necessary.

5.5 *Desiccators*, containing anhydrous calcium chloride (or other suitable desiccant) for storage of the preconditioned specimens.

5.6 *Conditioning Chamber*, for conditioning the specimens at the desired test temperature prior to testing. The conditioning shall be done either in an insulated storage chamber of the circulating-air type or in the insulated test chamber. If the specimens are conditioned in the insulated test chamber they shall be placed on a wire-mesh rack or other suitable support during the conditioning period.

5.7 *Side-Supporting Plates* used for Method A, 0.3 by 2.5 by 7.6 cm ($^1/_8$ by 1 by 3 in.).

5.8 *C-Clamps*, 2.5-cm (1-in.), for clamping steel plates to test specimens.

6. Test Specimens

6.1 *Configuration*—Test specimens for both methods shall conform to the dimensions and shape given in Fig. 1. They shall have a minimum thickness of 0.32 cm ($^1/_8$ in.) and shall be 2.54 cm (1 in.) wide by 20 cm (8 in.) long. The length of the specimens may be varied to accommodate requirements of the available testing equipment. The edges of the specimen shall be smooth but not round or beveled.

6.2 *Preparation*—Two parallel cuts, one on each opposite face of the specimen and 1.25 cm ($^1/_2$ in.) apart, shall be sawed across the entire width of the specimen. The incision shall be of sufficient depth to sever the center laminate located midway between the two faces of the laminate, as shown on Fig. 1.

6.3 *Number*—Five specimens shall be tested whenever isotropic materials are under test. Ten specimens, five normal to and five parallel with the principal axis of anisotropy, shall be tested whenever anisotropic materials are under test. Specimens that fail prematurely or at some fortuitous flaw shall be discarded and retests made, unless such flaws constitute a variable the effect of which is to be studied.

7. Temperature Control and Measurement

7.1 Temperature variation of the specimen from the indicated nominal test temperature during load application shall not exceed ±5 F or ±1 percent of the nominal test temperature (whichever is greater) at a particular monitoring point.

7.2 The time of heating prior to the start of the test should be governed by the time necessary to ensure that the temperatures can be maintained within the limits specified above. Since plastics have a comparatively low thermal conductivity, sufficient time must be allowed for the specimen to come to a constant temperature throughout its cross section. This

[1] *Annual Book of ASTM Standards*, Parts 40 and 41.

heating time should be as nearly as possible the same for all specimens to be compared. Both the time-to-temperature and the time-at-temperature prior to testing should be reported. Where the heating time required to bring a specimen to equilibrium is in doubt, it may be determined by embedding a thermocouple in a representative specimen and determining the actual time-to-temperature requirement. This time should be correlated with a thermocouple or thermocouples at the specimen surface.

7.3 The method of heating and temperature measurement must be sufficiently sensitive and reliable to ensure that the temperature of the specimen is within the limits specified. Extreme care must be taken to prevent overheating of the specimen surface. Where there is an indication that the specimen was damaged due to temperature in excess of the limit specified, the result for that specimen shall be discarded.

8. Conditioning

8.1 In general, the physical properties of plastics are influenced by relative humidity in a manner that significantly affects test results. In order that reliable comparisons may be made of different materials and between different laboratories, it is necessary to standardize the humidity conditions. When comparisons of this nature are to be accomplished and unless otherwise specified, the following conditioning procedure is to be followed:

8.2 *Preconditioning* All test specimens shall be preconditioned in accordance with Procedure B of ASTM Methods D 618, Conditioning Plastics and Electrical Insulating Materials for Testing.[4] At the higher temperatures, tests will necessarily be on the basis of dried specimens, regardless of the type of preconditioning. Consequently, in order that tests at all temperatures be made on the same basis so far as moisture content is concerned, a preconditioning treatment that removes all moisture is specified.

8.3 *Conditioning* Test specimens shall be placed in the conditioning or test chamber at the specified temperature and allowed to remain until thermal equilibrium is attained.

NOTE 6 Suggested minimum conditioning time is 2 h.

8.3.1 If conditioning is done in a separate conditioning chamber, the time necessary for attainment of the thermal equilibrium in the test chamber after transfer of the specimen shall be determined by appropriate measurements (see 7.2).

9. Speed of Testing

9.1 Speed of testing shall be the relative rate of motion of the grips or test fixtures during test. Rate of motion of the driven grip or fixture when the machine is running idle may be used if it can be shown that the resulting speed of testing is within the limits of variation allowed.

9.2 The standard speed of testing for either Method A or B shall be 0.50 cm (0.20 in.) to 0.65 cm (0.25 in.)/min.

10. Procedure

10.1 If conditioned in a separate conditioning chamber, place such temperature conditioned specimens as rapidly as possible in the tension grips (between the side-supporting steel plates if Method A is used). This entire transfer shall not require longer than 30 s. After exposure for a period 1.3 times the time found necessary for the control specimen to attain thermal equilibrium in the test chamber (8.3 or 8.3.1), ±10 percent, test the specimen in accordance with either Method A or B.

NOTE 7 The time requirement may be modified if it can be demonstrated that no appreciable error is introduced by so doing, and all concerned parties agree.

10.2 *Method A* The side-supporting steel plates required for this method shall be held snugly against the faces of the test specimen by means of two small clamps, located 6.5 cm (2 ½ in.) apart. With the steel plates in place, stress the specimen in the grips of the testing machine until rupture occurs.

10.3 *Method B* Stress the specimens in the grips of the testing machine without side-supporting steel plates until rupture occurs.

11. Calculations

11.1 Calculate interlaminar shear strength at rupture as follows:

$$S = P/wa$$

where:

S = interlaminar shear strength, MPa (or psi),

P = total applied load, N (or lbf),

w = width of the specimen (2.54 cm (1 in.)), and
a = distance between sawcuts, (1.25 cm ($^1/_2$ in.)).

11.2 *Standard Deviation*—The estimated standard deviation shall be calculated and reported to two significant figures as follows:

$$s = \sqrt{(\Sigma X^2 - n\bar{X}^2)/(n-1)}$$

where:
s = estimated standard deviation,
X = value of single observation,
n = number of observations, and
$\bar{X}$ = arithmetic mean of the set of observations.

12. Report

12.1 The report shall include the following:

12.1.1 Complete identification of the materials tested, including type, source, manufacturer's code number, and any other pertinent information,

12.1.2 Number of specimens tested and test method used,

12.1.3 Method of preparing the test specimen and dimensions of the test specimen,

12.1.4 Conditioning time (time-to-temperature and time-at-temperature prior to beginning of test),

12.1.5 Mean temperature in the test enclosure at any time,

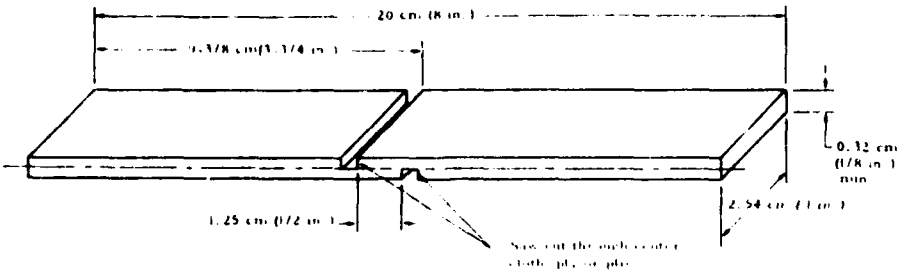
12.1.6 Maximum temperature in the test enclosure at any time,

12.1.7 Average deviation from the mean temperature in the test enclosure during the test,

12.1.8 Average interlaminar shear strength, and standard deviation at each temperature tested,

12.1.9 Atmospheric conditions in the test room (temperature and relative humidity), and

12.1.10 Date of test.



* Saw cuts must be parallel within 0.08 cm (0.030 in.).
* Depth of saw cut shall be as follows:
(*a*) $^1/_2$ laminate thickness plus thickness of 1 ply, or
(*b*) $^1/_2$ laminate thickness plus 0.01 cm (0.005 in.) and minus 0 if thickness per ply or number of plies is unknown

FIG. 1 Test Specimen.

AMERICAN NATIONAL STANDARD ANSI/ASTM D 3167 - 76

Standard Test Method for
FLOATING ROLLER PEEL RESISTANCE OF ADHESIVES[1]

This Standard is issued under the fixed designation D 3167; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

INTRODUCTION

The purpose of this test procedure is to provide for the determination of the metal to metal peel strength of adhesives by a method that will provide good reproducibility at low, as well as at high, strength levels and yet allow for a simple method of test specimen preparation and testing.

The accuracy of the results of strength tests of adhesive bonds will depend on the conditions under which the bonding process is carried out. Unless otherwise agreed upon by the manufacturer and the purchaser, the bonding conditions shall be prescribed by the manufacturer of the adhesive. In order to ensure that complete information is available to the individual conducting the tests, the manufacturer of the adhesive shall furnish numerical values and other specific information for each of the following variables:

(*1*) Procedure for preparation of the surfaces prior to application of the adhesive, the cleaning and drying of metal surfaces, and special surface treatments such as sanding, which are not specifically limited by the pertinent test method.

(*2*) Complete mixing directions for the adhesive.

(*3*) Conditions for application of the adhesive, including the rate of spread or thickness of film, number of coats to be applied whether to be applied to one or both surfaces, and the conditions of drying where more than one coat is required.

(*4*) Assembly conditions before application of pressure, including the room temperature, length of time, and whether open or closed assembly is to be used.

(*5*) Curing conditions, including the amount of pressure to be applied, the length of time under pressure, and the temperature of the assembly when under pressure. It should be stated whether this temperature is that of the glue line, or of the atmosphere at which the assembly is to be maintained.

(*6*) Conditioning procedure before testing, unless a standard procedure is specified, including the length of time, temperature, and relative humidity.

A range may be prescribed for any variable by the manufacturer of the adhesive, if it can be assumed by the test operator that any arbitrarily chosen value within such a range or any combination of such values for several variables will be acceptable to both the manufacturer and the purchaser of the adhesive.

1. Scope

1.1 This method covers the determination of the relative peel resistance of adhesive bonds between one rigid adherend and one flexible adherend when tested under specified condi-

[1] This method is under the jurisdiction of ASTM Committee D 14 on Adhesive and is under the jurisdiction of Subcommittee D 14.80 on Metal Bonding Adhesives.

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tions of preparation and testing.

1.2 A variation in thickness of the adherends will generally influence the test values. For this reason, the thickness of the sheets used to make the test specimens shall be specified in the material specification. When no thickness is specified, the flexible adherend shall be 0.63 mm (0.025 in.) thick and the rigid adherend shall be 1.63 mm (0.064 in.) thick.

2. Applicable Documents

2.1 *ASTM Standards:*

B 209 Specification for Aluminum-Alloy Sheet and Plate[4]

D 1781 Climbing Drum Peel Test for Adhesives[5]

E 4 Verification of Testing Machines[3]

3. Significance

3.1 This method is of value for acceptance and process control testing. The method may be used as an alternative to the Metal to Metal Climbing Drum Peel Test, Method D 1781, when that facility is not available. This method should be considered more severe since the angle of peel is greater.

4. Apparatus

4.1 *Testing Machine*, conforming to the requirements of Methods E 4. The testing machine shall be so selected that the breaking load of the specimens falls between 15 and 85 % of the full-scale capacity. The machine shall be capable of maintaining a constant crosshead rate of 152 mm (6 in.)/min, unless otherwise specified. It shall be provided with a suitable self-aligning grip to hold the specimen. It is recommended that the jaws of this grip shall engage the outer 25.4 mm (1 in.) of the end of the flexible adherend firmly. The grip and attachments shall be so constructed that they will move into alignment with the test specimen as soon as the load is applied, so that the flexible member of the test specimen will coincide with the direction of the applied pull through the center line of the grip assembly. The machine shall be autographic, giving a chart that can be read in terms of millimetres (or inches) of separation as one coordinate and applied load as the other coordinate. The applied load as measured and recorded shall be accurate within ± 1 %.

4.2 A fixture as shown in Fig. 1 for support of the test specimen shall be attached to one of the testing machine cross arms. The 1-in. diameter rollers on this test fixture shall roll freely.

5. Test Specimens

5.1 Laminated test panels (see Fig. 2) shall consist of two adherends properly prepared and bonded together in accordance with the adhesive manufacturer's recommendations.

5.2 Unless otherwise specified, clad aluminum alloy conforming to the specification for aluminum alloy sheet and plate (Method B 209) Alloy 2024-T3 shall be used.

5.3 The bonded panels shall be cut into 12.7-mm (0.5-in.) wide test specimens (see Fig. 2) by a means that is not deleterious to the bond. Edge members may or may not be discarded dependent on desire to measure peel strength in this area. The method of cutting test specimens is controlled by adherend and adhesive compositions and the accuracy desired. Shearing, milling, and band-saws can all be used successfully. The unbonded end of the flexible adherend shall be bent, perpendicular to the rigid adherend, for clamping in the grip of the testing machine. Specimens shall be two in number for each temperature tested from each of three bonded panels.

NOTE 1—Direct comparison of different adhesives can be made only when specimen construction and test conditions are identical.

NOTE 2—Within the limitations imposed by 5.3, other specimen widths may be used provided the test machine grip and peel test fixtures are of ample width to apply the load uniformly across the width of the adherends.

NOTE 3—Direct comparison of different adhesives can be made only when the angle of peel is identical. The operator must ascertain that the flexible adherend is bending over the mandrel and not at some irregular angle.

6. Procedure

6.1 Insert the test specimen into the peel test fixture as shown in Fig. 1, with the unbonded end of the flexible adherend gripped in the test machine jaw. Peel the specimen at 152 mm (6 in.)/min bond separation rate by applying the load at a constant head speed of 152 mm (6 in.)/min. If back up plate bends or is distorted during test it is recommended that the speci-

[3] *Annual Book of ASTM Standards*, Part 7.
[4] *Annual Book of ASTM Standards*, Part 22.
[5] *Annual Book of ASTM Standards*, Parts 14, 32, 35 and 41.

men be redesigned with a back up member stiff enough to assure even peel.

6.2 During the peel test make an autographic recording of load versus head movement (load versus distance peeled).

6.3 Record the load over at least a 7.6 mm (3 in.) length of the bond line disregarding the first 2.54 mm (1 in.) of peel.

7. Calculations

7.1 Determine from the autographic curve or at least 7.6 mm (3 in.) of peeling (disregarding the first 25.4 mm (1 in.) the average peeling load in pounds-force per inch (or kilonewtons per metre) of the specimen width required to separate the adherends. It is preferred that the average load be determined from the curve by means of a planimeter.

NOTE 4—In case a planimeter is not used the average may be calculated as the average of load readings taken at fixed increments of crosshead motion. For example, the load may be recorded at each 12.7-mm (½-in.) interval of heat motion (discarding the first inch) until at least six readings have been attained.

8. Report

8.1 The report shall include the following

8.1.1 Complete identification of the adhesive tested including type, source, manufacturer's code number, batch or lot number, form, etc.

8.1.2 Complete identification of adherends used, including material thickness, surface preparation, and orientation.

8.1.3 Description of bonding process, including method of application of adhesive, glueline thickness, drying or precuring conditions (where applicable), curing time, temperature and pressure

8.1.4 The average thickness of adhesive layer after formation of the joint shall be reported within 0.0127 mm (0.0005 in.) The method of obtaining the thickness of adhesive layer shall be described including procedure, location of measurements and range of measurements.

8.1.5 Complete description of the test specimen, including dimensions and construction of the test specimen, conditions used for cutting individual test specimens, number of test panels represented, and number of individual test specimens.

8.1.6 Conditioning procedure prior to testing.

8.1.7 Testing temperature.

8.1.8 Type of test machine and crosshead separation rate used.

8.1.9 Method of recording load and determining average load.

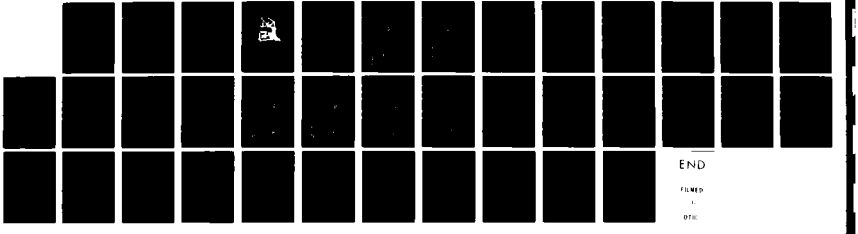
8.1.10 Average, maximum, and minimum peeling load values for each individual specimen.

8.1.11 Average peel strength in pounds-force per inch (or kilonewtons per metre) of width for each combination of materials and constructions under test.

8.1.12 Type of failure, that is, cohesive failure within the adhesive or adherend, adhesion to the adherend, or combination thereof, for each individual specimen.

AD-A122 067 DEVELOPMENT OF IMPROVED PRINTED WIRING BOARD INNER LAYER ADHESION(U) RAYTHEON CO SUDBURY MA EQUIPMENT DIV T E BAKER JUN 82 AFWAL-TR-82-4054 F33615-79-C-5131 3/3

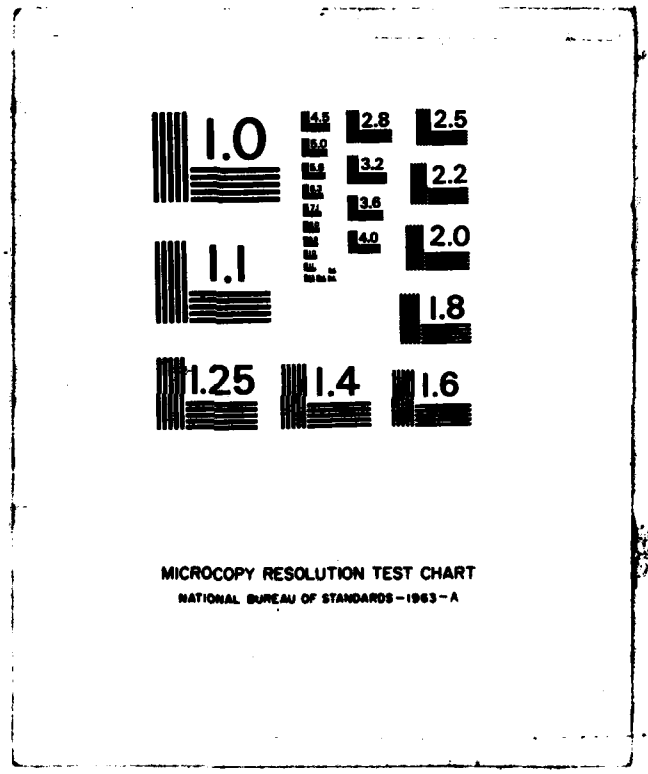
UNCLASSIFIED F/G 11/1 NL



END

FILMED

DTIC


1.0
1.1
1.25
1.4
1.6
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.8
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

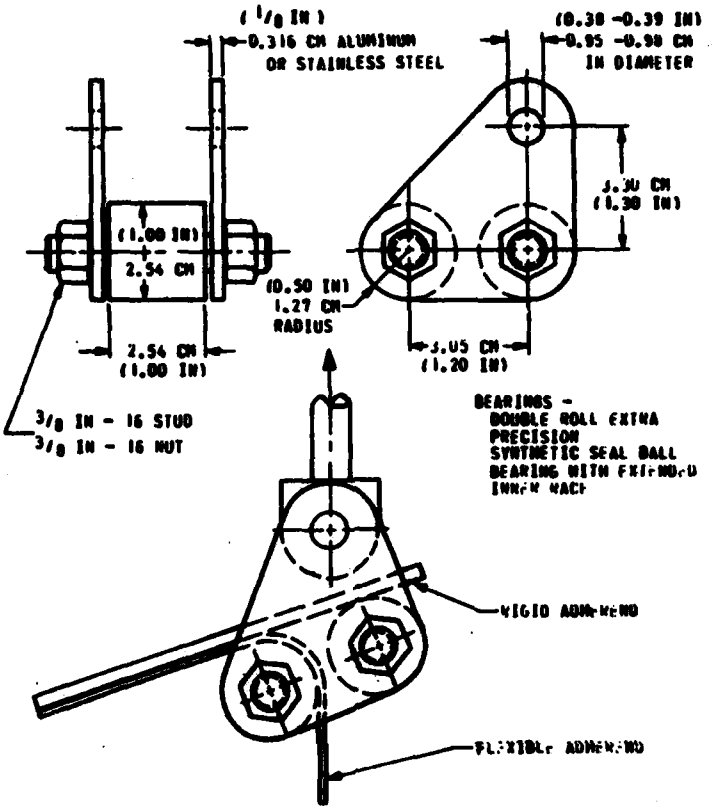
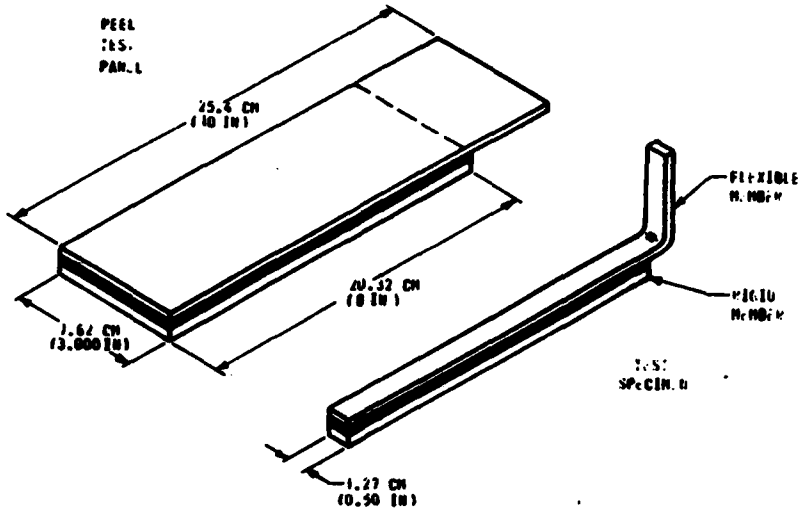


FIG. 1 Roller Drum Peel Test Fixture.



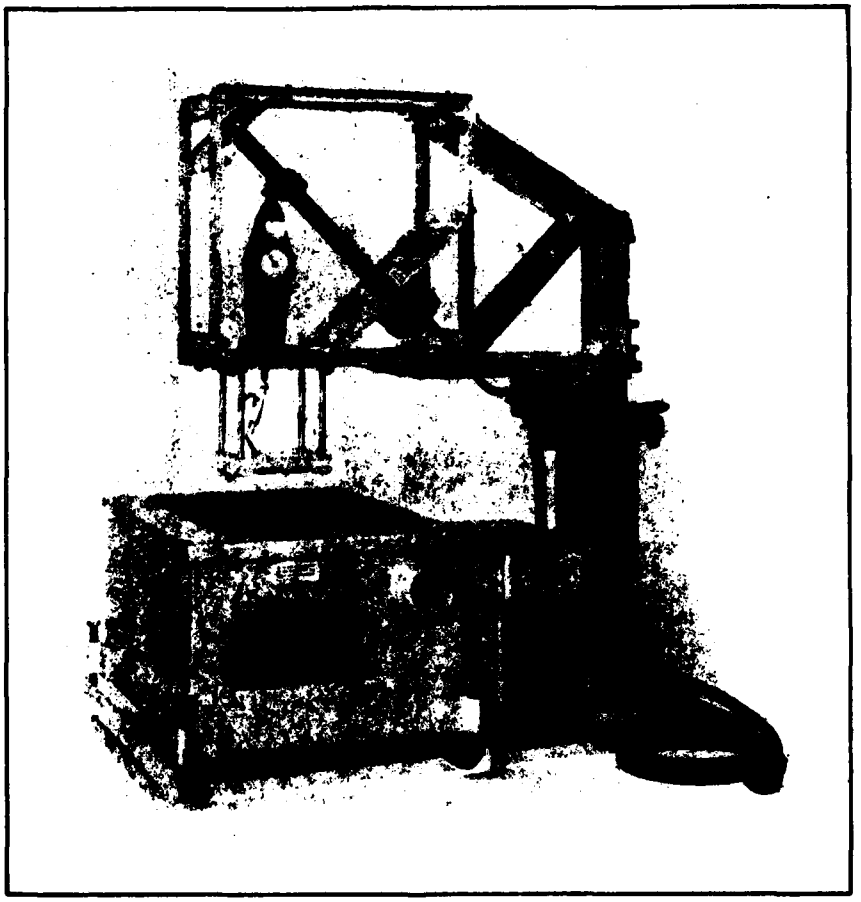
NOTE—A 1.5 to 3.0-in. (38.1 to 74.2-mm) shim can be used to facilitate the start of peel.

FIG. 2 Test Panel and Test Specimen.

APPENDIX D

LUSTER-JORDAN MANUFACTURING CO.

520 HAMILTON STREET NORRISTOWN, PA 19401



DESCRIPTION OF HOT PEEL STRENGTH TESTER

This machine consists of a reversing motor driven screw set on an angle of 45° to horizontal, which operates a quick disengage nut to which is attached a force gauge. On this force gauge is a clamping device which is engaged to the copper strip to be peeled from the laminate. The laminated specimen is inserted in a spring clip under a glass melamine pad with a slot through which the copper strip is pulled and as it is pulled at approximately 90° with the plastic, the force gauge indicates the pull required.

When the strip is clamped properly the specimen in the clamp is lowered along with the supporting and operating frame until the specimen is in the heated oil to the proper depth.

This lowering is accomplished through a rack and pinion operated by a hand crank. A catch is provided at the top position and an adjusting screw sets the low position. A negator spring partially counterbalances the weight of the moving parts. When the specimen is immersed, the operator starts the motor which moves the nut at 3" per minute.

The weight of the machine proper is 125 pounds and the solder pot is 100 pounds, packed for export.

Packed for domestic shipment the machine weighs 110 pounds and the solder pot 80 pounds.

APPENDIX E

ESCA SPECTRA OF COPPER OXIDES

FIGURE 1

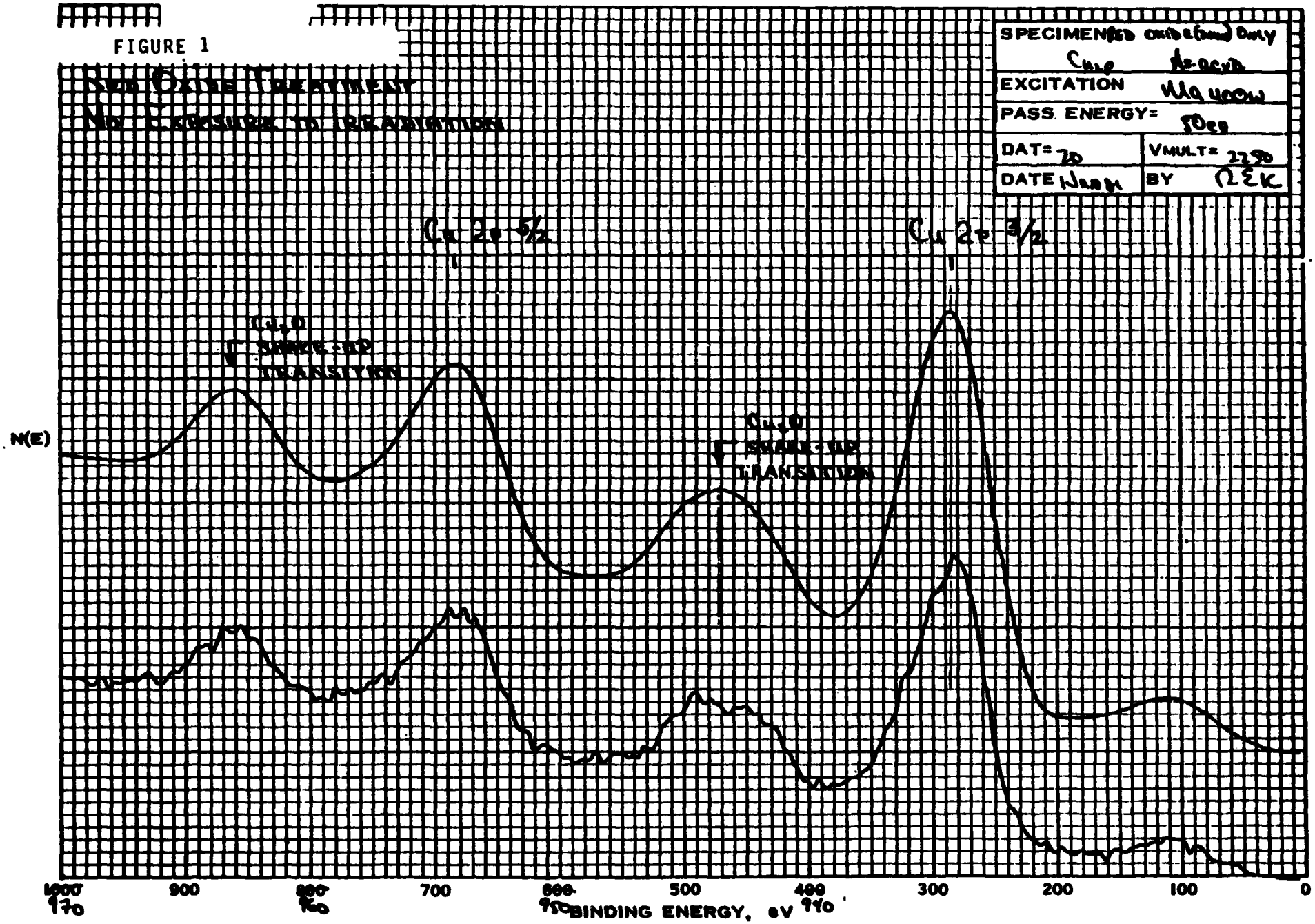
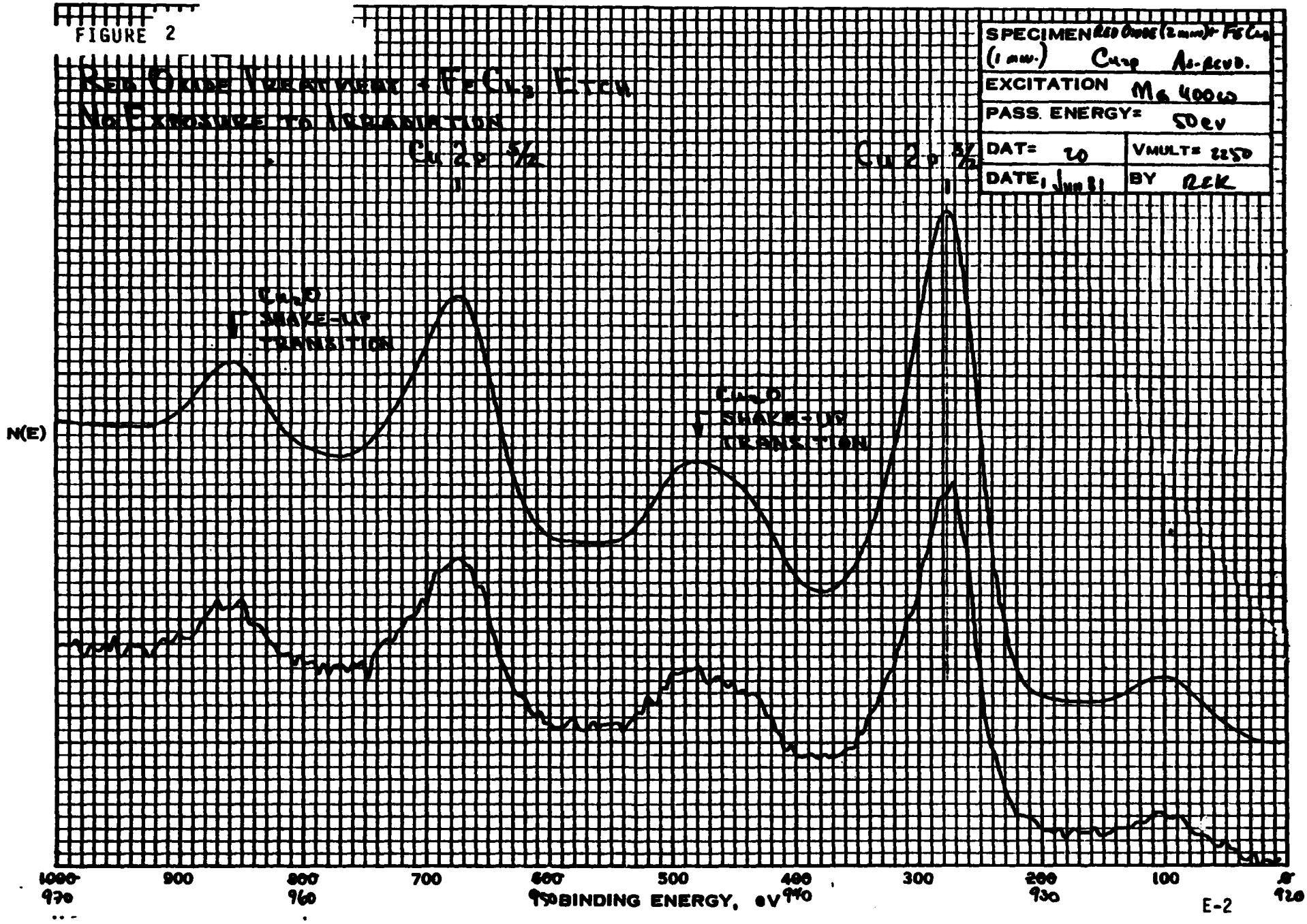

SPECIMEN
EXCITATION
PASS ENERGY=
DAT=
VMULT=
DATE
BY
Cu 2p 3/2
Cu 2p 1/2
Cu+O SHAKE-UP TRANSITION
Cu+O SHAKE-UP TRANSITION
N(E)
1000
900
800
700
600
500
400
300
200
100
0
BINDING ENERGY, eV

FIGURE 2


SPECIMEN Red Oxide (2 mm) + FeCl3 (1 mm.) Cu2p As-Recvd.
EXCITATION Mg 400 W
PASS ENERGY= 50 eV
DAT= 20
VMULT= 2250
DATE: 1 JUN 81
BY REK
Cu 2p 3/2
Cu 2p 3/2
Cu2O SHAKE-UP TRANSITION
Cu2O SHAKE-UP TRANSITION
N(E)
1000
900
800
700
600
500
400
300
200
100
970
960
950
940
930
920
BINDING ENERGY, eV

E-2

FIGURE 3

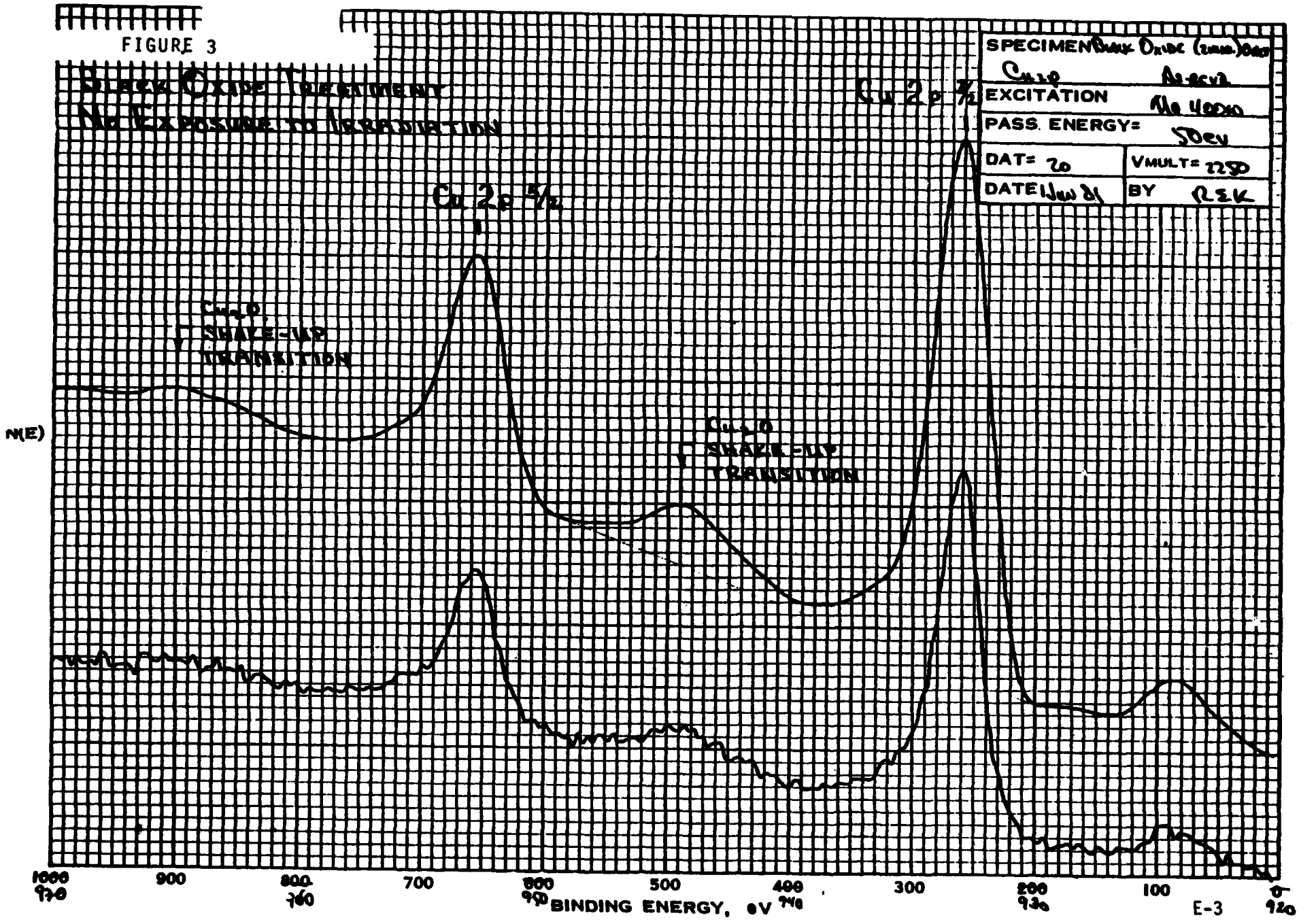
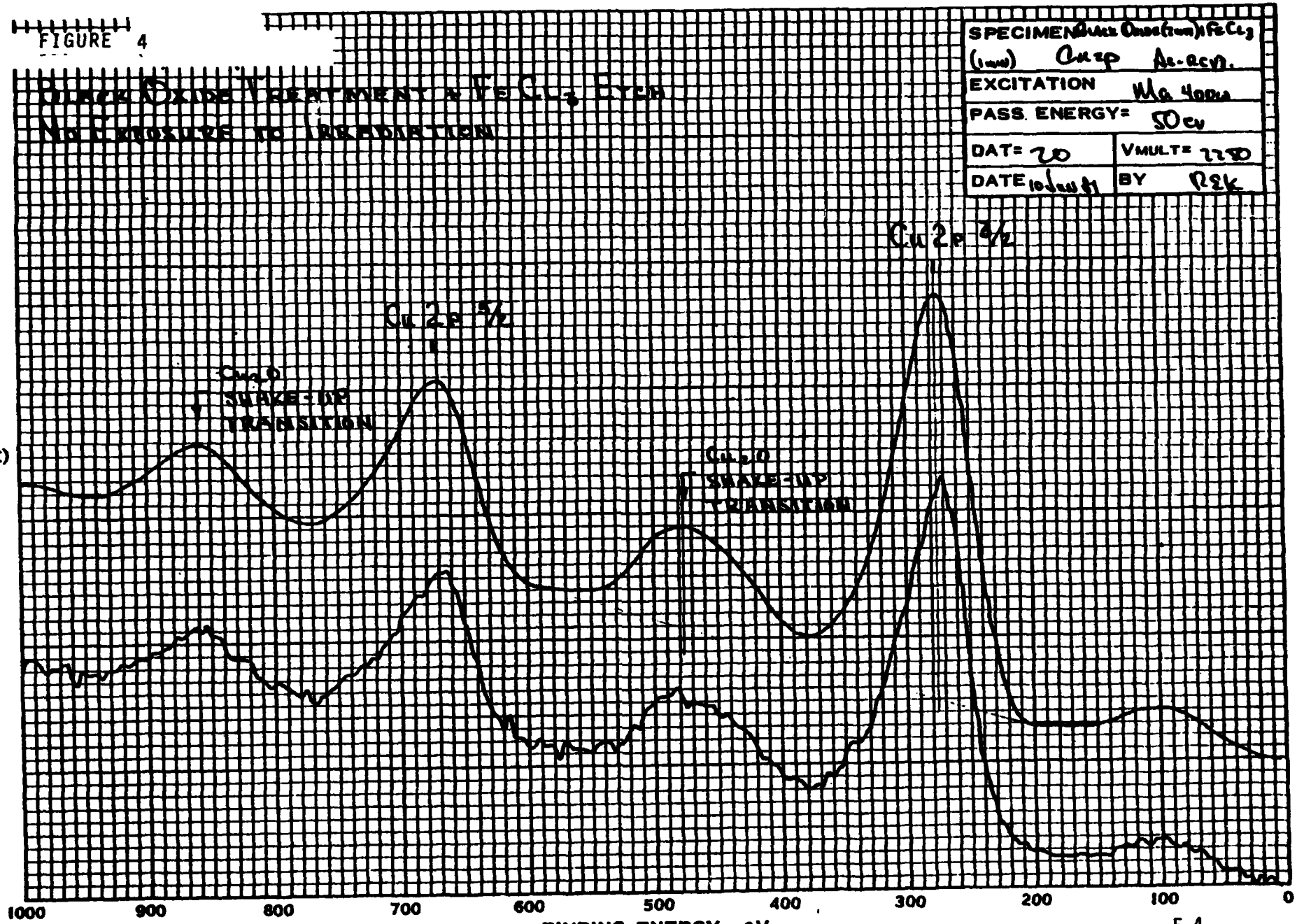

BLACK OXIDE TREATMENT
NO EXPOSURE TO IRRADIATION
SPECIMEN Black Oxide (2min.) Cu
Cu 2p
Al-Kα
EXCITATION Mg Kα 400W
PASS ENERGY= 50eV
DAT= 20
VMULT= 2250
DATE Jan 84
BY R.S.K
Cu 2p 3/2
Cu 2p 1/2
Cu 2p SHAKE-UP TRANSITION
Cu 2p SHAKE-UP TRANSITION
N(E)
1000
970
900
800
760
700
600
550
BINDING ENERGY, eV
500
400
348
300
200
930
100
0
920
E-3

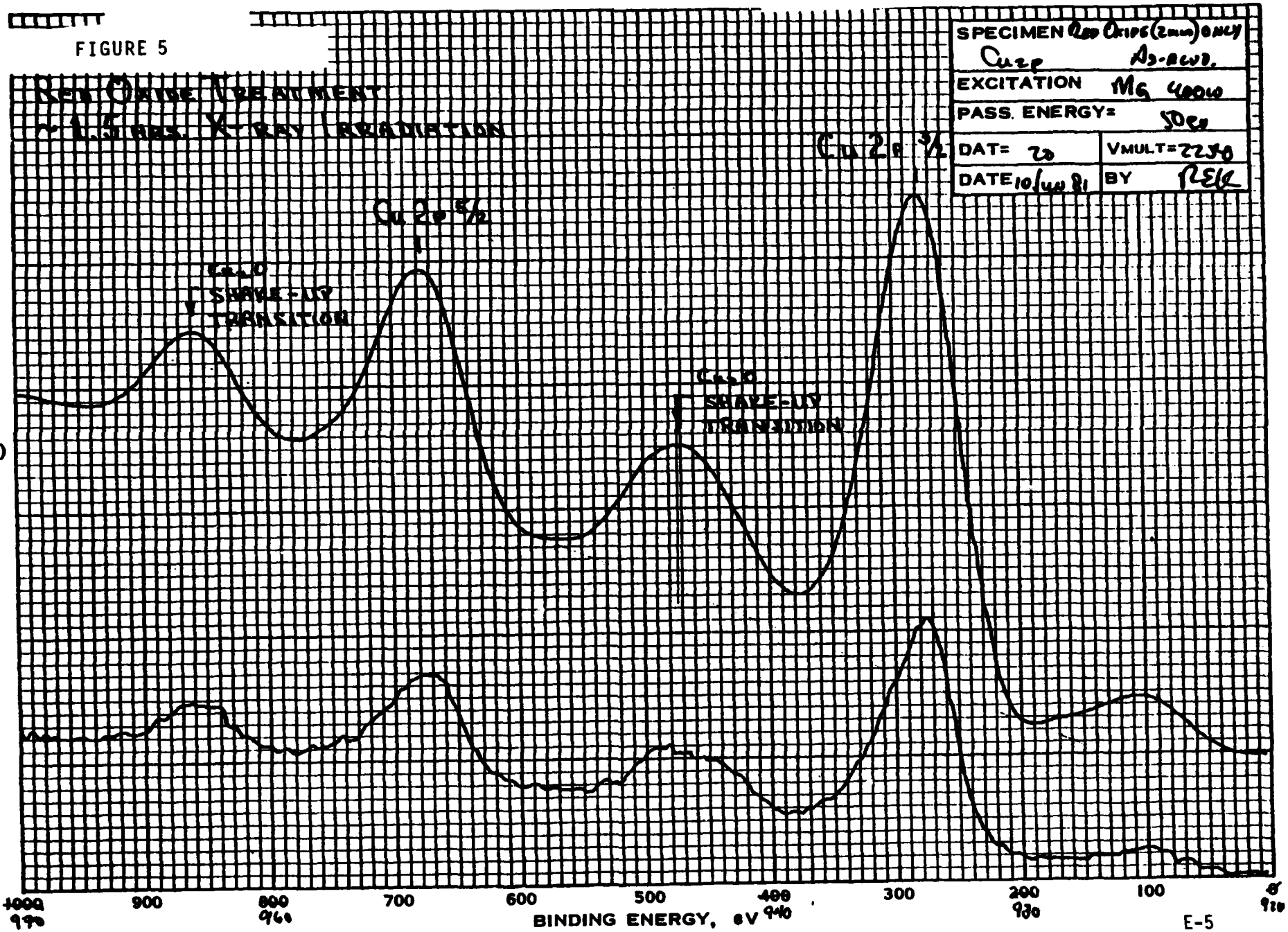
FIGURE 4



BLACK OXIDE TREATMENT w/ $FeCl_3$ ETCH
NO EXPOSURE TO IRRADIATION

E-4

FIGURE 5


SPECIMEN Cu2p Oxide (2min) ONLY
Cu2p As-Rcvd.
EXCITATION Mg 400W
PASS. ENERGY= 50eV
DAT= 20
VMULT=2250
DATE 10/4/81
BY RSK
Cu 2p 3/2
Cu 2p 1/2
Cu+2 SHAKE-UP TRANSITION
Cu+2 SHAKE-UP TRANSITION
N(E)
1000
900
800
700
600
500
400
300
200
100
0
BINDING ENERGY, eV

E-5

FIGURE 6

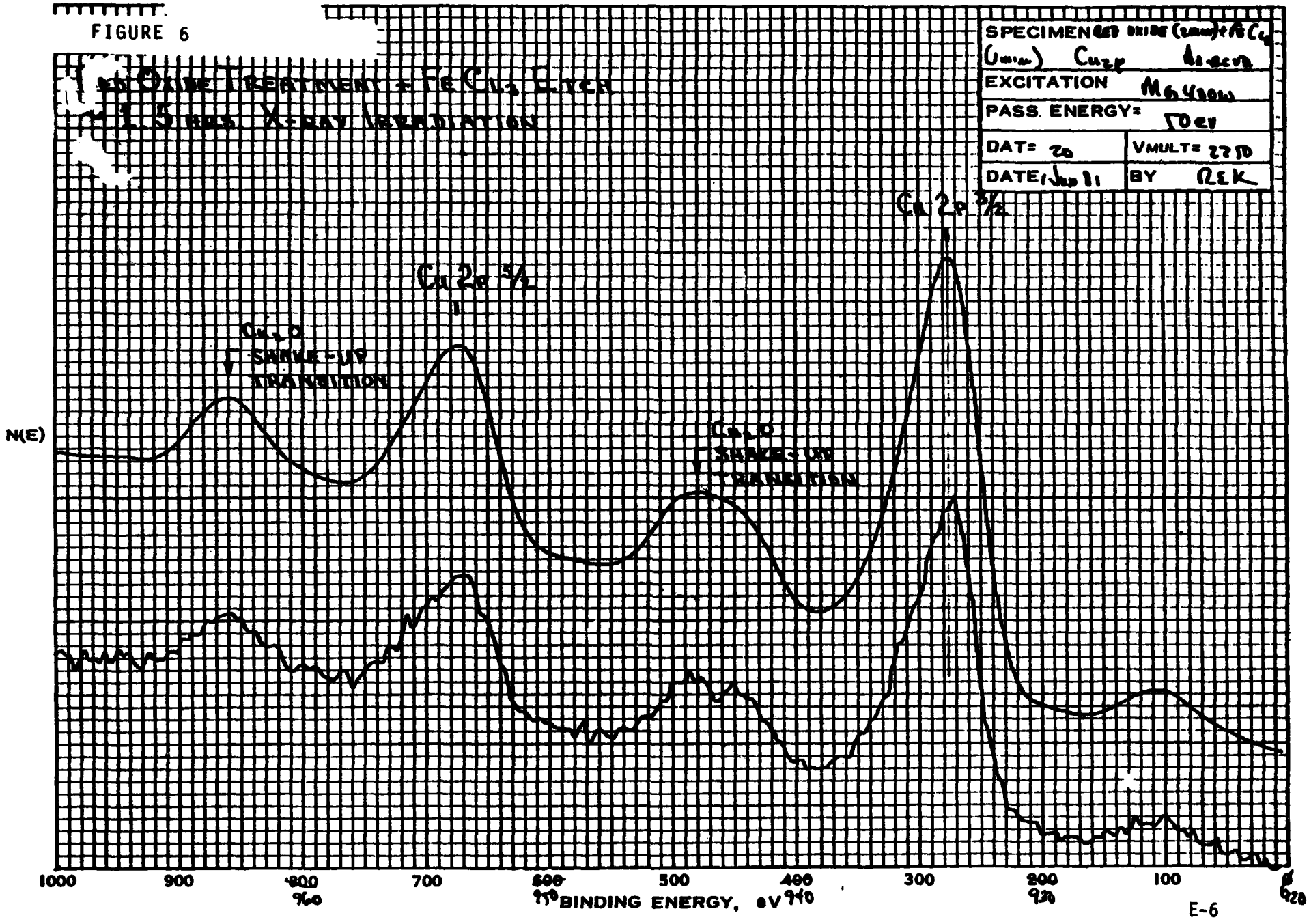

SPECIMEN
EXCITATION
PASS. ENERGY=
DAT=
VMULT=
DATE
BY
Cu 2p 3/2
Cu 2p 3/2
Cu LMM
SHAKE-UP TRANSITION
Cu LMM
SHAKE-UP TRANSITION
N(E)
1000
900
800
700
600
500
400
300
200
100
BINDING ENERGY, eV

FIGURE 7

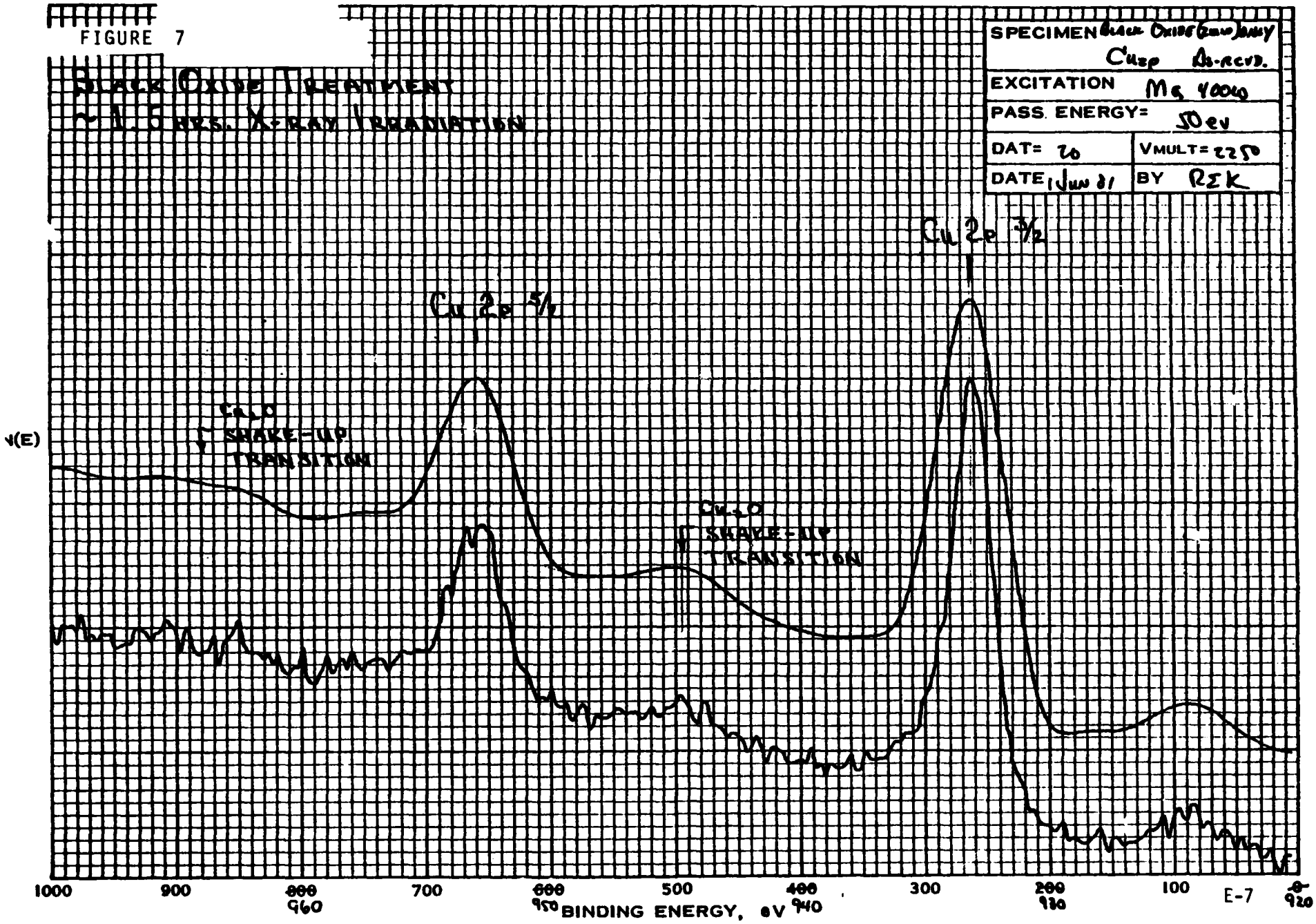
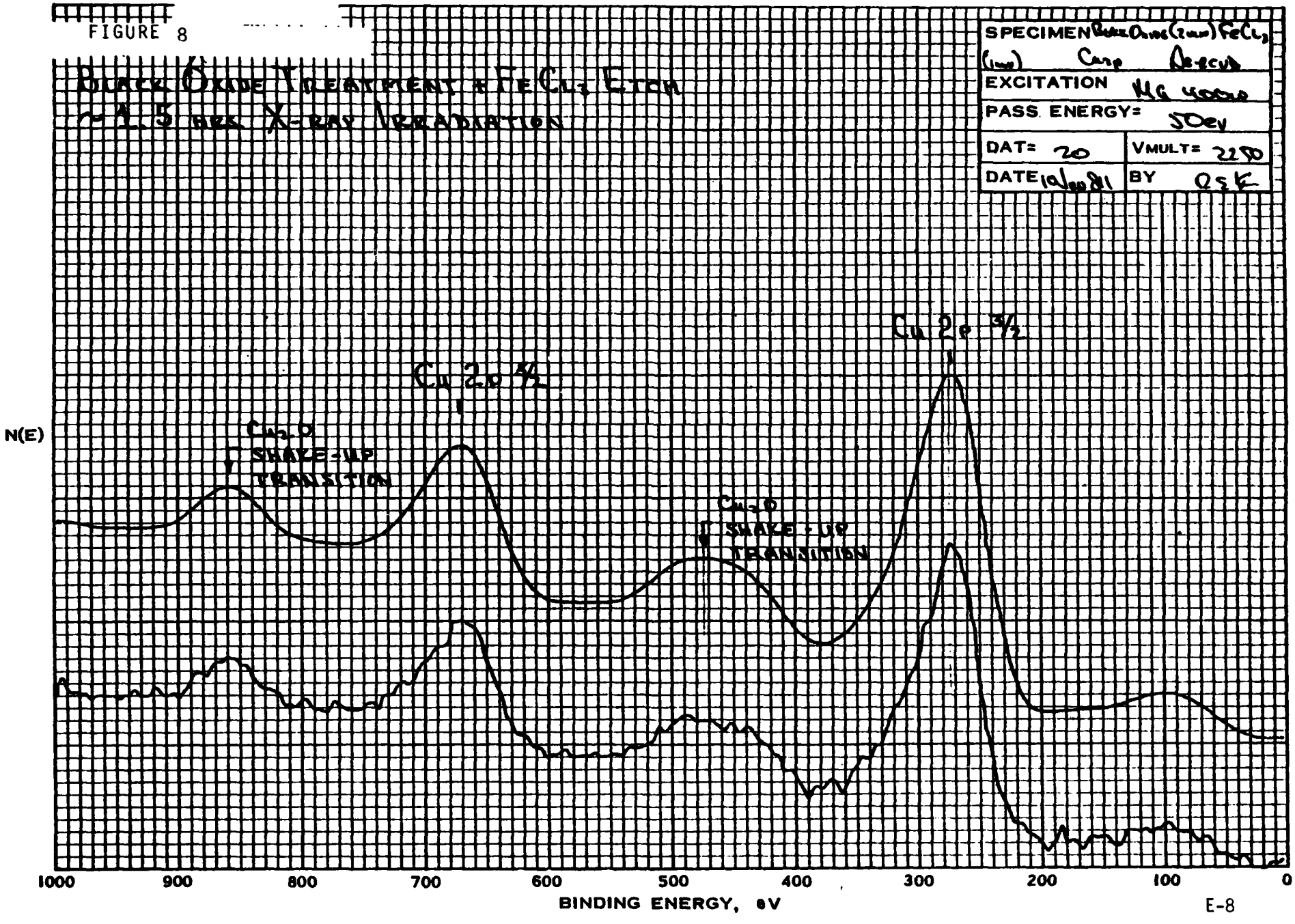

BLACK OXIDE TREATMENT
~1.5 HRS. X-RAY IRRADIATION
SPECIMEN Black Oxide (Low Temp) Alloy
Cu 2p As-Rcvd.
EXCITATION Mg 400eV
PASS ENERGY= 50 eV
DAT= 20
VMULT= 2250
DATE 1 Jun 81
BY RSK
Cu 2p 3/2
Cu 2p 1/2
Cu 2p SHAKE-UP TRANSITION
Cu2O SHAKE-UP TRANSITION
N(E)
1000
900
800
960
700
600
950
500
400
940
300
200
930
100
E-7
920
BINDING ENERGY, eV

FIGURE 8


BULK OXIDE TREATMENT + FeCl3 ETCH
~1.5 KEV X-RAY IRRADIATION
SPECIMEN
EXCITATION
PASS ENERGY=
DAT=
VMULT=
DATE
BY
Cu 2p 3/2
Cu 2p 1/2
Cu 2p SHAKE-UP TRANSITION
Cu 2p SHAKE-UP TRANSITION
N(E)
1000
900
800
700
600
500
400
300
200
100
0
BINDING ENERGY, eV

E-8

FIGURE 9

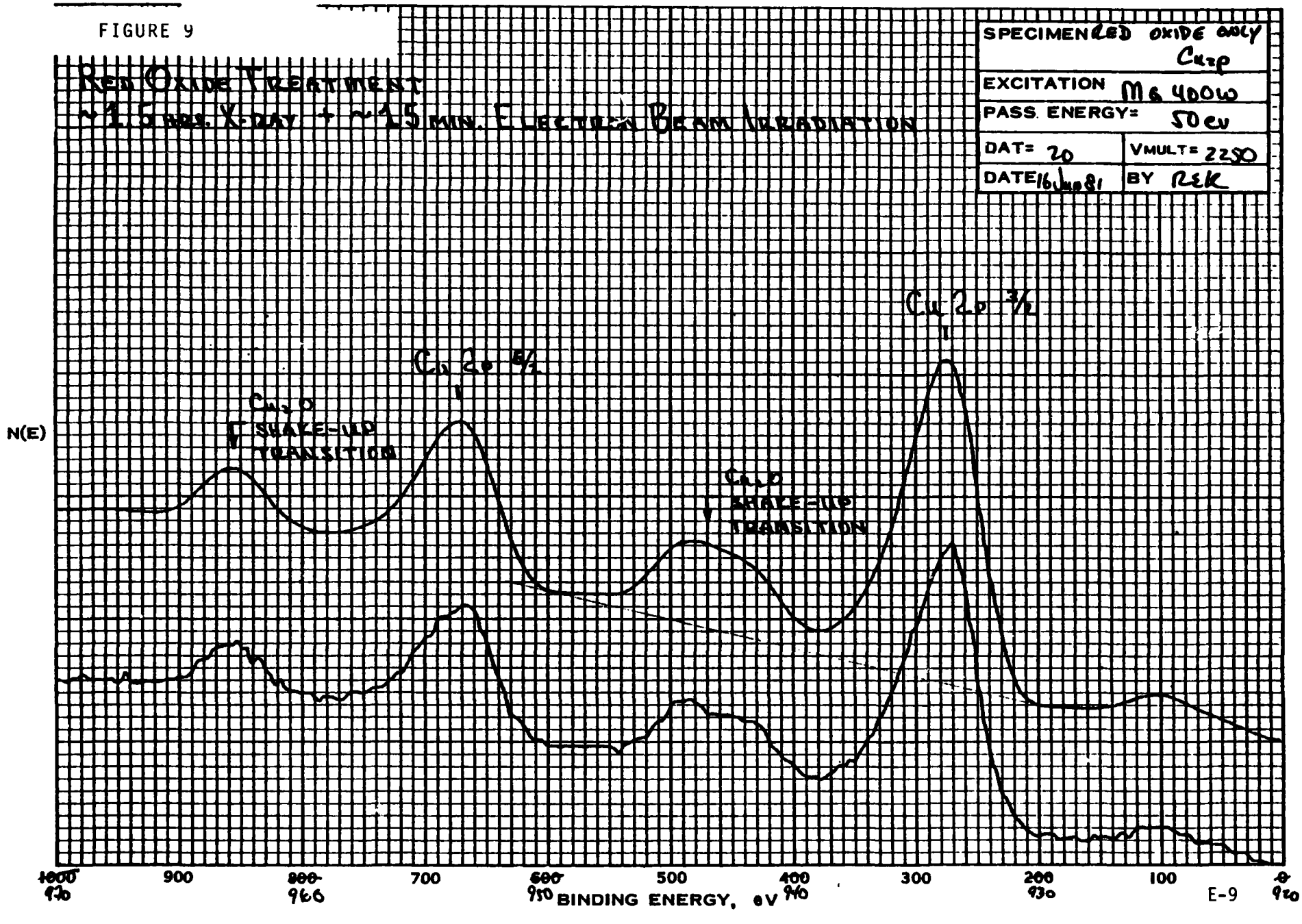

RED OXIDE TREATMENT
~1.5 HRS. X-RAY + ~15 MIN. ELECTRON BEAM IRRADIATION
SPECIMEN RED OXIDE ONLY
Cu2p
EXCITATION Mg 400W
PASS. ENERGY= 50 eV
DAT= 20
VMULT= 2250
DATE 16 JAN 81
BY REK
Cu 2p 3/2
Cu 2p 1/2
Cu 2p 3/2 SHAKE-UP TRANSITION
Cu 2p 1/2 SHAKE-UP TRANSITION
N(E)
1000
900
800
700
600
500
400
300
200
100
0
BINDING ENERGY, eV
E-9

FIGURE 10

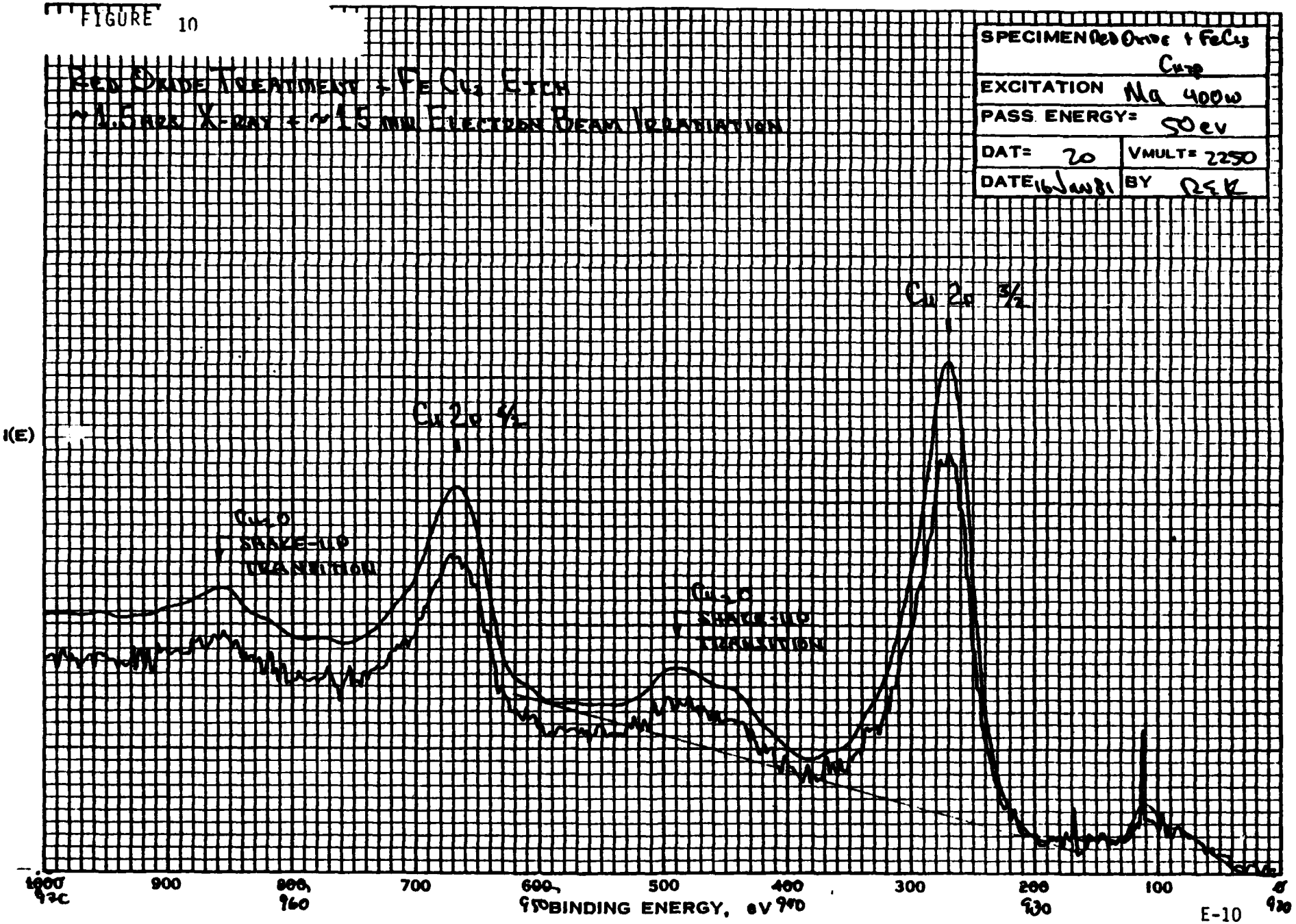

RED OXIDE TREATMENT + FeCl3 ETCH
~1.5 KEV X-RAY & ~15 MA ELECTRON BEAM IRRADIATION
SPECIMEN Red Oxide + FeCl3 Cu2p
EXCITATION Mg 400w
PASS ENERGY= 50 eV
DAT= 20
VMULT= 2250
DATE 16 JAN 81
BY RSK
Cu 2p 3/2
Cu 2p 1/2
Cu-O SHAKE-UP TRANSITION
Cu-O SHAKE-UP TRANSITION
I(E)
1000
900
800
700
600
500
400
300
200
100
0
BINDING ENERGY, eV

FIGURE 11

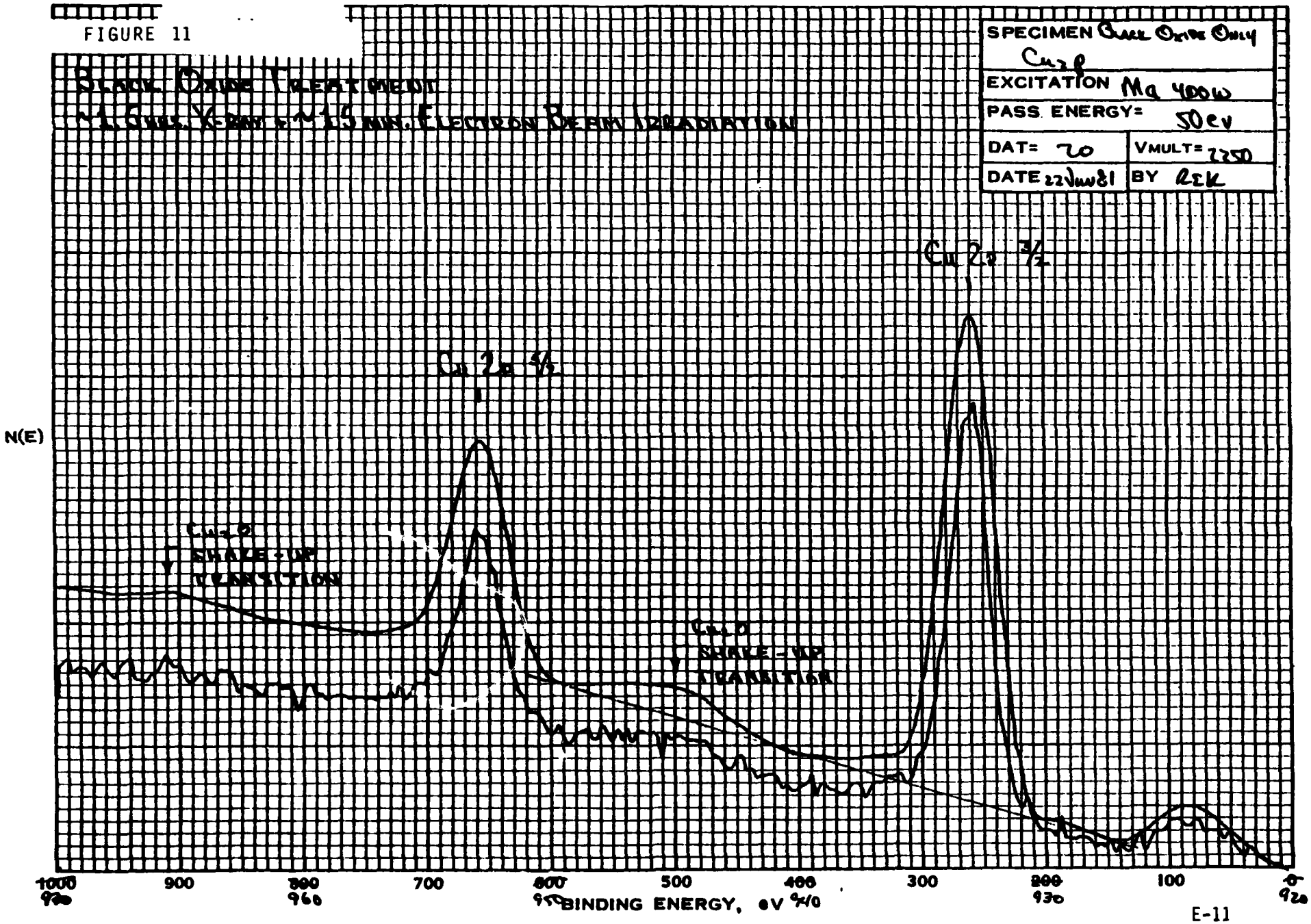
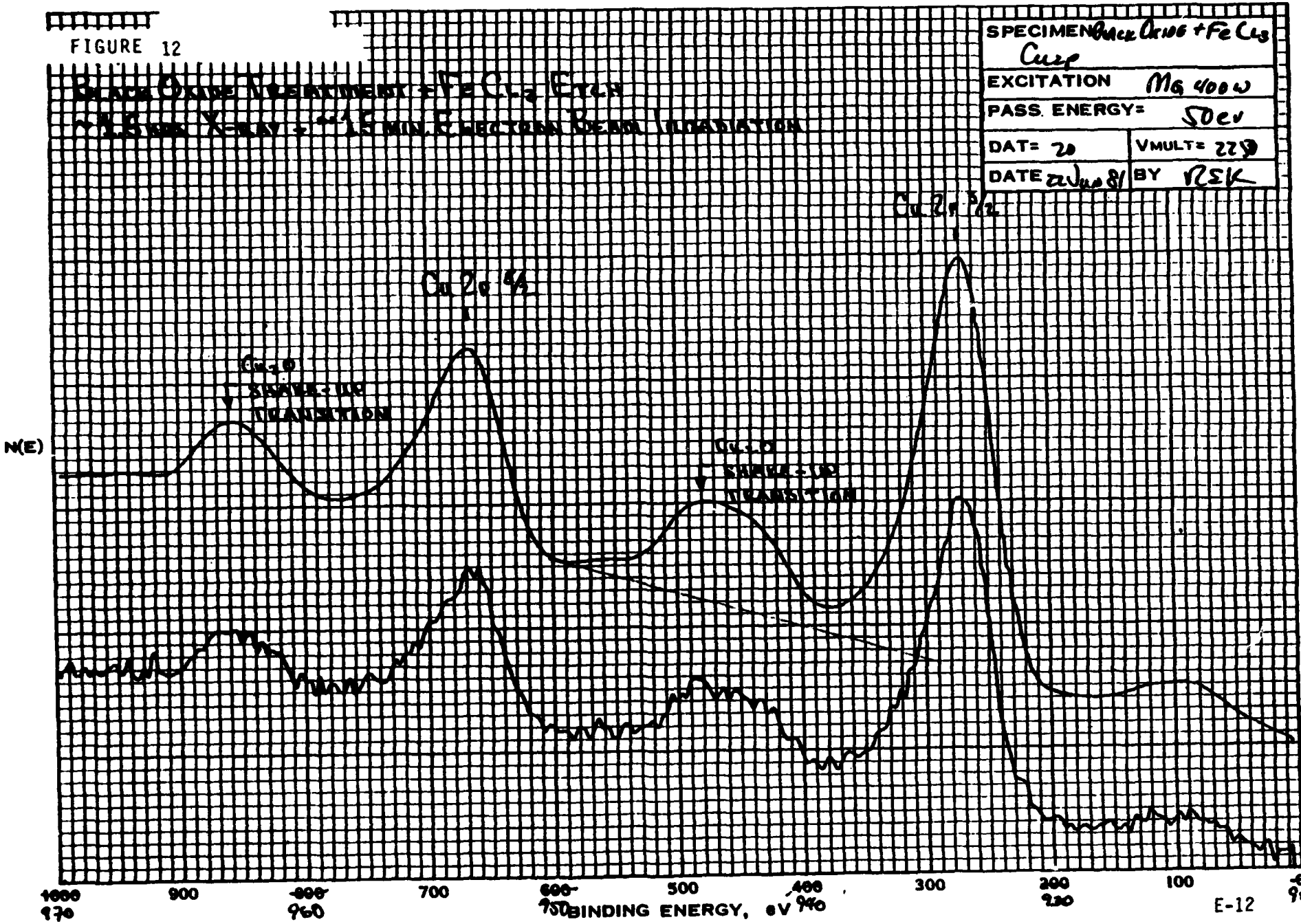

BLACK OXIDE TREATMENT
~1.5 KILL. X-RAY x ~1.5 MIN. ELECTRON BEAM IRRADIATION
SPECIMEN BLACK OXIDE ONLY
Cu2p
EXCITATION Mg 400W
PASS ENERGY= 50eV
DAT= 70
VMULT= 2250
DATE 22JAN81
BY RSK
Cu 2p 3/2
Cu 2p 1/2
Cu+2 SHAKE-UP TRANSITION
Cu+1 SHAKE-UP TRANSITION
N(E)
1000
900
800
700
600
500
400
300
200
100
0
BINDING ENERGY, eV

FIGURE 12



E-12

FIGURE 13

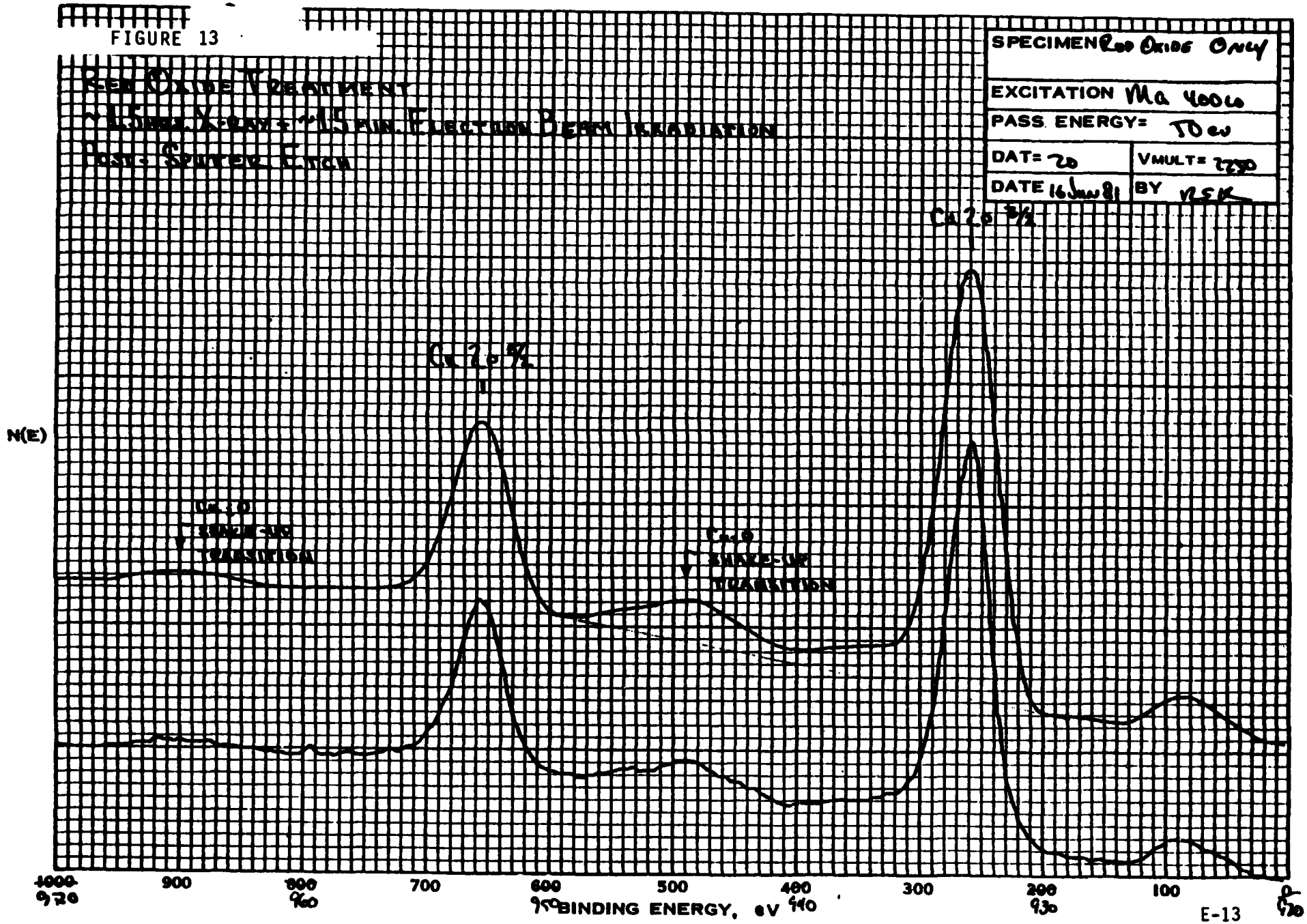

SPECIMEN Ru Oxides Only
EXCITATION Mg 400W
PASS ENERGY= 50 eV
DAT= 20
VMULT= 2250
DATE 16 Jun 81
BY RSK
Cls 2p 3/2
Cls 2p 1/2
Cls 1s
SHAKE-UP TRANSITION
Cls 1s
SHAKE-UP TRANSITION
N(E)
1000
920
900
800
960
700
600
980
500
940
400
300
200
930
100
0
920
BINDING ENERGY, eV

FIGURE 14

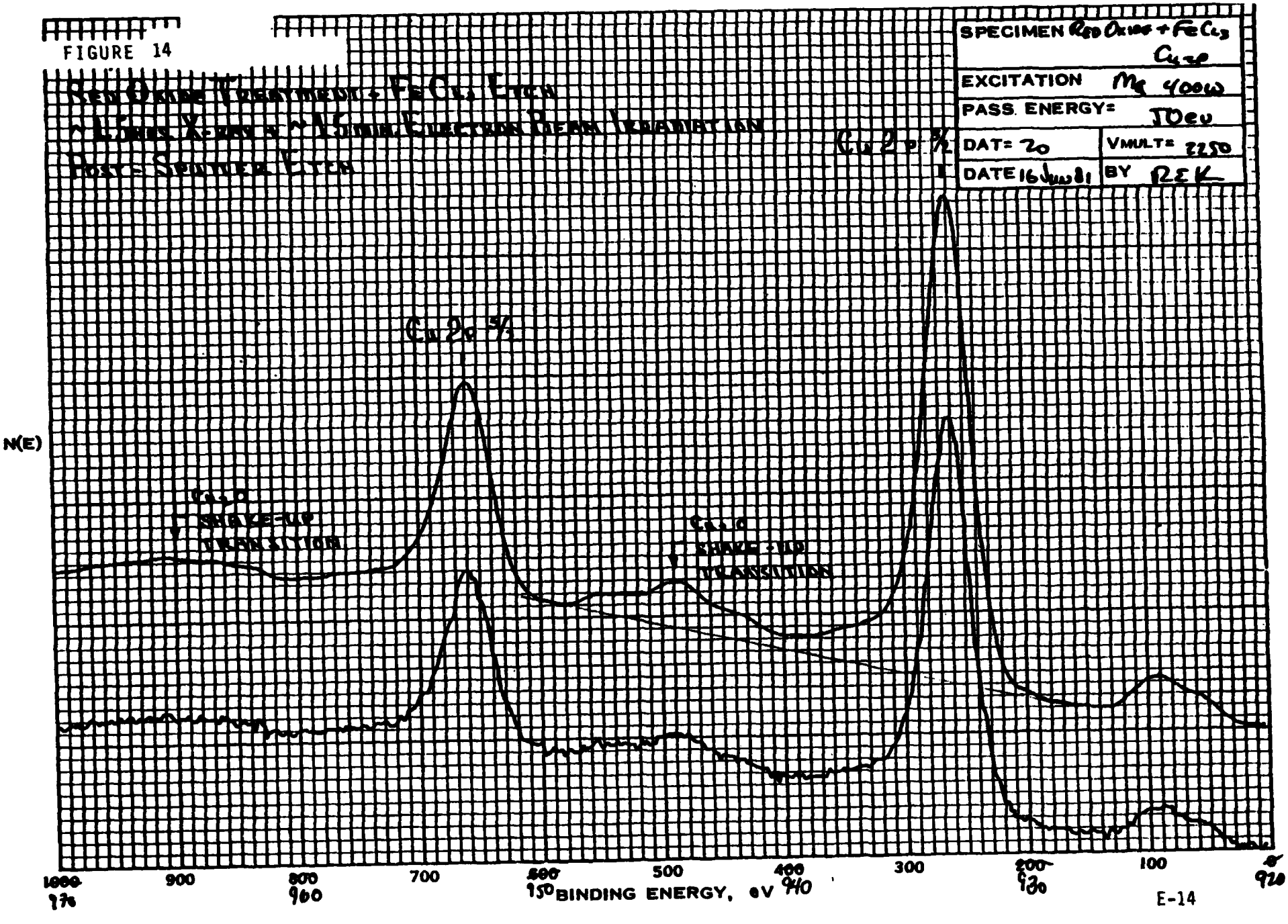

RED OXIDE TREATMENT + FeCl3 ETCH
~1.0 KeV X-RAY & NORMAL ELECTRON BEAM IRRADIATION
POST-SPUTTER ETCH
SPECIMEN Red Oxide + FeCl3 Cu 2p
EXCITATION Mg 400W
PASS. ENERGY= 100eV
DAT= 20
VMULT= 2250
DATE 16 JUN 81
BY REK
Cu 2p 3/2
Cu 2p 3/2
SHAKE-UP TRANSITION
Cu 2p 1/2
SHAKE-UP TRANSITION
N(E)
1000
900
800
700
600
500
400
300
200
100
BINDING ENERGY, eV
976
960
950
940
930
920

FIGURE 15

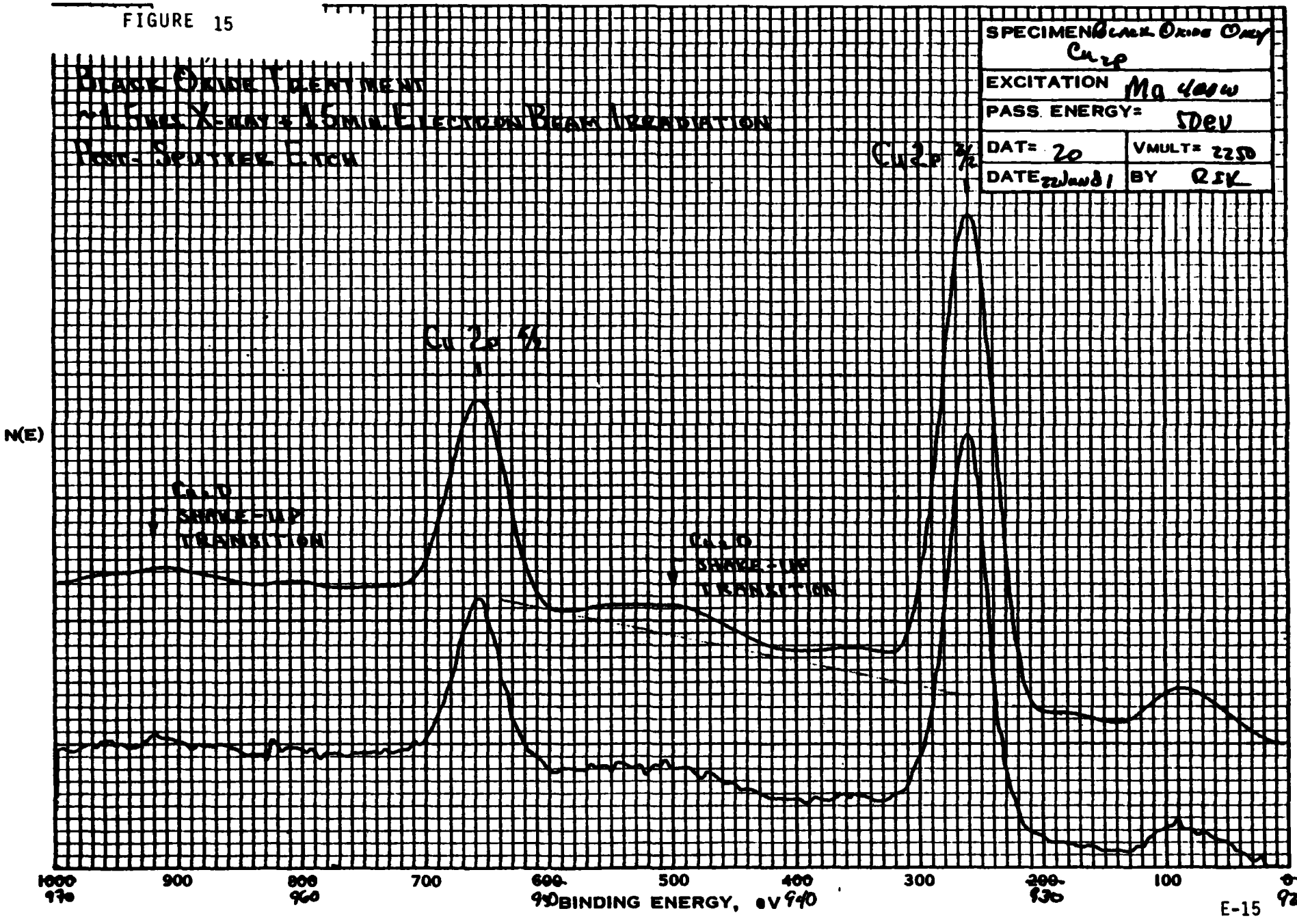
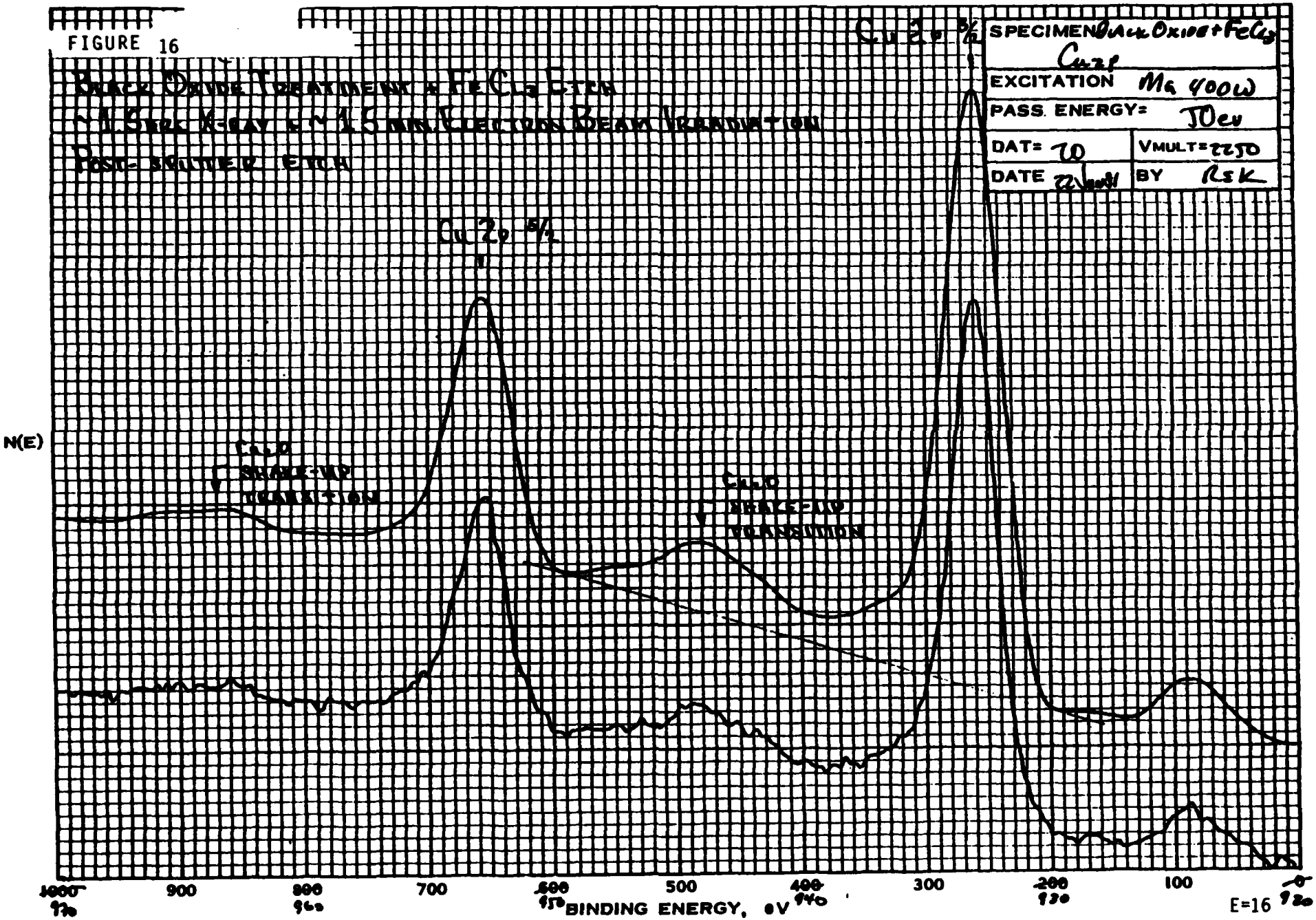

SPECIMEN Black Oxide Only Cu 2p
EXCITATION Mg 400W
PASS ENERGY= 50eV
DAT= 20
VMULT= 2250
DATE 22Jan81
BY RSK
Cu 2p 3/2
Cu 2p 1/2
Cu LMM SHAKE-UP TRANSITION
Cu LMM SHAKE-UP TRANSITION
N(E)
1000
900
800
700
600
500
400
300
200
100
0
BINDING ENERGY, eV

FIGURE 16


BLACK OXIDE TREATMENT + FeCl3 ETCH
Al Kα X-RAY + Ar+ ION/ELECTRON BEAM IRRADIATION
POST-SPUTTER ETCH
Cu 2p 3/2
Cu 2p 1/2
Cu+2 O SHAKE-UP TRANSITION
Cu+1 O SHAKE-UP TRANSITION
SPECIMEN Black Oxide + FeCl3
Cu2p
EXCITATION Mg 400W
PASS. ENERGY= 50eV
DAT= 70
VMULT=2250
DATE
BY RSK
N(E)
1000
900
800
700
600
500
400
300
200
100
0
BINDING ENERGY, eV
E=16

APPENDIX F

DETERMINATION OF FREE 4,4'-METHYLENEDIANILINE (MDA) IN KERIMID 601

1. Principle

- Colorimetric determination of MDA by reaction of N - α - naphtyl - N', N' - diethylpropylenediamine hydrochloride on an aliquot portion of a KERIMID 601 solution obtained by sequential dissolution of the resin in sulfuric acid, precepitation by addition of water, and filtration.

2. Reagents

- Reagent grade sulfuric acid (specific gravity : 1.83).
- 0.1 N. sulfuric acid
- Reagent grade sodium nitrite; 1% solution; maximum shelf life : 1 week.
- Ammonium sulfamate; 5% solution;maximum shelf life: 1 week.
- Reagent grade crystallized sodium acetate; solution at 408.3 g/l.
- N - α - naphtyl - N', N'-diethylpropylenediamine hydrochloride; 1% solution; maximum shelf life: 1 day.
- Reagent grade hydrochloric acid (specific gravity : 1.19).
- Spectral grade ethanol.
- Standard solution of MDA:

  Place a carefully weighed quantity (Wc) of MDA (28 to 32 mg within +.05 mg) in a 100 ml volumetric flask. Make up to 100 ml with 0.1 N sulfuric acid.

3. Equipment

- Thermostated bath at 20 ± 0.5°C.
- JEAN et CONSTANT spectrophotometer.
- Calibrated flasks : 20 ml, 25 ml and 100 ml.
- Pipettes.
- 50 µl HAMILTON type syringe.

4. Remark

Colorimetric determination must be carriedout as soon as possible after dissolution of reagent in KERIMID 601 solution.

5. Procedure

Sample Preparation

Weigh within ±. 1 mg a 150-200 mg KERIMID 601 sample (W_a). Put it in a test tube (18 mm x 180 mm). Add 0.5 mg sulfuric acid (specific garvity : 1.83) and stir with a glass rod to get an homogeneous dispersion (30 mn max).

Add drop by drop 2 ml of water with stirring and then, more quickly, 10 ml of water.

Filter and collect liquid in a 25 ml calibrated flask; complete to 25 ml with water, rinsing the filter and test tube. Mix well.

Colorimetric measurement

In three 20 ml flasks, pour 15 ml of 0.1N sulfuric acid; one of them will be used as a blank test sample.

Add 50 µl of MDA standard solution in one of the flasks and 50 µl of the KERIMID 601 solution in the other.

Add 0.5 ml of sodium nitrite to each flask and mix well.

After 10 mn, add 0.5 ml of ammonium sulfamate. Mix well.

After 2 mn, add 2.0 ml of sodium acetate.

Mix vigorously and add 0.5 ml of N -α- naphtyl - N', N' - diethylpropylenediamine hydrochloride. Mix well.

After 2 mn, add 1 ml of hydrochloric acid (specific gravity: 1.19). Mix well.

After 20 mn at 20°C, add 0.1 ml of ethanol as antifoaming agent. Complete to 20 ml with water. Mix well.

Colorimetric determination is carried out under the following conditions:

- determine baseline with the blank test sample
- wave length : 545 nm (1 nm = 10^{-9} meter)
- cell : antimony (or other material optically transparent in the 545 nm range)
- optical cell wall thickness : 40 mm.

5. Procedure

Colorimetric measurement (Continued)

Dd is the number of divisions read for the KERIMID sample.

De is the number of divisions read for the MDA reference sample.

6. Results

$$\text{NDA \%} = 25 \frac{W_c \times D_d}{W_d \times D_c}$$

(1 % of free MDA corresponds to 10.1 meg/100 g of primary amine groups.)

N -α- naphthyl - N', N' - diethylpropylene diamine hydrochloride is available (catalog item #25789) from Prolabo -

Prolabo; BP 200; 75526 - Paris Cedex 11;
Telex - Prolabo Paris 680566

APPENDIX G

HUMIDITY TESTS OF POLYIMIDE COUPONS

ENVIRONMENTAL LABORATORY
SUDBURY
FORM NO 93-0230P1 (12/73) **TEST DATA**

JOB NUMBER | SHEET ___ OF ___

TYPE OF COMPONENT: POLYIMIDE COUPON, PATTERN E

PROJECT: AIR FORCE POLYIMIDE INNER LAYER ADHESION STUDY

REQUESTED BY: T. BAKER

TEST: HUMIDITY EXPOSURE

SPECIFICATION AND PARAGRAPH: MIL-STD-202, METHOD 106

COMMENTS: COUPON 1 BIAS: 100VDC

MEASUREMENT	INITIAL I.R.	I.R.	I.R.	I.R.	I.R.	FINAL I.R.
UNITS	OHMS	OHMS	OHMS	OHMS	OHMS	OHMS
LAYER 1(+) ÷ 1(-)	$>5.0\times10^{13}$	1.5×10^{11}	2.5×10^{11}	1.3×10^{11}	1.5×10^{11}	$>5.0\times10^{13}$
1(+) ÷ 2(-)		3.0×10^{11}	8.0×10^{11}	8.0×10^{11}	5.0×10^{11}	
1(-) ÷ 2(+)		3.0×10^{11}	5.0×10^{11}	3.0×10^{11}	4.0×10^{11}	
2(+) ÷ 2(-)		4.0×10^{12}	3.0×10^{12}	3.0×10^{12}	3.0×10^{12}	
2(+) ÷ 3(-)		9.0×10^{9}	1.0×10^{10}	3.0×10^{10}	1.0×10^{11}	
2(-) ÷ 3(+)		1.5×10^{12}	1.5×10^{12}	2.0×10^{12}	1.5×10^{12}	
3(+) ÷ 3(-)		$>5.0\times10^{13}$	$>5.0\times10^{13}$	$>5.0\times10^{13}$	$>5.0\times10^{13}$	
3(+) ÷ 4(-)		1.0×10^{12}	1.0×10^{12}	1.0×10^{12}	1.0×10^{12}	
3(-) ÷ 4(+)		4.0×10^{9}	2.0×10^{10}	2.0×10^{10}	3.0×10^{10}	
4(+) ÷ 4(-)		2.0×10^{13}	3.0×10^{12}	3.0×10^{12}	2.0×10^{12}	
4(+) ÷ 5(-)		5.0×10^{9}	2.0×10^{10}	1.5×10^{10}	3.0×10^{10}	
4(-) ÷ 5(+)		4.0×10^{12}	3.0×10^{12}	3.0×10^{12}	3.0×10^{12}	
5(+) ÷ 5(-)		9.0×10^{9}	3.0×10^{10}	3.0×10^{10}	8.0×10^{10}	
5(+) ÷ 6(-)		1.0×10^{11}	3.0×10^{10}	3.0×10^{10}	4.0×10^{10}	
5(-) ÷ 6(+)		1.5×10^{8}	3.0×10^{9}	3.0×10^{9}	4.0×10^{9}	
6(+) ÷ 6(-)		2.0×10^{8}	4.0×10^{9}	4.0×10^{9}	4.0×10^{9}	
						71°F
						4-15-81
						15%
READ BY	RCN	RCN	RCN	RCN	RCN	
TEMPERATURE	70°F	65°C	65°C	65°C	65°C	
DATE	3-27-81	4-3-81	4-7-81	4-9-81	4-13-81	
CONDITION 1 R.H.	28%	95%	95%	95%	95%	
CONDITION 2 TIME		0950 HRS.	1030 HRS.	1010 HRS.	1015 HRS.	
CONDITION 3 DAYS IN HUMIDITY		1	5	7	11	
CONDITION 4						
CONDITION 5						
CONDITION 6 HUMIDITY STARTED:	4-2-81					
CONDITION 7 HUMIDITY [illegible]	4-13-81					

EQUIPMENT

A		G	
B		H	
C		I	
D		J	
E		K	
F		L	

CHECKED BY: ___

APPROVED BY: ___

FORM NO 93-9236P1 (12'73)

SUDBURY
TEST DATA

TYPE OF COMPONENT: POLYIMIDE COUPON, PATTERN E

PROJECT: AIR FORCE POLYIMIDE INNER LAYER ADHESION STUDY

REQUESTED BY:

TEST: HUMIDITY EXPOSURE

SPECIFICATION AND PARAGRAPH: MIL-STD-202, METHOD 106

COMMENTS: COUPON 2 BIAS: 100VDC

MEASUREMENT	INITIAL I.R.	I.R.	I.R.	I.R.	I.R.	FINAL I.R.
UNITS	OHMS	OHMS	OHMS	OHMS	OHMS	OHMS
LAYER 1(-) to 1(-)	$>5.0\times10^{13}$	1.0×10^{11}	3.0×10^{11}	2.0×10^{11}	2.5×10^{11}	$>5.0\times10^{13}$
1(-) to 2(-)		5.0×10^{11}	5.0×10^{11}	5.0×10^{11}	5.0×10^{11}	
1(-) to 2(-)		7.0×10^{11}	5.0×10^{11}	4.0×10^{11}	4.0×10^{11}	
2(-) to 2(-)		5.0×10^{12}	3.0×10^{12}	4.0×10^{12}	3.0×10^{12}	
2(-) to 3(-)		1.5×10^{12}	2.0×10^{12}	2.0×10^{12}	1.0×10^{11}	
2(-) to 3(-)		9.0×10^{11}	1.5×10^{12}	1.0×10^{12}	1.5×10^{12}	
3(-) to 3(-)		2.0×10^{13}	5.0×10^{12}	7.0×10^{12}	3.0×10^{12}	
3(-) to 4(-)		9.0×10^{11}	1.0×10^{12}	1.0×10^{12}	9.0×10^{11}	
3(-) to 4(-)		2.0×10^{12}	1.0×10^{12}	1.0×10^{12}	1.0×10^{12}	
4(-) to 4(-)		3.0×10^{13}	4.0×10^{12}	5.0×10^{12}	3.0×10^{12}	
4(-) to 5(-)		1.5×10^{12}	8.0×10^{11}	4.0×10^{11}	4.0×10^{11}	
4(-) to 5(-)		8.0×10^{12}	2.0×10^{12}	3.0×10^{12}	1.0×10^{12}	
5(-) to 5(-)		1.0×10^{12}	2.0×10^{11}	3.0×10^{11}	1.0×10^{11}	
5(-) to 6(-)		6.0×10^{11}	4.0×10^{11}	4.0×10^{11}	2.0×10^{11}	
5(-) to 6(-)		4.0×10^{11}	2.0×10^{11}	1.5×10^{11}	1.5×10^{11}	
6(-) to 6(-)		2.0×10^{11}	3.0×10^{11}	2.0×10^{11}	2.0×10^{11}	
						71°F
						4-15-81
						15%

READ BY	RCN	RCN	RCN	RCN	RCN	EQUIPMENT
TEMPERATURE	76°F	65°C	65°C	65°C	65°C	A G
DATE	3-30-81	4-3-81	4-7-81	4-9-81	4-13-81	B H
CONDITION 1 R.H.:	34%	95%	95%	95%	95%	C I
2 TIME:		1015 HRS.	1100 HRS.	1100 HRS.	1130 HRS.	D J
3 DAYS IN HUMIDITY:		1	5	7	11	E K
4						F L
5						CHECKED BY:
6 HUMIDITY STARTED:	4-2-81					APPROVED BY:
7 HUMIDITY COMPLETE:	4-13-81					

FORM NO 53-0230P1 (12/73) **TEST DATA**

TYPE OF COMPONENT	POLYIMIDE COUPON, PATTERN E
PROJECT AIR FORCE POLYIMIDE INNER LAYER ADHESION STUDY	REQUESTED BY
TEST HUMIDITY EXPOSURE	SPECIFICATION AND PARAGRAPH MIL-STD-202, METHOD 106

COMMENTS
COUPON 3 BIAS: 100VDC

MEASUREMENT	INITIAL I.R.	I.R.	I.R.	I.R.	I.R.	FINAL I.R.	
UNITS	OHMS	OHMS	OHMS	OHMS	OHMS	OHMS	
LAYER 1(+)+1(-)	$>5.0 \times 10^{13}$	1.0×10^{11}	1.0×10^{11}	1.5×10^{10}	1.0×10^{10}	$>5.0 \times 10^{13}$	
1(+)+2(-)		4.0×10^{11}	3.0×10^{11}	2.0×10^{11}	2.0×10^{11}		
1(-)+2(+)		6.0×10^{11}	4.0×10^{11}	3.0×10^{11}	2.0×10^{11}		
2(+)+2(-)		2.0×10^{12}	5.0×10^{12}	1.5×10^{12}	1.5×10^{12}		
2(+)+3(-)		1.0×10^{12}	8.0×10^{11}	4.0×10^{11}	4.0×10^{11}		
2(-)+3(+)		6.0×10^{11}	9.0×10^{11}	5.0×10^{11}	5.0×10^{11}		
3(+)+3(-)		2.0×10^{13}	4.0×10^{12}	3.0×10^{12}	2.0×10^{12}		
3(+)+4(-)		7.0×10^{11}	8.0×10^{11}	7.0×10^{11}	6.0×10^{11}		
3(-)+4(+)		8.0×10^{11}	8.0×10^{11}	4.0×10^{11}	4.0×10^{11}		
4(+)+4(-)		1.0×10^{13}	5.0×10^{12}	4.0×10^{12}	2.0×10^{12}		
4(+)+5(-)		7.0×10^{12}	4.0×10^{12}	3.0×10^{12}	1.0×10^{12}		
4(-)+5(+)		2.0×10^{12}	2.0×10^{12}	2.0×10^{12}	1.0×10^{12}		
5(+)+5(-)		3.0×10^{12}	2.0×10^{12}	2.2×10^{12}	7.0×10^{11}		
5(+)+6(-)		3.0×10^{11}	4.0×10^{11}	3.0×10^{11}	2.0×10^{11}		
5(-)+6(+)		4.0×10^{11}	4.0×10^{11}	3.0×10^{11}	1.0×10 [illegible]		
6(+)+6(-)		2.0×10^{11}	4.0×10^{11}	2.0×10^{11}	1.0×10^{11}		
						91°F	
						4-15-81	
						15%	

						EQUIPMENT
READ BY	RCN	RCN	RCN	RCN	RCN	A / G
TEMPERATURE	76°F	65°C	65°C	65°C	65°C	B / H
DATE	3-30-81	4-3-81	4-7-81	4-9-81	4-13-81	C / I

CONDITION						
1 R.H.		95%	95%	95%	95%	D / J
2 TIME		1040 HRS.	1120 HRS.	1115 HRS.	1050 HRS.	E / K
3 DAYS IN HUMIDITY:		1	5	7	11	F / L
4						
5						CHECKED BY
6 START HUMIDITY:	4-2-81					APPROVED BY
7 HUMIDITY COMPLETE:	4-13-81					

FORM NO 53-0234P1 (12-73)

SUDBURY TEST DATA

TYPE OF COMPONENT: POLYIMIDE COUPON, PATTERN 6

PROJECT: AIR FORCE POLYIMIDE INNER LAYER ADHESION STUDY

REQUESTED BY:

TEST: HUMIDITY EXPOSURE

SPECIFICATION AND PARAGRAPH: MIL-STD-202, METHOD 106

COMMENTS: COUPON 4 (CONTROL) NO BIAS

MEASUREMENT	INITIAL I.R.	I.R.	I.R.	I.R.	I.R.	FINAL I.R.
UNITS	OHMS	OHMS	OHMS	OHMS	OHMS	OHMS
LAYER 1(+) & 1(-)	$>5.0\times10^{13}$	1.5×10^{10}	3.0×10^{10}	2.0×10^{10}	2.0×10^{10}	$>5.0\times10^{13}$
1(+) & 2(-)		1.0×10^{11}	1.0×10^{11}	6.0×10^{10}	5.0×10^{10}	
1(+) & 2(+)		1.0×10^{11}	6.0×10^{10}	3.0×10^{10}	3.0×10^{10}	
2(+) & 3(-)		4.0×10^{11}	2.0×10^{11}	1.0×10^{11}	7.0×10^{10}	
2(+) & 3(-)		1.5×10^{11}	1.5×10^{11}	7.0×10^{10}	7.0×10^{10}	
2(-) & 3(+)		2.0×10^{11}	2.0×10^{11}	9.0×10^{10}	1.0×10^{11}	
3(+) & 3(-)		4.0×10^{11}	3.0×10^{11}	1.5×10^{11}	1.5×10^{11}	
3(+) & 4(-)		3.0×10^{11}	2.0×10^{11}	1.0×10^{11}	7.0×10^{10}	
3(-) & 4(+)		1.5×10^{11}	1.5×10^{11}	9.0×10^{10}	8.0×10^{10}	
4(+) & 4(-)		4.0×10^{11}	3.0×10^{11}	1.5×10^{11}	1.0×10^{11}	
4(+) & 5(-)		1.0×10^{11}	1.0×10^{11}	7.0×10^{10}	7.0×10^{10}	
4(+) & 5(+)		3.0×10^{11}	2.0×10^{11}	1.0×10^{11}	6.0×10^{10}	
5(+) & 5(-)		7.0×10^{10}	4.0×10^{10}	4.0×10^{10}	4.0×10^{10}	
5(+) & 6(-)		5.0×10^{10}	4.0×10^{10}	2.5×10^{10}	2.0×10^{10}	
5(-) & 6(+)		2.0×10^{10}	2.0×10^{10}	1.5×10^{10}	2.0×10^{10}	
6(+) & 6(-)		1.0×10^{10}	1.5×10^{10}	9.0×10^{9}	1.0×10^{10}	
						71°F
						4-15-81
						15%
READ BY	RCN	RCN	RCN	RCN	RCN	
TEMPERATURE	76°F	65°C	65°C	65°C	65°C	
DATE	3-31-81	4-3-81	4-7-81	4-9-81	4-13-81	
CONDITION 1 R.H.		95%	95%	95%	95%	
CONDITION 2 TIME		1105 HRS.	1140 HRS.	1320 HRS.	1230 HRS.	
CONDITION 3 DAYS IN HUMIDITY		1	5	7	11	
CONDITION 4						
CONDITION 5						
CONDITION 6 START HUMIDITY:	4-2-81					
CONDITION 7 HUMIDITY COMPLETE:	4-13-81					

EQUIPMENT

A		G	
B		H	
C		I	
D		J	
E		K	
F		L	

CHECKED BY:

APPROVED BY:

SUDBURY

FORM NO 53-02368P1 (12/73) **TEST DATA**

TYPE OF COMPONENT: POLYIMIDE COUPON, PATTERN 5

PROJECT: AIR FORCE POLYIMIDE INNER LAYER ADHESION STUDY

REQUESTED BY:

TEST: HUMIDITY EXPOSURE

SPECIFICATION AND PARAGRAPH: MIL-STD-202, METHOD 106

COMMENTS: COUPON 5 (CONTROL) NO BIAS

MEASUREMENT	INITIAL I.R.	I.R.	I.R.	I.R.	I.R.	FINAL I.R.	
UNITS	OHMS	OHMS	OHMS	OHMS	OHMS	OHMS	
LAYER 1(-) + 1(-)	$>5.0\times10^{13}$	3.0×10^{9}	1.0×10^{9}	3.0×10^{8}	3.8×10^{8}		
1(-) + 2(-)		2.0×10^{10}	1.0×10^{10}	4.0×10^{9}	2.0×10^{9}		
1(-) + 2(+)		3.0×10^{10}	1.5×10^{10}	8.0×10^{9}	6.0×10^{9}		
2(+) + 2(-)		5.0×10^{10}	3.0×10^{10}	1.0×10^{10}	9.0×10^{9}		
2(+) + 3(-)		4.0×10^{10}	2.0×10^{10}	1.0×10^{10}	7.0×10^{9}		
2(-) + 3(+)		1.5×10^{10}	1.5×10^{10}	6.0×10^{9}	4.0×10^{9}		
3(+) + 3(-)		4.0×10^{10}	2.0×10^{10}	8.0×10^{9}	5.0×10^{9}		
3(+) + 4(-)		1.5×10^{10}	1.5×10^{10}	6.0×10^{9}	5.0×10^{9}		
3(-) + 4(+)		3.0×10^{10}	1.0×10^{10}	4.0×10^{9}	3.0×10^{9}		
4(+) + 4(-)		4.0×10^{10}	2.0×10^{10}	8.0×10^{9}	5.0×10^{9}		
4(+) + 5(-)		3.0×10^{10}	1.0×10^{10}	4.0×10^{9}	3.0×10^{9}		
4(-) + 5(+)		1.5×10^{10}	2.0×10^{10}	9.0×10^{9}	1.5×10^{10}		
5(+) + 5(-)		3.0×10^{10}	1.0×10^{10}	7.0×10^{9}	8.0×10^{9}		
5(+) + 6(-)		2.0×10^{10}	1.0×10^{10}	5.0×10^{9}	6.0×10^{9}		
5(-) + 6(+)		8.0×10^{9}	4.0×10^{9}	2.0×10^{9}	1.5×10^{9}		
6(+) + 6(-)		7.0×10^{9}	6.0×10^{9}	3.0×10^{9}	2.0×10^{9}		
						71°F	
						4-15-81	
						15%	

READ BY	RCN	RCN	RCN	RCN	RCN	EQUIPMENT
TEMPERATURE	76°F	65°C	65°C	65°C	65°C	A G
DATE	3-31-81	4-3-81	4-7-81	4-9-81	4-13-81	B H
CONDITION 1 R.H. :		95%	95%	95%	95%	C I
CONDITION 2 TIME :		1130 HRS.	1200 HRS.	1345 HRS.	1845 HRS.	D J
CONDITION 3 DAYS IN HUMIDITY :		1	5	7	11	E K
CONDITION 4						F L
CONDITION 5						CHECKED BY
CONDITION 6 START HUMIDITY :	4-2-81					APPROVED BY
CONDITION 7 HUMIDITY COMPLETE :	4-13-81					

APPENDIX H

SUMMARY OF LITERATURE RELATED TO INNER LAYER ADHESION OF MLPWB

Reference	Highlights Related to Inner Layer Adhesion of MLPWB
1	The objective of this program was to establish and document the processes for fabricating polyimide/glass printed wiring boards (PWB's), both double-sided and multilayered, and to compare costs and performance of polyimide and epoxy printed wiring boards. Data are presented relative to material availability, material and process characterization, and performance tests. It is concluded that polyimide is a superior material for printed wiring applications and that fabricated polyimide boards/assemblies exhibit substantially lower life cycle costs and improved performance characteristics, particularly when subjected to adverse environments.
2	Measurements of temperature histories of epoxy/glass prepreg layers during multilayer printed wiring board lamination have been recently obtained. It is shown that the temperature histories may be predicted by an analysis of the transient heat flow process within the multilayer board (MLB). The analysis requires a knowledge of the press platen temperature history during lamination and the thermal resistance of the padding material. Theoretically predicted results show close agreement with the experimental data for both 5-layer and 15-layer MLB's using the "hot press" as well as the "cold press" cycles. The present theory has been applied to study the effect of kraft paper padding on the prepreg temperatures. Results are shown for both 15- and 5-layer laminations employing the hot press as well as the cold press cycles. The number of kraft paper sheets used is shown to have a significant bearing on the temperature.
3	The work described herein was initiated in order to generate resin characterization data that could describe a B-stage epoxy material via the viscosity-time-temperature interactions that are inherently related to the nature of the lamination process. The technique of chemo-rheology, or isothermal polymeric flow-cure analysis, is explored as a means of characterizing the viscosity-time-temperature behavior of the B-stage epoxy resins. The B-staged epoxy resins studied are typical of those available as glass impregnated prepreg bonding sheets used to manufacture multilayer printed wiring boards.

SUMMARY OF LITERATURE RELATED TO INNER LAYER ADHESION OF MLPWB (Cont'd)

Reference	Highlights Related to Inner Layer Adhesion of MLPWB
4	Presented are details of an Air Force sponsored manufacturing technology study to establish improved fabrication processes for polyimide printed wiring boards. Comparisons are made between polyimide and conventional epoxy material systems, and data are presented relative to material availability, material and process characterization performance tests, and life cycle cost analysis. On the basis of comparative tests, it is concluded that polyimide is a superior material for printed wiring applications and that fabricated polyimide boards/assemblies exhibit lower life cycle costs and improved performance characteristics particularly when subjected to adverse environments.
5	This paper presents the results of a study to identify the thermal characteristics of the laminating process for multilayer printed wiring boards (MLB's). MLB's with 5 and 15 conducting layers were studied by embedding thermocouples into the epoxy/glass bonding sheets during the "hot press" lamination process. An effort was made to isolate the important parameters governing thermal variation during hot-press lamination and to determine the thermal timing "window" for cure-pressure application necessary for uniform resin flow. The results show that whereas the temperature of the bonding sheets in a 5-layer MLB are practically identical, the temperature in 15-layer MLB's differs in excess of 37°F (20.5°C). The study also concludes that the lag between the time the lay-up is inserted and the press is closed governs temperature differences for a given MLB.
6	A recently developed epoxy/glass multilayer printed wiring board (PWB) presently being manufactured experienced severe delamination problems early in its developmewnt program. This multilayer PWB had several differences from other multilayer designs. The new multilayer PWB utilized GF (general purpose epoxy/glass, flame retardant) material, while the previous multilayer PWB's utilized a GE (general purpose epoxy/glass) material. The newer design used large internal ground planes, while the older design incorporated no ground planes. The new boards were solder dipped and leveled, compared to tin-lead electroplate and reflow for the older design. Finally, the new boards were drag soldered after the solder dip and level, as opposed to hand soldering for the older design. The delamination which had presented early problems occurred at the copper/epoxy prepreg interface during the solder dip, solder level, and drag solder processes. A project was initiated to develop a lamination process to consistently produce quality multilayer PWB's which were not subject to to delamination problems.

SUMMARY OF LITERATURE RELATED TO INNER LAYER ADHESION OF MLPWB (Cont'd)

Reference	Highlights Related to Inner Layer Adhesion of MLPWB
7	The rapid progress in reliability and performance of electronic equipment in recent years calls for further improvement in circuit density, reliability and electrical properties of printed circuit boards on which IC or LSI is installed. This problem can be solved only by new development in such as board material, plating, and manufacturing process and technologies. To meet these requirements, two new kinds of laminates for printed circuit boards were developed; one is a thin copper foil clad laminate, clad with copper foil which is thinner than the usual 1/2 oz. and further protected by aluminum foil, and the other is a transcribed rough surface laminate on which circuits can be printed directly by electroless plating.
8	A two year study describes a series of unidirectional glass reinforced epoxy laminates that can exhibit different initial and aged properties depending on the properties of the resin matrix and glass-resin matrix combination.
9	Developed high-performance polyimide laminates, especially thin laminates and prepregs, for multilayer printed wiring boards and then compared their properties with those of epoxy material. (Note: This article is in Japanese and not available in English. The tables and figures, however, are English-captioned and give the reader the fundamental results of this study.)
10	In the past, epoxy resin, fiberglass-reinforced multilayer printed wiring boards have met the end use requirements of most electronic packages used in Air Force systems. However, more demanding Air Force requirements have made epoxy resin boards either electrically or mechanically unsuitable. Since recently-developed polyimide resin systems showed promise of overcoming these shortcomings, a program was undertaken to thoroughly characterize polyimide resin thin laminate prepregs and completed multilayer boards while subjecting them to comprehensive electrical, mechanical, and environmental tests far exceeding the capabilities of other systems. The polyimide resin systems performed reliably during the tests with no evidence of degradation. It can be concluded from this program that polyimide resin, fiberglass-reinforced board materials are available that can produce multilayer printed wiring boards capable of continuous operation at over 150°C and thermal cycling up to 200°C without plated-through failure or degradation of electrical characteristics.

SUMMARY OF LITERATURE RELATED TO INNER LAYER ADHESION OF MLPWB (Cont'd)

Reference	Highlights Related to Inner Layer Adhesion of MLPWB
11	RADC had undertaken a comprehensive study program to evaluate polyimide resin systems and compare them with commonly used epoxy systems. This report outlines the study in progress.
12	In order to ensure the acceptance of reliable and stable laminate material, realistic incoming inspection criteria must be set. Since these criteria must be based on a complete and thorough characterization study of existing materials, a comprehensive program was established to evaluate materials supplied by prominent vendors. Nine suppliers provided general-purpose and flame-retardant epoxy-glass laminates in thicknesses from 0.002 to 0.030 in., which were then evaluated for more than 15 electrical, physical and mechanical properties. It was necessary in some cases to develop unique test methods in order to obtain data on certain characteristics. The program was intended to characterize the materials objectively as they are available today. One result has been the promulgation of military specification MIL-P-55617(EL).
13	A high density multilayer (15-layer) printed wiring board has been developed for ACOS series 77 NEAC System 800/900 computers. Special polyimide laminate has been developed for this multilayer board. Dimensional stability in the X, Y, and Z directions and heat resistance of special polyimide laminate, are all extremely superior to G-10 laminate. 15-layer multilayer board with special polyimide laminate shows good interconnection reliability even in 100 cycle heat shock test (NEC method). The board with special polyimide laminate is considered to fulfill the high density packaging system where LSI's are widely used.
14	Kerimid 601 resin allows, for the first time, the preparation, under epoxy processing conditions, of polyimide multilayer printed wiring boards which perform reliably under demanding environmental service conditions. Void-free laminates offer order of magnitude improvements over epoxies in the areas of z-dimensional stability, 500°F heat resistance, non-smearing and moisture resistance. In any application, where epoxy boards have proven marginal or deficient or where past polyimide boards have proven improcessable, Kerimid 601 laminates offer an opportunity to significantly upgrade the properties of electronic packaging.

SUMMARY OF LITERATURE RELATED TO INNER LAYER ADHESION OF MLPWB (Cont'd)

Reference	Highlights Related to Inner Layer Adhesion of MLPWB
15	The most important improvement in printed wiring boards since the development of plated through holes has been the production growth of polyimide resin as an alternative to the limitations of epoxy. The knowledge of the application and uses of the polyimide resin laminate systems has been extensively researched and tested. The use of the polyimide systems have put thousands of multilayer boards into field service without any failures.
16	Differential scanning calorimetry has been applied to the study of epoxy-glass and Kerimid 601 (polyimide-glass) prepregs used in making multilayer printed wiring boards. The data generated through thermal analysis are thermodynamic and kinetic. Thermodynamic properties of B-stage prepregs obtained are endothermal and exothermal peak temperatures, glass transition temperatures, and heats of residual cure. They were obtained from thermograms made at fixed scanning rates. Kinetic information obtained from isothermal cure scans gave rates of residual cure, cure times, and energies of activations. This information gives the process engineer useful information for controlling the processing of multilayer printed wiring boards.
17	In an effort to control the variables during lamination, a recent study identified the thermal characteristics of the lamination process and determined the process dependent thermal timing windows necessary for cure pressure application. These timing windows are indicative of the necessary processing flexibility of prepreg resins. Extending the results of that study, this article examines temperature history extremes of a B-stage resin within an MLPWB during lamination. Temperature histories are combined with an analytical resin flow model to predict thickness-time behavior of the B-stage epoxy resin during lamination.
18	Moisture diffusion in fiber reinforced plastics is characterized by two observables: the saturation level, which is the weight percent moisture uptake at equilibrium and the susceptibility parameter which is determined by the initial absorption rate. A relatively quick method for determining these parameters is discussed along with the possibility of using the results to screen composite materials for consistency of mechanical properties that depend on resin composition and cure quality. This approach is called the incremental grinding method.

SUMMARY OF LITERATURE RELATED TO INNER LAYER ADHESION OF MLPWB (Cont'd)

Reference	Highlights Related to Inner Layer Adhesion of MLPWB
19	High Pressure Liquid Chromatography (HPLC) as a quality control tool for polyimide resins and prepregs is presented. A data base to help establish accept/reject criteria for these materials was developed. This work is intended to supplement, not replace, standard quality control tests normally conducted on incoming resins and prepregs. To help achieve these objectives, the HLPC separation of LARC-160 polyimide precursor resin was characterized. Room temperature resin aging effects were studied.
20	The properties of laminated composite materials are strongly affected by many fabrication variables including temperature, time, and molding pressure. It is therefore necessary to have reliable quality control tests to check the properties of manufactured materials. The short term shear test is used widely by both manufacturers and researchers as a quality control test in the production of materials and development of new material systems. There are, however, several limitations to the standard test method. This paper presents the results of short beam shear tests on graphite-polyimide laminates and reports on stiffness-strength relationships and nondestructive evaluation methods which aid in the interpretation of the test data.
21	The Clark-Schwebel Research and Development Division worked with Kerimid 601 polyimide resin in developing finishing agents CS-290 and CS-309. These two finishes offer significant elevated temperature performance with the Kerimid resin system. The test results obtained for both structural and electrical applications are discussed.
22	Improvements in multilayer bond strengths can be achieved using a modified solution to produce an oxide surface with a finer crystal structure. The structure of the surface is described and bond strengths with both epoxy-glass and polyimide laminates are reported.
23	Delamination resistance at soldering temperatures is a property required of multilayer printed wiring boards and is a function of material conditioning, inner layer surface treatments, and port-lamination storage conditions. A recently completed project determined how to optimize the delamination resistance of multilayer boards by controlling these process variables.

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