2

WL-TR-91-2105

HIGH TEMPERATURE POLYMER DIELECTRIC FILM INSULATION

ROBERT J. JONES
WARD F. WRIGHT

TRW SPACE AND DEFENSE
ONE SPACE PARK
REDONDO BEACH, CA 90278

FEBRUARY 1992

Final Report for period November 1988 - May 1991

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION IS UNLIMITED

AERO PROPULSION AND POWER DIRECTORATE
WRIGHT LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433-6563

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely Government-related procurement, the United States Government incurs no responsibility or any obligation whatsoever. The fact that the government may have formulated or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication, or otherwise in any manner construed, as licensing the holder, or any other person or corporation; or as conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

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

John G Nairus

John G. Nairus
Program Manager
Power Components Branch
Aerospace Power Division
Aero Propulsion and Power Directorate

Joseph A. Weimer
Technical Area Manager
Power Components Branch
Aerospace Power Division
Aero Propulsion and Power Directorate

FOR THE COMMANDER

William Borger

WILLIAM U. BORGER
Chief, Aerospace Power Division
Aero Propulsion & Power Directorate

If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify WL/POOC-1, WPAFB, OH 45433-6563 to help us maintain a current mailing list.

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

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

1b. RESTRICTIVE MARKINGS
N/A

2a. SECURITY CLASSIFICATION AUTHORITY
N/A

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE
N/A

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release;
distribution is unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)
WL-TR-91-2105

6a. NAME OF PERFORMING ORGANIZATION
TRW SPACE & DEFENSE

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION
AERO PROPULSION AND POWER DIRECTORATE,
(WL/POOC), WRIGHT LABORATORY

6c. ADDRESS (City, State and ZIP Code)
ONE SPACE PARK
REDONDO BEACH, CA 90278

7b. ADDRESS (City, State and ZIP Code)
WRIGHT-PATTERSON AFB, OH
45433-6563

8a. NAME OF FUNDING/SPONSORING ORGANIZATION
STRATEGIC DEFENSE INITIATIVE OFFICE

8b. OFFICE SYMBOL (If applicable)
SDIO/T-KT

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
F33615-88-C-2909

8c. ADDRESS (City, State and ZIP Code)
THE PENTAGON
WASHINGTON,DC 20310-7100

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
63224C	L210	00	37

11. TITLE (Include Security Classification)
High-Temperature Polymer Dielectric Film Insulation

12. PERSONAL AUTHOR(S)
ROBERT J. JONES AND WARD F. WRIGHT

13a. TYPE OF REPORT
FINAL

13b. TIME COVERED
FROM 8811 TO 9105

14. DATE OF REPORT (Yr., Mo., Day)
1992 February

15. PAGE COUNT
114

16. SUPPLEMENTARY NOTATION
N/A

17. COSATI CODES

FIELD	GROUP	SUB. GR.
01	03	-
22	02	-

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
HIGH-TEMPERATURE POLYMERIC DIELECTRIC FILM, UPILEX^R S POLYIMIDE, EYMYD^R POLYIMIDE, 300°C THERMAL-ELECTRICAL PROPERTIES, CERAMIC COATED POLYIMIDE FILM, POLYIMIDE INSULATED WIRE

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

The overall objective of this program was to identify and evaluate advanced aromatic/heterocyclic film forming polymers having improved electrical and thermal properties over Kapton^R for wire insulation applications in future spacecraft.

Five polymeric candidates were screened for high (300°C) and low temperature (-269°C) behavior, initial electrical properties and oxidative/solvent resistance versus Kapton^R film as the control material for which a replacement was sought. It was experimentally determined that EYMYD^R L-30N, IP-200 PPQ and UPILEX^R S films possessed a very promising initial combination of properties versus Kapton^R indicative of high promise for 300°C insulation service.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
JOHN NAIRUS

22b. TELEPHONE NUMBER (Include Area Code)
513-255-6016

22c. OFFICE SYMBOL
WL/POOC-1

DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE.

19. ABSTRACT (Continued)

The promising EYMYD^{R} L-30N, IP-200 PPQ and UPILEX^{R} S film materials were subjected to long-term exposure in environments known to degrade state-of-the-art insulation materials prior to launch and/or during prolonged mission exposure in space versus Kapton^{R} as the control film material. Isothermal aging of the three candidate film materials and Kapton^{R} in humidity, ultraviolet radiation, vacuum, basic solution and polar solvent determined that the EYMYD^{R} L-30N and UPILEX^{R} S films possessed superior environmental resistance versus both IP-200 PPQ (generally better performance) and Kapton^{R} (significantly better performance).

Thin ceramic surface coatings were studied to optimize the electrical properties of EYMYD^{R} L-30N and UPILEX^{R} S, including breakdown voltage and arc/track resistance. Kapton^{R} film was again employed as the control material. It was determined on uncoated and silicon dioxide ceramic coated (up to 5000 Angstroms thick) that UPILEX^{R} S offers greater potential than either EYMYD^{R} L-30N or Kapton^{R} for arc/track resistance at nearly equivalent high ac and dc breakdown voltage performance. Both UPILEX^{R} S and Kapton^{R} film were double wrapped on 14 gauge bare copper conductor using Teflon^{R} FEP as an adhesive according to standard industry practice. Breakdown voltage tests both before and after aging at 300°C in air verified that UPILEX^{R} is a superior candidate wire insulation material versus Kapton^{R} for advanced spacecraft power generation and management applications.

FOREWORD

This document is the Final Report on Contract F33615-88-C-2909 sponsored by the USAF Wright Laboratory/Aero Propulsion and Power Directorate. The technical period of performance described herein is from November 1988, through May 1991. The USAF Program Manager responsibilities were successively provided by Lt Thomas King, Mrs. Sandra Fries-Carr and Mr. John Nairus, all during prior or current assignments in WL/POOC-1.

The program was conducted in the Applied Technology Division of TRW's Space and Defense Sector. Dr. Robert J. Jones served as TRW's Program Manager throughout the contract. Mr. Richard Griese and Mr. Ward Wright, Materials Engineering and Technology Department, provided the key polymeric film materials development and support during the program. Mr. Walter Dinkins, Lawrence Technology (formerly TRW's Oilwell Cable Division), provided the key electrical engineering support. The Chemistry Technology Department provided the thermal and morphology characterization support.

A select number of vendors provided key polymeric materials supply, materials conversion and property testing services during the program. The vendors, along with their contributed support function to the program, are provided alphabetically as follows:

- Cemota: Polyphenyquinoxaline polymer varnish,
- Du Pont: Kapton^R polyimide film and Pyralin^R polyimide varnish,
- Ethyl Corporation: EYMYD^R polyimide varnish,
- ICI, Inc.: UPILEX^R polyimide film,
- Lawrence Technology Division of CAMCO Corporation: Film electrical property testing and wire wrapping/testing,
- Rexham Corporation: Continuous film casting,
- Sheldahl Corporation: Ceramic surface coating of film and
- Wyle Laboratories: Cryogenic film exposure.

Table of Contents

Table of Contents (Continued)

Figures

Figures (Continued)

Tables

Tables (Continued)

SUMMARY

This program, Contract F33615-88-C-2909, entitled High Temperature Polymer Dielectric Film Insulation, was sponsored and directed by the USAF Aero Propulsion and Power Directorate with funding provided by the Strategic Defense Initiative Organization. A highlight summary of the problem addressed, program objective, program approach and technical accomplishments is provided in the paragraphs below.

At the inception of this program, a comprehensive data base on new/improved polymeric film insulation materials was not available to address and solve the critical problems identified for current materials making their use very suspect for advanced power generation in advanced Strategic Defense Initiative spacecraft systems. State-of-the-art high performance, aromatic/heterocyclic dielectric film insulation materials (exemplified by Kapton^R) currently suffer from several critical deficiencies as follows:

- Variations in dissipation factor (or loss) as a function of temperature from approximately -80^oC to +100^oC and above +200^oC (at all frequencies from 60 Hz to 10^{11} Hz),
- High equilibrium moisture gain of ~3 percent by weight and generally poor moisture resistance,
- Poor long-term oxidation resistance at $\geq$280^oC and
- High incidence of arcing/tracking failure.

Based upon the problem stated above for now qualified state-of-the-art wire insulation materials, the overall objective of this program was to identify and evaluate advanced aromatic/heterocyclic film forming polymers having improved electrical and thermal properties over Kapton^R for wire insulation applications in future spacecraft. Ideally, the new insulation material would demonstrate equally superior performance for aircraft applications. The goal performance temperature range was from -269^oC to $\geq$ +300^oC.

The technical approach selected for this program focused on selecting five promising high temperature resistant, commercially available film forming polymeric materials (based upon available data). Each candidate was screened for key electrical, thermal and chemical property tests employing Kapton^R as the control film material. The program was conducted according to the following sequential task summary:

TASK	KEY TESTS	OUTPUT OF TASK
1	Screen five candidates for: ● High temperature properties ● Low temperature flexibility ● Initial electrical properties ● Oxidation resistance ● Initial cleaning solvent stability	Down select to three promising candidates; document test plan for conducting remainder of program
2	Perform detailed tests on three candidates: ● Humidity resistance ● Ultraviolet resistance ● Basic and polar fluid resistance ● Vacuum aging	Down select to two most promising candidates
3	Perform process optimization and test on two candidates in terms of: ● Ceramic coatings ● Continuous casting of film	Down select to best candidate
4	Wrap film on wire and test for: ● Electrical properties before and after air aging	Wire test data/samples and recommendations for further work

The five specific candidate polymers investigated in this program are summarized in Table 1 in the Introduction. A highlight summary of technical accomplishments achieved during each of the four program sequential tasks is provided below.

The five polymeric candidates were screened for high (300^{o}C) and low (-269^{o}C) temperature behavior, initial electrical properties and oxidative/solvent resistance versus Kapton^{R} film as the control material for which a replacement was sought. It was experimentally determined that EYMYD^{R} L-30N, IP-200 PPQ and UPILEX^{R} S films possessed a very promising initial combination of properties versus Kapton^{R} indicative of high promise for 300^{o}C insulation service. These three candidate film materials were selected for detailed testing in Task 2.

The promising EYMYD^{R} L-30N, IP-200 PPQ and UPILEX^{R} S film materials were subjected in Task 2 to extended long-term exposure in environments known to degrade state-of-the-art insulation materials prior to launch and/or during prolonged mission exposure in space. Again, Kapton^{R} was employed as the control film material. Isothermal aging of the three candidate film materials and Kapton^{R} in humidity, ultraviolet radiation, vacuum, basic solution and polar solvent determined that the EYMYD^{R} L-30N and UPILEX^{R} S films possessed superior environmental resistance versus both IP-200 PPQ (generally better performance) and Kapton^{R} (significantly better performance). Preliminary optimization studies on the two most promising films were conducted as described below.

The Task 3 study was focused on the promise of thin ceramic surface coatings to optimize the electrical properties of EYMYD^{R} L-30N and UPILEX^{R} S, particularly for breakdown voltage and arc/track resistance. Kapton^{R} film was again employed as the control material. It was determined on uncoated and silicon dioxide ceramic coated (up to 5000 Angstroms thick) that UPILEX^{R} S offers greater potential than either EYMYD^{R} L-30N or Kapton^{R} for arc/track resistance at nearly equivalent high ac and dc breakdown voltage performance. UPILEX^{R} S was, therefore, selected as the single most promising candidate for insulated wire production and testing to complete the program as described below.

The final effort on the program, Task 4, was focused on demonstrating that the superior performance of UPILEX^{R} S versus Kapton^{R} in film tests could be realized in actual insulated wire performance. Both UPILEX^R S and Kapton^R film were double wrapped on 14 gauge bare copper conductor using Teflon^R FEP as an adhesive according to standard industry practice. Breakdown voltage tests both before and after aging at 300^{o}C in air verified that UPILEX^R S is a truly superior candidate wire insulation material versus Kapton^R for advanced spacecraft (and probably aircraft) power generation and management applications.

This success oriented exploratory development program has shown conclusively that polymeric dielectric materials exist today which are truly superior in a combination of high perforamnce properties to the qualified Kapton^R state-of-the-art insulation material. UPILEX^R S polyimide, directly available as a film material, is strongly thought to be ready for system specific advanced development and qualification as an outstanding insulation material. EYMYD^R L-30N, because of its generally superior combination of properties versus Kapton^R, is thought to be very attractive, domestically available alternative material worthy of equal advanced development and qualification consideration for selected very high performance power generation/distribution applications. Detailed experimental test results demonstrating the superior dielectric film performance of UPILEX^R S and EYMYD^R L-30N are documented throughout the remainder of this Final Report.

1. INTRODUCTION

This Final Report describes the work performed by TRW on Contract F33615-88-C-2909, High Temperature Polymer Dielectric Film Insulation, during a 30-month technical period of performance from November 1988, through May 1991. The program was conducted by performing four sequential technical tasks. This Introduction provides an overview of the technical approach by describing the work performed in each task. The statement of the problem and the program objective were provided in the Summary and are not repeated in this Introduction.

1.1 TASK 1 - SCREENING, SELECTION OF PROMISING CANDIDATES AND DOCUMENTATION OF TEST PLAN

A total of five promising aromatic/heterocyclic polymers were screened for selected electrical, thermal, chemical and mechanical properties over the temperature range of $-269^{o}C$ to $\geq +300^{o}C$. All properties were compared with those of Kapton^{R} employed as a control. The tests were conducted on procured or TRW cast films at a nominal thickness of 0.001 inch.

A summary description of Kapton^{R} and the five polymer candidates are provided in Table 1. A summary of key known properties of Kapton^{R} and the five polymer candidates as reported by the vendors and/or the open literature is provided in Table 2.

On the basis of experimental test results determined in Task 1, EYMYD^{R} L-30N, IP-200 PPQ and UPILEX^{R} S were selected and approved as promising candidates for development and detailed testing in Task 2. A Program Test Plan was documented and approved prior to undertaking the remaining program tasks.

1.2 TASK 2 - DEVELOPMENT AND DETAILED TESTING

The three promising candidates selected in Task 1 were subjected to experimental development and detailed testing work along with the

TABLE 1

POLYMERIC MATERIAL CANDIDATES

POLYMER TRADE NAME	GENERIC POLYMER TYPE/ABBREVIATION	VENDOR/PRODUCT FORM SOLD	RATIONALE FOR SELECTION a)	REFERENCE
Kapton^R	Polymide/PI	DuPont/Film	Control film	1
Pyralin^R PI-2566	Polymide/PI	DuPont/Varnish	Improved electrical properties	2
Eymyd^R L-30N	Polymide/PI	Ethyl Corporation/Varnish	Improved thermal-oxidation stability	3
IP-200	Polyphenylquinoxaline/PPQ	Cemota/Varnish	Improved electrical and thermal properties	4
Sixef^R 44	Polymide/PI	American Hoechst/Powder	Improved electrical properties	5
Upilex^R S	Polymide/PI	UBE Industries (Distributed by ICI in US)/Film	Improved thermal-oxidation properties	6

TABLE 2

COMPARISON OF CONTROL AND POLYMER CANDIDATE REPORTED KEY PROPERTIES$^{a)}$

	ELECTRICAL PROPERTIES		THERMAL PROPERTIES			OTHER
POLYMER	DIELECTRIC CONSTANT (1000 Hz 1-MIL RT)	DISSIPATION FACTOR (1000 Hz, 1-MIL, RT)	GLASS TRANSITION TEMPERATURE (Tg IN ^{o}C)	CONTINUOUS USE TEMPERATURE (^{o}C IN AIR)	COEFFICIENT OF THERMAL EXPANSION (CTE IN/IN/^{o}Cx10^{-6})	EQUILIBRIUM MOISTURE REGAIN (PERCENT)
KAPTON^{R} (CONTROL	3.5	0.0025	360-410	220-250	20	2.9
PYRALIN^{R} PI2566	<3.0	<0.003	TBD	>280	--	<2.0
EYMYD^{R} L-30N	2.9	<0.003	400	>280	36	1.1
IP200	3.2	TBD	370	TBD	35	<2.0
SIXEF^{R}	2.6	TBD	322	TBD	--	1.1
UPILEX^{R} S	3.5	0.0013	>500	280	12	1.2

a) Reported by vendor or others in open literature publications.

b) TBD = To be experimentally determined in this program.

Kapton^R control. The types of experimentation conducted in Task 2 are summarized below:

- Polymer modification studies
  - Postcure effects on mechanical properties,
- Detailed Testing
  - Electrical properties from 25°C to 300°C at 1000 Hz,
  - Isothermal aging in vacuum at 300°C,
  - Humidity aging at 90°C/100 percent RH,
  - Ultraviolet aging at 25°C and 365 nm wavelength,
  - Base solution exposure at pH 10 and 93°C and
  - Refluxing in methylethylketone polar solvent at 80°C.

Based upon the experimental test results, EYMYD^R L-30N and UPILEX^R S were selected as the two promising candidates for optimization work in Task 3.

1.3 TASK 3 - MODIFICATION, OPTIMIZATION AND TESTING OF MOST PROMISING POLYMERIC FILM CANDIDATES

The two most promising candidates selected in Task 2 were subjected to further modification and/or preliminary process optimization. The work conducted in Task 3 is summarized below:

- Casting of continuous lengths of EYMYD^R L-30N film material by a solvent method,
- Vapor deposition of protective silicon dioxide ceramic coating on the promising films and Kapton^R and
- Electrical property testing of uncoated and coated films, including arc/track determinations.

Based upon the experimental results determined in Task 3, UPILEX^R S was selected as the single most promising dielectric film candidate for wire insulation work in Task 4.

1.4 TASK 4 - INSULATED WIRE PRODUCT FABRICATION, TEST AND DELIVERY

UPILEX^R S dielectric film candidate and the Kapton^R control were wrapped onto copper conductor and key electrical property tests were conducted on the insulated wire. A summary of the work conducted is as follows:

- Development of wrapping process for UPILEX^R S,
- Wrapping of insulated wire in sufficient lengths to complete the program and
- Testing electric properties of the insulated wire before and after air aging exposure.

Testing of the insulated wire verified the film results determined in Tasks 1 through 3 and showed that UPILEX^R S is a superior dielectric film insulation versus Kapton^R.

1.5 REMAINING FINAL REPORT ORGANIZATION

This Final Report on Contract F33615-88-C-2909 is divided into the following additional sections:

- Section 2 - Technical result details of Task 1,
- Section 3 - Technical result details of Task 2,
- Section 4 - Technical result details of Task 3,
- Section 5 - Technical result details of Task 4,
- Section 6 - Conclusions,
- Section 7 - Recommendations for further work and,
- References.

All key technical data determined in this program are tabularized and comments are provided in the context. Representative thermal analysis and other characterization tracings and photographs of tests in progress and equipment utilized are provided throughout Sections 2 through 5. Plots of selected tabularized data are provided for emphasis of particularly key test results.

2. TASK 1 EXPERIMENTATION

This section describes the work performed in Task 1 - Screening, Selection of Promising Candidates and Documentation of Test Plan. The experimentation described herein on the five polymeric dielectric candidates, EYMYD^R L-30N, IP-200 PPQ, PYRALIN^R PI-2566, SIXEF^R 44 and UPILEX^R S, plus the Kapton^R control, is as follows:

- Preparation or procurement of film materials,
- Thermal analysis determinations,
- Cryogenic exposure at -269^{o}C,
- Isothermal aging at 300^{o}C,
- Preliminary electric property determinations and
- Cleaning solvent exposure.

Each of the experimental areas listed above is separately described below. For simplicity, the trademark designation for the films has been dropped from the technical discussion in Sections 2 through 5.

2.1 PREPARATION OR PROCUREMENT OF FILM MATERIALS

Samples of the Kapton control and UPILEX S were obtained as films in a nominal 0.001 inch thickness from DuPont and ICI, respectively. The remaining four polymer candidates not available as films were cast into films from vendor supplied varnishes at TRW employing established procedures and cured (or imidized) into a final state for evaluation employing vendor recommended processing conditions.

Two casting procedures were employed to prepare essentially defect-free films for testing. The first procedure was used for the polyimides, PYRALIN PI-2566, EYMYD L-30N, and SIXEF 44. The second procedure was used to cast IP-200 PPQ.

The procedure used for EYMYD L-30N serves as an example for the polyimides. The EYMYD was obtained as a thick red-colored varnish at a 25 percent by weight solids content in a N-Methyl-2-Pyrrolidinone (NMP) solvent. The EYMYD varnish was poured onto a clean, flat, tempered glass plate in a fume hood. A doctor blade was drawn across the varnish, resulting in a 0.004 inch thick coating (including solvent). The plate was placed in an oven and vacuum applied for 15 minutes at room temperature. While still under vacuum, the temperature was raised in increments of ~50^{o}C every hour until 200^{o}C was reached. The temperature was held for 2 hours at 200^{o}C, then the vacuum was released and the glass plate removed from the oven and cooled to room temperature. The EYMYD film was peeled from the glass plate and the reverse side taped to the glass. The assembly was placed into a circulating air oven at 200^{o}C for 1 hour, followed by raising the temperature by ~50^{o}C increments per hour until the film reached 371^{o}C, then held at this temperature for 1 hour. The oven was then cooled to 200^{o}C and the glass plate removed and cooled to room temperature. This technique yielded 0.001 inch thick films which were removed from the plate, tagged, and retained for subsequent testing.

The procedure for casting PPQ films involved spreading a 15 percent by weight solids solution in meta-cresol solvent onto a clean tempered glass plate. The film/plate was placed on a hot plate in a fume hood and allowed to stand at ~100^{o}C for 4 hours. After initial solvent removal, the film was removed, taped onto a fresh glass plate and placed into a circulating air oven for 2 hours at 200^{o}C. The temperature was raised in 50^{o}C increments for 1 hour each until 371^{o}C was reached, then held at this temperature. After 1 hour at 371^{o}C, the plate was cooled to 200^{o}C and removed from the oven.

2.2 THERMAL ANALYSIS DETERMINATIONS

Samples of 0.001 inch thick Kapton^{R} and the five candidate films were subjected to Thermal Gravimetric Analysis (TGA) in vacuum, Differential Scanning Calorimetry (DSC) and Rheometrics Dynamic Analysis (RDA). These tests and results are described below.

2.2.1 Thermal Gravimetric Analysis (TGA) in Nitrogen and Vacuum

A problem associated with Kapton and all aromatic structure polymers are their tendency to form carbonaceous char on thermal decomposition which may contribute to poor resistance to arcing and tracking. Consequently, the nature of the Kapton replacement materials to yield less or more char on thermal decomposition were determined by TGA in nitrogen (to approximate terrestial behavior) and vacuum (to approximate space behavior). The TGA test results are discussed below.

The thermal behavior of Kapton and each of the five new polymer candidates was determined by TGA analysis in nitrogen over the temperature range of 25^oC to 800^oC employing a $5^oC/min$ heat-up rate on a DuPont 9900 thermal analyzer. As expected, each polymer demonstrated excellent thermal stability to 500^oC, followed by varying percent weight losses from 500^oC to 800^oC. When the temperature reached 800^oC, each polymer had apparently formed a stable char as evidenced by a plateau in the weight loss curve. The percent weight loss obtained on each polymer at 500^oC, 600^oC, 700^oC and 800^oC is given in Table 3. As can be seen from these data, IP-200 and UPILEX S gave a higher char yield than Kapton, whereas the three partially fluorinated polyimide candidates, EYMYD L-30N, PYRALIN PI-2566 and SIXEF 44, were slightly lower than Kapton. A more dramatic difference in char yields were obtained in vacuum as discussed below. Representative TGA tracings for EYMYD L-30N and UPLIEX S in nitrogen are shown in Figures 1 and 2, respectively.

The thermal behavior of Kapton and each of the five new polymer candidates was also determined by TGA in vacuum (<10 Torr). The same heat-up rate and instrument was employed. Again, each film material demonstrated excellent weight retention up to 500^oC and similar weight retentions were obtained up to 600^oC as in nitrogen. Above 600^oC, a significantly higher weight loss was obtained in vacuum versus nitrogen

TABLE 3

THERMAL GRAVIMETRIC ANALYSIS (TGA) SCREENING RESULTS OBTAINED IN NITROGEN AND VACUUM[a]

	Weight Retention as a Function of Temperature (Percent)							
Film	Nitrogen Environment				Vacuum Environment			
Material	500°C	600°C	700°C	800°C	500°C	600°C	700°C	800°C
KAPTON (Control)	97	82	62	58	97	82	58	47
EYMYD L-30N	95	67	58	55	95	67	51	31
IP 200 PPQ	98	87	80	76	98	84	76	66
PYRALIN PI-2566	97	70	57	55	95	67	51	36
SIXEF 44	97	58	52	50	96	55	42	35
UPILEX S	98	95	75	62	98	93	63	53

a) Determined on 0.001 inch thick film samples at a heat-up rate of 5°C/min on a DuPont 9900 Thermal Analyzer; the nitrogen flow rate was 80 ml/min and the vacuum employed was <10 Torr.

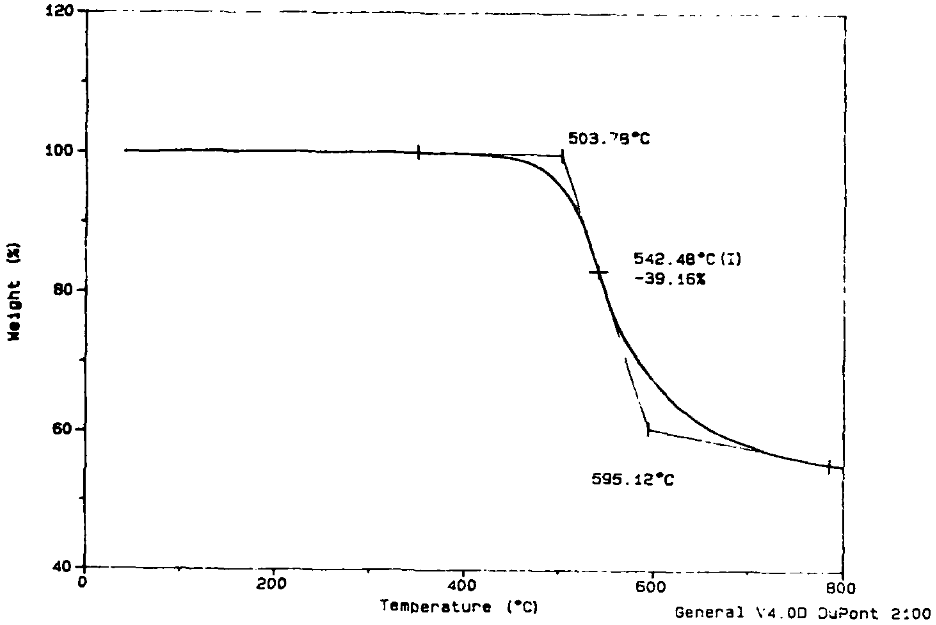

Figure 1. TGA Tracing of EYMYD L-30N in Nitrogen.

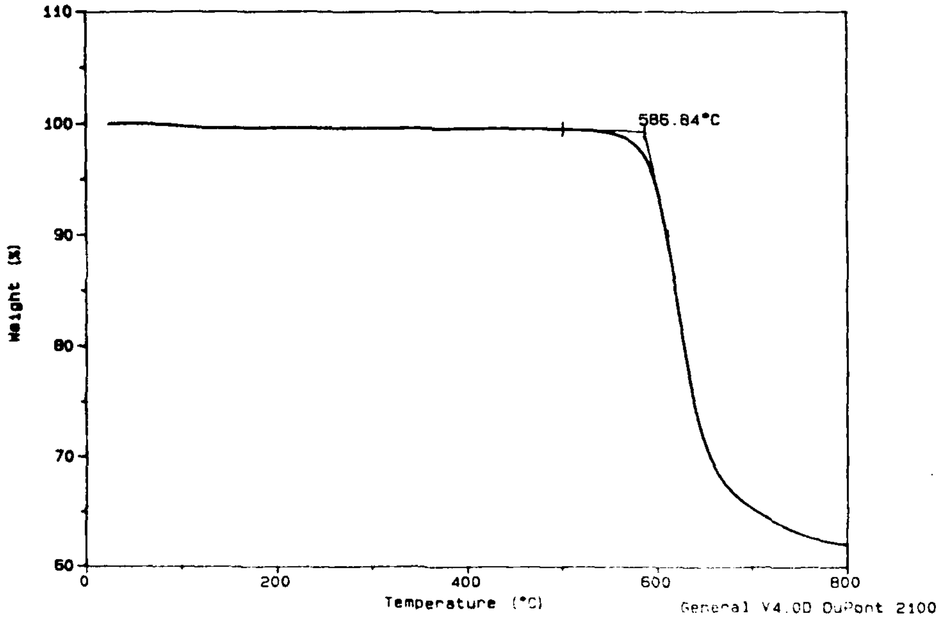

Figure 2. TGA Tracing of UPILEX S in Nitrogen.

out to char formation at 800°C. The percent weight losses obtained at 500°C, 600°C, 700°C and 800°C in vacuum are also presented in Table 3. As can be seen from these data, IP-200 PPQ and UPILEX S again gave a higher char yield than Kapton. Conversely, EYMYD L-30N, PYRALIN PI-2566 and SIXEF 44 gave significantly lower char yields than Kapton of at least 10 percent at 800°C. Representative TGA tracings for EYMYD L-30N and UPILEX S in vacuum are presented in Figures 3 and 4, respectively.

The TGA testing on Kapton and the five polymer candidates are conclusive that the three polyimide candidates containing a partially fluorinated structure, EYMYD L-30N, PYRALIN PI-2566 and SIXEF 44, each form less carbonaceous char than Kapton in a vacuum environment. This behavior infers that these materials could perform better than Kapton in resistance to arcing/tracking in the high vacuum environment encountered in space applications as wire insulation.

In all the TGA testing, in nitrogen and vacuum, Kapton nor any of the five other candidate films demonstrated any severe initial weight loss tendencies out to 500°C. These results are very important and strongly infer that none of the films should present a source of spacecraft outgassing problems.

2.2.2 Differential Scanning Calorimetry (DSC) Screening Analysis

Kapton and each of the five polymer candidates were screened as films by static (i.e., no applied load) Differential Scanning Calorimetry (DSC) analysis. The film samples were scanned over the temperature range of -150°C to +600°C in a nitrogen environment employing a DuPont 2100 thermal analyzer at a 5°C/min heat-up rate. The purpose of the DSC screening was to assess major endothermic temperatures indicative of polymer transitions (e.g., glass transition temperature-Tg) and major exothermic temperatures indicative of polymer melting or decomposition. The results obtained from the DSC work are presented and discussed below.

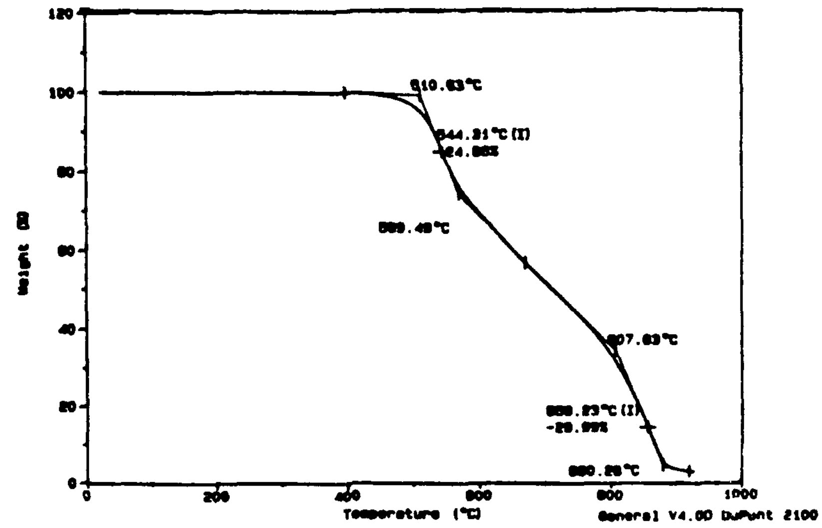

Figure 3. TGA Tracing of EYMYD L-30 in Vacuum.

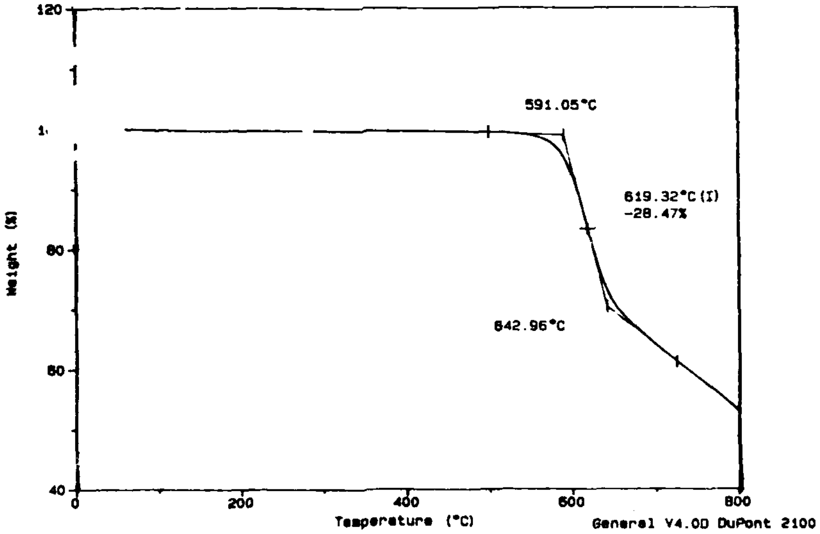

Figure 4. TGA Tracing of UPILEX S in Vacuum.

The DSC screening analysis showed no unexpected results in terms of major or clearly discernible endothermic transitional changes in Kapton or the five candidate polymers up to at least $+350^{\circ}C$. Minor, wide temperature range endotherms in selected polymers, including Kapton, occurred from $+50^{\circ}C$ to $+200^{\circ}C$ indicating effects assumed to be loss of absorbed moisture. These observations and thermal phenomena occurring above $+350^{\circ}C$ are presented in Table 4. The data summarized in Table 4 are worthy of highlight comments as follows:

- Kapton, IP-200 and UPLEX S show some very minor thermal endotherms in the range of $+50^{\circ}C$ to $+200^{\circ}C$,
- Kapton, EYMYD L-30N and UPILEX S gave evidence of a transition above $400^{\circ}C$ and
- All polymers except UPILEX S show a melting or decomposition phenomena in the temperature range of $+370^{\circ}C$ to $+560^{\circ}C$.

The DSC screening data are interpreted to mean that each of the five new polymers do not possess severe thermal problems below the goal level of $>300^{\circ}C$. Representative DSC tracings are presented for EYMYD L-30N and IP-200 PPQ in Figures 5 and 6, respectively.

Dynamic thermal behavior determined for Kapton and the five new polymer candidates is discussed in Section 2.2.3.

2.2.3 Rheometrics Dynamic Analysis (RDA) Screening

Kapton and each of the five polymer candidates were screened by Rheometrics Dynamic Analysis (RDA). The film samples were scanned over the temperature range of $-100^{\circ}C$ to $+500^{\circ}C$ in circulating air environment employing a Rheometrics RDA-700 instrument at 60 Hz (377 Radians/second) under a load of approximately 100 g. The purpose of the RDA scanning was to measure the stability of modulus (E') from very low to very high temperatures and detect the temperature (or range) at which the storage modulus breaks significantly indicating a dynamic work loss breakpoint or transition (TAN DELTA). The results obtained from the RDA screening work are presented and discussed below.

TABLE 4

DIFFERENTIAL SCANNING CALORIMETRY (DSC) SCREENING ANALYSIS RESULTS[a)]

Film Material	Endothermic and Exothermic Behavior Versus Temperature (^{o}C) Endotherms: Minor from Probable Loss of Absorbed Moisture	Endotherms: Major Indicative of Tg	Exotherms: Major Indicative Melting or Decomposition
KAPTON	50-200	540-560	>560
EYMYD L-30N	None	400-440	>440
IP-200 PPQ	90-170	None	>480
PYRALINE PI-2566	None	None	>400
SIXEF 44	None	None	>370
UPILEX S	70-200	510	None

a) Determined on 0.001 inch thick films under 80 ml/min nitrogen flow at a $5^{o}C$/min heat-up rate employing a DuPont 2100 thermal analyzer.

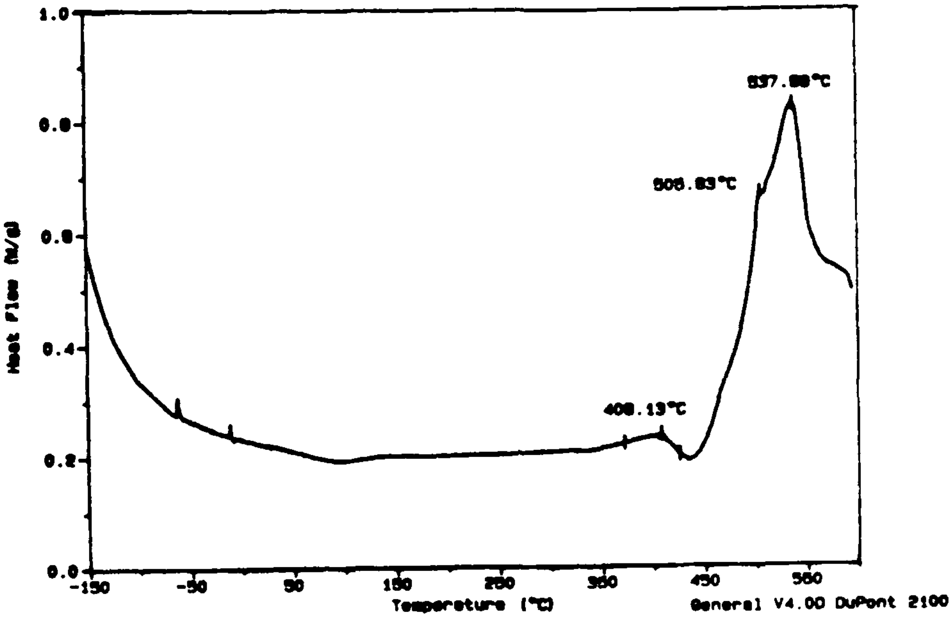

Figure 5. DSC Tracing of EYMYD L-30N.

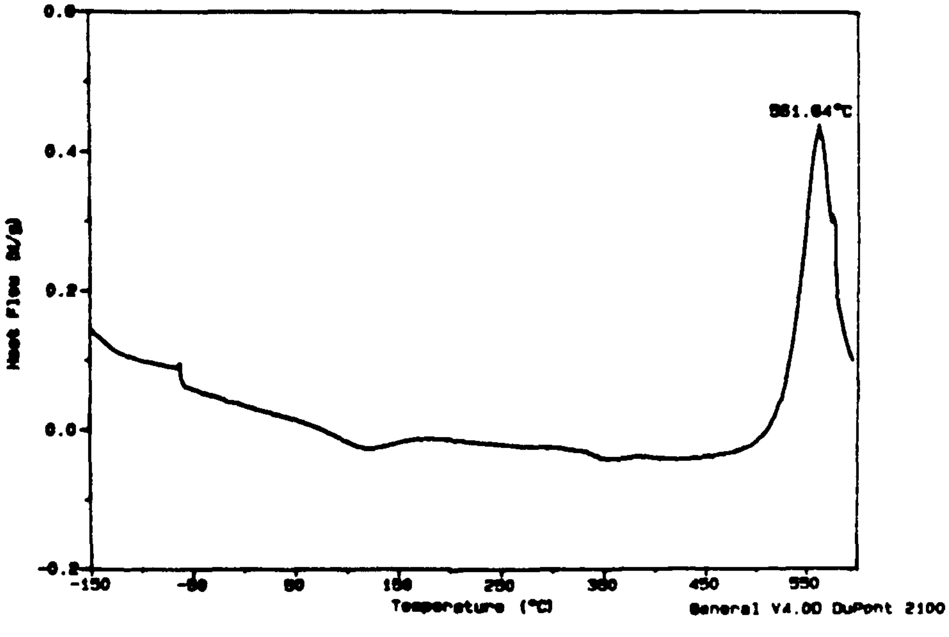

Figure 6. DSC Tracing of IP-200 PPQ.

The RDA screening analysis work indicated that each of the five new polymer candidates possess a high retention of mechanical properties as evidenced by retention of modulus to above the goal of +300^{o}C. All the films are apparently very "tough" as evidenced by their ability to withstand the probe acceleration of 60 Hz during the approximately 120 minutes required to complete the test. As was also evidenced by DSC static thermal analysis, some films gave evidence of plasticization or effect by moisture in the temperature range of -100^{o}C to +200^{o}C as shown in Table 5. Very importantly, each new polymer candidate gave strong evidence in the RDA screening to possess a high retention of mechanical properties to greater than the 300^{o}C goal. Representative RDA tracings for IP-200 PPQ and PYRALIN PI-2566 are presented in Figures 7 and 8, respectively.

2.3 LIQUID HELIUM IMMERSION STUDIES

Film samples of Kapton and the five new polymer candidates were subjected to liquid helium immersion to test their resistance to embrittlement and cracking at a low cryogenic temperature (-269^{o}C). The sample configuration and the test results are described below.

Film samples of dimensions 0.001 inch thick x 1.0 inch wide x 4.0 inch long of the Kapton control and the five new polymer candidates were wrapped on individual 0.5 inch OD copper tubes at an approximately 45^{o} helical angle and a 0.5 inch overlap. The end obtained after wrapping was secured with copper wire.

The samples were subjected to cryogenic immersion at Wyle Laboratories, El Segundo, CA. The samples were initially equilibrated to a low temperature (-196^{o}C) by immersion in liquid nitrogen in a Dewar flask for several minutes, then transferred into a second Dewar flask containing liquid helium (-269^{o}C). The samples were immersed in liquid helium for 15 minutes, then removed and allowed to warm to room temperature in an ambient air environment.

TABLE 5

RHEOMETRICS DYNAMIC ANALYZER SCREENING ANALYSIS RESULTS[a)]

Polymeric Film Material	Temperature(s) at which Modulus Effects Occurred (°C)	
	Potential Moisture Effects or Transitions	Apparent Onset of Major Dynamic Work Loss
Kapton	-50 to +200	340
EYMYD L-30	None	350
IP-200 PPQ	None	300
PYRALIN PI-2566	+200 to +300	320
SIXEF 44	+170 to +300	330
UPILEX S	-50 to +80 +260 to +300	310

a) Determined on 0.001 inch thick films in an circulating air environment under a 60 Hz cycling load of 100 g using a 5°C/min heat-up rate employing a Rheometrics Model 700 instrument.

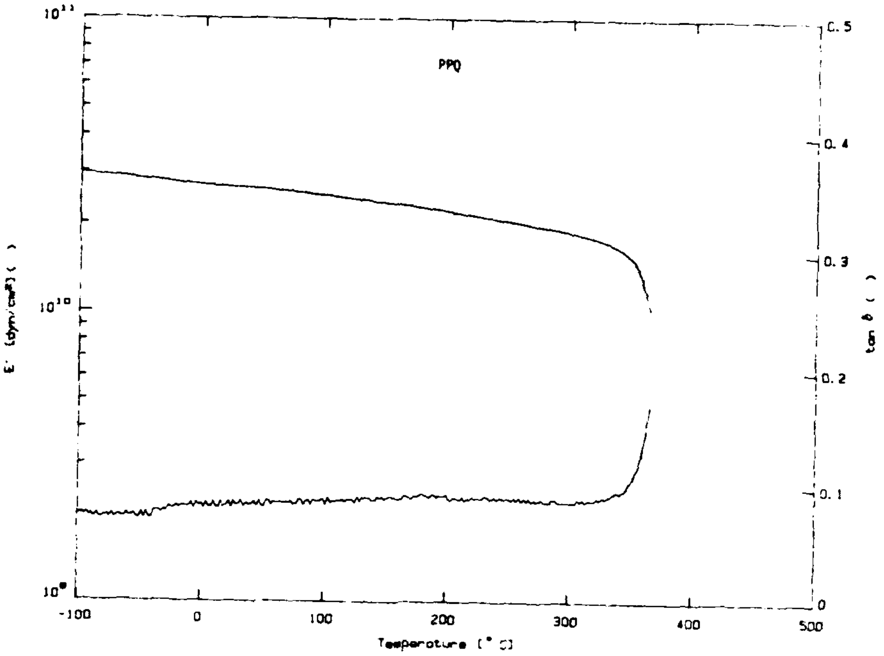

Figure 7. RDA Tracing of IP-200 PPQ.

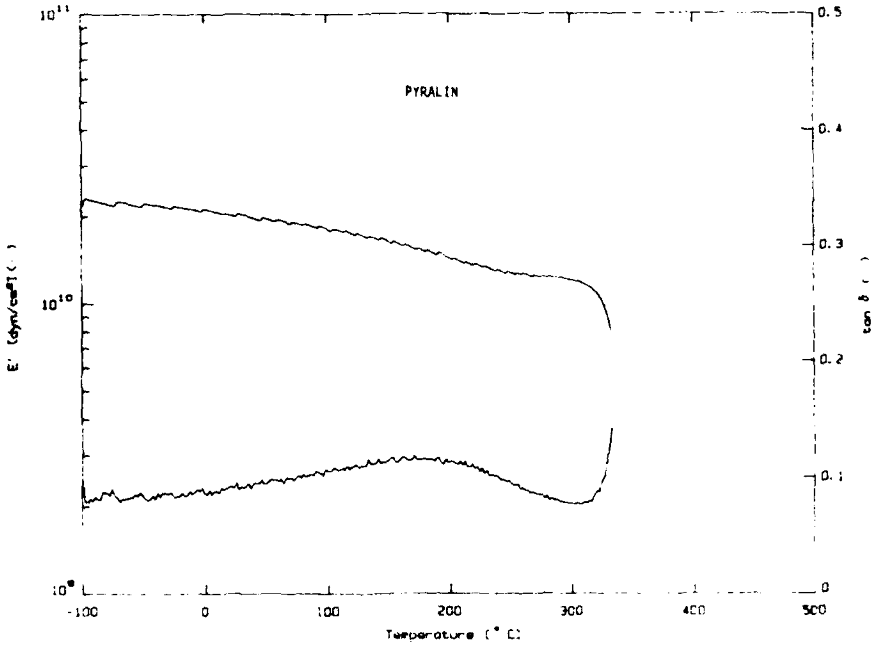

Figure 8. RDA Tracing of Pyralin PI-2566.

No stress cracking or apparent failures of any kind were visually observed for the exposed Kapton and five new polymer candidates and each material was judged to have passed this critical cryogenic temperature exposure test. This result, combined with the isothermal aging results discussed in Section 2.4, is interpreted to mean that EYMYD L-30N, IP-200, PYRALIN PI-2566, SIXEF 44 and UPILEX S have potential for superior thermal performance over the very wide temperature range of -269°C to +300°C.

2.4 ISOTHERMAL AGING OF FILM CANDIDATES

Isothermal aging of Kapton and the five new polymer candidates was conducted in air at 300°C to test their high temperature oxidative stability. The samples were aged for 1000 hours to accurately gauge the five polymer candidate's performance against Kapton which had been shown (Reference 7) to degrade at 300°C after several hundred hours. A discussion of the aging methodology and the results obtained are presented below.

Duplicate film samples of Kapton and the five new polymer candidates of dimensions 0.001 inch thick x 1.0 inches wide x 2.0 inches long were cut from larger films, then weighed and measured. The films were placed into individual 100 ml beakers, then placed in an air circulating oven (400 cubic feet/minute flow) at 300°C. The samples were removed from the oven at selected time durations, placed in a dessicator and allowed to cool to RT, then weighed, and replaced in the oven to continue the aging. Weighings on the duplicate samples of each material were made after 24, 48, 96, 144, 192, 264, 306, 528, 672, 768 and 1000 hours of aging. All five new polymer candidates demonstrated a significantly higher weight retention than Kapton. A summary of the duplicate average aging results obtained at each weighing point is presented in Table 6. A curve plotted from the 264, 528, 768 and 1000 hour data points is shown in Figure 9.

As we can see from the data presented in Table 6, all five new polymer candidates were significantly more oxidative stable than Kapton from shortly after initiation to conclusion of the aging test. This performance of the new candidates was expected based upon the >300°C

TABLE 6

RESULTS OF ONE THOUSAND HOUR AGING OF KAPTON AND THE FIVE NEW POLYMER CANDIDATES IN AIR AT 300°C[a]

Lapsed Time Duration at which Samples were Weighed (Hours)	Percent Weight Loss Determined					
	Kapton	EYMYD L-30N	IP-200 PPQ	Pyralin	SIXEF	UPILEX S
24	1.4	0.6	0.8	0.5	0.2	0.8
48	1.4	0.7	0.9[b]	0.5	0.4[b]	0.8
96	1.8	0.8	0.7[b]	0.4[b]	0.3[b]	0.9
144	2.1	0.9	0.8[b]	0.8	0.3	1.0
192	2.9	1.2	1.3[b]	1.0	0.6	1.0
264	3.3	1.2	1.1[b]	1.2	0.6	1.1
360	4.2	1.7	1.3	1.6	0.7	1.3
528	6.0	2.2	1.8	2.6	0.9	1.5
672	7.7	2.7	2.2	3.2	1.1	1.8
768	8.8	3.1	2.7	3.7	1.3	1.8
1000	13.0	4.1	4.0	5.9	1.9	1.8

---

a) Percent weight loss measured and reported as an average of two candidates.

b) Attributed to minor humidity weight gain during weighing operation.

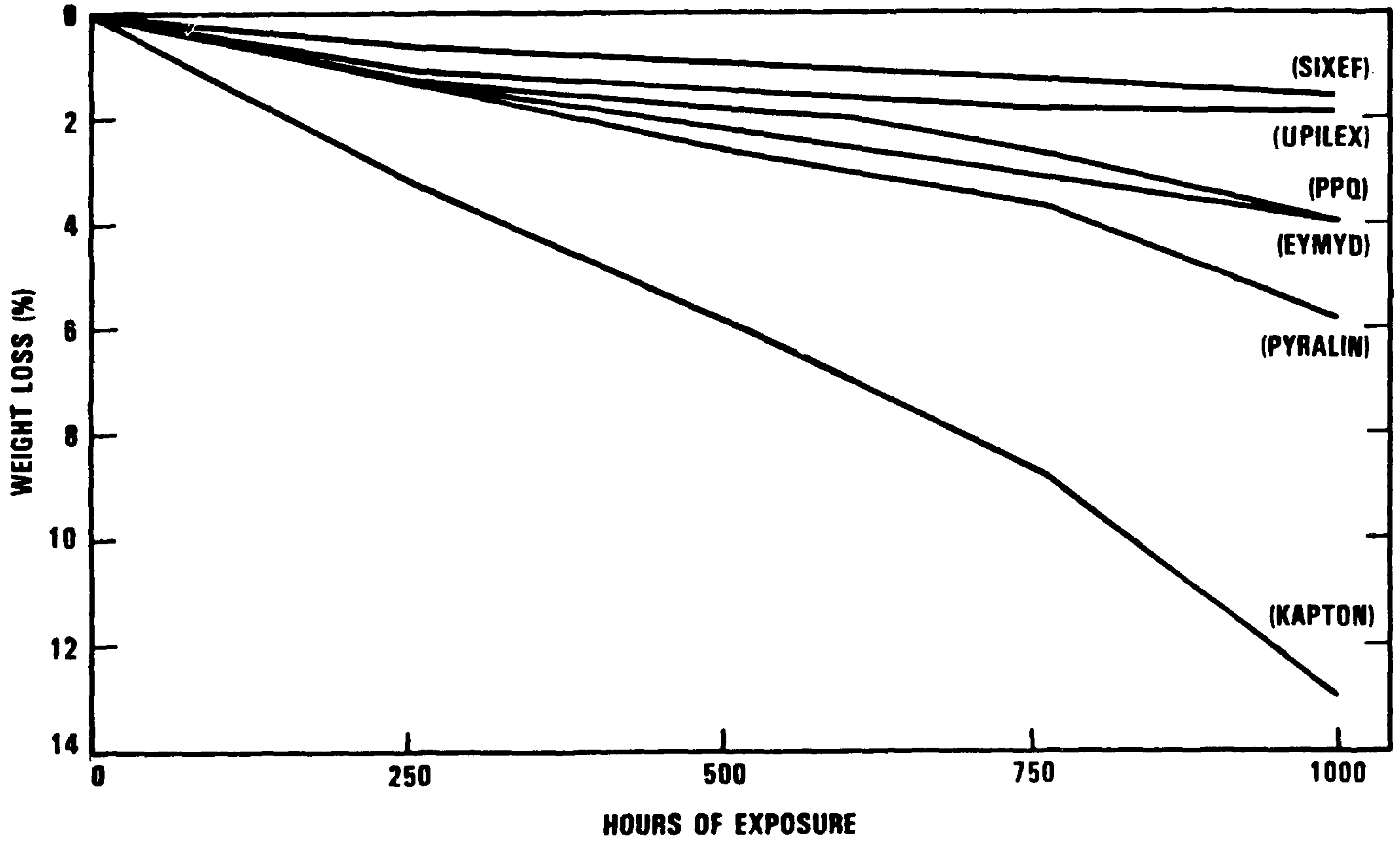

Figure 9. Plot of Isothermal Aging in Air at 300^{o}C for the Five Polymeric Film Candidates and the Kapton Control.

Differential Scanning Calorimetry (DSC) and Rheometrics Dynamic Analysis (RDA) transition data described in Section 2.2. At the conclusion of the aging test, only the Kapton and PYRALIN samples had begun to significantly embrittle. No significant dimensional change in the samples could be detected at the conclusion of the test.

2.5 INITIAL ELECTRICAL PROPERTY TESTING

A key Task 1 property screening test on the Kapton control and the five new polymer candidates was accomplished by conducting dielectric constant, dissipation factor and breakdown voltage measurements. The promising initial electrical properties obtained on the new polymer candidates at temperatures up to 300^{o}C are discussed below.

2.5.1 Dielectric Constant and Dissipation Factor

The dielectric constant and dissipation factor for Kapton and the five new polymer candidates were determined at 24^{o}C and 300^{o}C at a 1000 Hz frequency using method ASTM D-150 on 0.001 inch thick samples. These initial tests were conducted at Pacific Testing Laboratory, Sylmar, CA under the direction of a representative from Lawrence Technology. The promising initial electrical property test results, an average of duplicate data point for most samples, are provided in Table 7.

As can be seen from the dielectric constant and dissipation factor results obtained at 24^{o}C and 300^{o}C, all of the five new polymer candidates possessed promising properties indicative of superior insulation capacitance performance at temperatures up to 300^{o}C, minimum. In particular, the dissipation factor for each new candidate at 300^{o}C did not give evidence of a very significant increase as was measured for Kapton (these results correlate with those reported in the DuPont literature) at this temperature. These results correlate well with additional capacitance measurements performed in Tasks 2 and 3 and reported in Sections 3 and 4, respectively. Painted silver electrodes

TABLE 7

SUMMARY OF INITIAL ELECTRICAL PROPERTY TESTING[a]

	ELECTRICAL PROPERTIES				
	DIELECTRIC CONSTANT		DISSIPATION FACTOR		BREAKDOWN VOLTAGE
POLYMERIC FILM SAMPLES	24°C (1000 Hz)	300°C (1000 Hz)	24°C (1000 Hz)	300°C (1000 Hz)	24°C (60 Hz) (V/mil)
KAPTON	3.4 (3.5)[b]	2.8 (2.9)[b]	0.0020 (0.0025)[b]	0.0150	6800 (6700)[b]
EYMYD L-30N	3.2 (2.9)[b]	2.4	0.0020	0.0050	5700
IP-200 PPQ	2.9	2.3	0.0019	0.0040	5200
PYRALIN	2.9	2.6	0.0023	0.0065	5400
SIXEF 44	2.7 (2.6)[b]	2.4	0.0028	0.0060	5100
UPILEX S	3.3 (3.5)[b]	2.9	0.0049	0.0060	5700

a) Performed by Methods ASTM D-150 (capacitance) and D-149 (breakdown).

b) Data reported in vendor literature.

were used for the Task 1 study had a tendency to quickly oxidize at 300°C. This potential problem was resolved by switching to sputtered gold electrodes for the Tasks 2 and 3 work in further testing at Lawrence Technology.

2.5.2 Breakdown Voltage

The breakdown voltage for Kapton and the five new polymer candidates was determined at 24°C and 60 Hz ac. The tests were conducted at Lawrence Technology using method ASTM D-149. The tests results are described below.

The breakdown voltage values (V/mil) determined on Kapton and the five new polymer candidates are also summarized in Table 7. Although the polymer candidate values were below Kapton, TRW believes that the values are respectable and indicative of superior insulation performance when coupled with the capacitance results shown in Table 7. The breakdown voltages obtained for selected new polymer candidates increased as development and optimization work on selected candidates were conducted in Tasks 2 and 3, respectively.

2.6 FLUID IMMERSION TESTING

Film samples of Kapton and the five new polymer candidates were also exposed in two common cleaning solvents. Details of the individual exposure of all film materials in both methylethylketone (MEK) and 1,1,2-trichloroethane (Trichlor) are presented below.

2.6.1 Immersion in Methylethylketone (MEK)

Film samples of dimensions 0.001 inch thick x 1.0 inch wide x 3.0 inches long of Kapton and the five new polymer candidates were subjected to exposure in refluxing MEK (80°C) for 1 week (168 hours). The film samples were fitted with a clip at each end. One clip was attached to a circular metal ring at the top of a 1 liter resin kettle. The samples were collectively placed in the resin kettle so that approximately one-half of each sample was immersed in the fluid. The kettle was placed in a heating mantle and the MEK was refluxed for 168 hours. The test results are described below.

During the first day of the MEK exposure test, it was observed that the fluid was having a significant effect on both the SIXEF 44 and PYRALIN candidates. The SIXEF 44 sample completely dissolved and the PYRALIN sample partially dissolved during the 168 hour exposure period at 80^{o}C. Examination of the other exposed films at the conclusion of the test indicated no visual effect of the MEK solvent on Kapton, EYMYD L-30N, IP-200 PPQ and UPILEX S.

The dissolving of SIXEF 44 and PYRALIN in the MEK fluid exposure test was a key test factor leading to the recommendation that these polymeric film candidates not be considered for further study in Task 2 of the program. (See Section 2.7.)

2.6.2 Immersion in 1,1,2-Trichloroethane (Trichlor)

Film samples of Kapton and the five new polymer candidates were also exposed in refluxing Trichlor (75^{o}C), another common cleaning solvent, for 1 week (168 hours). This exposure test is described below.

Film samples of Kapton and the five new polymer candidates were wrapped onto individual 0.5 inch OD copper tubes. The wrapped film dimensions and configuration were identical to those described for the liquid helium immersion tests in Section 2.3.

The Kapton control and the five new polymer candidates, wrapped on their individual copper mandrils, were placed in a 1 liter resin kettle containing Trichlor fluid. The kettle was placed in a heating mantle, the Trichlor heated to reflux (75^{o}C) and the samples were collectively exposed, fully immersed, for 1 week (168 hours), except for the SIXEF 44. (See below.)

During the first day of the trichlor fluid exposure, it was observed that the SIXEF 44 sample had begun to dissolve in the fluid. The SIXEF 44 sample was removed at that time, then the exposure of the remaining film materials was continued for the remainder of the 168 hour exposure period. The Kapton control and the other four new polymer candidates did not apparently suffer any degradation or attack during the 168 hour exposure period at 75^{0}C in Trichlor.

The failure of SIXEF 44 polymeric film to resist attack by another common cleaning solvent, Trichlor, reinforced TRW's recommendation that this material should be eliminated from further program evaluation. (See also Section 2.7.)

2.7 PRELIMINARY SELECTION OF CANDIDATES FOR TASK 2 SUMMARY

Based upon their very promising combination of thermal analysis, isothermal aging, liquid helium exposure, fluid immersion and electrical property data performance versus the Kapton control, EYMYD L-30N, IP-200 PPQ and UPILEX S were recommended and approved as the polymeric dielectric film candidates for further development and evaluation in Task 2. The failure of SIXEF 44 and PYRALIN to resist a common cleaning solvent such as methylethylketone (MEK see Section 2.6.1) was the deciding factor in the dropping of these polymers from consideration for further evaluation.

2.8 DOCUMENTATION OF TEST PLAN FOR TASKS 2, 3 AND 4

In parallel with the experimental work described above in Sections 2.1 through 2.7, TRW prepared a Test Plan for conducting the technical work in Tasks 2, 3 and 4 to complete the program. The major elements of this Test Plan were summarized in the Introduction as Sections 1.2, 1.3 and 1.4 for Tasks 2, 3 and 4, respectively.

This Test Plan and the recommendation of EYMYD L-30N, IP-200 PPQ and UPILEX S polymer candidates for further study were submitted to the USAF Program Manager and approved prior to initiation of Task 2.

3. TASK 2 EXPERIMENTATION

This section describes the work performed in Task 2 - Development and Detailed Testing. The experimentation described herein on the three promising polymeric candidates, EYMYD L-30N, IP-200 PPQ and UPILEX S, plus the Kapton control, is as follows:

- Postcure study on EYMYD L-30N and IP-200 PPQ,
- Isothermal aging in vacuum at 300°C,
- Humidity aging at 90°C/100 percent RH,
- Ultraviolet radiation aging at 25°C and 365 nm wavelength,
- Basic solution exposure at 93°C and pH 10,
- Exposure in methylethylketone polar solvent at 80°C and
- Electrical property testing at 25°C and 300°C.

Each of the experimental areas listed above is separately described below.

3.1 POSTCURE STUDIES

The film samples of EYMYD L-30N and IP-200 PPQ, prepared as discussed in 2.1, were tested for 25°C tensile properties after one, two, four and eight hour postcure cycles at 371°C (700°F) in nitrogen. The 1 hour postcure was employed for all initial film sample preparation in Task 1. The additional postcure durations were investigated to determine if the Tg of the polymeric film candidates could be increased without significant embrittlement or loss of tensile elongation. The tensile testing and Tg results are presented and discussed below.

3.1.1 Film Mechanical Property Test Results

The tensile properties of EYMYD L-30N and IP-200 PPQ, determined at 25°C, after the increased postcure durations given above, are presented in Table 8. As can be seen from the data in Table 8, both polymeric film

TABLE 8

ROOM TEMPERATURE TENSILE PROPERTIES OF EYMYD L-30N AND IP-200 PPQ AS A FUNCTION OF POSTCURE DURATION IN NITROGEN AT 371°C (700°F)a)

POLYMERIC FILM SAMPLE	POSTCURE DURATION AT 371°C IN NITROGEN	RT TENSILE PROPERTIES b)		
		STRENGTH (PSI)	ELONGATION AT BREAK (PERCENT)	MODULUS (KSI)
EYMYD L-30N	1	9.4	6.2	246
	2	7.1	4.7	245
	4	7.3	3.7	276
	8	7.9	3.6	324
IP-200 PPQ	1	12.3	5.6	392
	2	11.9	4.5	397
	4	11.3	4.0	401
	8	11.6	3.8	430

a) Determined on an Instron Tester Model 1132 equipped with a 1000-lb load cell.

b) Average of minimum of duplicate breaks on 1.0 inch x 4.0 inch x 0.001 inch samples.

candidates followed an expected trend to "stiffen" when subjected to increasingly longer postcure exposure at 371°C. This "stiffening" is evidenced by a decrease in elongation to break and an increase in modulus. Both polymeric candidates demonstrated a decrease in tensile elongation to what is felt to be an unacceptable level of $\leq$4.0 percent after 4 hours of postcure. In comparison, RDA testing (see Section 3.1.2) showed that Tg essentially "leveled off" after 2 hours of postcure (i.e., more than 2 hours postcure only embrittles the film samples without any benefit in Tg increase). Because the 2 hour postcure tensile properties were deemed to be acceptable and the Tg values increase in going from a 1 hour to 2 hour postcure (again, see Section 3.1.2), a 2 hour postcure at 371°C in nitrogen was selected and employed for all subsequent curing of EYMYD L-30N and IP-200 PPQ during the remainder of the program.

3.1.2 Rheometrics Dynamic Analysis Testing Results

The glass transition temperature (Tg) of EYMYD L-30N and IP-200 PPQ was determined by Rheometrics Dynamics Analysis (RDA) after the 1, 2, 4 and 8 hours postcure of EYMYD L-30N and IP-200 PPQ in nitrogen at 371°C. The RDA method employed Tan Delta measurement by the identical technique employed successfully in Task 1. (See Section 2.2.3.) The RDA results are presented and discussed below.

The Tan Delta Tg values determined on EYMYD L-30N and IP-200 PPQ as a function of postcure duration are presented in Table 9. As we can see from the Tg results in Table 9, an increase in postcure duration from 1 to 2 hours does effect the desired increase in Tg by 10°C for EYMYD L-30N and 20°C for IP-200 PPQ. Further postcure has no effect in elevating the Tg of IP-200 PPQ and a further increase in the Tg of EYMYD L-30N does not occur until greater than 4 hours. Because the objective of the postcure study was to increase Tg without an unacceptable decrease in the tensile elongation to break (see Section 3.1.1), TRW interpreted the combined tensile property/Tg results to show that a 2 hour postcure at 371°C in nitrogen is the most satisfactory treatment condition and this film processing temperature was employed henceforth in the program.

TABLE 9

RHEOMETRICS DYNAMIC ANALYSIS OF EYMYD L-30N AND IP-200 GLASS TRANSITION TEMPERATURE AS A FUNCTION OF POSTCURE DURATION AT 371°C (700°C)a)

POLYMERIC FILM SAMPLE	POSTCURE DURATION AT 700°F IN NITROGEN	TAN △ GLASS TRANSITION TEMPERATURE (°C)
EYMYD L-30N	1	350
	2	360
	4	360
	8	370
IP-200 PPQ	1	350
	2	370
	4	370
	8	370

a) Determined on 0.001 inch thick films in a circulating air environment from -100°C to +500°C under a 60 Hz cycling load of 100 g using a 5°C/min heat-up rate employing a Rheometrics Model 700 instrument.

3.2 ISOTHERMAL AGING IN VACUUM 300°C

As was reported and discussed in Section 2.4, all polymeric film candidates and the Kapton control were isothermally aged in air at 300°C. All of the polymeric film candidates were determined to be significantly more oxidatively stable than Kapton in the air aging test. Because exposure in vacuum presents a realistic exposure condition for films in space environments, the most promising polymeric film candidates and the Kapton control were isothermally aged in vacuum at 300°C. The results of this test is described below.

Duplicate samples of EYMYD L-30N, IP-200 PPQ, UPILEX S and the Kapton control were isothermally aged for 504 hours in a vacuum oven at 300°C and a reduced pressure of 1 Torr. The weight loss results from this vacuum exposure are presented in Table 10 along with those in air, given in parentheses, for approximately the same duration of air exposure.

As we can see from the data presented in Table 10, exposure in vacuum at 300°C presents less of a degrading environment than exposure in air at 300°C. The most significant improvement in resistance to weight loss in vacuum versus air was determined for Kapton, with lesser weight losses observed for the three polymeric film candidate materials. The 300°C aging in vacuum test results were interpreted to mean that this environment presents no unexpected or severe degrading effect on the EYMYD L-30N, IP-200 PPQ and UPILEX S polymeric film candidates.

3.3 HUMIDITY AGING AT 90°C/100 PERCENT RELATIVE HUMIDITY (RH)

A very critical environmental exposure test conducted in this program was assessment of the effect of combined high temperature (i.e., 90°C) and high humidity (i.e., 100 percent RH represent the "worst case" which the film materials may encounter in a terrestial environment) on the EYMYD L-30N, IP-200 PPQ and UPILEX S polymeric film candidates. The criticality of this test focuses on the fact that Kapton moisture sensitivity is

TABLE 10

INITIAL FILM RESULTS ISOTHERMAL AGING IN VACUUM AT 300°C a),b)

POLYMERIC FILM SAMPLE	WEIGHT LOSS AFTER INDICATED DURATION (PERCENT) 233 HOURS	504 HOURS
KAPTON (CONTROL)	1.6 (3.0) c)	1.7 (6.0) c)
EYMYD L-30N	1.1 (1.7)	1.2 (2.2)
IP-200 PPQ	0.8 (1.1)	1.6 (1.8)
UPILEX S	1.0 (1.1)	1.0 (1.5)

a) Samples aged at ~1 Torr; Sample dimensions 1.0 inch x 4.0 inch x 0.001 inch.

b) Average of two samples.

c) Weight loss percent in air at approximately the same exposure durations. (See Table 6.)

known to be an "Achilles heel" of this material (Reference 1). The moisture sensitivity of Kapton casts some dispersion on the general humidity resistance of polyimides as a generic polymer family. Very significantly, all the polymeric film candidates passed this critical environment exposure test, whereas Kapton, as expected, completely failed. This important humidity testing is discussed below.

The humidity aging test results obtained after 1222 hours exposure at $90^{o}C$/100 percent RH on EYMYD L-30N, IP-200 PPQ and UPILEX S, plus the Kapton control, are presented in Table 11. As expected, the Kapton film material became very tacky on the surface between the 324 hour and 501 hour exposure periods and was unsuitable for weight loss measurements and further testing. Conversely, the three polymeric film candidates demonstrated very little or no weight loss after the entire exposure period and remained very "tough" on flexing and bending and possessed no tackiness on the surface. This very significant resistance to long-term, very high humidity exposure demonstrated by EYMYD L-30N, IP-200 PPQ and UPILEX S was not totally surprising due to their much lower reported equilibrium moisture regain (less than 2 percent by weight) versus 2.9 percent by weight regain reported for Kapton. (See Table 2.)

These humidity test results, combined with the numerous other tests conducted during this program and reported herein, very strongly support TRW's conclusion that truly outstanding dielectric film candidate alternatives to Kapton do exist and are worthy of optimization and qualification for advanced spacecraft (and aircraft) dielectric insulation applications.

3.4 ULTRAVIOLET RADIATION EXPOSURE

The ability of the three polymeric film candidates to withstand the effects of ultraviolet radiation, a very important property dictating

TABLE 11

FILM TEST RESULTS FROM
ISOTHERMAL AGING
IN 90°C/100 PERCENT RH ENVIRONMENT[a)]

POLYMERIC FILM SAMPLE	WEIGHT CHANGE AFTER INDICATED HOURS EXPOSURE DURATION (PERCENT)[b)]						
	69	156	324	501	742	886	1222
KAPTON (CONTROL)	-2.1	-2.0	-2.3	c	-	-	-
EYMYD L-30N	-0.1	-0.2	+0.5	+0.7	-0.4	-0.5	-0.4
IP-200 PPQ	-0.1	-0.2	0.0	0.0	+0.2	+0.9	-0.6
UPILEX S	-1.0	-0.9	-0.1	-0.7	-0.7	-0.8	0.0

a) Samples aged in a closed glass container in the presence of distilled water which in turn was placed in an oven at 90°C; sample dimensions 1.0 inch x 4.0 inch x 0.001 inch.

b) Average of three samples.

c) Test terminated because samples developed surface tackiness and weights weights could not be obtained.

stability in space versus Kapton was conducted. This exposure test was conducted at 25°C for 1008 hours employing a 365 nm ultraviolet radiation source. The results obtained in this exposure test are presented below.

Three film samples each of EYMYD L-30N, IP-200 PPQ and UPILEX S, along with the Kapton control, were exposed for 1008 hours in a fume hood employing a 365 nanometer radiation source. The film samples were exposed at a 12.0 inch distance from the source rated at 1600 microwatts/square centimeter at this distance. The weight loss data obtained in the ultraviolet exposure are presented in Table 12. As we can see from the experimental results presented in Table 12, Kapton demonstrated a weight loss greater than double that of all the polymeric film candidates. Further, the weight loss of IP-200 PPQ was at least double that of EYMYD L-30N and UPILEX S. This weight loss of the PPQ may mean that this polymer type is more susceptible to ultraviolet degradation than the polyimide structures possessed by the EYMYD and UPILEX films. Regardless, it is conclusive that all three polymeric film candidates should degrade significantly less than Kapton in space. The weight loss measured for IP-200 PPQ was a deciding factor in the elimination of this candidate from further study at the conclusion of Task 2. (See Section 3.8.)

3.5 BASIC SOLUTION EXPOSURE AT 93°C AND PH 10

Kapton is reported by DuPont to have low resistance to hydrolysis upon exposure to alkaline environments (Reference 1). Because dielectric film materials may be exposed to caustic cleaning solutions, it was deemed important to assess the performance of the three candidate film materials versus Kapton in a basic media. The exposure conditions selected for the test, immersion in a pH 10 sodium hydroxide solution at 93°C for 96 hours, are those reported by DuPont for their evaluation of Kapton (Reference 1).

TABLE 12

FILM RESULTS FROM ISOTHERMAL AGING AT 25°C IN ULTRAVIOLET LIGHT[a)]

POLYMERIC FILM SAMPLE	WEIGHT LOSS AFTER INDICATED HOURS EXPOSURE DURATION (PERCENT)[b]	
	500	1008
KAPTON	5.3	6.7
EYMYD L-30N	1.5	1.4
IP-200 PPQ	2.7	2.9
UPILEX S	0.4	0.5

a) Samples aged in a positively vented fume hood at 25°C; sample dimensions 1.0 inch x 4.0 inch x 0.001 inch.

b) Average of three samples.

The pH 10 basic solution immersion results obtained for EYMYD L-30N, IP-200 PPQ and UPILEX S versus the Kapton control are presented in Table 13. As we can see from the results presented in Table 13, the EYMYD L-30N and UPILEX S were determined to be approximately twice as stable as Kapton in the basic solution as evidenced by one-half or less weight loss. Conversely, the IP-200 PPQ gave a weight loss that was greater than Kapton and approximately three times that shown by EYMYD and UPILEX. This higher than expected degradation of IP-200 PPQ was another deciding factor in eliminating this candidate from further study in the program. (See Section 3.8.)

A significant technical study performed by NASA Langley Research Center was released after TRW completed the work described above (Reference 8). It was conclusively demonstrated in the NASA work that UPILEX S is indeed significantly more stable than Kapton in several basic solution media. In fact, most high performance polyimides performed astonishingly better than Kapton in their resistance to caustic or basic solution exposure. EYMYD L-30N was not included in the NASA study.

3.6 EXPOSURE IN METHYLETHYLKETONE SOLVENT AT 80°C

The effect of 1 week exposure in 80°C refluxing methylethylketone (MEK) solvent on all polymeric film candidates and Kapton was conducted in Task 1. (See Section 2.6.1.) Because the MEK dissolved two candidate polymers, PYRALIN PI-2566 and SIXEF 44 polyimides, it was deemed prudent to subject the remaining three polymeric film candidates and the Kapton control for a longer time exposure to MEK during the Task 2 studies. The results of this MEK exposure testing is described below.

Film samples of EYMYD L-30N, IP-200 PPQ and UPILEX S, along with the Kapton control, were exposed in refluxing MEK polar solvent at 80°C for a period of 500 hours (versus the 168 hour exposure period employed in Task 1). (See Section 2.6.) The film samples were one-half immersed in

TABLE 13

FILM TEST RESULTS FROM IMMERSION IN 93°C/pH 10 BASIC SOLUTION[a)]

POLYMERIC FILM SAMPLE	WEIGHT LOSS AFTER 96 HOUR EXPOSURE DURATION (PERCENT)[b]
KAPTON (CONTROL)	2.57
EYMYD^R L-30N	1.32
IP-200 PPQ	3.65
UPILEX^R S	1.15

a) Samples aged in immersed state in a pH 10 sodium hydroxide solution maintained at 93°C (200°F); sample dimensions 1.0 inch x 4.0 inch x 0.001 inch.

b) Average of two samples.

the MEK fluid and the remainder exposed to the refluxing fluid vapors. The results of the MEK exposure of the film samples are presented in terms of percent weight gain or loss in Table 14. As we can see from the results presented in Table 14, Kapton and IP-200 PPQ gained weight during the MEK exposure, probably due to solvent penetration into the film material. Conversely, EYMYD L-30N and UPILEX S experienced a minor weight loss, probably due to solvent removal of absorbed surface moisture. In all cases, the films remained tough and flexible after the MEK exposure conclusively showing that these materials should not be susceptible to degradation in the presence of a polar cleaning solvent.

3.7 ELECTRICAL PROPERTY AND TESTING AT 25°C AND 300°C

Additional capacitance (i.e., dielectric constant and dissipation factor) electrical property determinations were made at 25°C and 300°C at 1000 Hz during Task 2. In the Task 2 property measurements, sputtered gold electrodes were employed versus the painted silver electrodes employed to perform the electrical property tests in Task 1. (See Table 7 for the Task 1 results.) Also the Task 2 testing was performed in a minimum of quintuplicate data points versus duplicates performed in Task 1. Thus, the capacitance results obtained in Task 2 are thought to be more truly representative of those to be expected for the three polymeric film candidates, particularly at 300°C. Kapton was again employed as the control material. The Task 2 capacitance property measurements are described below.

The dielectric constant and dissipation factor measurements were determined on EYMYD L-30N, IP-200 PPQ and UPILEX S, along with the Kapton control, at 25°C and 300°C at a frequency of 1000 Hz. The Task 2 test results are presented in Table 15. The Task 1 test results from Table 7 are shown in parentheses next to the Task 2 values.

As we can see from the capacitance data presented in Table 15, the dielectric properties of the EYMYD L-30N, IP-200 PPQ and UPILEX S polymeric film candidates are excellent at both 25°C and 300°C and may be considered to generally exceed program goals of 3.5 dielectric

TABLE 14

FILM TEST RESULTS FROM REFLUXING IN METHYLETHYLKETONE[a)]

POLYMERIC FILM SAMPLE	WEIGHT GAIN OR LOSS AFTER 500 HOUR EXPOSURE DURATION (PERCENT)
KAPTON (CONTROL)	+5.8
EYMYD L-30N	-2.9
IP-200 PPQ	+6.1
UPILEX S	-1.7

a) Samples refluxed in MEK at 80°C (176°F); sample dimensions 1.0 inch x 4.0 inch x 0.001 inch.

TABLE 15

TASK 2 ELECTRICAL PROPERTY TEST RESULTS[a]

POLYMERIC FILM CANDIDATE	ELECTRICAL PROPERTIES			
	DIELECTRIC CONSTANT (1000 Hz)[b]		DISSIPATION FACTOR (1000 Hz)[b]	
	25°C	300°C	25°C	300°C
KAPTON (CONTROL)	3.1 (3.4)	2.8 (2.8)	0.001 (0.002)	0.063 (0.015)
EYMYD L-30N	3.1 (3.2)	2.9 (2.4)	0.001 (0.002)	0.004 (0.005)
IP-200 PPQ	3.0 (2.9)	2.7 (2.3)	0.001 (0.002)	0.002 (0.004)
UPILEX	3.3 (3.3)	3.3 (2.9)	0.002 (0.005)	0.003 (0.006)

a) Average of triplicate tests determined on ~0.001-inch-thick film samples.

b) ASTM D-150.

constant and 0.005 dissipation factor at 300°C. Again, Kapton experienced a very large dielectric loss when measured at 300°C (0.063) versus 25°C (0.001). These capacitance values obtained on uncoated films are compared with silicon dioxide ceramic coated film values in the Task 3 discussion. (See Section 4.)

3.8 SELECTION OF TWO MOST PROMISING POLYMERIC FILM CANDIDATES FOR TASK STUDIES

Based upon the key experimental results obtained in Tasks 1 and 2 of the program, TRW selected eight property tests thought to be most critical to judge the performance of a truly superior polymeric candidate for future dielectric film applications in spacecraft (and potential aircraft) applications. These eight property tests are given in Table 16 along with a numerical grade for each of the EYMYD L-30N, IP-200 PPQ and UPILEX S candidates. The numerical grade was assigned wherein 1 = best, 2 = second best and 3 = worst in comparison of property values obtained on the three film candidates. The (+), (0) or (-) value next to the numerical grade refers to comparison with the value obtained for Kapton. Adding the numerical grades for each polymeric film candidate, the lowest additive score being best, clearly showed that EYMYD L-30N and UPILEX S were superior to IP-200 PPQ. Therefore the latter candidate was dropped from further study and EYMYD L-30N and UPILEX S were selected and approved for further evaluation in Task 3 as described in Section 4.

TABLE 16

RANKING OF EYMYD L-30N, IP-200 PPQ AND UPILEX S BASED UPON TASKS 1 AND 2 TEST RESULTS

Test Results Considered	Relative Performance of Three Candidates versus Each Other (also Each to Kapton Results)[a] EYMYD L-30N	IP-200 PPQ	UPILEX S
1. Breakdown Voltage at RT (Table 7)	1.5 (-)[b]	3 (-)	1.5 (-)[b]
2. Char Yield in Vacuum (from Table 3)	1 (+)	3 (-)	2 (-)
3. Isothermal Aging in Humidity Environment (Table 11)	2 (+)	3 (+)	1 (+)
4. Isothermal Aging in Ultraviolet Light (Table 12)	2 (+)	3 (+)	1 (+)
5. Dissipation Factor at 300°C/1000 Hz (Table 15)	3 (+)	1 (+)	2 (+)
6. Immersion in Hot Base Solution (Table 13)	2 (+)	3 (-)	1 (+)
7. Isothermal Aging in Vacuum at 300°C (Table 10)	3 (+)	1 (+)	2 (+)
8. Isothermal Refluxing in Cleaning Solvent (Table 14)	2 (0)	3 (-)	1 (+)
Total Score	16.5	20.0	11.5

---

a) The designation in parentheses reflects the quantitative relative performance of each candidate compared to Kapton^R using the code of (+) = better, (0) = approximately equivalent and (-) = worse.

b) The 1.5 reflects a tie for the breakdown voltage results.

4. TASK 3 EXPERIMENTATION

This Section describes the work performed in Task 3 - Modification, Optimization and Testing of most Promising Film Candidates. The experimentation described herein on the two most promising polymeric film candidates, EYMYD L-30N and UPILEX S, plus the Kapton Control, is as follows:

- Casting of continuous lengths of EYMYD L-30N film method from precursor polymer varnish,
- Vapor deposition of silicon dioxide ceramic coating on the promising films and Kapton and
- Electrical property testing of uncoated and ceramic coated films, including capacitance, breakdown voltage and dry arc/track determinations.

Each of the experimental areas listed above is separately described below. A section is also included which describes X-ray morphological testing of uncoated and ceramic coated films and the potential effect of crystallinity on the electrical properties measured. Graphics of selected processes, equipment and tests are included where pertinent during the Task 3 discussion.

4.1 CONTINUOUS CASTING OF EYMYD L-30N FILM MATERIAL

A key requirement at this stage in the program was the availability of EYMYD L-30N and UPILEX S in sufficient quantity to complete Task 3 and, depending on which polymeric film candidate was selected as the single most promising material, be available in a minimum of hundreds of feet of continuous length for wire wrapping and testing in Task 4. Continuous film was not necessary for evaluation work in Tasks 1 and 2, because small samples (up to 12.0 inch x 12.0 inch x 0.001 inch) laboratory cast films of EYMYD L-30N and the other candidates evaluated or purchased (UPILEX S) were sufficient to complete all the evaluation work described in Sections 2 and 3. The potential availability of UPILEX S posed no problem, because large quantities of up to 60 inch width x 1000s of feet length of 0.001 inch thick film was readily available from ICI/Ube. The challenge in Task 3 was to demonstrate a feasible process to produce EYMYD L-30N in continuous film lengths, because only the poly(amic-acid) polymer precursor to the polyimide, not film, was available from Ethyl Corporation as a solution varnish in N-methylpyrrolidone. This varnish material was used throughout Tasks 1 and 2 by TRW to laboratory cast all EYMYD L-30N samples for evaluation and testing. (See Section 2.1 for a description of small film sample casting and curing.) Attention therefore was focused on selection of a casting process and an appropriate vendor to produce continuous (i.e., several hundred feet lengths) of EYMYD L-30N. The methodology followed to secure the desired continuous length EYMYD film is described in the following subsections.

4.1.1 Selection of a Continuous Film Production Process and Manufacturer

Commercially available high performance films such as DuPont's Kapton and Ube's UPILEX S are produced by proprietary solution casting processes, because the polyimide polymers (this also includes EYMYD L-30N polymer) possess too high a melting point (or they do not truly melt) to allow practical melt extrusion of high quality film. A proprietary aqueous dispersion powder technology is used by selected sources to prepare very high melting thermoplastic materials such as the Teflon^R family of fluoropolymers. However, the latter method must depend at some stage in very high temperature melt fusion of finely divided polymer powders. This powder fusion process was assessed to be highly risky to produce high quality polyimide films for reliable dielectric insulation applications. Consequently, it was decided to use a solution casting process to produce continuous lengths of EYMYD L-30N film. Prior to the initiation of Task 3, TRW and Ethyl Corporation (the commercial source of EYMYD L-30N varnish) did an industry survey of potential film casting sources that were both capable of and willing to attempt a small-scale continuous solution process casting of the film. The survey identified Rexham Corporation, Industrial Products Division, Matthews, NC, as the only company willing to attempt the solution process casting of EYMYD L-30N on a scale (~20 lbs), turn-around-time and cost commensurate with that which fit within the scope and schedule of Task 3. The film casting performed by Rexham is described and discussed in Section 4.1.3. Procurement and qualification of the EYMYD L-30N varnish for the film casting is discussed below.

4.1.2 Procurement of EYMYD L-30N Poly(amic-acid) Varnish for Solution Film Casting

A quantity of 10 gallons of EYMYD L-30N poly(amic-acid) precursor varnish to the polymeric polyimide film material was procured from Ethyl Corporation. The solution varnish contained approximately 20-pounds of poly(amic-acid) dissolved at a 25 percent by weight solids loading in N-methylpyrollidone (NMP) solvent.

The varnish was assessed for acceptable quality by determining the inherent viscosity of the poly(amic-acid) polymer and electrical properties of laboratory cast polyimide film samples. The inherent viscosity was determined to be 1.6 deciliters/gram (dl/g) at 20°C in NMP which significantly exceeded the minimum level of 1.2 dl/g set by TRW as indicative of superior molecular weight for obtaining high quality cast films. Determination of capacitance and breakdown voltage values on polyimide film prepared from the varnish paralleled those prior values given in Tables 7 and 15 for EYMYD L-30N. The 10 gallon lot of EYMYD L-30N poly(amic-acid) varnish was thus deemed to be of high and acceptable quality. This varnish material was then shipped to Rexham Corporation for continuous film casting as described below.

4.1.3 Continuous Solution Process Casting of EYMYD L-30N Poly(amic-acid) Film

The EYMYD was cast as the polyamic-acid precursor at an 11 percent polymer solids loading by weight in N-methylpyrollidone (NMP) (solvent diluted with NMP from the original 25 percent polymer solids loaded varnish processed from Ethyl Corporation) from a total solution volume of 20 gallons. The film was cast on a modified Faustel slot-die caster operating at throughput rate range of 6 to 20 feet/min. The EYMYD was cast at a 20 inch width on a continuously fed 30 inch width MYLAR A-3000 (0.005 inch thick) film webbing. The cast film was dried in-line by passing through a 30 foot long, ventilated oven equipped with three zones of forced air heating attaining a 140°C (285°F) maximum temperature during the casting run, then wound in a continuous roll employing a polyethylene film to sandwich the dried film to prevent any damage to the exposed side. Several ≥100 foot long samples of the EYMYD film were obtained under various oven drying temperature ranges. A 400 foot continuous length roll was obtained from midrun that met the desired goals of low defect film and a thickness of 0.0009 inch to 0.0011 inch.

Although the continuous film casting run was very successful in producing the desired continuous EYMYD L-30N poly(amic-acid) film, the material obtained in the run at Rexham contained 25 to 30 percent by weight residual NMP solvent. The 400 foot length of apparent high quality film was rerun through the Rexham drying oven at 171°C (340°F), the maximum oven temperature capability at Rexham. This redry run reduced the NMP solvent content to ~15 percent by weight (i.e., approximately one-half the solvent content of the original cast film material). TRW took samples of the redry run and determined the additional time which would be required at 171°C to completely dry the film to zero NMP content. It was established that an additional 15 minutes, minimum, at 171°C was required to product the desired completely dry and imidized film. To obtain this duration of 171°C drying at Rexham, this would have involved a minimum of three additional redry operations at the minimum throughput feed of 6 feet/minute in the 30 foot drying oven. Because the MYLAR webbing was suspect to retain its dimensional stability and integrity for another three drying recycles (some evidence of deterioration was noted after the redry run), attempts to obtain high quality, fully dried polyimide film were terminated. The 400 foot length of high quality film was used as a source to prepare small (i.e., 12 inch x 12 inch) samples by laboratory oven drying/imidization/postcure up to 371°C according to the procedure given in Section 2.1.

Key steps in the continuous film casting run at Rexham Corporation including poly(amic-acid) NMP varnish solution feed container, slot-die coater, film feed into the drying oven and final film wind-up into a roll are depicted in Figures 10 through 13, respectively. Two Fourier Transform Infrared (FTIR) spectra depicting partially dried film containing ~15 percent by weight NMP solvent and near dried/imidized film are depicted in Figures 14 and 15, respectively. Attention is called to the absorption bands in the range of 1685 cm^{-1} to 1255 cm^{-1} in Figure 14 representative of carbon-oxygen contained in NMP solvent and poly(amic-acid) polymer which are essentially absent in Figure 15 giving spectral evidence that small sample oven drying/imidization to the polyimide had occurred.

The initial demonstration of the fact that EYMYD L-30N varnish can be directly cast into continuous film is considered to be a significant accomplishment for the program. It is strongly believed that future use of a webbing material with a higher thermal stability than MYLAR A-3000, coupled with an in-line oven with heaters capable of 260°C (500°F) minimum temperature will facilely overcome the mechanical difficulties encountered during this program to directly produce dry/imidized EYMYD L-30N film. Schedule and fiscal limitations of the program prevented modification of Rexham's equipment or selection of another vendor with higher oven temperature capability to upgrade/improve the initial EYMYD L-30N continuous film casting process study.

4.2 VAPOR DEPOSITION OF SILICON DIOXIDE CERAMIC ON EYMYD L-30N, UPILEX S AND KAPTON FILM SURFACES

A key objective of this program was to determine, and potentially improve, the breakdown voltage and/or the dry arc/track resistance of the polymeric film candidates versus the Kapton baseline control. Also, protection of film surfaces from potential degradation by atomic oxygen species encountered in spacecraft low earth orbit (LEO) was highly desirable. The ceramic coating methodology by which TRW investigated a single approach to accomplish both improved breakdown voltage and arc/track resistance as well as atomic oxygen degradation surface protection is described below.

Figure 10. Photograph of EYMYD L-30N Varnish in Reservoir to Feed Continuous Film Casting Equipment.

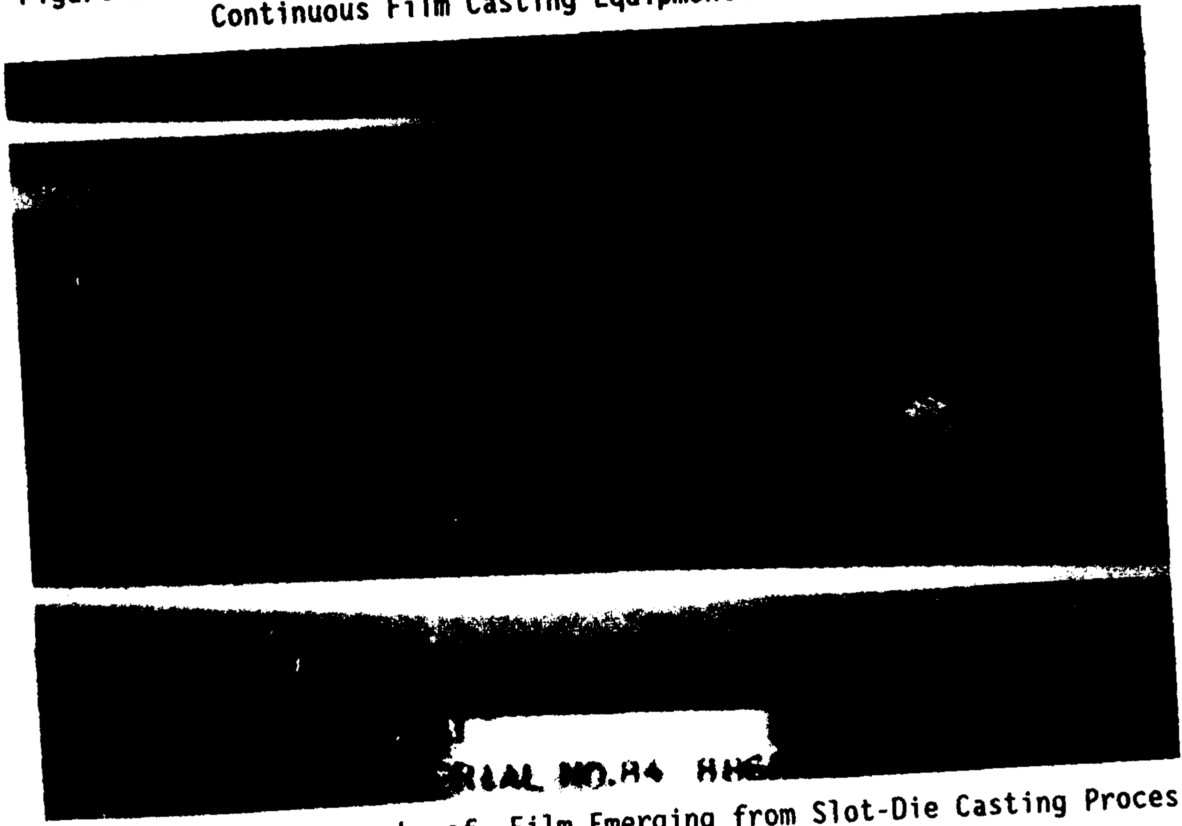

Figure 11. Photograph of Film Emerging from Slot-Die Casting Process Equipment.

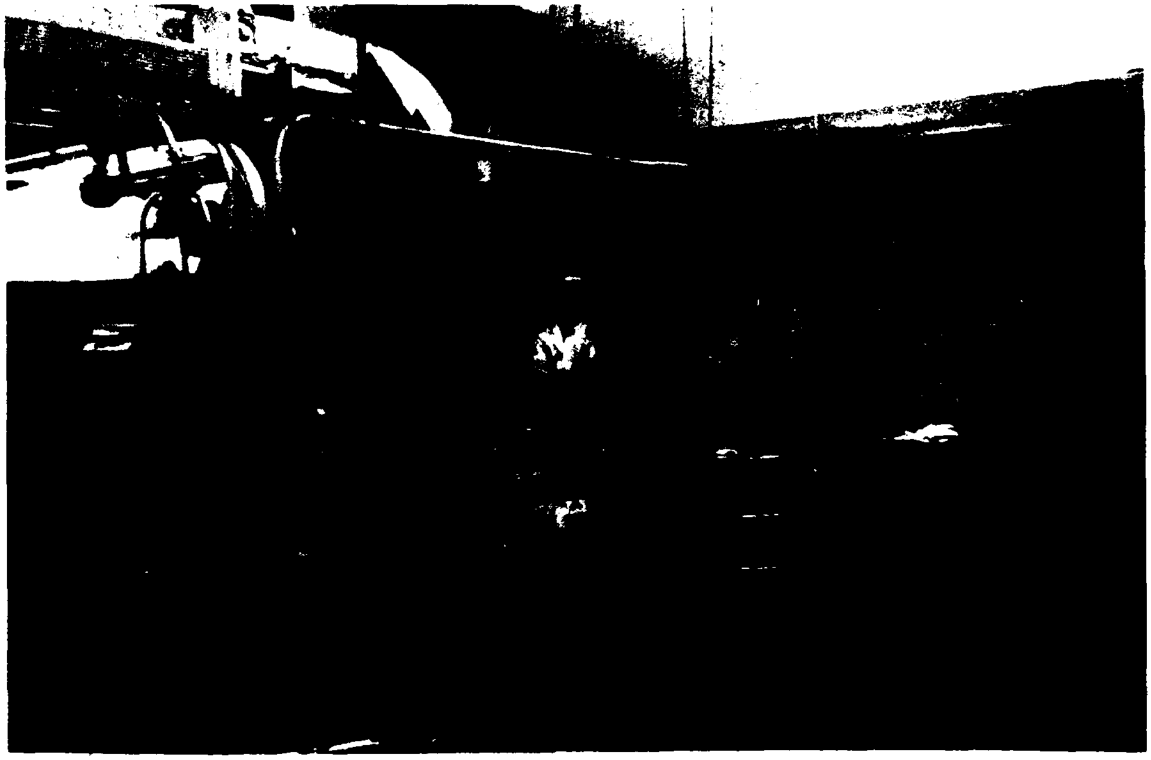

Figure 12. Photograph of Cast Film Entering On-line Drying Oven.

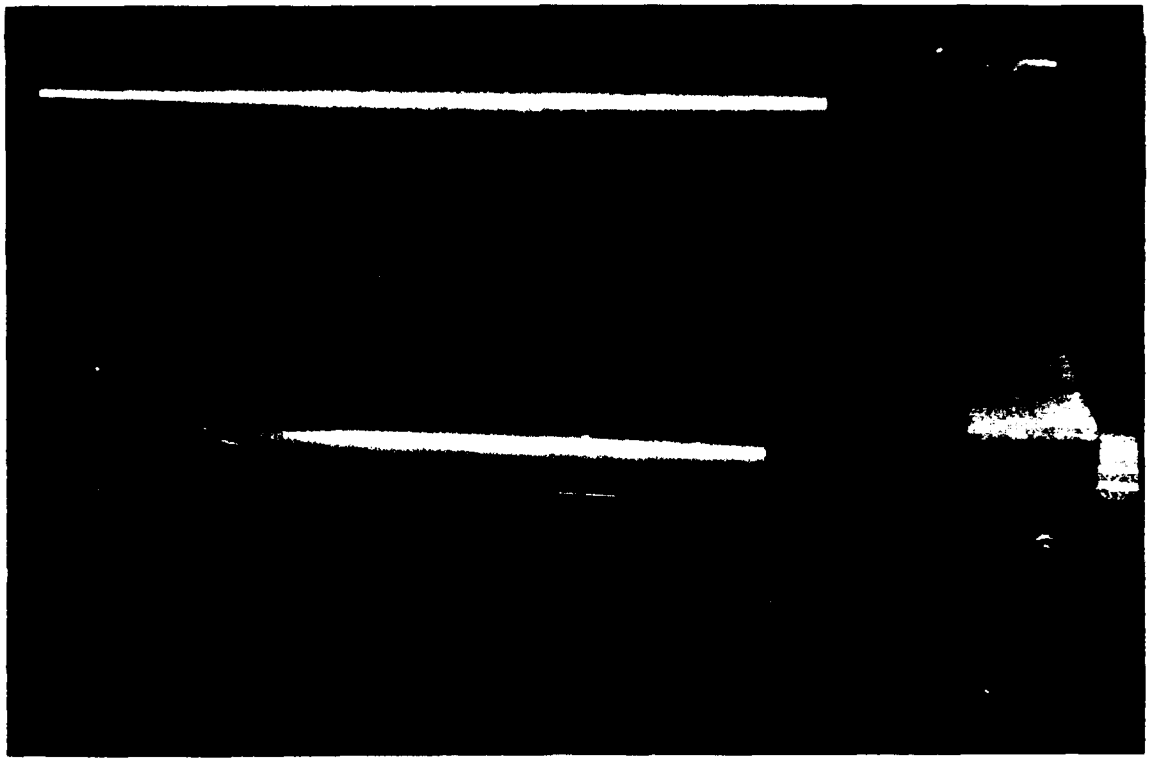

Figure 13. Photograph of Cast Film being Wound into a Roll after Drying.

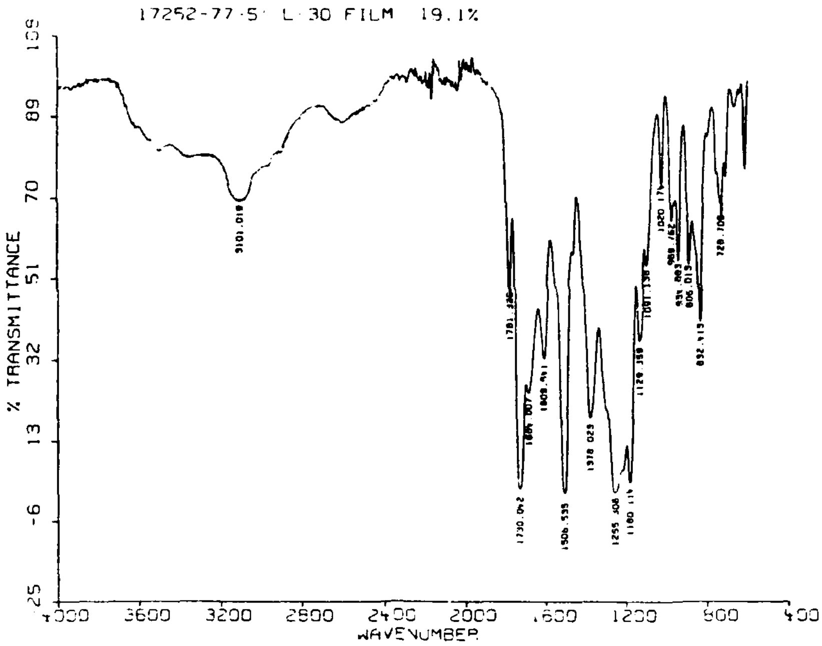

Figure 14. Fourier Transform Infrared Spectrum of EYMYD L-30N Poly(amic-acid) Containing NMP Solvent.

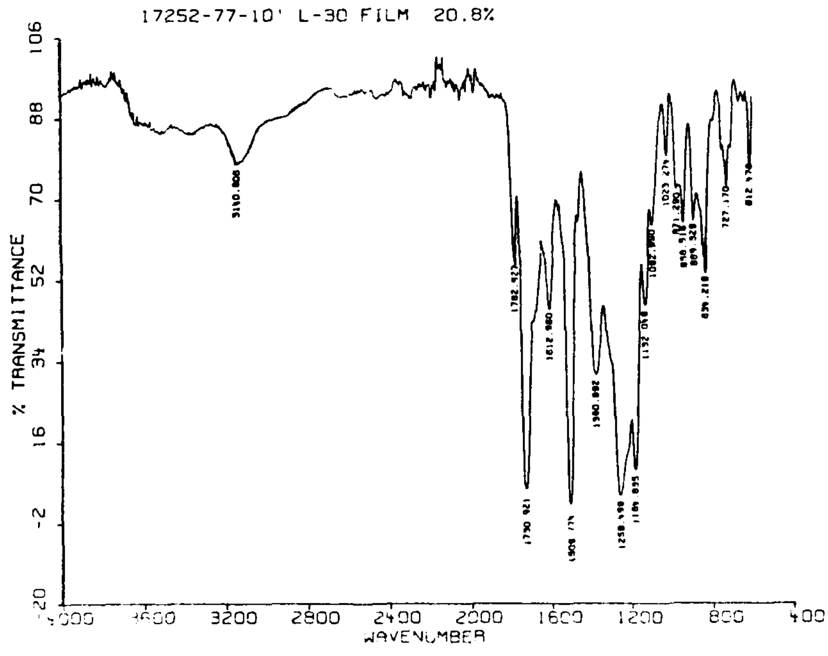

Figure 15. Fourier Transform Infrared Spectrum of EYMYD L-30N Polyimide Essentially Dry of NMP Solvent.

4.2.1 Background on Ceramic Coating Protection and Property Enhancement of Polymer Surfaces

Prior to undertaking this program, TRW had established the attractiveness of employing selective, very thin ceramic coatings to protect and/or enhance the properties of polymeric materials. The functioning of ceramics to protect Kapton film from atomic oxygen attack was being implemented in the mid-1980s (Reference 9). Similar approaches were known by TRW and NASA as a means to effect surface protection of matrix resin composite structures (Reference 10). However, little was known concerning the practical use of ceramic coatings to improve film electrical properties. The latter potential of ceramic coatings was therefore the subject of a key study conducted by TRW on this program as described in the remainder of this section.

4.2.2 Vapor Deposition of Silicon Dioxide Ceramic on EYMYD L-30N, UPILEX S and Kapton Film Surfaces

TRW selected the widely available amorphous silicon dioxide (SiO_2) as the choice for a film surface coating to study its effect on improving breakdown voltage and/or dry arc/track resistance of the EYMYD L-30N and UPILEX polymeric film candidates as well as the Kapton film control material. The choice of SiO_2 as the ceramic material was based upon its known surface protective potential (see Section 4.2.1) and the relative ease by which it can be vapor deposited in controllable thin layers on film material (Reference 9). The experimental work to obtain high quality vapor deposited amorphous SiO_2 ceramic on the dielectric film material candidates and the Kapton film control is described below.

TRW selected Sheldahl Corporation, Northfield, MN, as its vendor to vapor deposit varying thicknesses of amorphous SiO_2 on the dielectric film surfaces. This selection was based upon Sheldahl's proven ability to coat high quality ceramic and other materials on organic film surfaces as a commercial product line (Reference 9). TRW supplied EYMYD L-30N, UPILEX S and Kapton film samples to Sheldahl in surface areas of approximately 120 square inches x 0.001 inch and 0.005 inch thick. Sheldahl employed their proprietary vacuum deposition to coat individual film samples with 2500 angstroms and 5000 angstroms of SiO_2 on both sides. These thickness levels were selected based upon Sheldahl's experience that an ~1000 to 2000 angstrom range thickness represents the minimum level that a reproducible coating could be practically applied and ~5000 angstroms thickness represents a maximum coating level of SiO_2 before "stiffness" and adhesion problems became prevalent.

Sheldahl coated and returned the SiO_2 surface coated film samples to TRW, who, in turn transmitted them to Lawrence Technology to conduct extensive capacitance, breakdown voltage and dry arc/track electrical property tests. The electrical property test results conducted on both uncoated and SiO_2 coated film samples are described in Section 4.3.

4.3. ELECTRICAL PROPERTY TESTING OF UNCOATED AND SILICON DIOXIDE CERAMIC COATED EYMYD L-30N, UPILEX S AND KAPTON FILMS

Detailed electrical property testing was conducted on uncoated and SiO_2 ceramic coated films at Lawrence Technology Division of CAMCO Corporation in Lawrence, KS. Capacitance, breakdown voltage and dry arc/track property measurements are separately described and discussed below.

4.3.1 Capacitance Property Testing

The dielectric constant and dissipation factor at 25°C was determined on 0.001 inch thick samples of uncoated and SiO_2 coated EYMYD L-30N, UPILEX S and Kapton film samples at Lawrence Technology. The test method employed and the experimental results obtained are described below.

All dielectric film samples, uncoated and 5000 angstroms SiO_2 coated (both sides), were sputtered with ~10,000 angstroms (~1 micron) gold electrodes on both sides. The capacitance film samples were 4.0 inch x 4.0 inch squares and the gold electrodes were applied as three to five 1.0 inch diameter circles spaced at least one inch apart on the film surface.

The capacitance measurements were conducted by the ASTM D-150 method at 25^{o}C and 300^{o}C at 400 Hz and 1000 Hz employing a HP Precision LCR Meter, Model 4284A connected with a Blue M static air oven capable of achieving a maximum temperature of 316^{o}C (600^{o}F). A photograph of the test apparatus is presented in Figure 16. The 5000 angstroms SiO_2 coated film thickness was selected for the capacitance measurements, because this level gave the largest improvement in breakdown voltage values (see Section 4.3.2) and was reproducibility receptive to yield apparent high quality sputtered gold electrodes on the ceramic surface.

The capacitance measurement results obtained on the uncoated and SiO_2 coated EYMYD L-30N, UPILEX S and Kapton film materials are presented in Table 17. As we can see from these capacitance data, a trend was observed in that the dielectric constant decreased for EYMYD L-30N and dissipation factor increased for all films measured at both 25^{o}C and 300^{o}C. The loss factor values were higher than these capacitance measurements performed on the uncoated polymeric films at the same temperatures. Sample moisture absorption is probably not the cause for the higher dissipation factor values determined on the SiO_2 coated films, because each sample was preheated to at least 100^{o}C in the oven before either 25^{o}C or 300^{o}C measurements were performed. Rather, TRW believes that the capacitance values obtained are the result of an unknown, deleterious interaction between the gold electrode, ceramic coating and/or the polymeric film substrate, because the dissipation factor (0.001) of bulk silicon dioxide is equal to or lower than the uncoated polymeric film (Reference 11).

These higher capacitance results, if taken alone, would suggest that a SiO_2 coating is detrimental to electrical properties. However, and significantly, the ceramic coating was determined to have a positive effect on increasing breakdown voltage and arc/track resistance as discussed in Sections 4.3.2 and 4.3.3, respectively.

Figure 16. Photograph of Capacitance Test Equipment Employed at Lawrence Technology.

TABLE 17

TASK 3 CAPACITANCE ELECTRICAL PROPERTIES DETERMINED ON 5000 ANGSTROMS SILICON DIOXIDE COATED FILMS[a)]

POLYMERIC FILM MATERIAL	FILM SAMPLE CONFIGURATION	ELECTRICAL PROPERTY RESULTS							
		DIELECTRIC CONSTANT				DISSIPATION FACTOR			
		400 HZ		1000 HZ		400 HZ		1000 HZ	
		25°C	300°C	25°C	300°C	25°C	300°C	25°C	300°C
KAPTON (CONTROL)	UNCOATED	3.1	2.9	3.1	2.8	0.001	0.050	0.001	0.063
	5000A SiO_2 COATED	3.1	3.1	2.7	2.7	0.009	0.027	0.010	0.021
EYMYD	UNCOATED	3.1	2.9	3.1	2.9	0.001	0.004	0.001	0.004
	5000A SiO_2	2.9	2.2	2.9	2.2	0.004	0.011	0.010	0.008
UPILEX S	UNCOATED	3.3	3.2	3.3	3.3	0.002	0.003	0.002	0.003
	5000A SiO_2	3.1	3.0	3.1	3.0	0.012	0.011	0.011	0.010

a) Tests conducted by ASTM D 150 method employing nominal 0.001-inch-thick film samples and the results represent an average of three data points, minimum.

4.3.2 Breakdown Voltage Property Testing

The ac and dc breakdown voltages were determined at 25°C at Lawrence Technology on uncoated, 2500A SiO_2 coated and 5000A SiO_2 coated Kapton (control), EYMYD L-30N and UPILEX S. The measurements were performed according to method ASTM D 149 employing a Hipotronics ac/dc Mipot Tester, Model HD 140. The measurements were performed at 25°C only, because Lawrence Technology's past experience has shown that testing the breakdown voltage of Kapton and similar dielectric insulation materials at higher temperatures is not critical to assess and predict expected performance under severe exposure environments such as downwell oil recovery system applications.

The results from these tests are presented in Table 18. As we can see from the data summarized in Table 18, Kapton and EYMYD L-30N consistently gave higher ac and dc breakdown voltage values than UPILEX S regardless of an uncoated or coated state. The SiO_2 ceramic coating seems to have a positive effect in increasing the ac and dc breakdown of Kapton and EYMYD L-30N. The breakdown voltage values obtained on the uncoated films and given in Table 18 are slightly higher than those determined in Task 1. (See Table 7.) The values obtained on EYMYD L-30N and UPILEX S, although somewhat lower than Kapton, are thought to be the kV/mil range considered superior as dielectric insulation. In general, it is thought that the SiO_2 ceramic coatings do not increase the 25°C breakdown voltage results to a degree that would justify the coatings for this electrical property improvement alone. However, the SiO_2 coating does have a significant effect to improve dry arc/track resistance as discussed in Section 4.3.3.

The damage area due to breakdown of all uncoated and coated samples were determined by optical microscopy. No significant differences were observed in the damage area caused by breakdown on the surfaces of uncoated and coated films. A deposit of carbonaceous char forms around the burned through point of maximum film damage. Representative photographs of uncoated and 5000 angstroms SiO_2 coated UPILEX S are presented as Figures 17 and 18, respectively.

TABLE 18

AC AND DC BREAKDOWN VOLTAGE RESULTS AT RT ON UNCOATED AND SILICON DIOXIDE COATED FILMS

Polymeric Film Candidate	Breakdown Voltage (kV/mil)					
	Uncoated		2500A SiO_2 Coated		5000A SiO_2 Coated	
	AC	DC	AC	DC	AC	DC
KAPTON (Control)	7.7	11.6	7.8	12.5	7.8	12.7
EYMYD L-30N	6.1	12.4	6.4	12.6	6.4	12.9
UPILEX S	5.6	9.5	5.6	9.5	5.6	9.5

a) Tests conducted on nominal 0.001 inch thick film samples according to ASTM D-149 test method; the results reported represent an average of three breakdowns/results, minimum.

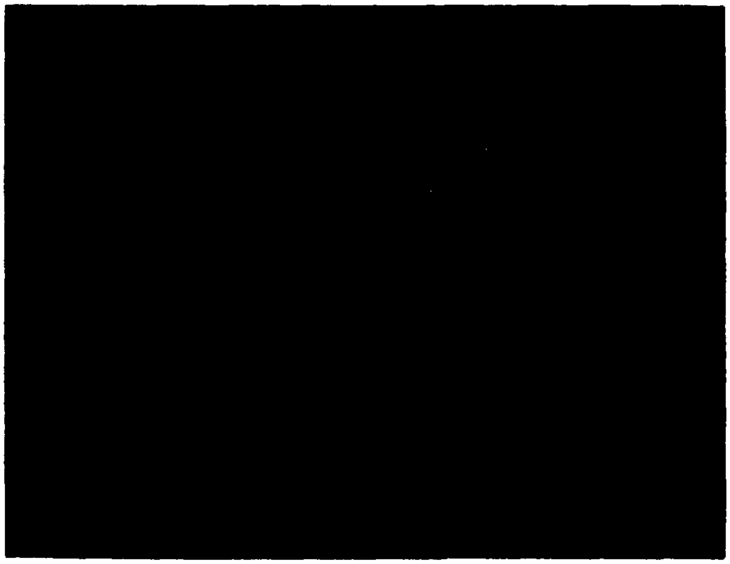

Figure 17. Photograph of Breakdown Damage Area Observed on Uncoated UPILEX S Film (75X Magnification).

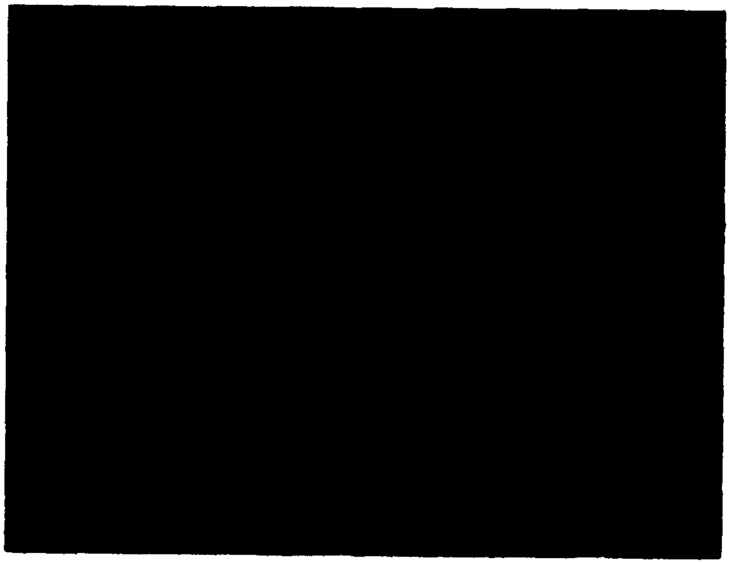

Figure 18. Photograph of Breakdown Damage Area Observed on 5000 Angstroms SiO_2 Coated UPILEX S Film (75X Magnification).

4.3.3 Dry Arc/Track Property Testing

The dry arc/track resistance of uncoated and SiO_2 ceramic coated EYMYD L-30N, UPILEX S and Kapton dielectric films was determined at Lawrence Technology. The measurements were performed at $25^{o}C$ according to method ASTM D 495-84. A test unit was specially assembled to perform the dry arc/track measurements according to the guidelines described by ASTM (Reference 12). A description of the tests performed and a discussion of the results obtained are presented below.

During calibration and testing of the dry arc/track apparatus it was determined that both uncoated and SiO_2 coated films of the nominal 0.001 inch thickness employed in all prior electrical property tests described herein distorted to an extent in the arc that reproducible test results could not be obtained. Upon a detailed examination of the DuPont Kapton product information (Reference 1), it was established that DuPont's dry arc/track database was determined on 0.005 inch thick samples. Kapton film at a thickness of 0.005 inch was consequently procured from DuPont and shown at Lawrence Technology not to distort in the dry arc/track test and values of ~180 seconds to failure were obtained which correspond to the Kapton data reported by DuPont. The necessity for 0.005 inch thick film samples required procurement of UPILEX S film material of this thickness, plus laboratory casting of EYMYD L-30N at the desired 0.005 inch thickness. Also, it was necessary for Sheldahl to coat the 0.005 inch thick samples with SiO_2 to test this ceramic's effect on arc/track resistance. For this coating work, TRW selected 5000 angstroms of SiO_2 on both sides of the dielectric film, because this ceramic thickness gave the largest increase in ac and dc breakdown voltage. (See Table 18, Section 4.3.2.)

The dry arc/track measurements, conducted according to method ASTM D 495-84, required that a procedure be developed to obtain consistency in the time to failure values obtained. After considerable experimentation to attempt to obtain consistency in the measurements, it was determined that cutting the uncoated and SiO_2 coated film samples into ~1.0 inch x 1.0 inch square samples, drying the samples in air at $100^{o}C$ for 1 hour and storing the samples in a desiccator prior to testing provided the best reproducibility in test results. Also, as part of the test methodology development, it was found that a time interval of 10 minutes before initiation of successive tests significantly assisted in obtaining reproducible test results. Additional test methodology employed is described below.

The dried uncoated and SiO_2 film samples were individually tested by placing the film on a 1.0 inch diameter SiO_2 ceramic disc. A spring placed below the ceramic disc was employed to ensure tension giving secure contact of the sample with the two tungsten electrodes spaced one-quarter inch apart according to ASTM D 495-84. The power to the unit was then turned on and the arc/track time to failure in seconds was determined at 25°C. The electric power transferred to the sample was automatically increased in a progressive step function according to ASTM D 495-84 as follows:

- 0 to 60 seconds at one-eighth step at 10-milliamps,
- 61 to 120 seconds at one-quarter step at 10-milliamps,
- 121 to 180 seconds at one-half step at 10-milliamps,
- 181 to 240 seconds at continuous 10-milliamps,
- 241 to 300 seconds at continuous 20-milliamps and
- >300 seconds at continuous 30-milliamps.

This progressive increase in electric power applied to the sample may be thought of as proceeding from a very benign intermittent load to a very severe continuous load over a time period of 6 minutes or less. Figures 19 through 22 trace the dry arc/track test procedure on uncoated Kapton from placement of test sample on the ceramic disc/electrode through application of power to sample, initiation by tracking and final tracking failure, respectively. Figure 23 presents a photograph of the entire arc/track apparatus constructed at Lawrence Technology.

Figure 19. Kapton Film Sample Inserted in Arc/Track Apparatus Prior to Initiation of Test.

Figure 20. Kapton Arc/Track Testing in Progress Prior to Initiation of Tracking Failure.

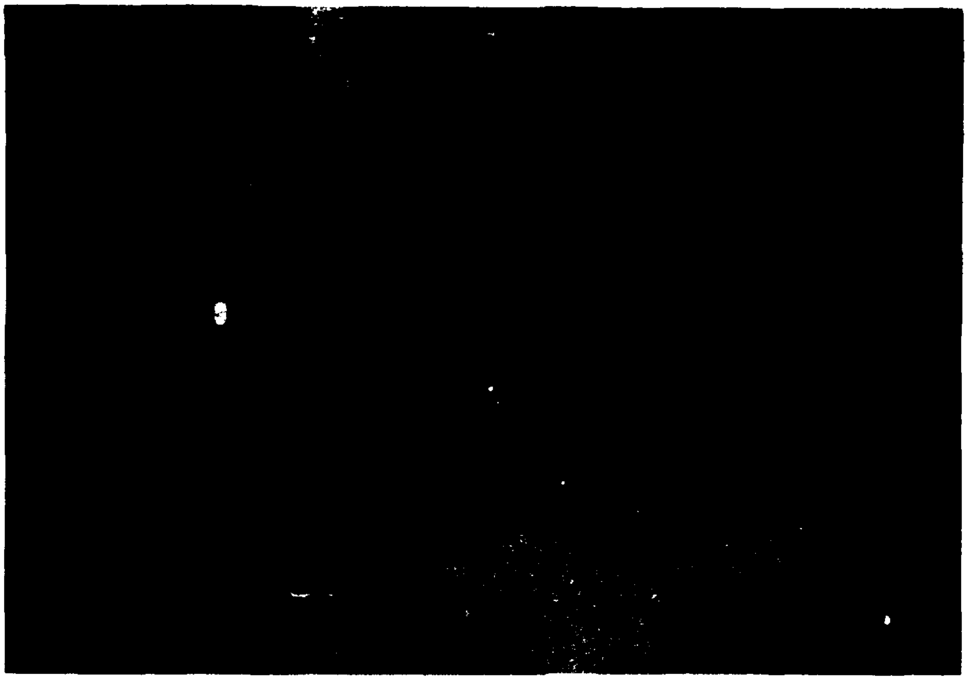

Figure 21. Initiation of Kapton Tracking Failure.

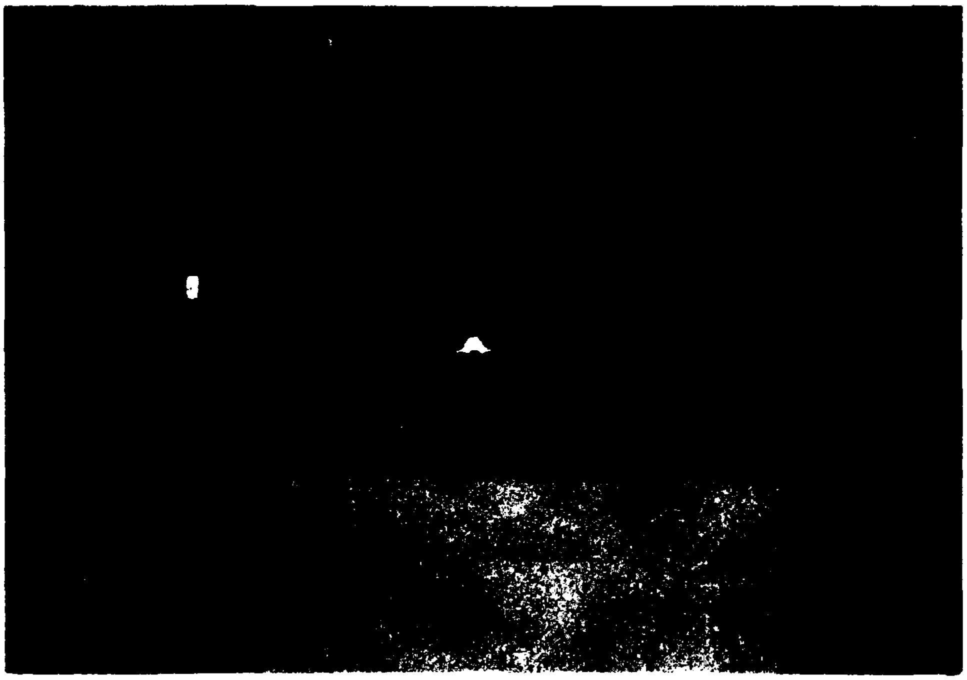

Figure 22. Completion of Kapton Tracking Failure.

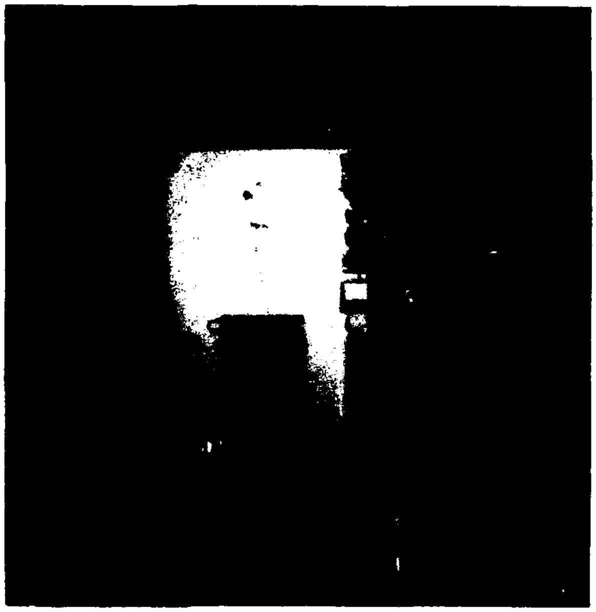

Figure 23. Arc/Track Apparatus Constructed at Lawrence Technology.

The average and median arc/track time to failure results obtained on 0.005-inch-thick film samples of uncoated and 5000 angstroms SiO_2 coated (both sides) Kapton, EYMYD L-30N and UPILEX S are summarized in Table 19. A summary of the total arc/track time to failure test data for Kapton, EYMYD L-30N and UPILEX S are presented in Figures 24, 25 and 26, respectively. The data presented in Table 19 and Figures 24 through 26 are interpreted to be very significant and highlight comments are as follows:

- Uncoated UPILEX S possesses a much greater potential resistance to dry arc/track failure than Kapton,
- A silicon dioxide coating both extends the average time to failure for all polymeric film materials as well as tends to eliminate premature (up to 120 seconds) sample failures and

TABLE 19

DRY ARC/TRACK RESULTS DETERMINED ON UNCOATED AND 5000 ANGSTROMS SILICON DIOXIDE COATED KAPTON, EYMYD L-30N AND UPILEX S[a)]

POLYMERIC FILM MATERIAL	FILM SAMPLE CONFIGURATION	TOTAL SAMPLES TESTED	TIME TO SAMPLE FAILURE (SECONDS)		
			Average	Median	Standard Deviation
KAPTON	Uncoated	44	150	181	51
	5000 Angstroms Silicon Dioxide Coated	30	193	183	48
EYMYD L-30N	Uncoated	8	126	129	27
	5000 Angstroms Silicon Dioxide Coated	20	150	141	30
UPILEX S	Uncoated	38	199	192	80
	5000 Angstroms Silicon Dioxide Coated	41	225	216	48

a) Tests conducted according to method ASTM D495-84 at 25°C on 1.0 inch x 1.0 inch x 0.005 inch samples.

Dry Arc-Track
5 Mil Kapton

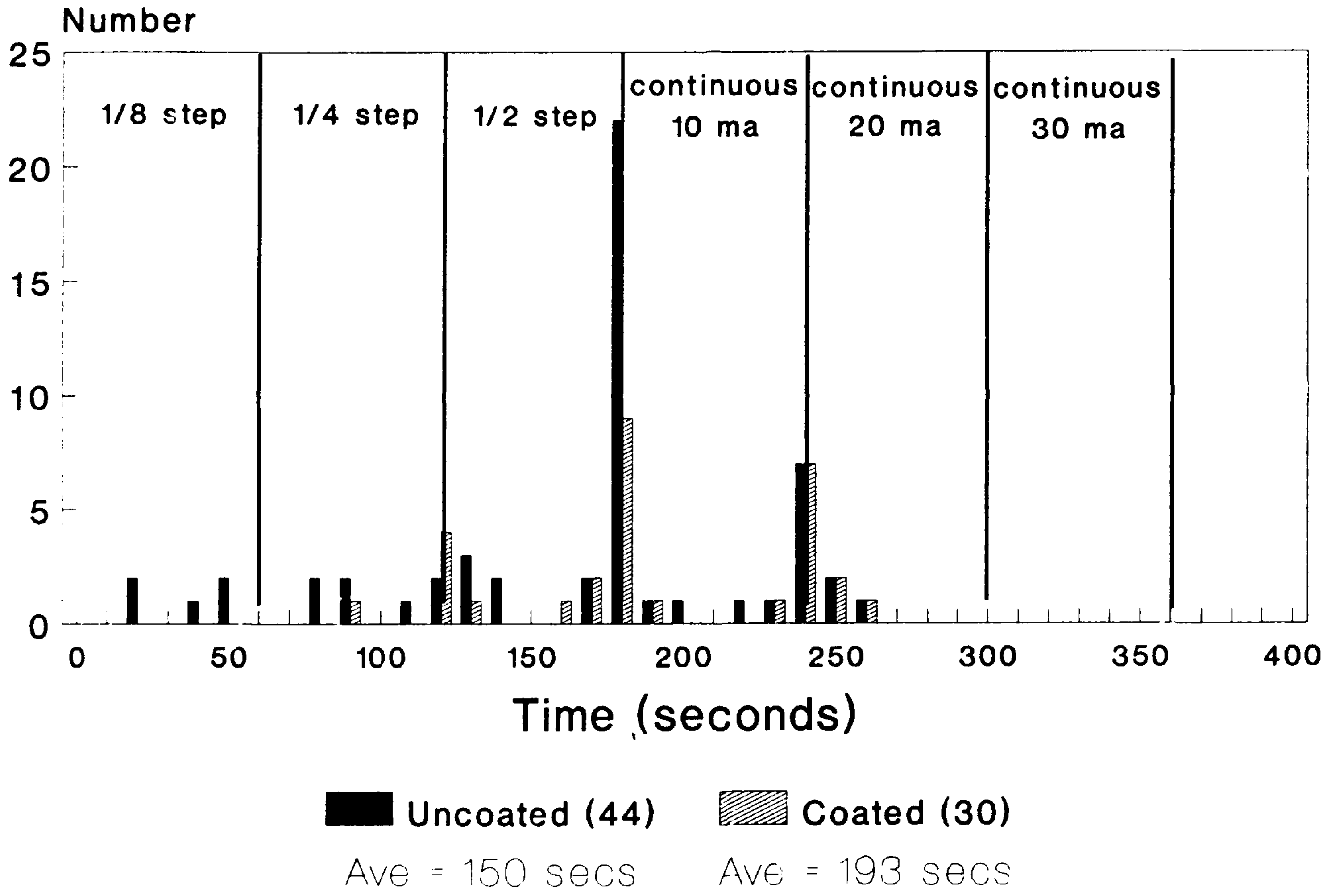

Figure 24. Summary of All Dry Arc/Track Test Results Determined on Uncoated and 5000 Angstroms SiO_2 Coated Kapton.

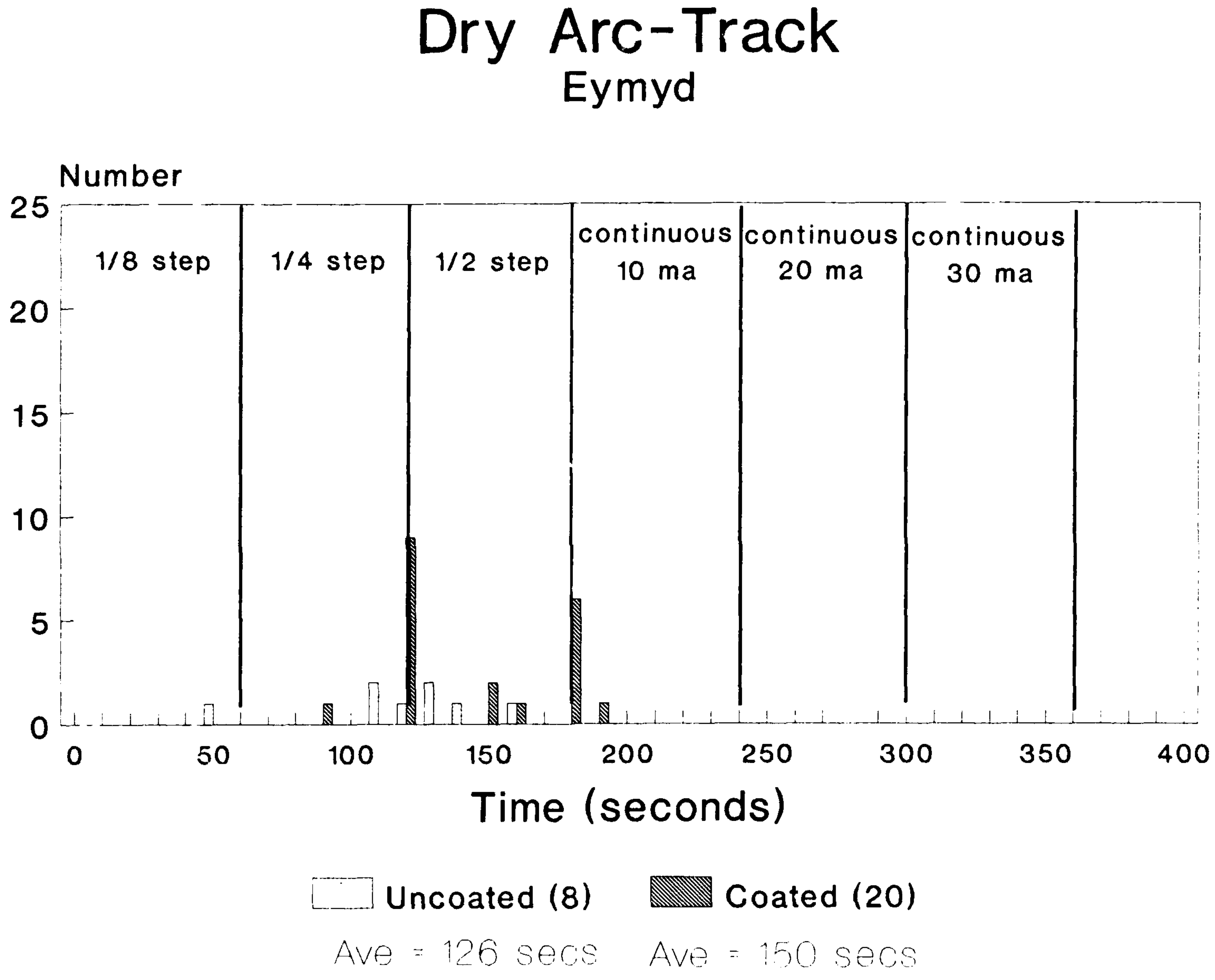

Figure 25. Summary of All Dry Arc/Track Test Results Determined on Uncoated and 5000 Angstroms SiO_2 Coated EYMYD L-30N.

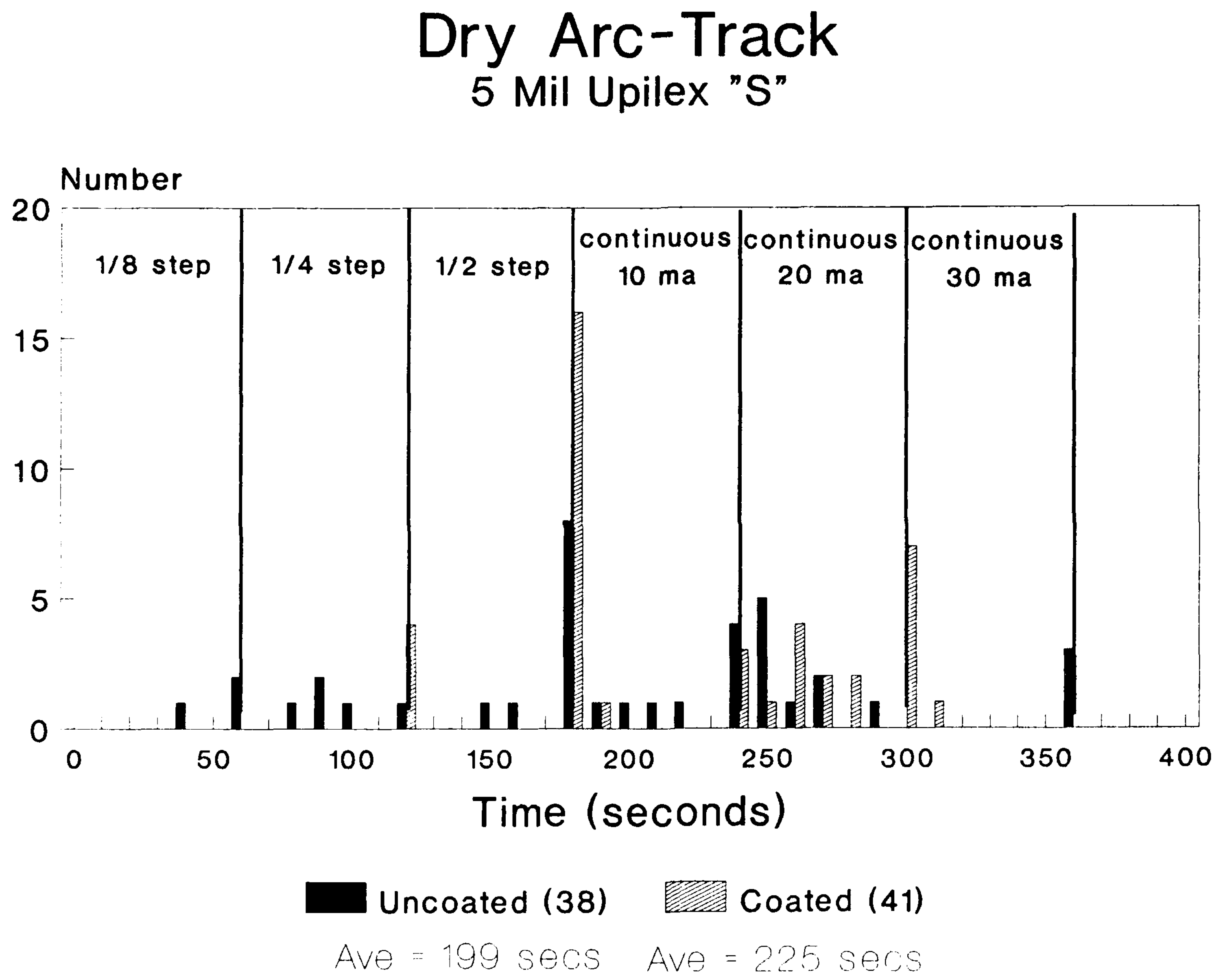

Figure 26. Summary of All Dry Arc/Track Test Results Determined on Uncoated and 5000 Angstroms SiO_2 Coated UPILEX S.

- Laboratory cast film samples of EYMYD (versus commercially produced Kapton and UPILEX S films) are susceptible to premature time to failure test results due to minute sample defects which could not be eliminated in the 0.005 inch thick test samples; the silicon dioxide coating seemed to assist in masking the effect of defect enhanced failures obtained on uncoated film samples.

The determination that UPILEX S possesses significantly higher resistance to dry arc/track resistance than Kapton (and EYMYD L-30N), coupled with its many other property improvements over Kapton presented and discussed in Sections 3 and 4, led to selection of UPILEX S as the single most promising candidate for wire insulation work in Task 4. (See Section 4.5.)

The arc/track results obtained in this program are worthy of additional comments. The very promising film results obtained on uncoated and silicon dioxide coated UPILEX S film must be verified in wrapped wire insulation configuration on appropriate copper-based conductors of various gauges (insulated wire testing of arc/track resistance was beyond the scope and schedule of this program). Also, the dry arc/track resistance of UPILEX S versus Kapton in insulated wire must also be compared with wet arc/track results under identical wire sample configurations. The data scatter encountered during the film dry arc/track testing on this program was expected, because of prior reported work on polymeric film materials other than those tested in this program as recently reported (Reference 13).

An additional physical property test, film sample morphology, is presented in Section 4.4 which may be fundamental to explain the arc/track experimental results based upon the physical state of the samples tested.

4.4 MORPHOLOGICAL TESTING OF POLYMERIC FILM CANDIDATES

The detailed electrical property testing presented in Section 4.3 concluded the evaluation of new polymer candidates in film form versus the state-of-the-art Kapton film material control. This film testing, plus the many tests conducted and described in Sections 2 and 3, have conclusively shown the significant combination property benefits of EYMYD L-30N and UPILEX S over Kapton both at 25°C and/or 300°C in achieving the program objectives. The ability of the non-optimized laboratory cast film samples of EYMYD L-30N to outperform Kapton in most tests conducted and, further, to compare very favorably with UPILEX S in most critical property assessments, must be viewed very positively. This performance of EYMYD L-30N versus Kapton and UPILEX S was very promising, because the latter two dielectric film materials represent commercially available, optimized film products. In-as-much, Kapton and UPILEX must be viewed as film materials which possess the "best" properties which have been engineered into the products during the film manufacturing process. This optimized production process normally introduces crystallinity or morphological order through draw orientation and cure/postcure treatment. This crystalline order significantly enhances the reproducible property attributes of Kapton and UPILEX S. Morphological data supporting the optimized state of Kapton and UPILEX S versus EYMYD L-30N is discussed below.

During the latter stages of Task 3, the physical crystalline state or morphorology of Kapton, EYMYD L-30N and UPILEX S were determined by X-ray crystallography. The percent crystallinity content of each uncoated polymeric film material was determined on 0.001 inch thick samples and the data determined are presented in Table 20. Plots of the X-ray crystallinity determinations on uncoated film samples are presented in Figures 27, 28, 29 for Kapton, EYMYD L-30N and UPILEX S, respectively. The X-ray plots for 2500 angstroms SiO_2 coated Kapton, EYMYD L-30N and UPILEX S are presented in Figures 30, 31 and 32.

TABLE 20

PERCENT CRYSTALLINITY OF UNCOATED KAPTON, EYMYD L-30N AND UPILEX S POLYMERIC FILM MATERIALS

POLYMERIC FILM MATERIAL	CRYSTALLINITY DETERMINED (PERCENT)
KAPTON	9
EYMYD L-30N	0
UPILEX S	37

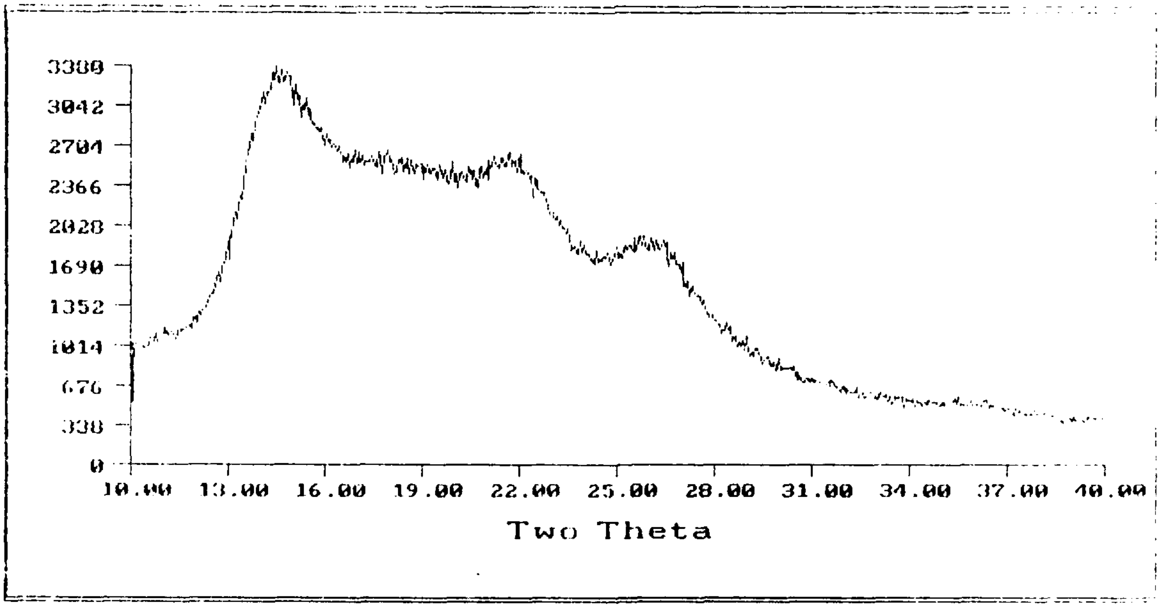

Figure 27. X-Ray Crystallography Plot of Uncoated Kapton.

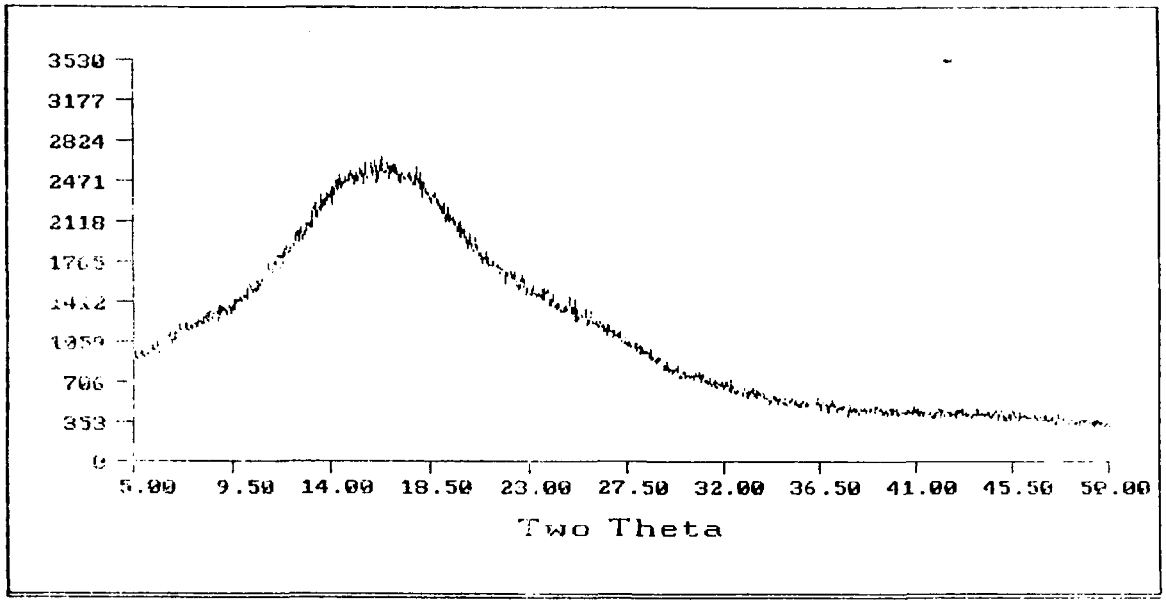

Figure 28. X-Ray Crystallography Plot of Uncoated EYMYD L-30N.

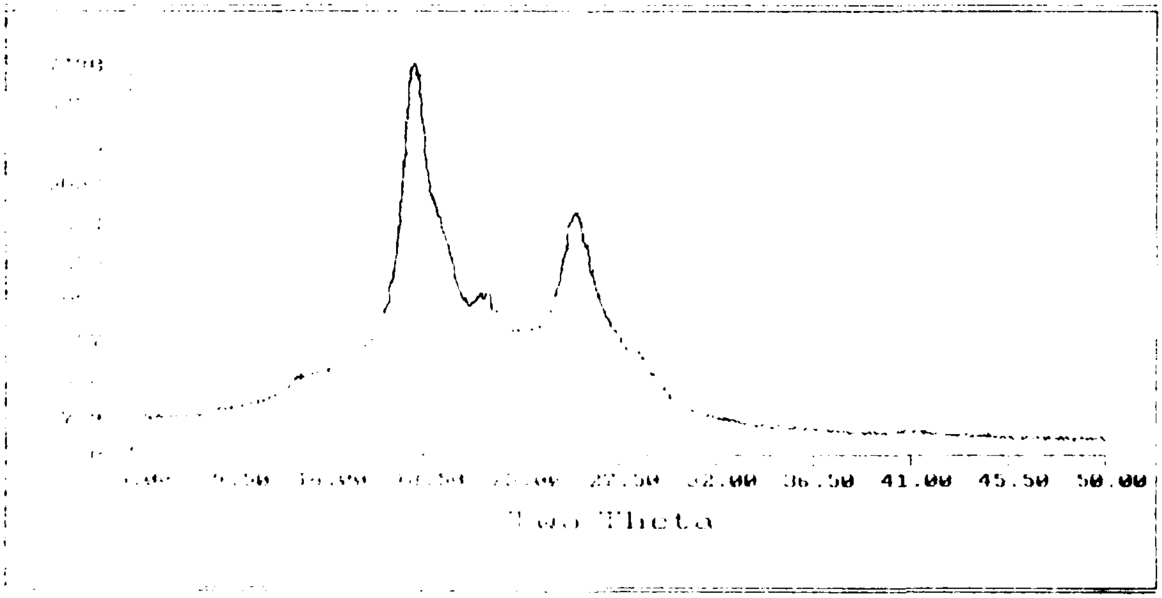

Figure 29. X-Ray Crystallography Plot of Uncoated UPILEX S.

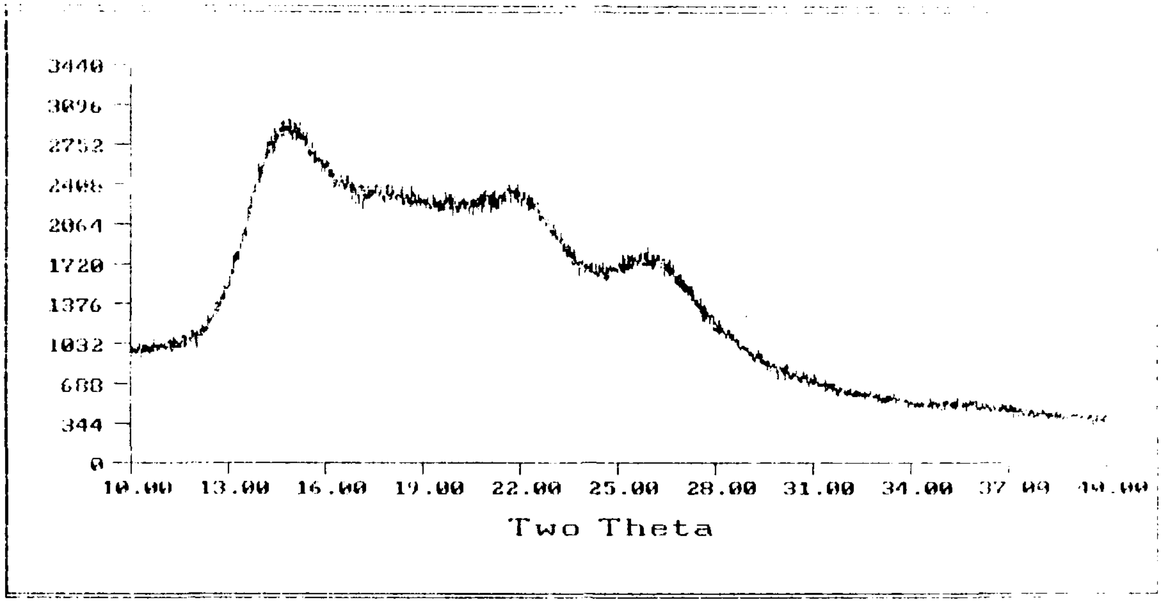

Figure 30. X-Ray Crystallography Plot of 2500 Angstroms SiO_2 Coated Kapton.

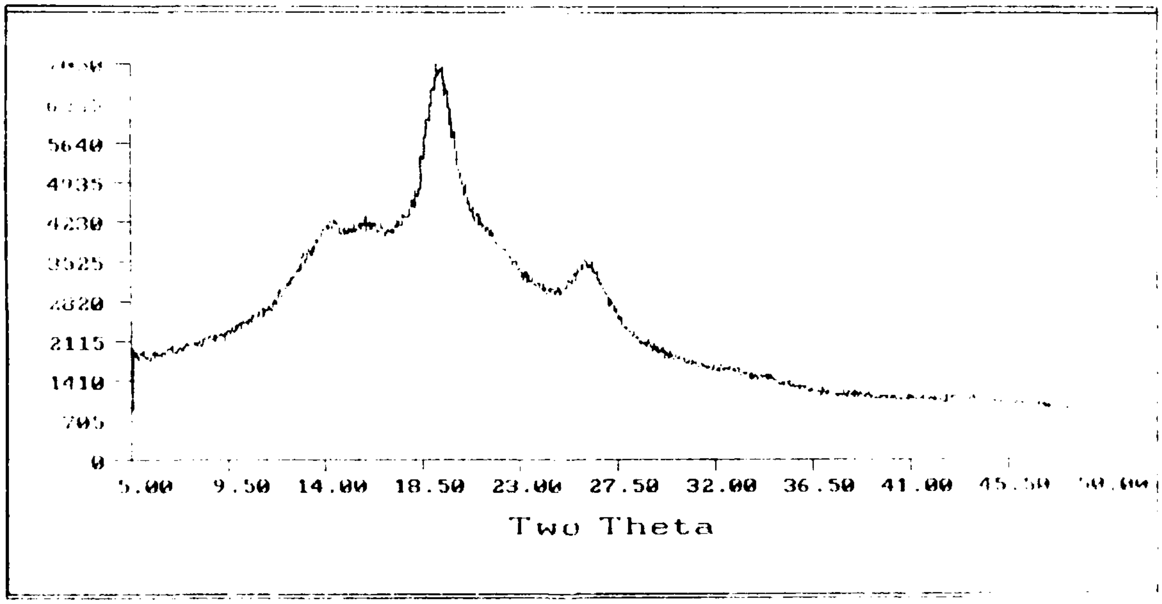

Figure 31. X-Ray Crystallography Plot of 2500 Angstroms SiO_2 Coated EYMYD L-30N.

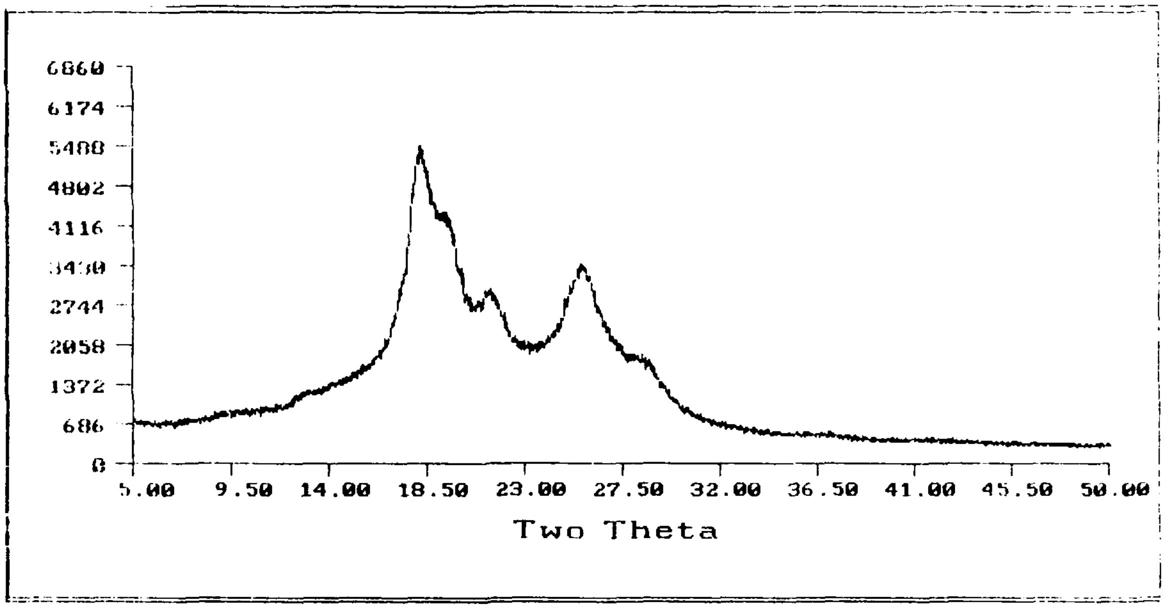

Figure 32. X-Ray Crystallography Plot of 2500 Angstroms SiO_2 Coated UPILEX S.

TRW believes that the X-ray crystallography test results summarized in Table 20 and shown graphically in Figure 27 through 32 are very significant for the following reasons:

- The test results clearly show that Kapton and UPILEX S contain crystalline order in the polymeric film verifying their existence as "ordered," optimized products,
- The much higher crystallinity content of UPILEX S (37 percent) versus Kapton (9 percent) is held to be a key contributing factor, along with molecular chemical structure, to the significantly improved combination of properties of UPILEX S versus Kapton,
- The absence of crystallinity in the uncoated EYMYD verifies that the film samples tested in this program represent a probable "worst case" physical state in that no order is present in the laboratory cast material,
- Comparison of the X-ray plot uncoated EYMYD L-30N in Figure 28 with the SiO_2 coated film in Figure 31 show that some crystalline order was introduced into the polymer by the vacuum deposition process used to coat the film; conversely, comparison

of Figures 27 and 30 for uncoated and coated Kapton, respectively, and Figures 29 and 32 for uncoated and coated UPILEX S, respectively, show that no apparent change occurred in these polymeric films during vacuum deposition of the amorphous SiO_2 coating.

This presence of crystallinity in Kapton and UPILEX S is not surprising, because the polymers become "ordered" in the optimized production process. The crystalline order of the UPILEX S film over Kapton and both films over EYMYD L-30N is held to be a significant contributor to the observed arc/track resistance ranking of UPILEX S > Kapton > EYMYD L-30N, because the energy of this test is directed at the film surface and tracking occurs at the film surface. The introduction of some crystallinity from the SiO_2 coating on EYMYD L-30N in Figure 31 is the most probable explanation for the improved arc/track resistance of this material versus the uncoated, amorphous film. The contribution of crystalline order to arc/track resistance is certainly worth additional study in future work comparing different types of dielectric film materials. The effect of film crystallinity on increasing arc/track resistance observed during this program correlates with the crystalline order of Teflon^R *perflurocarbon* polymers and their superior arc/track resistance (Reference 14). Thus, future work should place emphasis on evaluation of crystalline polymers and, most probably, crystalline ceramic coatings to optimize dry arc/track resistance.

In further work, film production process optimization of EYMYD L-30N, including bidirectional stretch-draw orientation of the film during imidization/cure/postcure thermal treatment, should introduce crystalline order into the material. By introduction of some degree of crystallinity into EYMYD L-30N film material, a significant improvement of the already superior combination of many electrical, thermal, chemical and physical properties may occur (i.e., EYMYD L-30N may surpass UPILEX S as an outstanding dielectric film insulation material, including arc/track resistance).

4.5. SELECTION OF UPILEX S AS THE SINGLE MOST PROMISING POLYMERIC FILM CANDIDATE

Based upon the outstanding balance of superior properties demonstrated by UPILEX S versus the Kapton control and the EYMYD L-30N polymeric film candidate as determined during back-to-back comparison throughout the program, UPILEX S was selected as the single most promising polymeric film candidate for conducting Task 4-Wire Insulation and Testing and completion of the program technical effort. It was also decided to proceed with evaluation of uncoated UPILEX S versus uncoated Kapton as the control for the following reasons:

- UPILEX S and Kapton were directly available from UBE Industries and DuPont, respectively, in 0.001 inch thick film tape with fluroethylenepropylene adhesive material at a thickness of 0.0005 inch one side of the tape and
- The non-optimized state of development of the silicon dioxide coating and its apparent tendency to lower capacitance properties made it suspect during this program to evaluate in wire insulation within the remaining scope and schedule upon completion of Task 3.

The promising results obtained on insulation and testing of UPILEX S film tape on wire versus a Kapton insulation material control are presented and discussed in Section 5.

5. TASK 4 EXPERIMENTATION

This section describes the work performed in Task 4 - Insulated Wire Product Fabrication, Test and Delivery. The work described herein on UPILEX S and Kapton insulated wire is as follows:

- Development of an acceptable tape wire wrapping process for UPILEX S,
- Wrapping of UPILEX S and Kapton insulated wire and
- Testing of insulated wire.

Each of these wire insulation and test areas is separately described below.

5.1 DEVELOPMENT OF WIRE WRAPPING PROCESS FOR UPILEX S

Task 4 was initiated by procuring approximately 4 pounds each of UPILEX S and Kapton film (Kapton F-Reference 1) tape from ICI/Ube Industries and DuPont, respectively. The tape furnished by each vendor was identical in construction consisting of 0.375 inch width x 0.001 inch thick polyimide film tape containing a 0.0005 inch thick layer of fluoroethylenepropylene (FEP) fluoropolymer adhesive deposited on one side of the polyimide film.

At the onset of Task 4, the performance of the FEP adhesive material was suspect as to its long-term performance at $300^{o}C$, because of its glass transition temperature (Tg) of $<300^{o}C$. Concerns, in general, of the FEP adhesive have been reported (Reference 15). However, this was the only common adhesive material available on both UPILEX S and Kapton polyimide film tape materials. The scope and schedule of this program did not provide for development of an alternative adhesive material tailored for service at $\geq 300^{o}C$. Failure of the FEP adhesive was observed upon aging of insulated wire at $300^{o}C$ in air as discussed in Section 5.3.

The initial film wrapping work conducted on the program was identification of a tape wrapping process suitable to yield acceptable quality UPILEX S insulated wire. For this work, Lawrence Technology selected initial conditions normally employed in their proprietary process to commercially produce Kapton F insulated motor lead and magnet wire. Their wrapping process employs a modified conventional tape machine coupled with resistive heaters to melt fuse the FEP adhesive to the copper conductor and successive layers of polyimide film (both overlap construction and multi-film tape insulation layers). The tape wrapping work employed bare, ultrasonically cleaned 14 gauge copper conductor wires. The wrapping process screening included varying line speed in the range of 40 feet/min to 60 feet/min and resistive oven temperatures up to ~430°C (~800°F), a 50 percent tape overlap and a double insulation layer (total insulation thickness: ~0.006 inch). Tape to conductor and tape to tape adhesion of ≥200 feet lengths of insulated wire at a given set of process conditions was employed to assess quality of the tape wrapped product produced. A twist fabrication tester was employed to assess adhesion.

The initial tape wrapping insulation work showed that a line speed of ~40 feet/min and a resistive heated oven temperature of ~400°C (~750°F) gave UPILEX S insulated wire with reasonably acceptable tape to conductor and tape to tape adhesion. Optimization of the wrapping process to yield UPILEX S tape adhesion equivalent to that normally achieved in the well-defined Lawrence Technology Kapton F wire insulation manufacturing were not achieved and considered to be beyond the scope of this program.

The process identified for wrapping UPILEX S tape was employed to produce insulated wire for testing as is described in Section 5.2.

5.2 WRAPPING OF FINAL UPILEX S AND KAPTON INSULATED WIRE SAMPLES

After completion of definition of acceptable UPILEX S wire wrapping process methodology as described in Section 5.1, Lawrence Technology proceeded to wrap the UPILEX S and Kapton insulated wire to conduct performance tests and deliverables to USAF/WL. A description of this final wire wrapping is provided below.

Quantities of 2000 linear feet each of UPILEX S and Kapton wrapped wire were produced by Lawrence Technology. Each wire sample was of identical construction consisting of 50 percent overlapped, double wrapped tape (thickness: 0.006 inch) on 14 gauge bare copper conductor.

The process employed to produce the UPILEX S insulated wire was identical to that described in Section 5.1. The process employed to produce the Kapton control insulated wire was the proprietary method used routinely by Lawrence Technology to manufacture motor leads and magnet wire. Each process employed two rolls of the film tape spirally wrapped in the same direction to afford the double wrap construction.

Each insulated wire product was assessed for tape to conductor and tape to tape adhesion. The adhesion measured for the UPILEX S material approximated the best attained in the process definition work described in Section 5.1. Both tape to conductor and tape to tape adhesion for the UPILEX S insulated wire was deemed to be acceptable for testing, but the adhesive bonds were not as strong as those measured for the Kapton control in the twist tester/~30 percent more revolutions were required adhesively to fail the Kapton wire samples versus the UPILEX S wire material. Photographs of the Kapton and UPILEX S wire wrapped in Task 4 are presented in Figures 33 and 34, respectively.

The Kapton control and UPILEX S insulated wire materials were tested for electrical properties and oxidative stability in air as described in Section 5.3.

5.3 ELECTRICAL PROPERTY AND 300°C AIR AGING TESTING OF INSULATED WIRE

The UPILEX S and Kapton insulated wire samples successfully produced by Lawrence Technology as described in Section 5.2 were isothermally aged

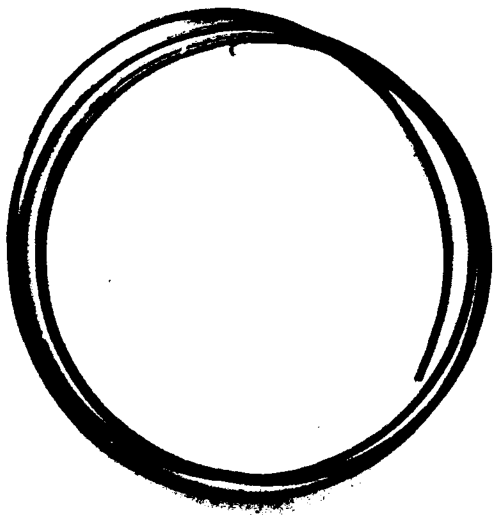

Figure 33. Photograph of Kapton Wrapped Wire Produced in Task 4.

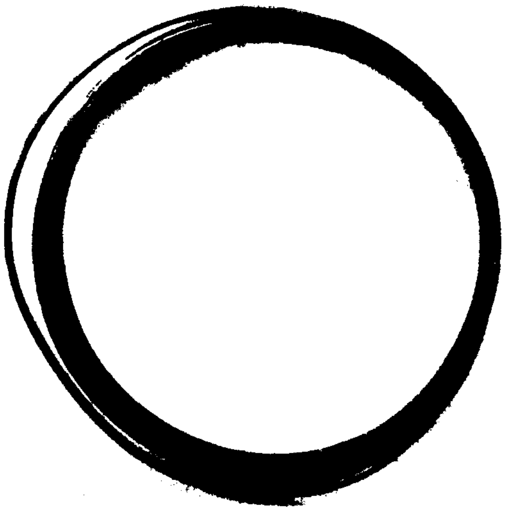

Figure 34. Photograph of UPILEX S Wrapped Wire Produced in Task 4.

in air at 300^{o}C for 504 hours to obtain comparative performance with film samples aged in Task 1. Also, breakdown voltages of the wire samples were determined before and after the air aging. These test results are separately discussed in the following sections.

5.3.1 Air Aging of UPILEX S and Kapton Insulated Wire at 300^{o}C

The UPILEX S and Kapton insulated wire samples were isothermally aged at TRW in air at 300^{o}C in the same oven that was utilized to age film samples in Task 1. (See Section 2.4.) The wire samples were aged as 3.0-inch-diameter coils containing approximately 8 linear feet of wire and weighed approximately 70 g/coil including approximately 61.6 g of copper conductor and 8.4 g of insulation material. The insulated wire samples were aged for 504 hours employing weight loss assessment methodology identical to that used for film aging in Task 1. The Kapton and UPILEX S polymeric insulation weight loss as a function of time at 300^{o}C in increments through 504 hours are reported in Table 21. The data presented in Table 21 reflect the actual weight loss percent determined on the wire sample and the percent weight loss of insulation material assuming none of the weight loss was contributed by the copper conductor. As we can see from the insulated wire weight loss results in Table 21, UPILEX S, as expected, significantly outperformed Kapton from inception to conclusion of the aging test at 300^{o}C. Most significantly, the weight loss observed for UPILEX S stabilizes to approximately one percent per 100 hour aging period, whereas the Kapton weight loss accelerates as the aging period continues. The UPILEX S insulation remained relatively flexible at the conclusion of the aging test, but the Kapton insulated turned almost black in color and had significantly embrittled.

Testing of breakdown voltage on the insulated wire samples before and after aging at 300^{o}C in air were consistent with the weight loss results summarized in Table 21 as discussed in the following section.

TABLE 21

300°C AGING IN AIR WEIGHT LOSS RESULTS OBTAINED ON KAPTON AND UPILEX S INSULATED WIRE[a]

INSULATION WIRE SAMPLE	SAMPLE BASIS	PERCENT WEIGHT LOSS DETERMINED AFTER INDICATED TIME DURATION (HOURS)				
		192	237	310	406	504
KAPTON (CONTROL)	INSULATION AND CONDUCTOR	1.41	1.79	2.54	3.07	3.66
	INSULATION ONLY	11.84	15.04	21.33	25.79	30.74
UPILEX S	INSULATION AND CONDUCTOR	0.47	0.51	0.59	0.59	0.76
	INSULATION ONLY	3.95	4.28	4.96	5.80	6.38

a) Average of duplicate test results determined on ~70 g insulated wire samples of the construction type described in Section 5.2.

5.3.2 Wrapped Wire Insulation Breakdown Voltage

The ac breakdown voltage of the unaged and 192 hour air aged (see Section 5.3.1 - Table 21) insulated wire samples of Kapton and UPILEX S were determined at 25°C employing method ASTM D-149. The test results are presented in Table 22. As we can see from the data in Table 22, the percent drop in ac breakdown voltage agreed very closely with the percent weight loss of film insulation material. (See Section 5.3.1.) As expected, the promising UPILEX S wire insulation material demonstrated superior retention of the insulation ac breakdown property versus Kapton. The lower absolute breakdown voltage of UPILEX S versus Kapton was expected and parallels the data determined on films as reported and discussed in Section 4.3.2. (See Table 18.) The absolute breakdown voltage results on UPILEX S are, none-the-less promising, because a simple double wrap construction yields an ac breakdown potential up to approximately 10,000 volts or greater.

TABLE 22

25°C INSULATED WIRE AC BREAKDOWN VOLTAGE[a)]

INSULATED WIRE SAMPLE	AC BREAKDOWN VOLTAGE (VOLTS) BEFORE AGING	AFTER AGING	PERCENT DECREASE	PERCENT INSULATION WEIGHT LOSS AT 300°C (FROM TABLE 21)
KAPTON	12,400[b)]	11,400[c)]	8	11.8
UPILEX S	9,900[b)]	9,500[c)]	4	4.0

a) Measured by ASTM D-149 on 18.0 inch length of insulated wire samples at 25°C before and after aging in air at 300°C for 192 hours.

b) Average of eight samples.

c) Average of seven samples.

It would have been desirable to obtain ac breakdown voltages after isothermal aging in air at 300°C at intervals up to 504 hours in concert with the insulation weight loss measurements over this time period as reported in Table 21. However, between the 192 hour data determination and the 310 hour point, the FEP fluoropolymer adhesive had apparently begun to flow in some areas along the length of the 300°C aged wire coils (tape to tape and tape to conductor) and attempts to determine the ac breakdown voltage after 310 hours aging at 300°C gave meaningless results. The possible problem with use of the state-of-the-art FEP material as the adhesive for Task 4, because it is not intended for use at 300°C, was discussed in Section 5.3.1. The 300°C aging study on the insulated wire has conclusively shown that the FEP adhesive material is not suitable for long-term service at 300°C and an adhesive stable at this temperature must be identified before the superior performance of UPILEX S (and EYMYD L-30N) at this temperature can be realized.

5.4 ASSESSMENT OF TASK 4 INSULATION WORK

TRW very strongly feels that the Task 4 work conducted and described in the sections above has proven the initial feasibility of the promise of UPILEX S as a superior insulation replacement for Kapton. This superior performance includes service at 300°C in air and, factoring in the film results shown and discussed in Tasks 1 through 3, applications at lower temperature in terrestial high humidity and space (vacuum and ultraviolet radiation) environments. Further comments concerning TRW's assessment of the Task 4 results are as follows:

- UPILEX S film (or tape) can be facilely wrapped on copper conductor employing the same general process employed in routine manufacture of Kapton insulated wire,
- UPILEX S demonstrates equivalent oxidative stability at 300°C in air as a wrapped insulation as it does in a non-wrapped film; in both forms UPILEX S is significantly more stable than Kapton,
- Additional work must be performed to optimize the UPILEX S tape wrapping process and

- A 300°C stable adhesive material alternative to FEP fluorocarbon must be identified or developed so that the advantages of UPILEX S at this temperature can be realized in wire insulations of various constructions.

These comments are also restated in Section 6 - Conclusions.

6. CONCLUSIONS

Based upon the significant number of tests conducted during performance of Contract F33615-88-C-2909 on newer (or improved) dielectric film materials offering potential superior performance to state-of-the-art Kapton, TRW offers the following conclusions:

- The program objective to identify and demonstrate polymeric dielectric films possessing a superior combination of electrical, thermal, chemical and physical properties to those possessed by Kapton over the temperature range of -269°C to +300°C has been achieved. UPILEX^R S and EYMYD^R L-30N polyimides possess the following key superior properties to Kapton^R polyimide:
    - Dielectric loss resistance at 300°C,
    - Oxidative and vacuum stability at 300°C,
    - Humidity resistance at 90°C/100 percent RH,
    - Ultraviolet radiation resistance at 25°C and
    - Basic solution (pH 10) hydrolysis resistance at 93°C,
- UPILEX^R S possesses higher dry arc/track resistance than Kapton^R,
- The overall properties of EYMYD^R L-30N (in the developmental state in film form) generally compare very favorable with UPILEX^R S (a commercially available, optimized commercial film product); optimization of EYMYD^R L-30N film may lead to superior film properties to UPILEX^R S,
- Ceramic coatings have the potential to significantly improve the breakdown voltage and/or dry arc/track resistance of high performance dielectric film materials, including Kapton,
- UPILEX^R S film can be converted into tape wrapped wire insulation by the same state-of-the-art commercial process currently employed to commercially produce Kapton^R wire and possesses superior 300°C oxidative stability versus Kapton^R as a wrapped insulation and
- An improved film wrap tape adhesive over Teflon^R FEP must be identified and developed to achieve the true potential of UPILEX^R S (and EYMYD^R L-30N) wire insulation for extended service at 300°C.

These key conclusions have been assessed to provide Recommendations for Further Work in Section 7.

7. RECOMMENDATIONS FOR FURTHER WORK

Based upon the overall work conducted and the accomplishments achieved on Contract F33615-88-C-2909 as well as the conclusions stated in Section 6, TRW strongly believes that further work is necessary and will almost certainly yield truly superior polymeric dielectric film insulation materials to state-of-the-art Kapton^R film and extruded or film wrapped fluorocarbon materials. The specific key technical areas recommended for advanced development (and manufacturing technology, if necessary) are as follows:

- Further detailed electrical, thermal, chemical and physical property testing of UPILEX^R S and EYMYD^R L-30N films and insulated wire such as the following:
  - Electrical properties (capacitance, ac/dc breakdown voltage, dry and wet arc/track, etc.) and mechanical tensile properties in the range of -269°C to +300°C before, during and after very long-term aging (up to $\geq$5000 hours) in the following environments:
    - Air at $\geq$300°C,
    - Humidity up to 90°C/up to 100 percent RH,
    - Thermal cycling, vacuum and ultraviolet radiation in the range of -269°C to +300°C,
    - Fuels and fluids up to boiling point and
    - Other potentially degrading environments (e.g., atomic oxygen).
  - Mechanical stress, tribological and other tests delineated in MIL-W-81381.
- Optimization of UPILEX^R S tape wrapping process and EYMYD L-30N film casting and wrapping processes,
- Identification and demonstration of a $\geq$300°C performing film tape adhesive,
- Optimization of ceramic coatings for selected high performance insulated wire applications and
- Identification and testing of emerging polymeric film materials for up to 400°C service.

Changes in future USAF spacecraft (and aircraft) mission requirements, of course, may necessitate modification and/or additions to the specific technical recommendations highlighted above.

REFERENCES

The references employed throughout this Final Report are cited below.

1. "KAPTON^R Polyimide Film," E. I. DuPont De Nemours and Company, Wilmington, Delaware.
2. D. N. Roark, "EYMYD^R Resins, High Temperature Thermoplastic Polyimides," March 22, 1988.
3. D. C. Hofer, "Polyimides in Packaging for Electronics," Proceedings of the ACS-sponsored Polyimide Symposium, Reno, Nevada, August, 1987.
4. "Pyralin^R Polyimides," E. I. DuPont De Nemours and Company, Wilmington, Delaware.
5. "SIXEF^R Polymers," Hoechst-Celanese Corporation, Specialty Products Group, Coventry, Rhode Island.
6. "UPILEX^R Polyimide Film," ICI Films, Wilmington, Delaware.
7. TRW - Unpublished Results.
8. C. I. Croall and T. L. St. Clair, NASA Technical Memorandum 102726, "The Mechanical Stability of Polyimide Films at High pH," October, 1990.
9. "Total Deposition Facility," Sheldahl Engineered Products Division, Northfield, Minnesota.
10. TRW - Unpublished Results.
11. W. D. Kingery, H. K. Bowen and D. R. Uhlmann, "Introduction to Ceramics," 2nd Ed., John Wiley and Sons, New York 1976.
12. ASTM D495-84, Standard Test Method for High-voltage, Low-current, Dry Arc Resistance of Solid Electrical Insulation.
13. T. Ikejeri, "A Statistical Study on Arc Resistance," Journal of the Society of Materials Science, Japan, Vol. 28, No. 307, April, 1979, pp. 332-8.
14. "Teflon Polymers," E. I. DuPont De Nemours and Company, Wilmington, Delaware.
15. L. Gordon, R. Druce and M. Wilson, "Failure Modes of Laminate Structures," Proceedings of Sixth IEEE Pulsed Power Conference, Arlington, Virginia, 1987, pp. 60-63.

U S Government Printing Office 1992—648-127/62564