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INVESTIGATION OF RESIN SYSTEMS FOR IMPROVED ABLATIVE MATERIALS

by

E. A. Burns, H. R. Lubowitz and J. F. Jones

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Contract NAS3-7949

DEPARTMENT OF DEFENSE
PLASTICS TECHNICAL EVALUATION CENTER
PICATINNY ARSENAL, DOVER, N. J.

TRW SYSTEMS

UNLIMITED

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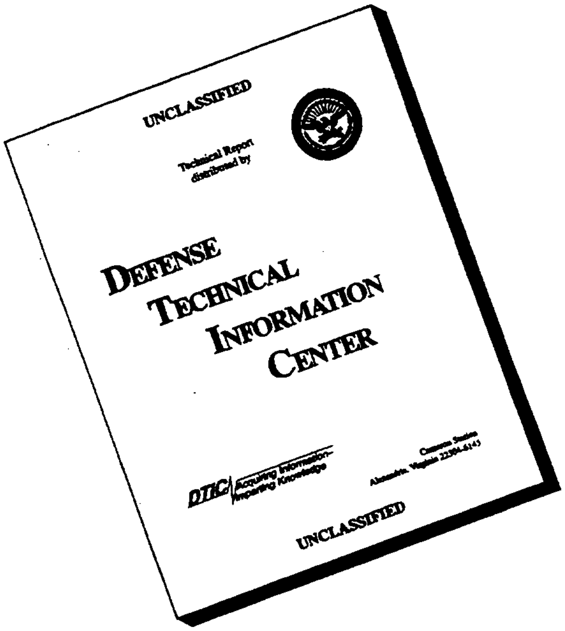
Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Liquid Rocket Technology Branch
Stephen M. Cohen

TRW SYSTEMS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FOREWORD

This document constitutes the final report for the work accomplished between 2 July 1966 and 12 April 1968 by TRW Systems for the National Aeronautics andSpace Administration, Lewis Research Center, under Contract NAS3-7949 on the Investigation of Resin Systems for Improved Ablative Materials.

The work was under the technical direction of Mr. Stephen M. Cohen of the Lewis Research Center, Cleveland, Ohio and the NASA Headquarters Project Manager was Mr. Frank E. Compitello.

The Chemistry and Chemical Engineering Laboratory of the Power Systems Division was responsible for the work performed on this program. Mr. B. Dubrow, Manager, of that Laboratory, provided overall program supervision, Dr. E. A. Burns, Manager, Chemical Research and Services Department, was Program Manager and Mr. H. R. Lubowitz, Head of the Polymer Research Section, was the Principal Investigator. The authors wish to acknowledge the technical assistance provided during this program by the following TRW Systems personnel:

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ABSTRACT

This final report describes the work performed to advance the state of the art of resin matrices required for improved ablative materials for use with high energy fluorine-containing liquid propellant systems. This experimental program was a continuation of a previously reported effort (NASA CR-54471) and consisted of a systematic materials development effort of resin synthesis and property determination of new and previously identified resin systems, optimization of composite processing parameters and fabrication and use testing of candidate ablative composites.

Two new high char forming polymer systems were synthesized, fabricated and evaluated in composite form for ablative use effectiveness. These aromatic/heterocyclic polymer systems were designed to be processed readily with the evolution of minimum quantity of volatile matter during cure. As a consequence, low void, high strength composites were prepared which exhibited ablative performance (combination of dimensional stability, weight retention and reistance to thermal shock) superior to commercially available ablative materials when tested in a FLOX/methane torch combustion environment. Tested composites were prepared using Refrasil, graphite and carbon cloth and titanium diboride fibrous reinforcements.

CONTENTS

CONTENTS (Continued)

CONTENTS (Continued)

CONTENTS (Continued)

CONTENTS (Continued)

ILLUSTRATIONS

ILLUSTRATIONS (Continued)

TABLES

TABLES (Continued)

NASA CR-72460
05937-6019-R0-00

INVESTIGATION OF RESIN SYSTEMS FOR IMPROVED ABLATIVE MATERIALS

By E. A. Burns, H. R. Lubowitz and J. F. Jones

SUMMARY

This report is the final project report describing the work performed by TRW Systems for the National Aeronautics and Space Administration, Lewis Research Center under Contract NAS3-7949 during the period 2 July 1966 through 12 April 1968. This project is an extension of initial studies conducted under Contract NAS3-4188. The work accomplished under this contract is contained in both this volume and the Interim Progress Report NASA CR-72022 dated 26 July 1966.

The primary objective of this project was to prepare ablative materials from improved resin matrices suitable for use with fluorine-propellant systems. In Contract NAS3-4188, 1) analytical and experimental determinations identified the critical parameters controlling the effectiveness of resins in an ablative use environment, 2) new resin systems were synthesized and evaluated experimentally to verify the criteria established for resin ablative utilization, and 3) advanced resins were recommended for future studies. The advanced resin systems identified in that contract were in various states of development. The present project (under Contract NAS3-7949) was initiated 1) to continue the development and testing of candidate resins through a systematic material development effort of synthesis, property determination, and optimization of composite processing parametric studies, and 2) to fabricate and test candidate ablative composites.

In a parallel NASA sponsored program (Contract NAS3-7948) conducted by Texaco Experiment, Inc., new fibers and reinforcing agents which improve the properties of composites in fluorine-containing high energy propellant combustion environments were synthesized and fabricated. In the program reported here, composite formulation studies were conducted to determine the processing and composition parameters required for preparation of composite structures from 1) the most promising resin matrices

identified in this program, and 2) the advanced fibers and reinforcing agents generated in the parallel program.

Two classes of high energy fluorine-containing propellant environments were identified in Contract NAS3-4188. Each present distinct differences in their reactivity with resins. One class consists of fluorine-containing propellant systems whose combustion products do not include oxygen in any free or combined form, e.g., fluorine/hydrogen; the other class includes propellant combinations which have both fluorine-and oxygen-containing exhaust species, e.g., FLOX/methane. In Contract NAS3-4188 it was determined that organic "stiff" polymers (polymers whose "backbones" are characterized by a multiplicity of aromatic/heterocyclic groups) were suitable for use in the fluorine/hydrogen combustion environment. It was recommended, although not tested, that inorganic resins, particularly those containing elements that had refractive fluorides and oxides were more likely to survive the FLOX/methane combustion environment. In experimental studies described in the Interim Report, it was determined that materials producing high chars also were excellent candidates for use in the FLOX/methane combustion environment. Consequently, the primary effort for this project was devoted toward the development of new aromatic/heterocyclic resin systems.

Two approaches were investigated for producing readily processable aromatic/heterocyclic polymer systems. The first method (A-type polymers) consisting of thermally induced aromatization or polymerization was found to be successful on pyrolysis of prepolymers which had been capped with specific alicyclic groups. The second method (B-type polymers) was found to be successful when a high molecular weight backbone containing thermally stable "flexible" chain segments was employed which permitted the use of fully cured, soluble "stiff" polymers in the preparation of ablative composites. Each of these approaches resulted in the synthesis of low void readily processable heterocyclic/aromatic polymers and easily fabricated reinforced laminates. The void content of the A-type polyimides were typically less than 2% v/v, and hence, (because of improved resin wetting of fibrous reinforcements) laminates exhibited mechanical properties superior to comparable commercially available polyimide composites.

Studies aimed towards the optimization of formulation and processing methodology of resin systems identified under Contract NAS3-4188 resulted in the selection of one system (of four candidates) namely, the polyamide-imide, for further detailed processing investigations. Previously identified cyclized and crosslinked polybutadiene urethanes, polyalkaline earth acrylates, phosphate bonded oxides, and zirconium diboride polymers were eliminated as contending resins at this stage on the basis of processing difficulties and/or ablative performance. Evaluation of commercially available heterocyclic/aromatic polymers (polyimides and polybenzimidazoles) showed that these systems cannot readily be processed into large ablative structures and hence, did not offer the potential available from the A-type and B-type heterocyclic polymer systems. As a consequence of these optimization studies, the A-type, and B-type and polyamide-imide systems were selected for processing and test evaluation using both Refrasil and graphite reinforcement as well as the advanced reinforcements prepared under the parallel effort.

Processing studies were conducted aimed at selecting optimum conditions for the processing of Refrasil, graphite, and titanium diboride fiber (as selected from the parallel program) reinforced composites prepared from selected candidate resin systems. Because of the scarcity of titanium diboride fibers, composites were prepared using only the A-type polyimide and a reference phenolic resin as matrices for this advanced fiber.

Small scale torch tests were conducted (termed PEET, for Propellant Exhaust Environmental Test) using both fluorine-hydrogen and FLOX(82.5% w/w fluorine, 17.5% oxygen)/methane combustion environments to determine the ability of candidate materials to withstand both the thermal and chemical combustion environment offered by these propellant systems. A series of recommended commercially available ablative materials were tested for PEET ablative performance to serve as a reference for comparison to judge the degree of improvement provided by the advanced composites prepared in this program. It was confirmed in these studies that the primary property characteristic for selection of improved ablative resin matrices is that of high char yield, as formed from aromatic/heterocyclic polymeric backbones.

Testing of the materials generated in this program showed that graphite and refrasil reinforced A- and B-type polyimides had superior char integrity and were not subjected to thermal shock fracture as were similar composites prepared from phenolic resins. Comparable composites prepared from the third candidate resin system, polyamide-imide, exhibited poorer performance. Composites prepared using titanium diboride fibrous reinforcement failed catastrophically during PEET evaluation, presumably caused by excessive heat transfer (high fiber thermal conductivity) to the resin beneath the FLOX/methane combustion gas ablative specimen interface inflicting severe resin degradation.

In summary, two new processable heterocyclic/aromatic polymer systems were developed in this program which when combined with suitable reinforcement demonstrated improved ablative performance in fluorine-containing combustion gas environments. These two new resin systems offer the advantage over state of the art resins in that they can be processed by conventional techniques and result in compact, dense materials, and hence, are suitable for use in fabrication of large size ablative composite materials.

1. INTRODUCTION

This report presents the work accomplished by TRW Systems for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-7949. This program entitled, "Investigation of Resin Systems for Improved Ablative Materials," is a continuation of studies performed under Contract NAS3-4188. The objective is the preparation of ablative composites with improved resin matrices suitable for use as advanced nozzles for rocket engines employing high energy propellants, such as fluorine/hydrogen and fluorine-oxygen/methane. Ablative composites employing improved resins will exhibit the following features: low ablation rates, resistance to severe chemical environments, ability to withstand extremely high temperatures for extended periods of time, and capability to perform successfully when subjected to engine duty cycles of varying durations.

In Contract NAS3-4188, analytical and experimental determinations provided 1) the critical parameters which control the effectiveness of resins in the ablative use environment, 2) new resin systems tailored and evaluated experimentally to verify the criteria established for resin ablative utilization, and 3) resins recommended for future studies (Ref. 1).

Advanced ablative resin systems identified in Contract NAS3-4188 were in various stages of development. The current program (under Contract NAS3-7949) was organized to continue the development and testing of candidate resins through systematic synthesis, property determination, and optimization studies in order to select the most promising resins for composite formulation studies.

In a parallel NASA sponsored program (Contract NAS3-7948), new fibers and reinforcing agents which improve the properties of composites in fluorine containing high energy propellant combustion environments were synthesized and fabricated. In this program (Contract NAS3-7949), composite studies were conducted to determine the processing and composition parameters required for preparation of composite structures from 1) the resin matrices selected under Contract NAS3-7949 and 2) the advanced fibers and reinforcing agents generated in the parallel program.

To accomplish the program objective it was necessary to conduct consecutive material development tasks for synthesis and property determinations, resin formulation optimization, composite processing parameter studies, synthesis scale-up, fabrication of ablative composites and test and evaluation of the most promising candidate formulations. The principal contribution of the overall effort was the synthesis and evaluation of two new thermally stable, high char forming resin systems which offer significant processing advantages over state of the art competitive systems. Ablative composites prepared from these systems demonstrated enhanced stability in fluorine-containing combustion gas environments, and hence, show promise for being processed into larger scale structures for comprehensive engine evaluations.

This report is divided into four principal sections covering consecutive program tasks:

- Synthesis of new resin systems and property characterizations,
- Optimization of previously identified candidate resin systems and selection of the more promising systems for further study,
- Development of processing technology for the preparation of reinforced candidate systems, and
- Ablative performance evaluation of the candidate composite materials.

The significant conclusions reached from evaluation and assessment of the test data are listed together with recommendations of activities that warrant further investigation. This report identifies in a separate section the new concepts originating from the program. The information presented in the main body of this report is supplemented by appendicies covering detailed descriptions of procedures, equipment and raw test data.

2. SYNTHESIS AND PROPERTY DETERMINATIONS OF RESINS

Under Contract NAS3-4188, materials were identified which offer the potential of yielding improved ablative resins in a fluorine-containing combustion environment. These materials were reviewed during the first six months of the current program under Contract NAS3-7949 (Ref. 2) with the conclusion that "stiff" polymers (polymers whose "backbones" are characterized by a multiplicity of aromatic groups) were the class of organic polymers best able to withstand the combustion environment of fluorine-containing propellant systems. In this review it was ascertained that current "stiff" polymers were difficult to process into the compact, void-free laminates required for ablative use. Consequently, polymers were investigated which would exhibit ease of processing into laminates yet exhibit the desirable stability of current "stiff" polymers.

In response to this need for thermally stable, yet readily processable polymers, TRW Systems proposed the synthesis of two types of "stiff" polymers:

A Type:	Polymer compositions whose "backbones" contain cyclic chemical groups which are amenable to thermally induced aromatization or polymerization. This curing mechanism is unique in plastic art.
B Type:	Polymer compositions whose "backbones" contain thermally stable, "flexible" chain segments. These polymers cure by conventional means, however, reduced volatile matter is achieved because of higher molecular weight of monomeric constituents. Because this type of "stiff" polymer is potentially soluble in common laminating solvents, the fully cured resin can readily be preimpregnated in ablative reinforcement materials and hence, is amenable to "dry bonding" processing, thereby eliminating the problem of volatile by-products.

The advantages of these two types of polymers in the processing of laminates were described in detail in the Interim Progress Report (Ref. 2). The initial A-type polymer planned for synthesis was that obtained by condensing bis(3,4-dicarboxy-2,3,4, 5-tetrahydrophthalic) sulfone dianhydride monomer with a diamine. Studies of model compounds to determine the temperatures required for thermally induced aromatization led to the identification of an alternative A-type polyimide approach, namely, preparation of relatively low molecular weight polyimide prepolymers capped with 3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalic anhydride which cure to load bearing plastics on pyrolysis at elevated temperature. The initial B-type polymer planned for synthesis was the polyimide obtained by condensing bis(3, 4-dicarboxyphenoxyphenyl) sulfone dianhydride monomers with a diamine. A second B-type polymer investigated was the polybenzimidazole produced by condensing bis(4-carboxyphenoxyphenyl) sulfone with a tetramine.

In this section of the report are presented detailed discussions of the accomplishments on the planned synthesis of the A- and B-type polymers, the results of thermal property measurements of model compounds and intermediates of A- and B-type polymers, and a discussion of an alternative synthesis route for achieving the Task I objective of preparation of readily processed "stiff" polymers.

2.1 SYNTHESIS OF NEW MONOMERS AND PREPOLYMERS

This section describes the accomplishments of the monomer synthesis program. Details of the compounds synthesized and their characterization are given in Appendix A.

2.1.1 A-Type Monomers and Prepolymers

2.1.1.1 Bis(3, 4-dicarboxy-2, 3, 4, 5-tetrahydrophthalic) Sulfone Dianhydride - Crude bis(3, 4-dicarboxylic acid-2, 3, 4, 5-tetrahydrophthalic) sulfone, the precursor to the monomer bis(3, 4-dicarboxy-2, 3, 4, 5-tetrahydrophthalic) sulfone dianhydride, was prepared in order to synthesize A-type polymers. The planned synthesis route to obtain this material was described in detail in the Interim Report (Ref. 2) and consists essentially of 1) reacting di-n-butyl tetrahydrophthalate with sulfur monochloride to form the bis-chloro sulfide adduct, 2) oxidizing the sulfide adduct to the sulfone, 3) dehydrochlorination of the sulfone, 4) saponification of the butyl ester, and 5) dehydration to bis(3, 4-dicarboxy-2, 3, 4, 5-tetrahydrophthalic) sulfone dianhydride. In the Interim Report the progress of this anhydride synthesis proceeded through the preparation of the bis-chloro sulfone intermediate.

During this report period, dehydrochlorination of bis(6-chloro-3, 4-n-butyl carboxy cyclohexyl) sulfone (an intermediate in the preparation of the desired anhydride) was effected using triethylamine. Evidence that the unsaturated intermediate was produced consisted of 1) the isolation of 93% of the expected yield of amine hydrochloride, and 2) the appearance in the infrared spectra of an infrared band at 1650 cm^{-1} indicating the presence of the carbon-carbon double bond. Transesterification of the unsaturated intermediate was effected using acetic acid in order to prepare the corresponding tetrabasic acid. (Note: Saponification with base, a technique usually employed for the isolation of acids from their corresponding esters, is not suitable here because the vinyl sulfone is destroyed by base.) The product isolated was found to exhibit a hydrogen ion equivalent of 9.34 meg/g (theoretical amount is 9.95 meg/g).

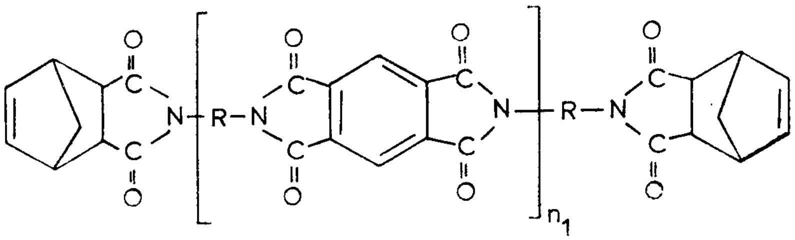
Isolation of polymer-grade tetrabasic acid was attempted by recrystallization of the crude material from water. It was found that the tetrabasic acid does not readily crystallize from aqueous solution. On the other hand, water was found to extract the tetrabasic acid from the impurities in the product. This phenomenon was useful for upgrading the product; nevertheless, recrystallization of the desired product was required in order to obtain polymer-grade material. Investigation of several organic liquids did not provide a suitable recrystallization matrix. Details of the synthesis and characterization of these products are presented in Appendix A.

2.1.1.2 A-Type Prepolymer - During the course of the synthesis of the new dianhydride described above (Section 2.1.1.1), property determinations of model compounds were conducted to determine the thermal and structural requirements for induced aromatization of partially unsaturated chemical groups. This activity was undertaken to insure that the theory proposed in the Interim Report for curing the A-type polymer by thermal treatment was feasible. The model compounds synthesized contain chemical configurations which simulated those planned to be in the backbone of the A-type polymers. During this study, discussed in detail in Section 2.3.1, it was found that pyrolysis of imide structures which were capped with 3,6-endomethylene-1,2,3,6-tetrahydrophthalic anhydride at temperatures above 280°C resulted in the formation of polymeric matter having relatively high char yields. This concept was extended to provide a facile means for producing high molecular weight resin masses. The approach here consists of preparing low molecular weight A-type prepolymers having a backbone chain terminated by nadic anhydride. The aromatic polyimide structure characterizes the "backbone" of the polymers. The molecular weights of these prepolymers would be formulated to be relatively low (1000-2000 g/mol) in order to facilitate subsequent fusion and/or dissolving them in suitable solvents. On fusion at elevated temperature, polymerization would occur in situ to form high molecular weight polyimide structures. Two types of A-type polyimides were prepared using this nadic anhydride capping approach. The differences between these classes of prepolymers was in the utilization of the following two different dianhydrides as part of the polyimide backbone:

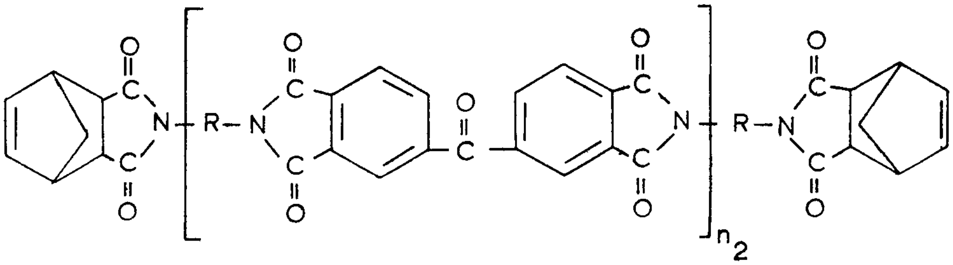
- Pyromellitic dianhydride (PMDA), and
- 3,3',4,4'-Benzophenone tetracarboxylic acid dianhydride (BTDA).

The prepolymers prepared had formulated number average molecular weights of approximately 1000 g/mol and consisted of the following:

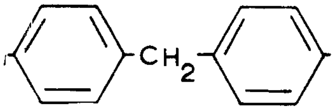
Group NP - Imides from Pyromellitic Dianhydride



Group NB - Imides from 3, 3'4, 4'-Benzophenone Tetracarboxylic Acid Dianhydride

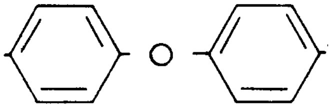


Where R =



as obtained from 4, 4'-methylenedianiline
and $n_1 = 1.3395$ and $n_2 = 1.0514$ (where n is the multiple required to yield a molecular weight of 1000 g/mol)

or where R =



as obtained from 4, 4'-oxydianiline
and $n_1 = 1.3272$ and $n_2 = 1.0430$ (where n is the multiple required to yield a molecular weight of 1000 g/mol)

Details of the synthesis of these prepolymers are given in Appendix A.

2.1.2 B-Type Monomers

2.1.2.1 Bis(3,4-dicarboxyphenoxyphenyl) Sulfone Dianhydride - The synthesis route for the preparation of bis(3,4-dicarboxyphenoxyphenyl) sulfone dianhydride (BSDA) is shown in Figure 1. Details of the synthesis of the intermediates, bis(3,4-dimethylphenoxyphenyl) sulfone and bis (3,4-dicarboxyphenoxyphenyl) sulfone, and the BSDA product are given in Appendix A. The coupling reaction is quite straightforward, however, the oxidation to the tetraacid intermediate must be performed under carefully controlled conditions in order to insure that complete oxidation takes place without attack of the aromatic backbone or decarboxylation. Because high purity monomeric starting materials are required to prepare polymers having high molecular weight, emphasis was placed on the purification and characterization of the B-type monomers. Two approaches to preparing high purity monomers were investigated:

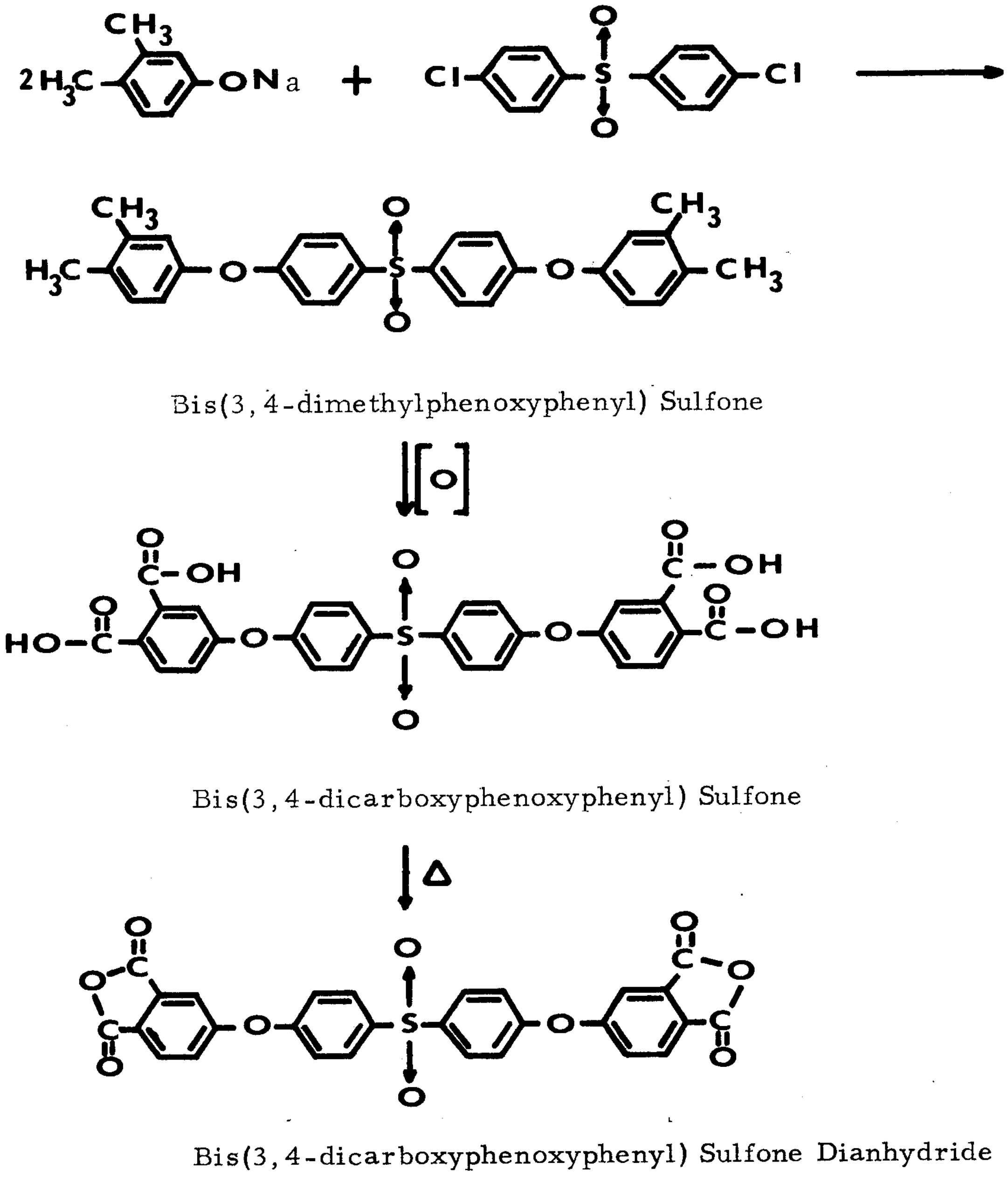


Figure 1. Synthesis of Bis(3,4-dicarboxyphenoxyphenyl) sulfone dianhydride

- Purification of the tetraacid intermediate after the oxidation step, and
- Improvement of the yield of the tetraacid obtained during the oxidation step.

Details of these studies are reported below.

2.1.2.1.1 Purification of the Tetraacid After Oxidation - Studies were undertaken to improve the purity of the bis(3,4-dicarboxyphenoxyphenyl) sulfone (tetraacid) after the oxidation step. The tetraacid was first recrystallized from acetic anhydride as the corresponding bis(3,4-dicarboxyphenoxyphenyl) sulfone dianhydride. The dianhydride obtained had a neutralization equivalent of 129 g/eq (theoretical = 135 g/eq) and a melting point range of 246° to 248°C. Further purification was accomplished by boiling the material in water for 15 minutes. The dianhydride was not soluble, hence, the procedure permitted the leaching of low molecular weight acids (acetic acid) which may have adsorbed on the dianhydride during crystallization. The product after leaching with water, isolation, and drying, had a neutralization equivalent of 133 g/eq. In previous I R and D studies at TRW, it was found that the corresponding tetraacid is soluble in hot water, hence, it is clear that the dianhydride is rather stable to hydrolysis. Infrared analysis of the leached product did not show the presence of carboxyl groups, whereas the preleached product did indicate the presence of this impurity.

It was possible to hydrolyze the bis(3,4-dicarboxyphenoxyphenyl) sulfone dianhydride by boiling the material in water for extended periods of time (approximately six hours). On cooling the solution, the tetraacid crystallized as fine needles. The crystals were isolated from the solution and dried under vacuum over P_2O_5.

The procedure described above permits the preparation of very pure tetraacid and dianhydride suitable for use in polymer synthesis.

2.1.2.1.2 Oxidation of Bis(3,4-dimethylphenoxyphenyl) Sulfone - The second approach to improve the purity of the B-type monomers consisted of investigation of the oxidation of bis(3,4-dimethylphenoxyphenyl) sulfone to bis(3,4-dicarboxyphenoxyphenyl) sulfone. The object of these studies was to synthesize a purer product from the oxidation step, thereby simplifying the subsequent purification procedures. As a direct consequence of this improvement, a greater yield of pure material should also result.

The stoichiometry of the constituents in the reaction vessel, and the conditions of the oxidation reaction, were varied systematically to determine the effect of these variables on the purity and yield of the oxidation product. Table I summarizes the more significant results of this study.

TABLE I

VARIATION OF THE EXTENT OF PRODUCT OXIDATION WITH REACTION CONDITIONS

Run Number	Reaction Time, hrs		Yield, %	Equivalent[a] Weight, g/eq
	1st Oxidation	2nd Oxidation		
84	2.0	0.5	63.4	159.0
94	7.0	1.0	71.7	141.6
99[b]	6.0	1.0	73.2	161.1

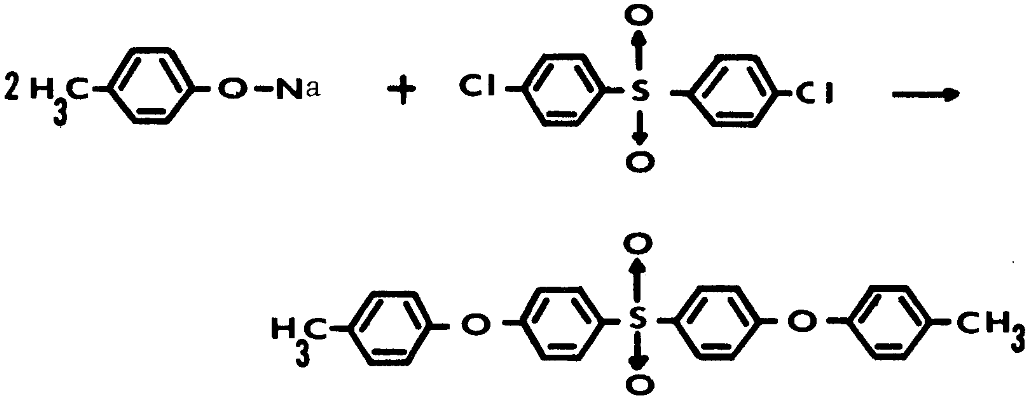
[a] Theoretical Equivalent Weight = 144.6 g/eq

[b] Run contains 20% theoretical excess of potassium permanganate in contrast to 10% excess in other runs.

These results show that product purity and yield was significantly improved by increasing the reaction time of the oxidation steps. On the other hand, employing additional oxidizer and increasing the reaction time did not increase the extent of oxidation of the product, (i.e., equivalent weight approximately the same as without enhanced conditions) nor did it increase the yield over that obtained from longer reaction time.

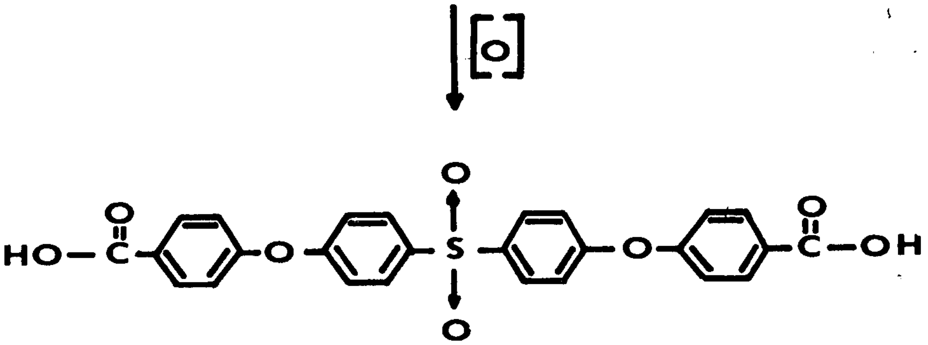
Scale up synthesis of the B-type dianhydride was straightforward and sufficient tetraacid was prepared to cover the requirements for the fabrication and evaluation of B-type composites (See Appendix E).

2.1.2.2 Bis(4-carboxyphenoxyphenyl) Sulfone - The synthesis route for the preparation of bis(4-carboxyphenoxyphenyl) sulfone (BCS) is shown in Equations 1 and 2. Details of the synthesis of the bis(4-methylphenoxyphenyl) sulfone intermediate and the BCS product are given in Appendix A.



(1)

Bis(4-methylphenoxyphenyl) Sulfone



(2)

The coupling and subsequent oxidation reactions were quite clean-cut yielding polymer grade purity material suitable for preparation of high molecular weight polymers.

2.2 POLYMER SYNTHESIS STUDIES

2.2.1 A-Type Polyimides

Group NB A-type polyimide prepolymers were prepared and isolated into two fractions as described in Appendix A. A soluble fraction (65%) and insoluble fraction (35%) were characterized by thermogravimetric analysis. During the heating of these prepolymers they were converted to A-type polyimides. The TGA curves obtained for the low molecular weight (soluble fraction) and high molecular weight (insoluble fraction products) are shown in Figure 2. It is seen from these curves that:

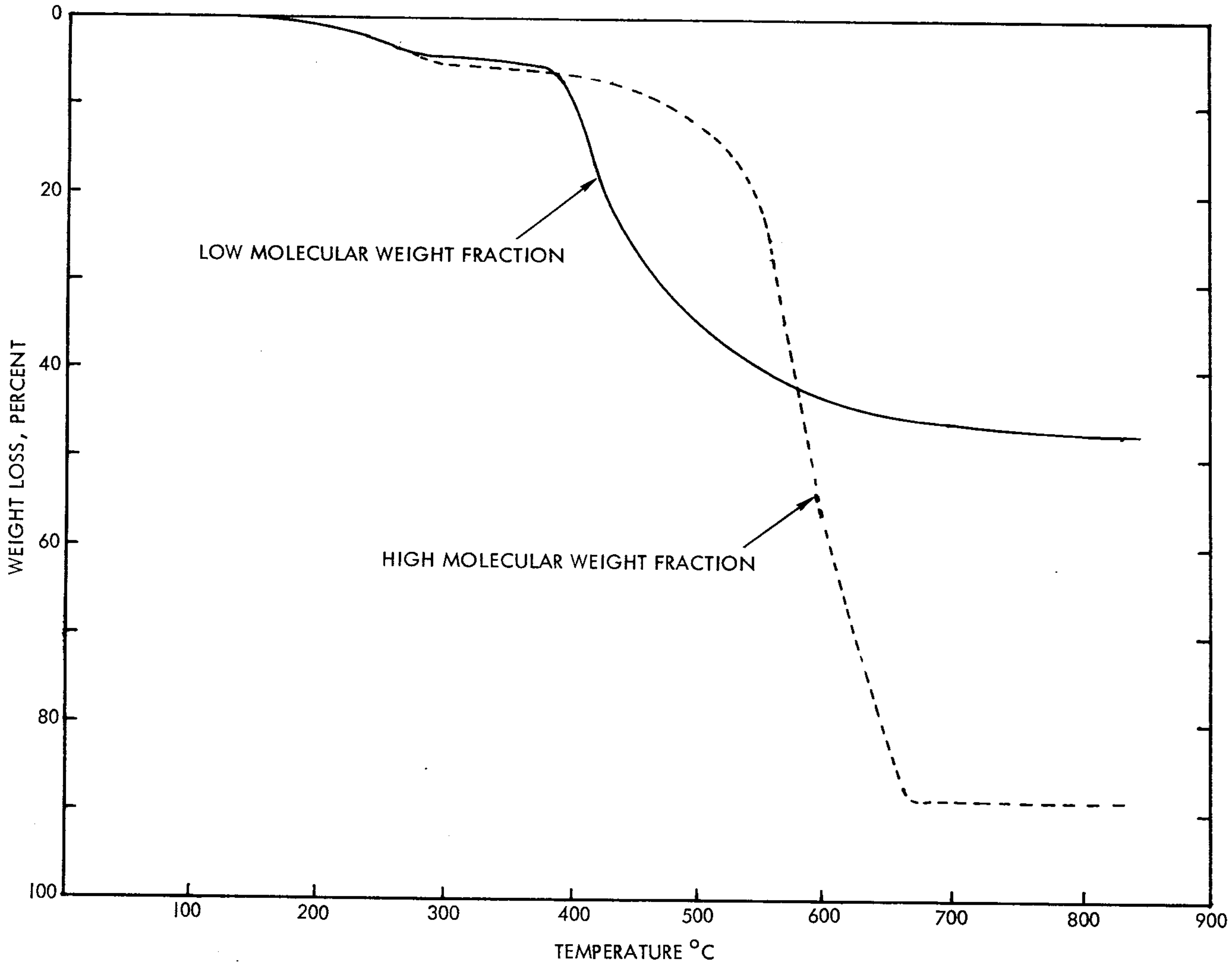


Figure 2. Thermogravimetric Analysis Curves of A-Type Group II High and Low Molecular Weight Fractions Prepolymers
Conditions: Heating Rate: 3°C/min
Conditions: Nitrogen Flow: 20 ml/min

- A weight loss of about 6% occurs at about 250°C;
- At 800°C the high molecular weight fraction retains only 12% of its mass as compared to 53% for the low molecular weight fraction.

The initial weight loss is attributed to the polymerization reaction. This observation is essentially identical to that reported for the model compounds described in Section 2.3.1. The differences between the curves shown in Figure 2 after about 400°C are attributed to differences in melting points which affect the mobility of the prepolymer molecules and hence, the degree of polymerization. That is, the low molecular weight fraction exists in a liquid state at 175°C and is amenable to chemical reaction at 250°C arising from the mobility of its molecules; conversely, the high molecular weight fraction is in a solid state at 250°C and chemical interaction is greatly reduced. This effect therefore, shows that lower molecular weight prepolymers ultimately polymerize to larger char-producing products than the higher molecular weight prepolymers. This observation indicates that a mixture of low and high molecular weight fractions would be desirable; the low molecular weight fraction would melt at 310°C (on the polymerization plateau of the curves in Figure 2) and wet the high molecular weight particles to cause interaction to produce greater amounts of char-forming products than with either of the high or low molecular weight fractions alone.

Resin masses were prepared from A-type Group NB prepolymers (methylenedianiline formulations) using equal weights of the high and low molecular weight fractions. The mixed powders were heated in a metal mold at 310°C under 2000 psig applied pressure for approximately 30 minutes. The resulting products were hard, tough and brown in color. This product is identified in this report as 50/50 MNB. The Barcol hardness of this product is compared with those of two commercial "stiff" polymer systems in Table II. The high value of the A-type resin masses was attributed to chemical crosslinking which is believed to have occurred during processing.

The thermogravimetric analysis curve of the moleded 50/50 MNB neat resin plug is shown in Figure 3. For comparison, the thermogravimetric analysis curve of a molded plug prepared from Amoco's AI-11 polyimide-

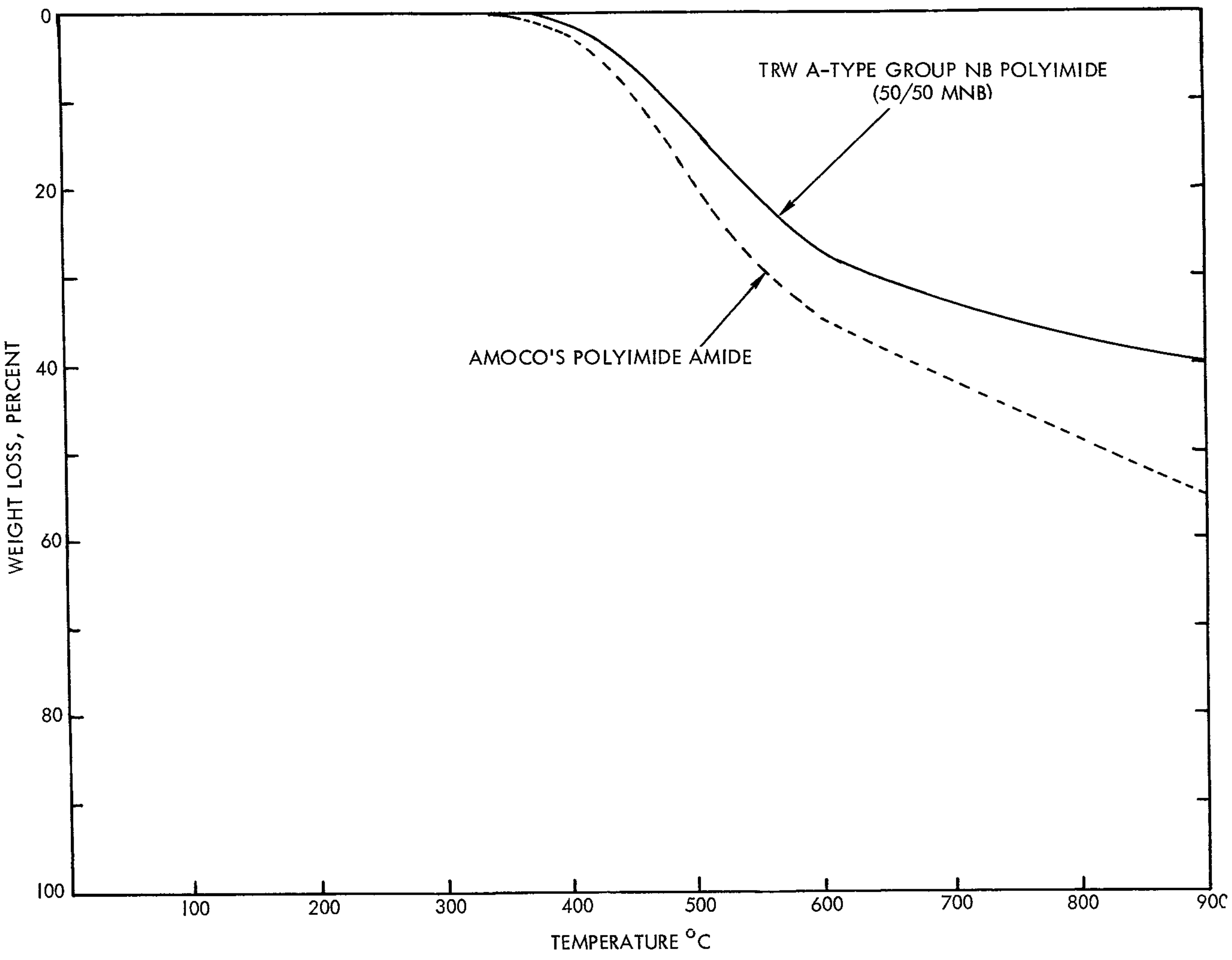


Figure 3. Thermogravimetric Analysis Curves of Molded 50/50 MNB A-Type Group NB Polyimide and Amoco's Polyimide Amide Heating Rate: 3°C/min Nitrogen Flow: 20 ml/min

TABLE II

HARDNESS OF NEAT POLYIMIDE RESINS

Polymer	Barcol Hardness
A-Type Group NB Polyimide	38
Amoco AI-11 Polyimide-Amide	28
DuPont SP-1 Polyimide	20

amide resin is also presented in Figure 3. It is seen that the A-type Group NB polyimide has approximately 15% more residue at 800°C than the comparable commercial resin. In addition, it is seen that the A-type molded product has no weight loss at 250°C (as compared to the prepolymers shown in Figure 2) and the weight retained at 800°C is greater than that of either the high or low molecular weight prepolymers.

In the preparation of the neat resin plugs it was observed that essentially zero volatile matter was evolved during cure. This observation shows that an addition-type polymerization reaction is occurring and hence demonstrates the high potential that this resin system has for preparing compact, void-free, thermally stable laminates. Details on the preparation and early results obtained using the A-type polyimide in preparation of laminates are presented in Appendix D.

2.2.2 B-Type Polymers

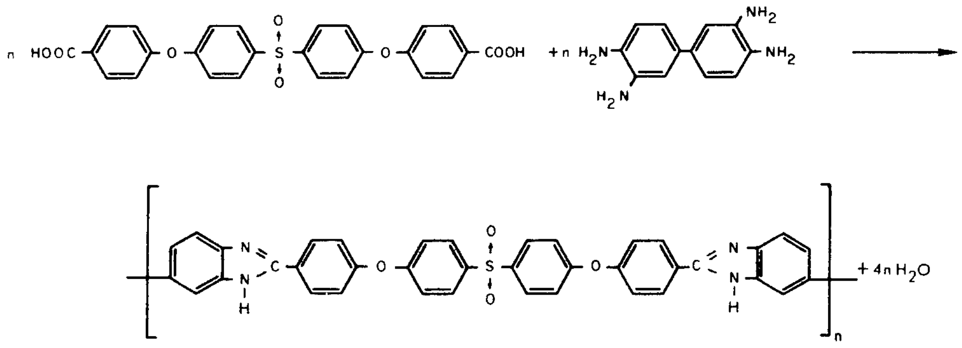
B-type polymer synthesis studies were conducted on the polybenzimidazole, polypyrrone and two polyimides. The scope of the overall activity in this phase of the work is shown in Table III which indicates the B-type condensation polymer class selected for laminating studies as a function of the B-type acid monomers and commercially available basic monomers constituents.

Although the major emphasis of the work is development of polyimides, with the pyrrone and polybenzimidazoles systems serving as comparative backup resins, the work on the polybenzimidazole (PBI) system progressed significantly faster because of the relative ease in isolating the necessary pure B-type monomer.

TABLE III
B-TYPE POLYMERS SELECTED FOR SYNTHESIS STUDIES

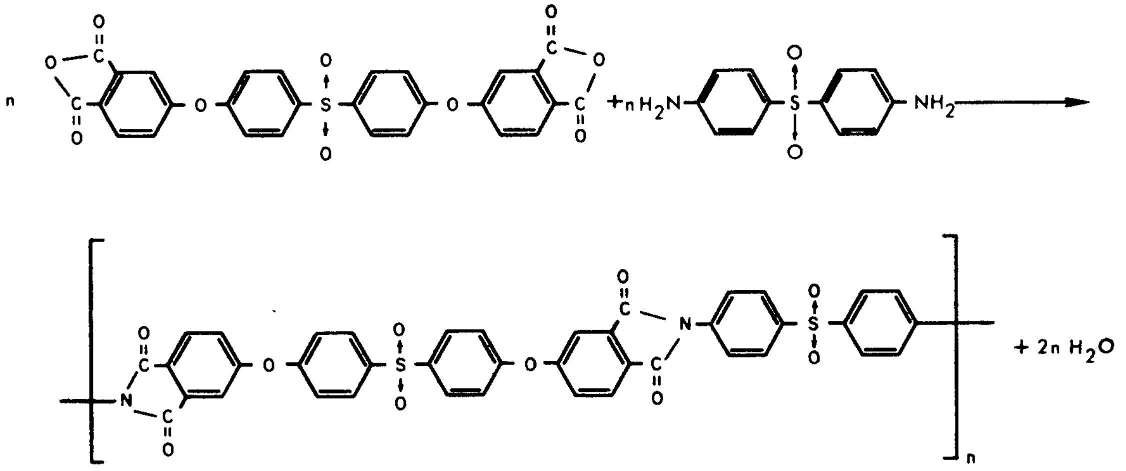
Basic Monomers	TRW Acid Monomers	
	bis(3, 4-dicarboxyphenoxyphenyl) sulfone	bis(4-carboxyphenoxyphenyl) sulfone
3, 3'-diaminobenzidene	Pyrrone	Polybenzimidazole
bis(4-aminophenyl) sulfone	Polyimide	
4, 4'-oxydianiline	Polyimide	

2.2.2.1 Polybenzimidazole - The polybenzimidazole was prepared by condensing bis(4-carboxyphenoxyphenyl) sulfone (BCS) with 3, 3'-diaminobenzidine in accordance with Equation 3. This polymer was soluble in dimethylformamide from which flexible films were cast. Characterization of this polymer is reported in Section 2.3.2. The thermal stability (840°F), incipient decomposition temperature, char forming capability (77% w/w) and apparent flow characteristics of the B-type polybenzimidazole were sufficiently promising to select this new polymer system for exploratory laminate studies. The results of these initial studies are presented in Section 4.



(3)

2.2.2.2 Polyimide - One B-type polyimide was prepared by condensing bis(3,4-dicarboxyphenoxyphenyl) sulfone dianhydride (BSDA) with bis(4-aminophenyl) sulfone in accordance with Equation 4. Similarly, B-type polyimides were formed by the condensation of bis(3,4-dicarboxyphenoxyphenyl) sulfone with 1) bis(4-aminophenyl) sulfone, and with 2) 4,4'-oxydianiline in dimethylformamide. The water evolved during condensation of these monomers was collected in both cases; the amount obtained was approximately 80% of the theoretical value. The apparent incomplete reaction was attributed to the relatively mild polymerization temperature of 130°C.



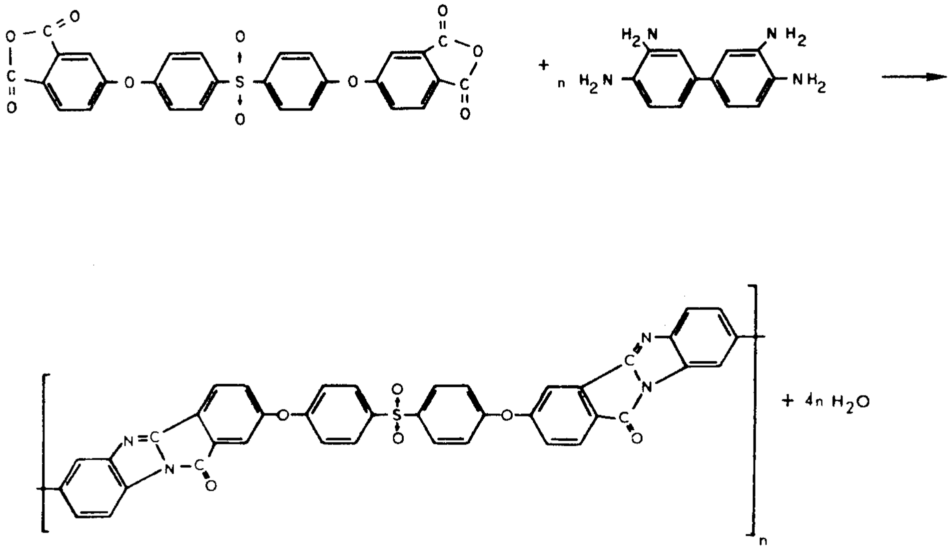
(4)

Higher reaction temperatures were employed in the polymerization of the tetraacid and oxydianiline. This was accomplished in two ways: 1) dimethylformamide was removed from the reaction vessel until the pot temperature reached 165°C and 2) dimethylsulfoxide was used as the solvent and the reaction carried out at 152°C. The reaction time for both preparations at these higher temperatures was 17 hours. In the studies described above, the polyimide polymer formed did not precipitate from solution during the reaction or on standing at room temperature. Infrared analysis of a polymer film obtained from the varnish showed that the elevated temperature reaction forced the reaction to near completion; there was evidence of only a trace of unreacted anhydride. Soluble aromatic polyimides have significance for use as resin matrices for ablative composites because they

- Facilitate the preparation of compact void-free composites by significantly reducing the volatile matter evolved during processing;
- Eliminate the necessity for use of hydrolytically and oxidative labile polyamic acids for coating reinforcing materials.

For the reasons listed above, the B-type polyimide prepared from 4, 4'oxydianiline and bis(3, 4-dicarboxyphenoxyphenyl) sulfone dianhydride was selected for exploratory laminate studies (See Appendix C).

2. 2. 2. 3 Polypyrrone - Polypyrrones were prepared by condensing bis-(3-4-dicarboxyphenoxyphenyl) sulfone dianhydride (BSDA) with 3, 3'-diaminobenzidine in accordance with Equation 5. Polypyrrone films were



(5)

heated in a tube under nitrogen in order to determine the resistance of the material to thermal distortion at elevated temperatures. It was found that heating at 400°C and 450°C, respectively for 3. 5 hours did not result in softening of the material. Inspection of the toughness of the polypyrrone indicated that the molecular weight obtained was relatively low. Studies using improved purity B-type monomers to yield higher molecular weight polymers were initiated and it was found that the pyrrone and its staged intermediates were insoluble. Further synthesis studies of the B-type pyrrone were terminated because 1) success was achieved in the polyimide system, and 2) it was desired to place additional emphasis on the polyimide laminate studies.

2.3 PROPERTY DETERMINATIONS

2.3.1 A-Type Polyimides

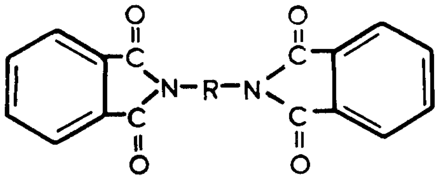
Model compounds which simulated the A-type polymers were prepared and were analyzed thermogravimetrically to obtain experimental evidence substantiating the occurrence of aromatization at relatively low temperatures. Details of these investigations are presented in this section because of the importance of these findings in establishing the A-type polyimide pyrolytic polymerization reaction.

2.3.1.1 Thermogravimetric Analysis of Model Compounds - The model compounds investigated in this program are classified in three different groups:

1. Fully aromatic dianhydrides
2. Partially unsaturated and bridged dianhydrides, and
3. Partially unsaturated dianhydrides.

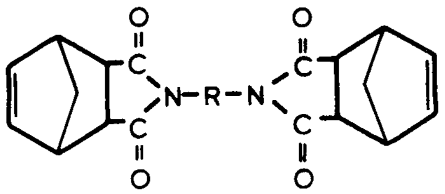
Specific compounds investigated in these three groups are listed below:

- Group I, Diimides from Phthalic Anhydride, having the general structure



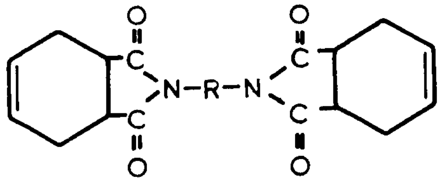
1. p, p'-Oxydiphenyl diphthalimide
2. p, p'-Methylenediphenyl diphthalimide
3. p, p'-Biphenyl diphthalimide
4. m-Phenylene diphthalimide

- Group II, Diimides from 3, 6-Endomethylene-1, 2, 3, 6-Tetrahydrophthalic Anhydride having the general structure of



1. p, p'-Oxydiphenyl-bis(3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalimide)
2. p, p'-Methylenediphenyl-bis(3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalimide)
3. p, p'-Biphenyl-bis(3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalimide)
4. m-Phenylene-bis(3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalimide)

- Group III, Diimides from 1, 2, 3, 6-Tetrahydrophthalic Anhydride having the general structure of



1. p, p'-Oxydiphenyl-bis(1, 2, 3, 6-tetrahydrophthalimide)
2. p, p'-Methylenediphenyl-bis(1, 2, 3, 6-tetrahydrophthalimide)
3. p, p'-Biphenyl-bis(1, 2, 3, 6-tetrahydrophthalimide)
4. m-Phenylene-bis(1, 2, 3, 6-tetrahydrophthalimide)

The syntheses of the model compounds which have not been described previously are given in Appendix A of this report. Thermograms of the methylenediphenylimides of the three dianhydrides are shown in Figure 4. These curves are representative of the three groups of model diimides. Thermograms of each of the model compounds are shown in Appendix A.

Inspection of Figure 4 provides some interesting insight concerning the thermal behavior of the three groups of model compounds. The order of increasing residue at elevated temperature was Group I (purely

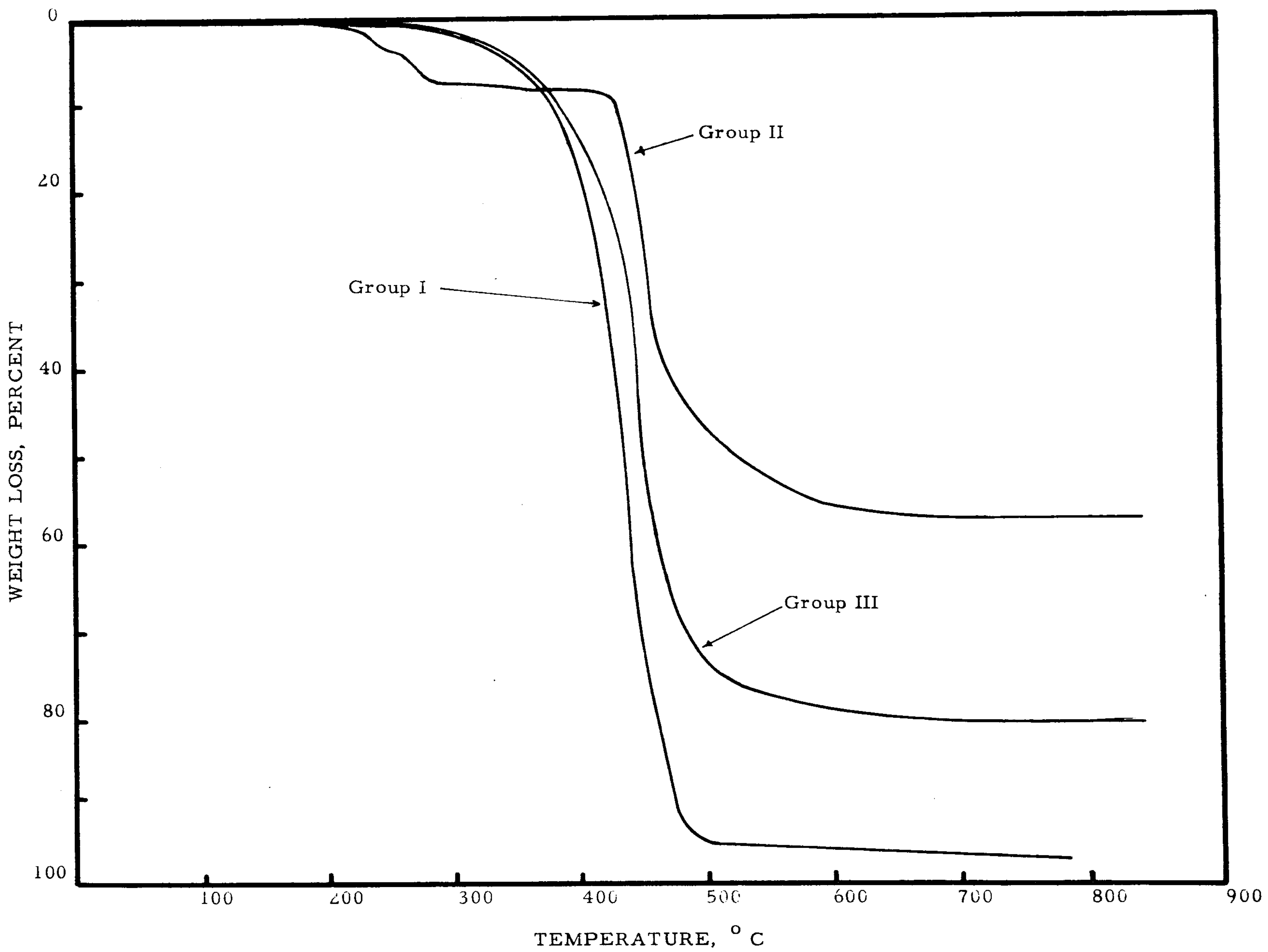


Figure 4. Thermograms of Model Diimide Compounds

aromatic structure)<Group III (partially unsaturated structure)<Group II (partially unsaturated bridged structure). The Group II analog had a loss of weight at a lower temperature (230° - 280°C). From 280° - 425°C, no apparent change in weight of the Group II compound was observed. In contrast, the Group I and Group II compounds exhibited continual weight losses in this temperature range.

2.3.1.2 Interpretation of TGA Curves - Interpretation of the facts presented above leads to the conclusion that macromolecules were formed on heating the Group II model compounds. In a sense this was accomplished by a thermal "polymerization" of the intermediate products arising from controlled pyrolysis of the bridged structure. Specifically, this conclusion resulted because

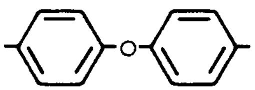
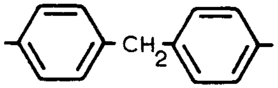
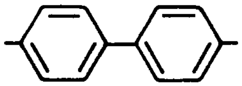
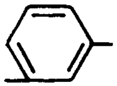
- The Group II models exhibited stability by displaying no weight loss over the 280° - 425°C temperature range.
- Without the formation of macromolecules, the resultant product formed at 280°C would be expected to volatilize, and hence, the curve would be similar to that of the Group I compound in the 280° - 425°C temperature range.

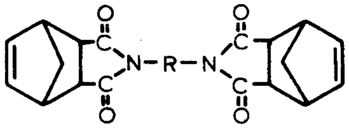
Table IV summarizes the experimental thermal properties of the Group II model compounds. These data indicate that the weight loss cannot be attributed to the quantitative reverse Diels-Alder reactions resulting in the evolution of cyclopentadiene because the weight losses associated with that mechanism would be about five times the observed results. In the range of 400° - 425°C, significant weight losses occur which give rise to the third inflection. Approximately 40-45% of the original weight of the compounds is retained at 800°C. It is believed that these significant amounts of thermally stable residues arise from thermally induced chemical compositional changes occurring at lower temperatures in which aromatization accompanies the formation of macromolecules.

Figure 5 provides a comparison of the thermograms obtained from polypyromellitimides with those exhibited by the Group II compounds. As can be seen, the sharp break in the thermogram of the Group II materials occurs at approximately 425°C which corresponds to the temperature region where significant pyrolytic weight loss begins in polypyromellitimides

TABLE IV

Thermal Properties of Di-3, 6-Endomethylene-1, 2, 3, 6-Tetrahydrophthalimides*
Group II Compounds
(R = diamine component)

Diamine Component R	Melting Point, °C	First Weight Loss Inflection		Second Weight Loss Inflection		Third Weight Loss Inflection	
		Temperature, °C	Weight Loss Percent	Temperature, °C	Weight Loss Percent	Temperature, °C	Weight Loss Percent at 800°C
	260-5	235	3.66	287	7.85	400	56.5
	254-7	190	3.05	240	7.64	425	60.9
	286-90	240	3.41	285	6.96	410	56.3
	243-7	200	3.89	230	16.9	410	60.6

* 

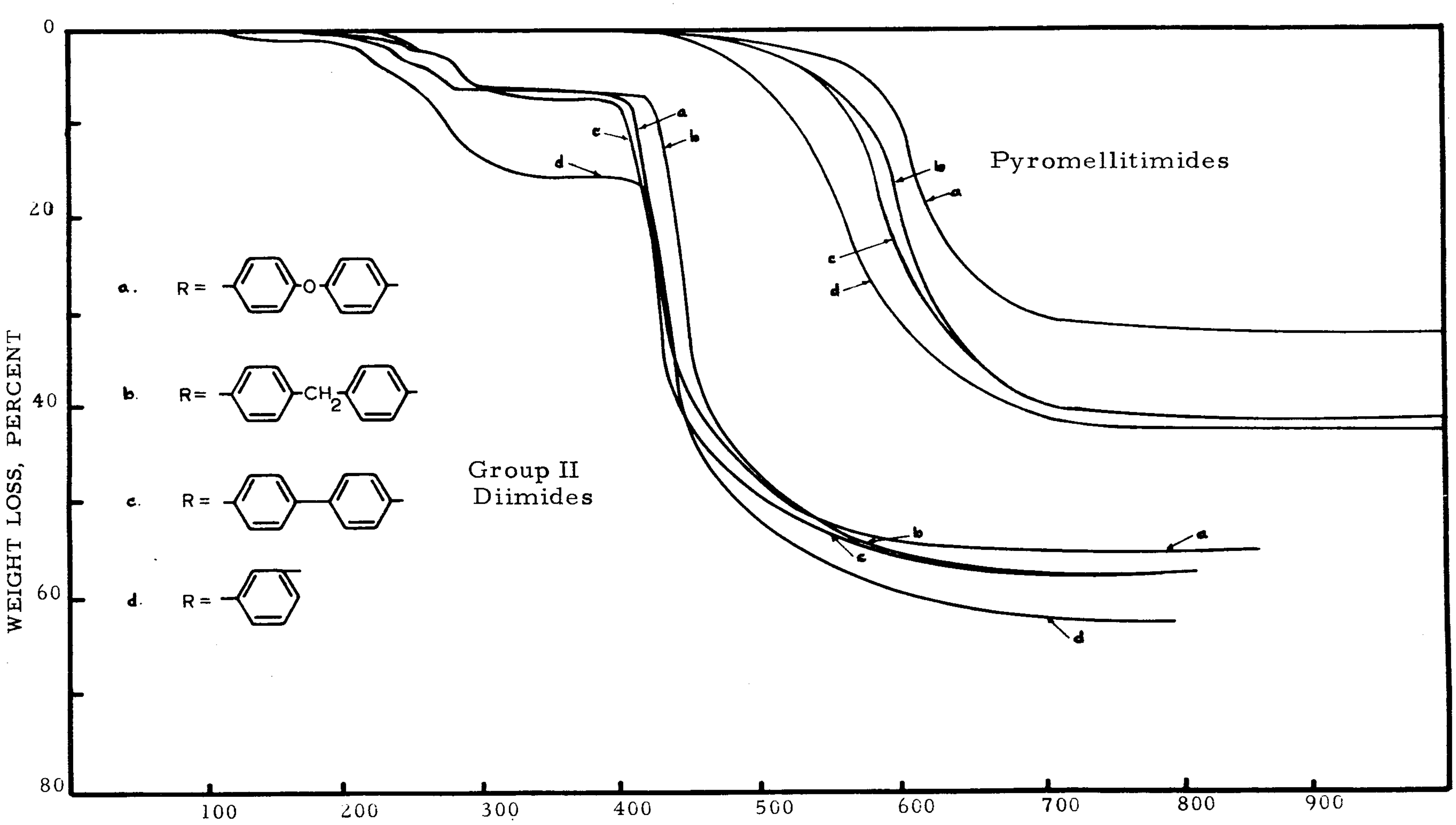
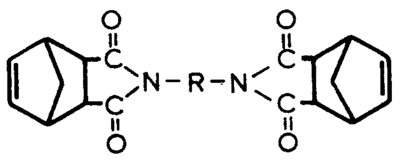
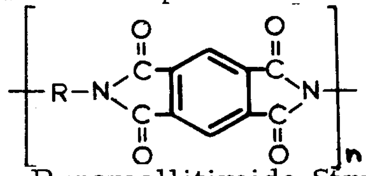


Figure 5. Effect of Diamine Structures on Weight Loss of Group II Diimides and Pyromellitimides



Group II Dimide Structure



Pyromellitimide Structure

Envirnoment: Dry helium Scan Rate: 3°C/Min.

prepared from methylene dianiline. The macromolecules formed from the Group II model compounds were speculated to have a greater amount of aliphatic structure than that of the corresponding polypyromellitimides. Consequently, it is believed that the differences in the shapes of the thermograms between the model compounds and the polymers arise strictly from pyrolysis of the different amounts of aliphatic structure.

The thermal properties of the Group I and Group III compounds are summarized in Table V. In general, the shapes of their thermograms (See Appendix A) were single S-shaped curves with incipient weight loss temperatures of around 300°C. It was interesting to note that the temperatures of initial weight losses are approximately the same for all the compounds examined although their melting points vary significantly. At 800°C, the preponderant amount of the original material was lost approximately 80-95% by weight. This weight loss was attributed principally to volatilization of the compound. The Group I compounds volatilize with a small amount of chemical decomposition, whereas a greater amount of chemical decomposition was found to accompany the volatilization of the Group III compounds.

Evidence to date indicates that Group III compounds aromatize at elevated temperatures without formation of appreciable quantities of macromolecules. This speculation is based on the following experimental facts:

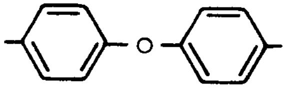
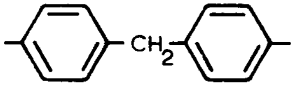
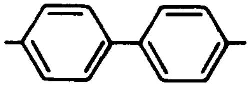
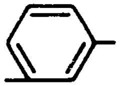
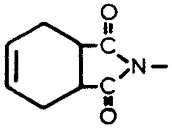
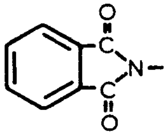
- The temperature of initial weight loss of Group I and Group III compounds are approximately the same (see Table V).
- The consistently greater amount of weight retention at 800°C of Group III compounds compared to Group I compounds indicates that some decomposition of the Group III compounds at elevated temperatures occurs to form thermally stable compositions of matter.

2. 3. 2 B-Type Polymers

2. 3. 2. 1 Theoretical Considerations - An assessment of the thermal stability of organic polymers of the B-type was made through a review of the literature of model compounds. Results of this assessment have shown that these compounds should produce advanced, thermally stable polymers.

TABLE V

Thermal Properties of Group I and Group III Compounds

Acid Anhydride Component	Thermal Properties	DIAMINE COMPONENT			
					
a. 	Melting Point Range, °C	242-4	212-6	299-02	200-1
	Temperature Initial Weight Loss, °C	300	310	280	290
b. 	Melting Point, °C	289-291	>300	>300	>300
	Temperature Initial Weight Loss, °C	330	320	330	310

a. Group I compounds

b. Group III compounds

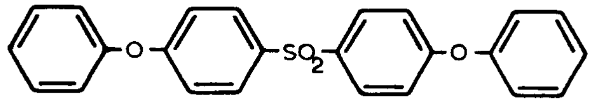
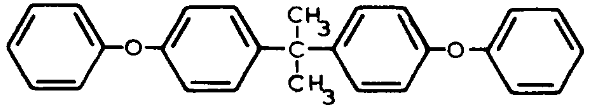
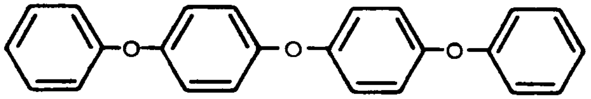
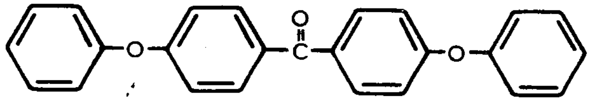
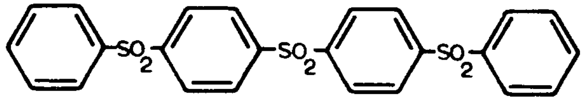
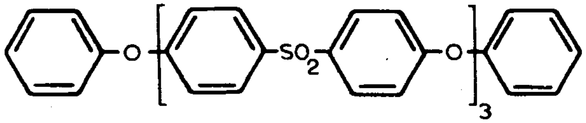
It was proposed that the B-type dianhydride-terminated monomer, which consist of four phenyl groups interconnected by a single atom (either with or without substituent groups), would be converted to polymers by condensation with di- or tetra-amines with greater processing ease than current polymers prepared from dianhydride monomers containing a single phenyl group (pyromellitic dianhydride). In a recent review (Ref. 3), 29 dianhydride monomers were evaluated which have two phenyl groups interconnected with one or two atoms. From this review, it was ascertained that two aryl anhydrides connected by a single atom was generally a far more thermally stable structure than comparable structures having two connecting atoms. Further, polymers prepared from anhydrides having a single atom connecting two aryl anhydrides offer modest improvement in processing over pyromellitic dianhydride.

In a recent paper discussing the thermal behavior of pertinent model compounds (Ref. 4), phenoxyphenyl sulfone was shown to be a highly thermally stable composition of matter. This reiterates and further supports the expected thermal stability of the dianhydride monomer as described in Section 2.3.2.2 below. The results of the thermal stability studies (Ref. 4) of this model compound and related analogs are shown in Table VI.

2.3.2.2 Experimental Determination of Thermal Stability - The B-type polybenzimidazole and polypyrrone products obtained from condensing diaminobenzidine with BCS and BSDA were examined by thermogravimetric analysis (TGA) to evaluate the thermal stability and char forming capability of polymers containing the phenoxyphenyl sulfone backbone. Thermogravimetric analysis of both the polypyrrone and the polybenzimidazole (Figures 6 and 7) show that these materials are stable in nitrogen to approximately 450°C (~ 840°F) and, in addition, yield appreciable char - this being indicated by approximately 70% weight retention of the materials at 900°C (~ 1650°F). The assymptotic nature of the TGA curve at increasingly high temperatures indicates that the resulting chars are stable at the elevated temperatures. In addition, the polybenzimidazole was found to be stable in air to 450°C as well as in nitrogen (Figure 7).

TABLE VI

THERMAL STABILITY OF B-TYPE POLYMER MODEL COMPOUNDS AT 400°C

Model	Time, Hour	Atmosphere	Weight Loss, %	Color[a]	Melting Point, °C	Original Melting Point, °C
	5	N_2	0.19	White	140-141-142	141-142
	5	Air	4.	Amber	115-121-133	141
	5	N_2	0.74	Lt. Yellow	55-58-60	62-63
	2.5	Air	4.7	Brown	Liquid	62
	5	N_2	0.37	White	107-109-110	108-109-110
	5	Air	11.1	Brown	85-87-105	108
	5	N_2	0.32	Lt. Yellow	145-146-147	146-147
	2.5	Air	1.89	Brown	135-140-144	146
	5	N_2	5.1	Amber	278-280-285	309-311-312
	5	N_2	0.2	Lt. Yellow	215-219-230	225-229-233

a. All compounds were initially white, crystalline solids.

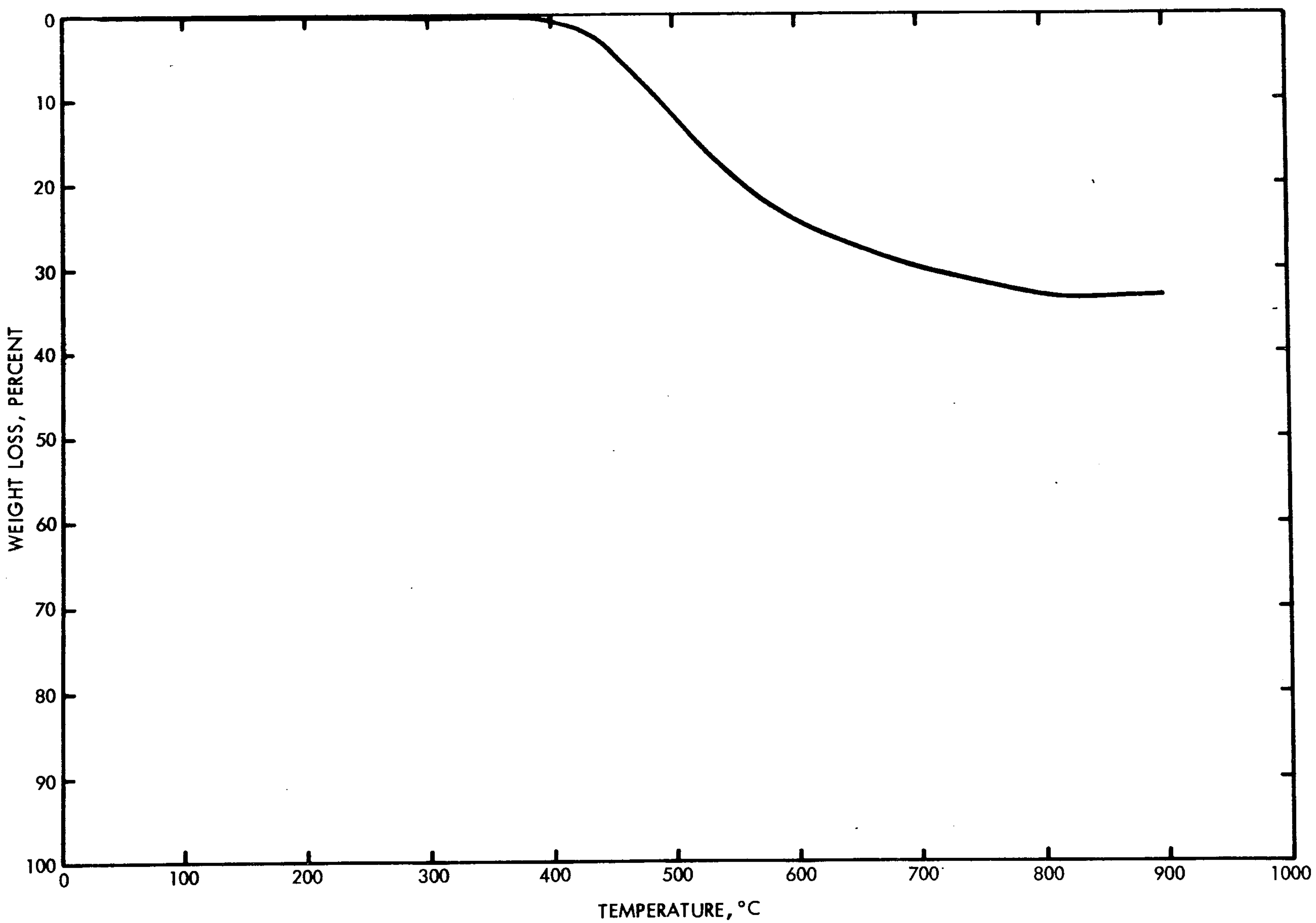


Figure 6. Thermogram of Polypyrrone Condensation Product of Bis(3, 4-dicarboxyphenoxyphenyl) Sulfone Dianhydride and Diaminobenzidine
Environment: 1 atm N_2 Flow Scan Rate: 3 ^{o}C/Minute

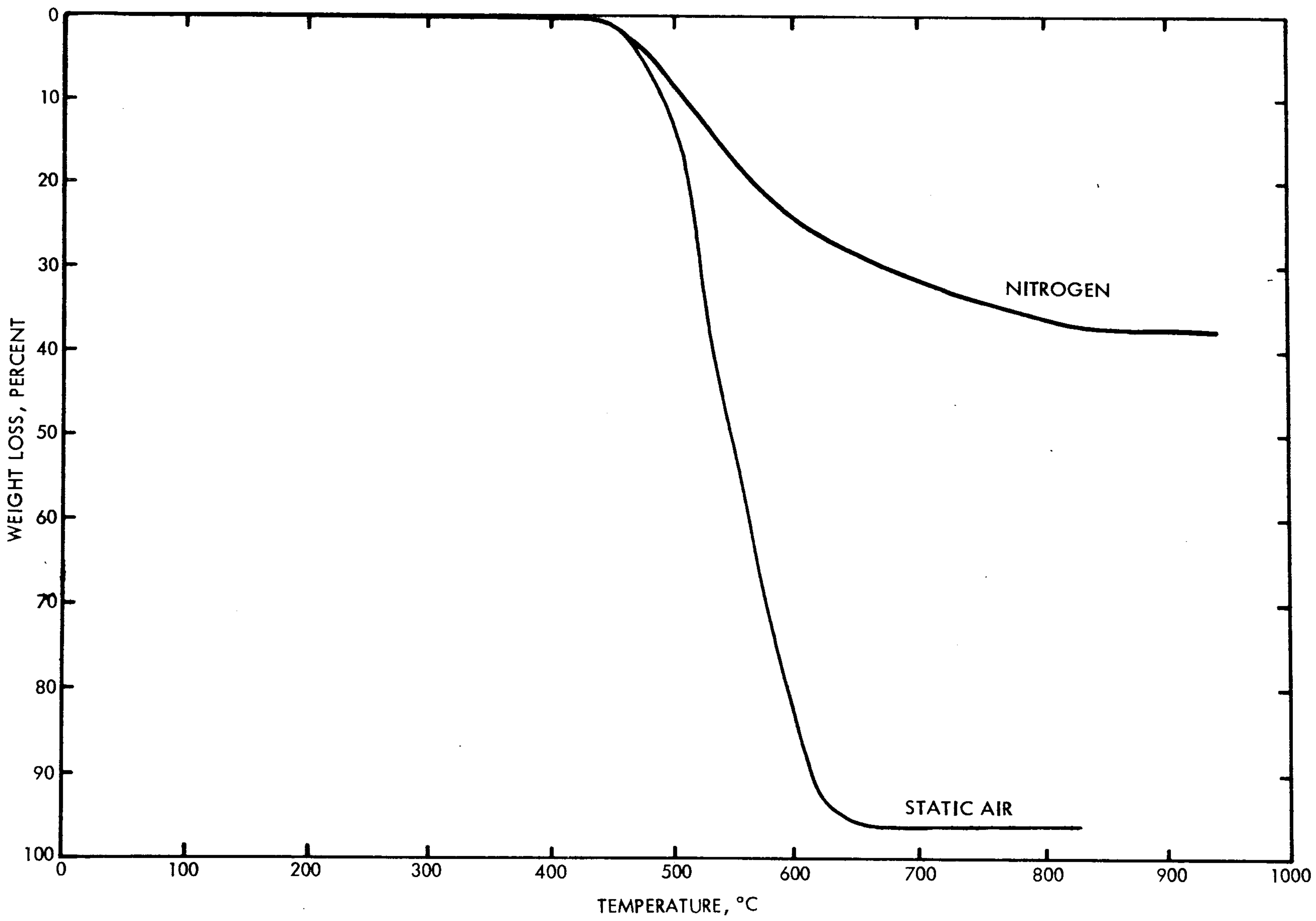


Figure 7. Thermograms of Polybenzimidazole Condensation Product of Bis(4-carboxyphenoxyphenyl) Sulfone and Diaminobenzidine in Flowing Nitrogen and Static Air Environments
Scan Rate: 3^{o}C/Minute

The apparent stability of the polymer in air indicates that this material may exhibit value as an adhesive matrix for high performance structural composites as well as ablative composites.

3. RESIN OPTIMIZATION

The investigations conducted during Contract NAS3-4188 identified either newly synthesized or commercially available resin systems suitable for future combination in fibrous reinforced composites as advanced ablative materials. Several of these resin systems required optimization to improve their overall ablative performance in fluorine-containing combustion environments. Optimization of resin matrices required an ordered investigation of resin properties and a determination of methods for improvement of properties. The objective of this task was to evaluate candidate resins, optimize the properties critical to ablative performance and select the most promising resins for investigation in the Composite Studies. (Section 4).

Resins from the following three sources were investigated for optimization in this program:

- Contract NAS3-4188: Cyclized polybutadiene urethane (CPBU), polyalkaline earth acrylates, phosphate bonded oxides, polyamide-imides, and zirconium borides.
- Contract NAS3-7949: Resin systems selected and synthesized in Task I.
- Commercial Sources: Monsanto - Skybond 700 (polyimide), and Narmco - Polybenzimidazole.

Optimization studies conducted in this program consisted of:

- Chemical tailoring of the polymer to enhance its usefulness as an ablative resin.
- Evaluation of the effect of new cure cycles, char promoters and aromatization catalysts.

In this task the optimized resin systems were evaluated without reinforcement to 1) determine the inherent ability of the resin to withstand ablative environments independent of the combined effect of resin-filler interaction and 2) provide a sensitive measure of ablative property improvement caused by optimized formulations. The evaluation of the optimized resin systems was accomplished through:

- Mechanical, thermal and chemical property assessments; and
- Propellant Exhaust Environmental Test (PEET) evaluation.

Selection of resin systems for incorporation into the subsequent Composite Studies, was made from data analysis of the evaluations performed and assessment of the degree of improvement to be imparted to the composite material. With the exception of the polyamide-imide resin systems, the optimization studies were unsuccessful. The highlights of the optimization studies are reported below and detailed information is reported in Appendix B.

3.1 POLY(CYCLIZED 1,2-POLYBUTADIENE) TOLYL URETHANE (CPBU)

Poly(cyclized 1, 2-polybutadiene) tolyl urethane (CPBU) was developed and recommended for future study during Contract NAS3-4188. Initial evaluations in ablative environments showed that CPBU had a very low char yield. Resin optimization studies were aimed toward increasing the char yield.

The saturated nature of this predominantly hydrocarbon resin suggested that optimization efforts be directed toward developing dehydrogenation methods for producing aromatic structures within the CPBU molecule. Highly aromatic structures will provide high char yields under ablative conditions. The following three dehydrogenation approaches were studied:

1) Controlled thermal dehydrogenation
2) Dehydrogenation catalyzed with a noble metal catalyst, and
3) Incorporation of metal acetonyl acetonates with and without tributyl phosphate as char forming additives.

Details of investigations on controlled thermal dehydrogenation and incorporation of finely divided metal catalysts on alumina substrates were reported in the Interim Report (Ref. 2). Several candidate thermal conditioning cycles, gaseous environments, and catalyst concentrations did not produce a product with an improved char yield (as evaluated by thermogravimetric analysis).

Studies incorporating metal acetonyl acetonates with and without tributyl phosphate as char forming additives resulted in only a modest improvement, which was far below that considered necessary for ablative resin use. In light of the unpromising results obtained in all three approaches examined, studies on CPBU were terminated.

3.2 POLYALKALINE EARTH ACRYLATES

Optimization investigations of polyalkaline earth acrylates were aimed at improving the processing characteristics to permit preparation of high density specimens exhibiting improved ablative properties. Previous attempts (Ref. 2) at developing a processing procedure for polycalcium acrylate which would be applicable to scale-up gave products with relatively poor ablative properties as exhibited in FLOX/methane PEET evaluation. Since the Interim Report period, two new approaches were studied which were designed to overcome the difficulty. These approaches were:

- Polycalcium acrylate - acrylic acid mixtures
- Polymerization of calcium acrylate during molding

These two processing modifications did facilitate the production of high density specimens. Details of these experimental processing studies are reported in Appendix B.

3.3 PHOSPHATE BONDED OXIDES

Phosphate bonded oxides, recommended for further studying during Contract NAS3-4188 (Ref. 1), have been studied for optimization of processing ability during this program. Initially the ablative performance of this inorganic resin was to be evaluated in a FLOX/methane propellant combustion environment in order to provide direction for the optimization studies. However the extreme friability of the material has caused major difficulties in obtaining standardized PEET specimens from sintered plugs. Attempts to machine PEET specimens nearly evolved into a major task in itself. It was evident, when special tooling employing ultrasonic machining techniques could not produce unfractured specimens, that further optimization studies were impractical. As a result, PEET evaluation was not possible and hence, further work was terminated.

3.4 POLYAMIDE-IMIDE RESINS

Polyamide-imide resins systems were recommended for further study during Contract NAS3-4188 as candidates for use in ablative environments. The polymers are formed from the reaction of trimellitic anhydride and an undisclosed diamine. The molding version, Amoco Type AI-11, was prereacted in such a manner that the ratio of ortho-amic acid groups to imide-amide groups is small. In this manner the compound can be compacted in a mold under heat and pressure causing condensation of the residual ortho-amic acid groups to complete the imide formation producing the finished polymer. Water, given off as a byproduct, was of concern in molding unreinforced specimens for PEET evaluations. A satisfactory molding procedure was developed and is described in Reference 2. Specimens made by this procedure were evaluated by PEET. The results given in Section 3.8 were sufficiently favorable for incorporation into candidate matrices investigated in the Composite Studies, Section 4.

3.5 ZIRCONIUM BORIDE POLYMERS

Zirconium boride polymers were suggested as possible inorganic resin matrices for withstanding advanced propulsion exhaust environments. The art of preparation of the polymers lies beyond the scope of this program; however, a simulant for these inorganic resins, zirconium diboride, is commercially available and provides a means for evaluating the stability of future resins containing these elements.

Difficulty was encountered in machining zirconium diboride (obtained from the Carborundum Co.) into specimens suitable for PEET ablative performance evaluation. The brittle nature of this compound necessitated its elimination from PEET evaluation.

3.6 SKYBOND 700 POLYIMIDE RESIN

Monsanto Chemical Company's Skybond 700 modified polyimide resin was selected for optimization studies, primarily for comparative evaluation purposes. This resin was under investigation in the Composite Studies (Section 4), and it was desirable to obtain ablative property information on the neat polyimide resin. Skybond 700 is much easier to process than other state of the art polyimide resins, e.g., DuPont's SP-1. Skybond 700 can be handled with lamination art similar to that used for polyamide-imides.

The moldings produced were homogenous and free from defects; however, after machining the center hole for the PEET specimen, every specimen displayed extreme brittleness and either cracked or shattered. Because it was not intended to make preparation of the comparative neat polyimides into a major task, further attempts to make and machine PEET specimens were terminated and the effort was shifted to the preparation of composite specimens. The cracked neat PEET specimens were not tested.

3.7 POLYBENZIMIDAZOLE RESIN

Polybenzimidazole resins were chosen for evaluation to represent the most advanced version of the "stiff" polymers. These resins have excellent heat resistance but very poor processability. Neat resin specimens were ordered from the resin supplier, Narmco Division of Whittaker Corporation early in this program. The difficulty in preparing neat polybenzimidazole is readily apparent in the fact that Narmco was unable to prepare satisfactory specimens suitable for evaluation.

3.8 PEET EVALUATION OF NEAT RESINS

Specimens of neat materials described earlier in this section, as well as neat materials for comparative purposes, were subjected to FLOX/methane Propellant Exhaust Environment Test (PEET) evaluation. This section 1) describes modifications incorporated in the PEET apparatus operation since the Interim Report period to provide increased confidence in the experimental test data and 2) presents the results obtained from candidate neat resin systems.

3.8.1 PEET Operational Modifications

Several inconsistencies were observed in comparison of test data on both neat and composite materials reported here with those previously obtained. Because this method is the principal means for determining ablative performance of candidate materials, a detailed effort was undertaken to determine the source of the suspect data. This effort included examination of the reproducibility of the FLOX/methane torch operational parameters (e.g., heat flux, mixture ratio, orifice tip integrity, torch-specimen movement, etc.) and examination of replicate samples.

Some early test data were eliminated as suspect because of non-uniform erosion (e.g., the erosion pattern was skewed and off-centered indicating movement of the torch or clogging during firing). The possibility of torch movement in recent tests was eliminated by utilization of a special mounting pin to fix the relative position at the torch tip to the specimen.

It was determined, after checking all of the equipment used in the PEET apparatus, that the flow calibration data (obtained from the vendor of the flowmeters) were about 20% below actual values determined experimentally for each flowmeter. The inconsistencies obtained in comparing previous test data have been related to use of vendor flowmeter calibration tables. Consequently, a variety of FLOX/methane mixture ratios have been used in previous PEET evaluations. Data in the Interim Report (Ref. 2) was obtained with a FLOX/methane volume ratio of 0.933. Recent data were obtained using the planned 2.44 volume ratio. With few exceptions, the data presented for specimens tested at the 2.44 volume ratio show greater consistency among samples from the same sets than did data presented with the lower volume ratios.

Calibration of the PEET apparatus for thermal flux was carried out for both fluorine/hydrogen and FLOX/methane propellant combinations. Details of this procedure are given in Appendix C.

3.8.2 Results

The results obtained on PEET evaluation of neat materials obtained in FLOX/methane (at 3 mixture ratios) and fluorine/hydrogen combustion environments are listed in Table VII. For convenience, all the data generated in this program and comparative data obtained during Contract NAS3-4188 are included in this Table.

Analysis of the data provides the following general observations:

TABLE

PEET Evaluation of Ne

Material Type	FLOX/M				
	Mixture Ratio . 933			Mixture Rat	
	Firing Time Sec.	Weight[a] Loss, g	Backwall[b] Temperature °C	Firing Time Sec.	Weig Loss
Pyrolytic Graphite (Supertemp)	10	0.0054	360		
	30	0.022	470	30	0.0
JTA Graphite (National Carbon)	10	0.014	340	10	0.0
	30	0.016	490	30	0.0
ATJ Graphite (National Carbon)					
SP-1 (DuPont)	10	0.21	140	10	0.5
				30	0.4
SP-2 (DuPont)[d]	10	0.41	140	10	0.2
				30	0.3
Epoxy Novalac[e]	10	0.53	190	10	1.
Polyamide-Imide[f]	10	0.15	160		
Polycalcium Acrylate[g]	10	0.85	120		
Polycalcium Acrylate[h]	10	1.14			
CPBU/Styrene[i]	10	2.39	290	10	1.2
CPBU Standard	10	2.32	290	10	0.

a. 1/2-inch diameter by 1-inch long specimens.

b. Thermocouple imbedded in center of specimen 0.5 inches from exposed end.

c. Weight gain.

d. Contains graphite powder filler.

e. D. E. N. 438/MNA system.

f. Amoco AI-13.

g. Acrylic acid binder.

h. No binder.

i. 75% CPBU/25% styrene.

j. Average of replicate samples.

②

TABLE VII
PEET Evaluation of Neat Ablative Materials

FLOX/Methane									Fluorine/Hydrogen[j]	
Mixture Ratio .933			Mixture Ratio 1.27			Mixture Ratio 2.44			Mixture Ratio 1.09	
ne	Weight[a] Loss, g	Backwall[b] Temperature °C	Firing Time Sec.	Weight[a] Loss, g	Backwall[b] Temperature °C	Firing Time Sec.	Weight[a] Loss, g	Backwall[b] Temperature °C	Firing Time Sec.	Weight[a] Loss, g
	0.0054	360							10	0.020
	0.022	470	30	0.023	831					
	0.014	340	10	0.00	369				10	0.030
	0.016	490	30	0.05	723					
						30	0.12[c]	807		
						30	0.10[c]	830		
						30	0.15[c]	743		
	0.21	140	10	0.51	56				10	0.21
			30	0.49	89					
	0.41	140	10	0.28	28	30	0.72	110	10	0.36
			30	0.35	92	30	0.31	120		
						30	0.59	94		
	0.53	190	10	1.03	40	10	1.0	64	10	0.55
						10	1.4	78		
						10	1.5	69		
	0.15	160				10	0.07	71	10	0.11
						10	0.14	47		
						10	0.15	46		
						10	0.21	46		
						10	0.14	48		
						10	0.17	62		
	0.85	120								
	1.14								10	0.30
	2.39	290	10	1.28	87					
	2.32	290	10	0.57	64	10	0.54	52	10	0.50
						10	0.62	55		
						10	0.48	48		
						10	1.0	64		

long specimens.

enter of specimen 0.5 inches from exposed end.

ler.

s.

- Parallel weight losses exist between specimens exposed to the combustion environments of FLOX/methane and fluorine/hydrogen. Three exceptions exist, namely, polycalcium acrylates and CPBU at all FLOX/methane mixture ratios examined and the epoxy novalac resin at high FLOX/methane mixture ratios. This severe attack of these resins seriously limits their usefulness in FLOX/methane environments.

- "Stiff" polymers, particularly the polyimide-amide show unusual resistance to the FLOX/methane combustion environment. This finding clearly shows that polyimide-amides, which decompose thermally to form carbonaceous chars, can withstand dynamic chemical reaction with the hot oxygen/water/hydrogen fluoride exhaust species arising from this hostile propellant combination.

- FLOX/methane combustion products did not exhibit the anticipated severe effect on carbon and graphite materials.

- Detailed interpretation of the variations observed for the du Pont polyimide polymers, SP-1 and SP-2, do not appear warranted. The differences observed at the low FLOX/methane mixture ratio were originally attributed to removal of the particulate graphite-filled material (SP-2); however, at the 1.27 mixture ratio, this trend is reversed and the graphite appears to be somewhat inhomogeneous as evidenced by the variability of replicate samples tested at a 2.44 FLOX/methane mixture ratio.

From these observations, it is clear that the polyimide-amide resin system and other "stiff" polymer systems will be useful in preparation of ablative composite materials for use with both FLOX/methane and fluorine/hydrogen propellant combinations. Other candidate resin systems do not appear to warrant further study in the neat form.

4. COMPOSITE STUDIES

Laboratory studies were conducted on the methods and processing variables required for preparing fiber reinforcement composites utilizing candidate resin systems selected and identified in Section 3, and other commercially available resin systems representing the advanced "state of the art." Reinforcements evaluated include silica and graphite fabrics (utilized in TRW molded materials), carbon, $Mg(OH)_2$, and Food Machinery Corporation's silica/cellulose and silica/carbon fabrics (utilized in commercially prepared materials). Evaluation of the composite materials for ablative performance in fluorine-containing combustion environments in the Propellant Exhaust Environment Test (PEET) provided background data necessary for selection of resin systems and processing methods for preparation of composite materials using an advanced reinforcement of titanium diboride. The advanced reinforcement was supplied from the parallel, NASA-sponsored, fibers program conducted by Texaco Experiment Incorporated (Contract NAS3-7948). The Texaco material was in the form of a continuous filament of titanium diboride coated on a tungsten core.

Processing studies with advanced resins and commercially available fabrics were conducted by successful preparation of laminates suitable for ablative performance evaluation. Extensive evaluation of the composite specimens in the FLOX/methane PEET apparatus was accomplished with replicate samples. This testing provided confidence in the results of this type of evaluation by permitting statistical treatment of the data and ascribing a repeatability and reproducibility to the method.

In addition, the processing procedures necessary for utilization of the advanced resins were evaluated in terms of application to the relatively large diameter titanium diboride fibers. Because of a limitation of available titanium diboride fibers, initial processing studies were conducted using 3-mil diameter tungsten wire. These considerations evolved into practical methods for the preparation of coherent uniform composite structures from the advanced resins and fibers.

The composite studies were performed in the following stages:

- Acquisition of commercially available reference ablative materials
- Preparation of test specimens from candidate resin classes and reinforcements
- Evaluation of ablative characteristics of candidate materials and selection of most promising for future optimization
- Optimization of advanced composite materials

The results of the subsequent evaluation of the advanced composite materials are reported in Section 5.

4.1 ACQUISITION OF REFERENCE ABLATIVE MATERIALS

As indicated in Section 3.8 an ablative performance of neat resin systems, the "stiff" polymer resin class appeared to provide superior performance in fluorine-containing combustion environments. It is recognized that the performance of a neat resin system is only indicative of its capability when prepared in a reinforced composite form. Consequently, testing of the resin class in composite form and comparison with available ablative materials is a prerequisite in ranking overall rocket ablative utility. Because the ablative performance of reinforcements varies significantly and the amount of reinforcement material in these composites is two to four times the amount of matrix resin, comparisons of the ablative effectiveness of resins can be made only with identical reinforcements at approximately the same degree of loading.

Several manufacturers and vendors of ablative materials were contacted to identify and procure commercially available composite materials to be used as a reference for comparison to judge degree of ablative performance improvement provided by the advanced composites prepared in this program. Upon review of the materials offered by the supplier and recommended for fluorine propellant combustion environment use, the 29 materials listed in Table VIII were obtained for ablative performance evaluation in this program.

4.2 PREPARATION OF CANDIDATE TEST SPECIMENS

Reinforced laminates were prepared from candidate resin systems identified in Section 3. Reinforcements utilized in these studies included

TABLE VIII

COMMERCIALLY AVAILABLE ABLATIVE REFERENCE MATERIALS SELECTED FOR ABLATIVE PERFORMANCE TESTING

Reinforcement Type	Resin Type	Supplier	Material Designation
Graphite	Phenolic	American Reinforced Plastics	185PHGRL
		Coast Manufacturing Co	4G 3036
		Fiberite Corp.	MX 4500
		U.S. Polymeric Corp.	X 5441 FM 5064
		Western Backing Co.	WB 8207 WB 8249
	Polyimide	U.S. Polymeric Corp.	M-4033
	Polybenzimidazole	Narmco Division	4824
Carbon	Phenolic	American Reinforced Plastics	218 PHC 259 PHC
		Coast Manufacturing Co	4C 1036 4C 1036-1
		Fiberite Corp.	MX 4926 MXC-51
		Narmco Division	X-5-96
		U.S. Polymeric Corp.	85592
		Western Backing Co.	WB 8217
	Polyimide	U.S. Polymeric Corp.	M-4032
Silica or Refrasil	Phenolic	Coast Manufacturing Co.	4S4136-1A 4S4136-1B 4S4133-X
		Fiberite Corp.	MX 2600 MXS-51
		TRW Systems	ECX-137[a]
	Polybenzimidazole	Narmco Division	4850
	Polyimide	TRW Systems	Skybond 700[b]
Silica/Cellulose	Phenolic	Western Backing Co.	AVC-RS-2223
Silica/Carbon	Phenolic	Western Backing Co.	AVC-CS-2223

[a] Prepared from Evercoat Chemicals Biphenol Phenolic Resin using manufacturer's processing instructions

[b] Prepared from Monsanto's Skybond 700 Polyimide Resin using manufacturers processing instructions

graphite and Refrasil fabric and tungsten and titanium diboride fibers. Candidate resin systems employed included A-type polyimide, B-type polyimide, B-type polybenzimidazole, and polyamide-imide. In addition, laminates were prepared for comparison purposes from Monsanto Skybond 700 polyimide and SC 1008 phenolic resin and Evercoat Chemicals biphenol phenolic. Details of the processing methodology employed in these studies are presented in Appendix E.

During the course of the program, two sets of candidate test specimens were prepared. Specific combinations of resins and reinforcements used to prepare the first set is shown in Table IX.

TABLE IX
CANDIDATE ABLATIVE MATERIAL COMPOSITION MATRIX

Resin	Reinforcement		
	Refrasil	Graphite	Tungsten
Phenolic[a]	x	x	
A-Type Polyimide	x	x	x
Polyamide-imide	x	x	x

[x] Specimens prepared
[a] Purchased specimens employed SC-1008 resin

These specimens were machined into cylindrical PEET specimens having dimensions of 0.5-inch diameter x 1.0-inch long.

The second set of candidate test materials were prepared later in the program to incorporate the titanium diboride fibrous reinforcement and the B-type polyimide and B-type polybenzimidazole resins. Because the total quantity of titanium diboride available for this program was limited to 15,200 feet (average fiber diameter of 0.00262-inch) it was necessary to reduce the size of the specimens used for ablative performance evaluations (PEET) so that a statistically adequate number of specimens could be prepared and tested. Implementation of the PEET size reduction also necessitated the fabrication of additional specimens previously evaluated to permit direct comparison of ablative performance independent of test specimen size. The reduced size specimens were molded in a 0.32-inch diameter x 1.0-inch long cyclindrical cavity and machined to a PEET specimen size of 0.25-inch diameter x 0.75-inch long. The resin-reinforcement composition matrix of the second set of test specimens prepared in this program to satisfy the reduced PEET specimen size requirements are listed in Table X.

TABLE X

REDUCED SIZE PEET SPECIMEN RESIN-REINFORCEMENT COMPOSITION

	Reinforcement		
	Refrasil	Graphite	Titanium Diboride
Phenolic (SC 1008)	x	x	x
A-Type Polyimide	x	x	x
B-Type Polybenzimidazole	x	x	
B-Type Polyimide	x	x	

x Specimen Prepared

4.3 ABLATIVE PERFORMANCE EVALUATION OF COMPOSITE MATERIALS

Extensive evaluation of reference and candidate composite ablative specimens was conducted through FLOX/methane propellant exhaust environmental testing (PEET). Testing was accomplished at FLOX/methane volume mixture ratios of 1.27 and 2.44.

Figure 8 shows three typical PEET specimens in the unfired, fired and sectioned conditions. The unfired specimens were cylindrical in shape - 0.50-inch diameter and 1.00-inch long. From the PEET evaluation, measurements were obtained for the following ablative performance parameters:

- Maximum depth of removal of material,
- Weight loss, and
- Backwall temperature.

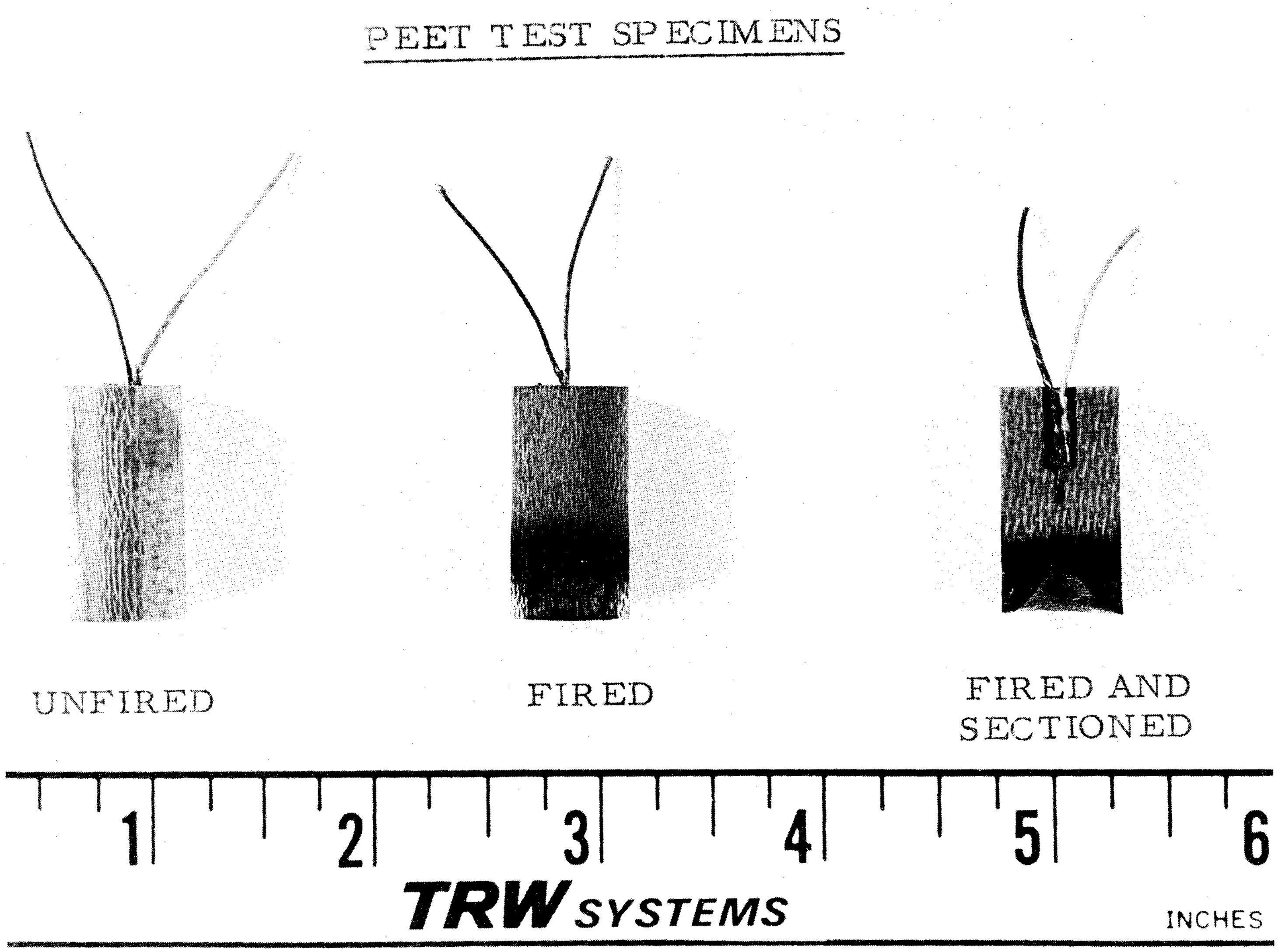
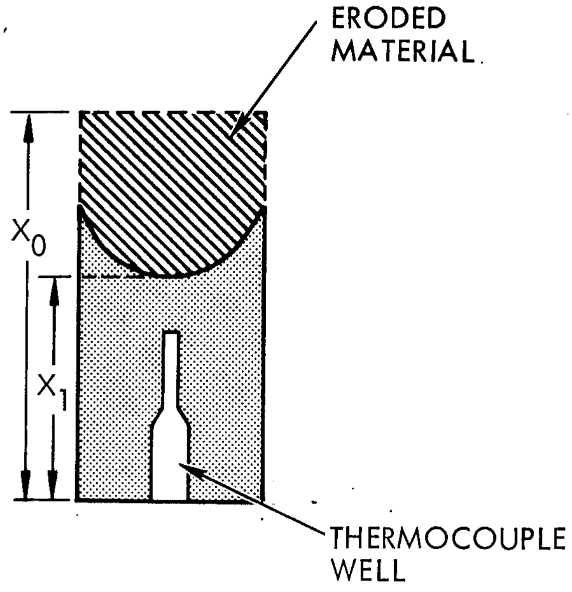


Figure 8. PEET Test Specimens

These parameters were obtained as described in the following paragraphs:

The depth of removal values represent the maximum depth of erosion resulting from a 30-second PEET evaluation. As shown in Figure 9 , a conical cross section resulted from the test with its maximum depth near the center of the cone. The depth of removal value presented in Table XI was calculated as the difference between the original length of the PEET specimen and the post-fired distance between the center of the eroded cone and the untested end of the specimen (See Figure 9).

The weight loss was determined as the net difference in weight of the specimen prior to and after PEET evaluation.



DEPTH OF REMOVAL = $X_0 - X_1$

Figure 9. Schematic of Eroded PEET Specimen

The backwall temperature measurement was obtained using a thermocouple located 0.50 inches from the exposed end of the specimen. The thermocouple was mounted through a 0.150-inch diameter hole drilled into one end of the specimen with a transition to a 0.040-inch diameter hole. The thermocouple was potted in the 0.040-inch diameter section with Bloomingdale Rubber Company's HT 424 adhesive.

Raw data obtained for the 1.27 and 2.44 volume mixture ratios of FLOX/methane are listed and were subjected to statistical evaluation in Appendix F. Assessment of these results revealed that insufficient data were obtained at the 1.27 volume mixture ratio to permit a meaningful statistical evaluation. Consequently, the discussion in this section of the report will deal with the ablative performance data obtained using the FLOX/methane volume mixture ratio of 2.44.

A summary of the statistically revised data is presented in Table XI. Inspection of these data in the light of the results reported in the Interim Progress Report (Ref. 2) shows that the previous guide used for evaluating ablative performance, namely, weight loss, was misleading. Indeed, the most important parameter for use in rocketry is dimensional stability as evaluated by depth of removal and the secondary factor is that of backwall temperature. Weight loss measurements are interesting but are difficult to interpret in the physical ablation phenomenon.

For convenience in evaluating the overall data presented in Table XI, the fabric resin combinations have been ranked in order of increasing depth of removal and increasing backwall temperature in Tables XII and XIII, respectively.

From these tables, the serious trade-off that rocket chamber designers must face is readily evident; namely, those materials and combinations which have good erosion resistance are generally poorer in backwall temperature performance and vice versa. Clearly the graphite polybenzimidazole, carbon-phenolic and the graphite-phenolic composites gave the best dimensional retention of the material classes tested, whereas the silica/cellulose-phenolic and the silica-biphenol phenolic composite mat-terials provided the best backwall temperature performance. As silica is introduced into the composite materials, the erosion resistance decreases. In a similar manner, as carbon and graphite are introduced as reinforcements in the composite, the backwall temperature increases. In general, surface recession is the foremost criteria in selection of ablative materials to be used for rocketry. However, there are some cases in design of combustion chamber geometric configurations where heat transfer may be the overriding consideration and the backwall temperature criteris is the more important.

TABLE XI

SUMMARY OF REVISED DATA FOR COMPOSITE SPECIMENS EXPOSED TO FLOX/METHANE (M.R. = 2.44 V/V) PEET EVALUATION

Material Fabric-Resin	Depth of Removal x 10^3, in.			Weight Loss x 10^2, in.			Backwall Temperature, °C		
	N[a]	Average	S[b]	N[a]	Average	S[b]	N[a]	Average	S[b]
Carbon-Phenolic	22	118	12.5	24	44	3.8	24	264	18.4
Carbon-Polyimide	3	141	7.3	3	41	2.5	2	302	41.0
Graphite-Phenolic	15	123	12.4	15	42	4.9	13	554	6.4
Graphite-Polyimide	3	145	3.0	3	48	1.0	2	441	1.4
Graphite-PBI	2	112	2.0	3	12	5.3	3	552	6.7
Silica-Phenolic	13	210	14.5	13	49	4.9	13	144	4.4
Silica-PBI	3	221	19.8	3	42	6.3	2	164	5.7
Silica-Polyimide	4	211	9.5	4	44	5.5	2	139	4.2
Silica-Biphenol Phenolic[c]	4	149	33.4	4	35	2.2	4	108	7.7
Silica/Cellulose-Phenolic	2	223	21.9	3	70	5.8	3	77	12.0
Silica/Carbon-Phenolic	2	134	16.3	3	60	8.0	3	177	6.6
Grand Pooled Standard Deviations			15.8			4.6			10.8

[a] N = Number of Tests

[b] S = Pooled Standard Deviation

[c] High Density Material

TABLE XII

RANKING OF DEPTH OF REMOVAL PERFORMANCE OF ABLATIVE COMPOSITES UNDER FLOX/METHANE (M.R. = 2.44 V/V) PEET EVALUATION[a]

Ranking	Material	Average Depth of Removal, Inch
1.	Graphite-polybenzimidazole	0.112
2.	Carbon-phenolic	0.118
3.	Graphite-phenolic	0.123
4.	Silica/carbon-phenolic	0.134
5.	Carbon-polyimide	0.141
6.	Graphite-polyimide	0.145
7.	Silica-biphenol phenolic	0.149
8.	Silica-phenolic	0.210
9.	Silica-polyimide	0.211
10.	Silica-polybenzimidazole	0.221
11.	Silica/cellulose-phenolic	0.223

[a] 30 second exposure

4.4 SELECTION OF MOST PROMISING CANDIDATE MATERIALS

The selection of the most promising candidate materials for detailed study resulted from assessment of the ablative performance results reported in Section 3 on resin optimization and those obtained for the reference commercial materials together with experience gained concerning the processability of these advanced and state of the art resin systems. Clearly the most significant important resin property determined in the earlier program (Ref. 1) in providing enhanced ablative performance (e.g., dimensional stability) namely, a resin capable of conversion in the ablative environment to a dense char (high char yield) was borne out by the experimental results. Processing characteristics

TABLE XIII

RANKING OF BACKWALL TEMPERATURE PERFORMANCE OF ABLATIVE COMPOSITES UNDER FLOX/METHANE (M. R. = 2.44 V/V) PEET EVALUATION[a]

Ranking	Material	Average Backwall Temperature, °C
1.	Silica/cellulose-phenolic	77
2.	Silica-biphenol phenolic	108
3.	Silica-polyimide	139
4.	Silica-phenolic	144
5.	Silica polybenzimidazole	164
6.	Silica/carbon-phenolic	177
7.	Carbon-phenolic	264
8.	Carbon-polyimide	302
9.	Graphite-polyimide	441
10.	Graphite-polybenzimidazole	552
11.	Graphite-phenolic	554

[a] 30 second exposure

of state of the art high char yield resins is subject to considerable difficulties. As a result the following three resin systems were selected for further processing optimization and detailed comparative ablative performance evaluation.

- Polyamide-imide
- A-type polyimide
- B-type polyimide and polybenzimidazole

Table XIV provides a brief summary of the disposition of the more important resin systems in the consecutive synthesis, formulation optimization, composite processing and ablative performance material development tasks.

TABLE XIV

DISPOSITION OF CANDIDATE RESIN SYSTEMS EVALUATED IN THIS PROGRAM

Resin System Source	Optimization Results	Composite Studies Including FLOX/CH_4 Evaluation	Selected for Detailed Study
Resin Systems from NAS3-4188			
CPBU	Low char yield	None	No
Polyalkaline earth acrylates	Prepared high density materials	Excessive spalling during FLOX/CH_4 test	No
Phosphate Bonded Oxides	Poor ductility	None	No
Polyamide-imide	Satisfactory composites processed	Ablative performance good	Yes
Commercial Sources			
Narmco Polybenzimidazoles	None	Material difficult to process; ablative performance excellent	No
Monsanto Skybond	None	Processing difficult; ablative performance erratic - related to processing	No
Resin Systems from NAS3-7949			
A-type polyimides	Readily processed into high performance composites	Ablative performance good	Yes
B-type polymers	Monomers synthesized composites prepared from polymers	Ablative performance good	Yes

5. EVALUATION OF CANDIDATE COMPOSITE MATERIALS

Candidate composite materials were tested for their ablative performance characteristics using the FLOX/methane Propellant Exhaust Environment Test (PEET). Testing of commercially available materials was performed to permit back-to-back evaluation. As mentioned in Section 4, two different sizes of test specimens were prepared because of limitations in availability of the titanium diboride reinforcement. Consequently, the results of these PEET evaluations of these composites will be reported in the two following sections relating to specimen size. The ablative performance parameters reported, namely, depth of material removal, weight loss and backwall temperature were measured by techniques identical to those reported in Section 3.8 and 4. Operational PEET parameters are discussed for the testing of the two different sample size specimens in Appendix C.

5.1 PEET EVALUATION OF STANDARD SIZE TEST SPECIMENS

The results of depth of removal and weight loss measurements obtained after FLOX/methane PEET evaluation of candidate and reference materials prepared into standard size (0.5-inch diameter x 1.0-inch long) cylindrical specimens are summarized in Table XV. Operational PEET conditions employed were a 2.44 volume mixture ratio of FLOX (82.5% w/w F_2) to methane for a 30-second exposure at heat fluxes in the range of 165-175 BTU/ft^2-sec. No apparent correlations were observed for the differences in heat flux, consequently, these data were pooled together and listed in Table XV. Detailed raw data obtained for these tests, including backwall and surface temperature measurements, pre and post test specimen diameter and significant observations, are presented in Appendix F, Table F.5. A discussion of the significant findings is presented below categorized by reinforcement material.

5.1.1 Refrasil Reinforcement

The depth of removal data in Table XV indicate that the A-type polyimide composites (both the Group II and Group I - pyromellitic dianhydride and benzophenone dianhydride versions, respectively) exhibited comparable ablative characteristics as the commercially available phenolic materials. In general, the weight loss data also appeared comparable. The polyimide-

TABLE XV

SUMMARY OF FLOX/METHANE PEET EVALUATION RESULTS

Reinforcement	Resin Type	Depth of Removal x 10^3, in			Weight Loss x 10^2, g		
		N^a	Average	s^b	N^a	Average	s^b
Refrasil	Phenolic MX2600	2	224	1	2	53	1.4
	Phenolic MXS51	8	229	17	8	59	8.5
	A-Type Polyimide (No post cure)	3	207	21	3	51	3.5
	A-Type Polyimide (600°F post cure)	4	236	7	4	58	1.8
	Polyamide-imide	4	252	23	4	54	1.7
Graphite	Phenolic MX 4500	9	125	29	9	44	1.7
	A-Type Polyimide	2	154	13	3	80	3.8
	Polyamide-imide	--	--	--	3	68	4.1

[a] N = Number of Tests

[b] S = Standard Deviation

amide, on the other hand, had a greater average depth of removal than the commercially available phenolic reinforced material. The major differences between these three types of matrix material is in their physical appearance after the PEET exposure (See Figure 10). The A-type polyimide did not form cracks and had only a minor carbon buildup on the side of the exposed surface; the phenolic matrix specimens had several quarter-inch long cracks or delaminations along the exposed surface; and the polyimide-amide matrix had a considerable black carbon residue on the side of the surface and the appearance that resin spalled away from the sample during test. These small delaminations suggest that under long term testing, larger cracks might develop which may lead to gross failure of the composite. On the basis of these observations, it appears that the A-type polyimide silica reinforced laminates are better suited for long term engine test than that of the comparable commercial product.

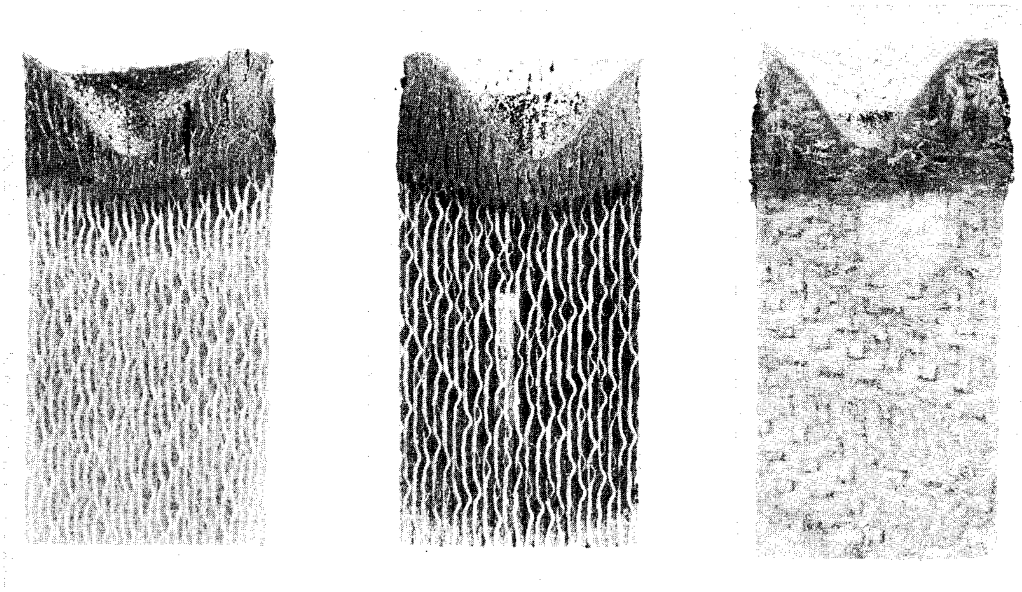
5.1.2 Graphite Reinforcement

Graphite reinforced specimens containing the A-type polyimide did not perform as well as the comparable commercial MX 4500 phenolic composite. Specimen delaminating and swelling, as well as excessive carbon deposition on the specimens' sides occurred during test. Comparable specimens prepared from the polyimide-amide matrix failed during test, consequently, no post test data could be obtained.

It appears as if further work should be performed to enhance the production of the A-type polyimide graphite reinforced composites. In the studies reported in Appendix E, considerable difficulty was encountered in preparing graphite reinforced laminates and all specimens appeared porous. Additional work is indicated to develop suitable processing procedures to enhance the wetting of the graphite reinforcement with the A-type polyimide during lamination.

5.1.3 Tungsten Reinforcement

From the data presented in Appendix F, Table F.5, it is seen that all experimental tungsten reinforcement resins failed. This failure was attributed to a direct consumption of the resin caused by conduction of the combustion surface temperature throughout the specimen via the tungsten

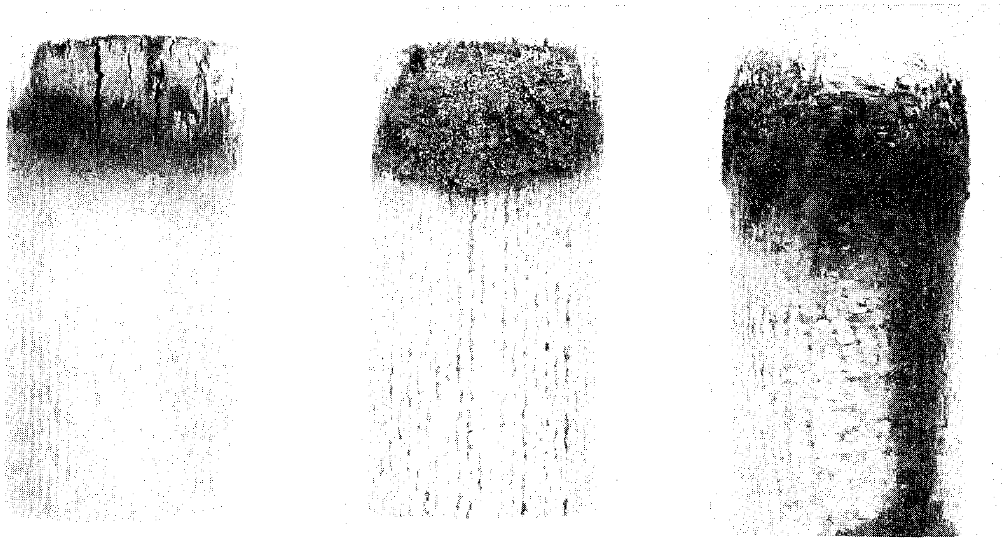


MXS-51

TRW A-Type Polyimide

Polyamide-imide

Section View of PEET Specimens
(2.5X)



MXS-51

TRW A-Type Polyimide

Polyamide-imide

Figure 10. Side View of PEET Specimens
(2. 5X)

filaments. Although it is clear the tungsten composites are not useful as an ablative material, the processing of the relatively coarse diameter fibers was directly applicable to the preparation of the titanium diboride reinforced composites.

5.2 PEET EVALUATION OF REDUCED SIZE TEST SPECIMENS

The results of depth of removal and weight loss measurements made on reduced size candidate and reference material test specimens (0.25-inch diameter x 0.75-inch long cylinders) after FLOX/methane PEET evaluation are summarized in Table XVI. Operational PEET conditions employed were a 2.44 volume mixture ratio of FLOX (82.5% w/w F_2) to methane for a 20-second exposure at a heat flux of 217.5 BTU/ ft^2-sec. Detailed raw data obtained for these tests, including surface temperature and significant test observations are presented in Appendix F, Table F.6. A discussion of the significant findings is presented below categorized by reinforcement material.

5.2.1 Refrasil Reinforcement

The depth of removal data in Table XVI indicate that comparable ablative performance is obtained on phenolic and A-type polyimide resins and B-type polyimide and polybenzimidazole resins which have been post cured at 950°F. On the other hand, post curing the B-type polymers at 850°F appears to effect a significant improvement in ablative performance. No significant differences were observed in surface temperatures (See Appendix F, Table F.VI). Typical photomicrographs of post tested ablative specimens are shown in Figure 11. Examination of the two pictures showed that the polybenzimidazole laminate did not crack or delaminate. Similarly, the A-type polyimide was not affected by thermal shock. The polybenzimidazole matrix (Figure 11) exhibited no evidence of melting; the MX 2600 phenolic resin underwent severe cracking and delamination. Weight loss data show a 25% less consumption of material with the 850°F post cured polybenzimidazole than with the phenolic composite. These findings demonstrate that the Refrasil reinforced B-type polybenzimidazole exhibits 1) resistance to thermal shock, 2) heat distortion temperatures greater than their pyrolysis temperature, and 3) superior ablative properties.

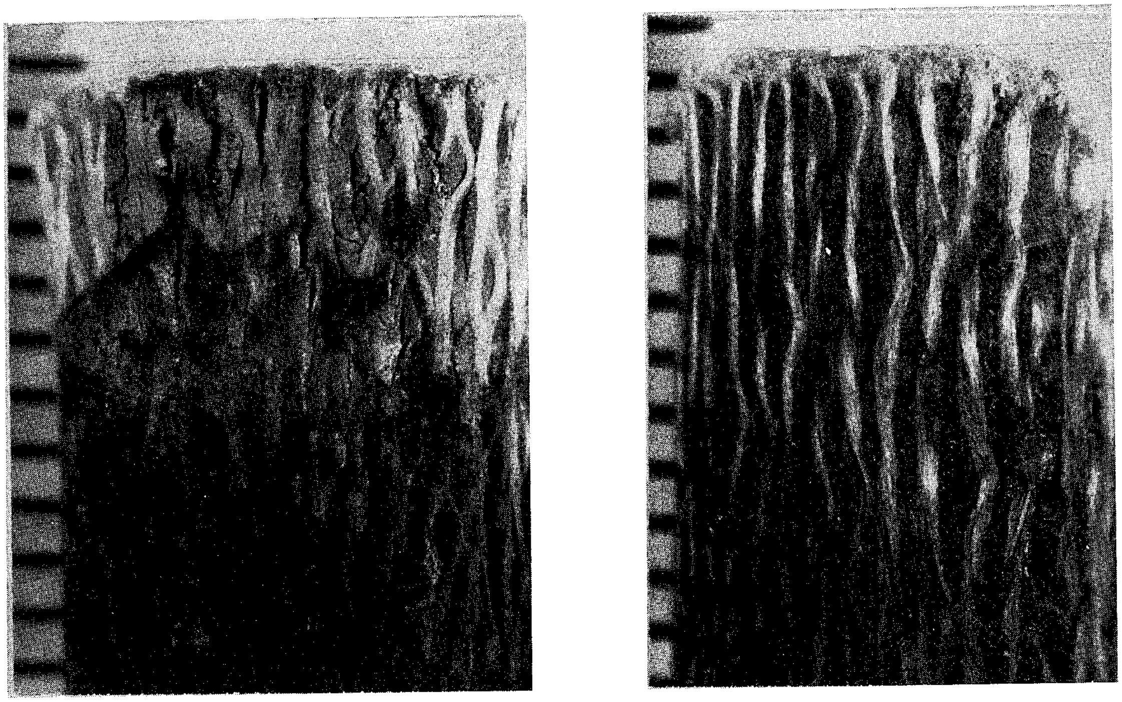
TABLE XVI

SUMMARY OF PEET RESULTS OBTAINED ON CANDIDATE MATERIALS USING SMALL TEST SPECIMENS

Reinforcement	Resin Type	Depth of Removal $\times 10^3$, g			Weight Loss $\times 10^2$, g		
		N[a]	Average	s[b]	N[a]	Average	s[b]
Refrasil	Phenolic	3	153	6.2	4	22.4	2.9
	A-Type Polyimide	3	150	11.0	3	22.1	1.3
	B-Type Polyimide (Post cured at 850°F)	3	135	5.7	3	18.1	1.2
	B-Type Polyimide (Post cured at 950°F)	3	161	7.6	3	17.9	0.4
	B-Type Polybenzimidazole (Post cured at 850°F)	4	138	6.2	4	16.7	1.6
	B-Type Polybenzimidazole (Post cured at 950°F)	2	144	0.7	2	16.3	1.0
Graphite	Phenolic	7	112	8.5	7	13.6	0.4
	A-Type Polyimide	2	131	21.2	5	23.2	3.0
	B-Type Polyimide	2	181	9.2	2	22.8	0.5
	B-Type Polybenzimidazole (Post cured at 850°F)	2	115	12.0	3	13.9	3.3
	B-Type Polybenzimidazole (Post cured at 950°F)	5	138	4.4	5	13.3	1.0
Titanium Diboride	Phenolic	1	116	---	2	31.3	6.9
	A-Type Polyimide	5	111	22.2	5	24.7	2.9

[a] N = Number of Tests

[b] S = Standard Deviation



a. Phenolic Resin Matrix

b. TRW Polybenzimidazole Resin Matrix

Figure 11. Silica Reinforced Ablative Specimens after Exposure to Identical FLOX/Methane Combustion Environment (Magnification 10X)

5.2.2 Graphite Reinforcement

Graphite reinforced specimens containing phenolic and B-type polybenzimidazole (post cured at 850°F) exhibited comparable erosion and weight loss properties (See Table XVI). The A-type polyimide, B-type polyimide and B-type polybenzimidazole (post cured at 950°F) had inferior ablative performance properties. As mentioned above, it appears that additional work should be devoted to enhancing the wetting of the graphite reinforcement with these experimental resin systems.

5.2.3 Titanium Diboride Reinforcement

The recession (depth of gross material removal) of titanium diboride reinforced phenolic and A-type polyimide specimens was comparable to that of the best of the graphite reinforced materials. However, it was evident that considerable detrimental ablative characteristics existed: excessive residue build-up was observed along the exposed surface together with swelling and severe longitudinal cracking. Apparently the relatively high thermal conductivity of the titanium diboride fibers transmitted the thermal environment rapidly throughout the specimen causing the large resin weight loss. The specimen surface temperature of these tests were consistently the highest of all specimens tested - all above the maximum measurement capability of Coloratio pyrometer (> 2760°C). For these reasons it does not appear that titanium diboride reinforcement offers an improvement in ablative composite material performance.

6. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this experimental effort to study new or improved resin systems suitable for a matrix material in ablative composites for combustion chambers in liquid rockets employing fluorine-containing propellant systems. Based on these findings recommendations are given for future ablative material improvement studies.

6.1 CONCLUSIONS

1. Based on experimental ablative performance evaluation of a number of resin systems and previous analytical studies, the primary property characteristic for selection of improved ablative resin matrices is that of high char yield. The advanced resin systems which possess this characteristic are those having aromatic/heterocyclic polymeric backbones.

2. Commercial aromatic/heterocyclic polymer systems are difficult to process primarily because 1) the evolution of condensation volatile matter during cure results in high void content composites, and 2) use of oxidative and/or thermally labile prepolymers necessitates special handling conditions.

3. Two new polymer systems which eliminate or minimize the difficulties attendant with processing commercial aromatic/heterocyclic polymers have been conceived and undergone preliminary development. The salient features of these new resins are:

A-Type:	Polymer compositions with "backbones" containing alicyclic chemical groups which cure by a pyrolysis curing mechanism which is unique in plastic art.
B-Type:	Polymer compositions with "backbones" containing thermally stable "flexible" chain segments. These polymers cure by conventional means, however, reduced volatile matter is achieved because of higher molecular weight of monomeric constituents. Because this type of "stiff" polymer is soluble in common laminating solvents, the fully cured resin can readily be preimpregnated in ablative reinforcement materials and hence, is amenable to "dry bonding" processing, thereby eliminating the problem of volatile by-products.

4. B-type polybenzimidazole Refrasil reinforced composites which had been post cured at 850°F possessed superior FLOX/methane ablative performance properties (lower material recession) than comparable Refrasil composites prepared from phenolic or A-type polyimides. Similar studies of B-type

polybenzimidazole and phenolic graphite-reinforced composites showed comparable recession properties.

5. Graphite and Refrasil A-type and B-type polymer systems had superior char integrity during ablation performance evaluation testing and were not subject to thermal shock fracture as were similar composites prepared from phenolic resins.

6. The high thermal conductivity of titanium diboride fibrous reinforcement causes severe resin decomposition during FLOX/methane ablative performance testing and results in products having low mechanical strength.

6.2 RECOMMENDATIONS

1. The promise offered from use of the A-type polyimide in ablative composites should be evaluated by preparing larger scale structures and testing by rocket engine firings.

2. The B-type polybenzimidazole and polyimide resin synthesis should be scaled up and large test composites should be prepared for rocket engine test evaluation.

3. Experimental studies are recommended to determine methods which will enhance wetting of graphite reinforcements by the A-type and B-type polymer systems.

4. Studies are recommended to investigate the use of advanced reinforcements with A-type polyimide resins. Two approaches for advanced reinforcement studies are encouraged. The first consists of determining the trade off of ablative properties (recession vs backwall temperature) on degree of blending graphite and silica reinforcements. The second approach would be an investigation of silica-type reinforcement having a smaller diameter than current Refrasil fabric to maximize the extent of the subsurface silica-carbon solid-state ablative reaction by enhancing the total surface area available for reaction.

5. Finally, it is recommended that the advantages offered by the A-type and/or B-type polymer systems in preparing graphitized graphite composites be examined. The ability to produce low void, dense structures from these resins, which yield significantly high char on pyrolysis, will reduce the number of processing steps currently required in producing graphitized-graphite composites using phenolic resins.

7. NEW TECHNOLOGY

In this section are presented discussions of the new resin and ablative material concepts generated in the course of this program. These concepts covering both composition of matter and applications are believed to be of sufficient novelty that invention disclosures have been submitted to the TRW Systems Patent Department. The subject matter of these disclosures are listed below:

Docket No.	Title
3789	Polyimide Polymers
3830	Reinforced Plastic Structures
3838	Plastic Molding Powder Compositions
4105	Polybasic Aromatic Carboxylic Acids, Esters, and Anhydrides
4800	Improved Process for Preparing Graphitized Graphite Composites
4801	Preparation of Improved Ablative Materials

A separate report covering these disclosures has been submitted to NASA, and brief discussions of these inventions, their novel features, and applications are presented below.

7.1 POLYIMIDE POLYMERS

This invention disclosure relates to a specific new polyimide prepolymer composition of matter prepared by condensing three types of chemical compounds, aromatic diamines, aromatic dianhydrides and a specific class of monoanhydrides, such as 3-6 endomethylene-1, 2, 3, 6-tetrahydrophthalic anhydride. The prepolymers are formulated to have moderate molecular weight (1000 to 3000) and have the monoanhydride at the terminal positions. The prepolymers coreact chemically on heating to form high molecular weight polymers. These polymers are formed with minimum evolution of volatile matter and hence, can be processed without the difficulties attendant with state of the art polyimide condensation polymers. The prepolymers are fully imidized and as such they are oxidatively and hydrolytically stable. Processing of the polymers is conducted using relatively short processing durations and good polymers can be produced without the requirement for post cure.

7.2 REINFORCED STRUCTURAL PLASTICS

This invention disclosure relates to the application of the A-type polyimide resin system for use as a plastic matrix in a reinforced structural plastic. This resin system yields reinforced structures which show high thermal and oxidative stability and can be readily prepared using conventional processing techniques. These reinforced structures may contain glass, silica, graphite, carbon, boron and other reinforcing fabrics, fibers or metals. The composite reinforced structure can be prepared using standard preimpregnation and molding methods. The resultant high strength reinforced structural plastic is prepared with the elimination of a relatively low amount of volatile matter. Other features of this invention include the utilization of a polyimide precursor that has long term storage stability and the economic preparation of a polyimide structural plastic. These structural plastics show promise for use in ablative materials, re-entry glider nose caps, high strength structures, leading edges, fins, high performance nose cones, hot structures and cryogenic structures.

7.3 PLASTIC MOLDING POWDER COMPOSITIONS

This invention disclosure relates to the application of the A-type polyimide resin system for use as a plastic matrix in molding powder compositions. This resin system yields molding powders which can be economically processed into useful objects having thermal and oxidative stability by conventional fabrication techniques, such as compression or transfer molding. The molding powders, as well as being useful without fillers, may contain fillers, such as glass, silica, sand, graphite, fibers, or metals in granular, powder or fibrous forms alone or in combinations. The plastic molding powder compositions of this invention have excellent shelf life and are processed with evolution of a small amount of volatile matter. Items prepared from these molded powder compositions show promise for use in ablative materials, high strength, high temperature and cryogenic applications and as a self-lubricating bearing materials.

7.4 POLYBASIC AROMATIC CARBOXYLIC ACIDS, ESTERS AND ANHYDRIDES

This invention relates to composition of matter, namely, polybasic aromatic carboxylic acids containing the bis(phenoxyphenyl) sulfone backbone. In addition, this invention relates to the ester and anhydride derivatives of the above specified acids. The novelty of these compositions of matter is their combination of unusual thermal stability and high molecular weight. Although other aromatic acids or derivatives may also be as thermally stable, the high molecular weight of this composition of matter permits preparation of polymers (such as polyimides, polybenzimidazoles and polypyrrones) by condensation polymerization with a lower amount of volatile matter than obtained from comparable thermally stable materials. Consequently, coherent fibers, films, adhesives, lubricants and surface coatings can be prepared without the usually associated void content.

7.5 IMPROVED PROCESS FOR PREPARING GRAPHITIZED GRAPHITE COMPOSITES

An improved process for the preparation of graphitized graphite composites has been conceived which relies on the use of the new high char forming A-type and B-type resin systems. Low void graphite composites can be prepared from these resin systems, which on pyrolysis yield products having a higher char yield than those obtained using conventional phenolic, epoxy or state of the art high char forming resins having a high volatile emission during cure. This process permits fabrication of graphitized composites using conventional impregnation-charring and graphite deposition methods, however, the final product is achieved with a significantly fewer number of repetitive processing steps. This improved process markedly reduces the cost of preparing graphitized-graphite composites and facilitates the fabrication of large, complex shaped structures.

7.6 PREPARATION OF IMPROVED ABLATIVE MATERIALS

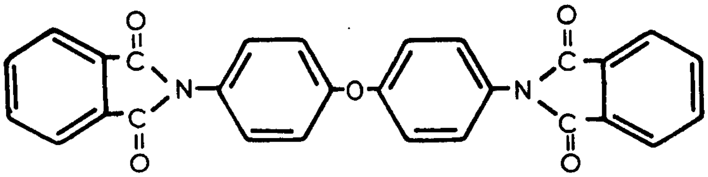
Improved silica-reinforced material formulations are prepared by maximizing the extent of the sub-surface silica-carbon reaction which occurs during ablation. Two methods have been conceived to insure a higher degree of completion of this highly endothermic reaction per unit weight. The first method consists of using the high char forming processable A-type and B-type resins in silica composites loaded to a greater level than that of commercial materials; this expedient would allow stoichiometric quantities to be present and permit about 15% more reaction capacity. The second approach consists of using beta glass fabric (leached to form a high silica product) which has an average diameter of 0.00015-inch per filament; this approach would permit a 2.3 fold increase in fiber surface area over standard Refrasil type reinforcement (0.00035-inch per filament) thereby facilitating the extent of the carbon-silica ablation reaction.

APPENDIX A
SYNTHESIZED MONOMERS AND PRECURSORS

The following compounds were prepared in the laboratory. The procedures used and the properties observed are reported below. The use of each material is reported in the text (Section 2).

A. 1 PREPARATION OF MODEL COMPOUNDS

A. 1. 1 p, p' - Oxydiphenyldiphthalimide



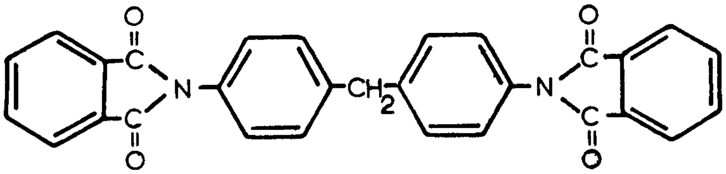
Procedure A. 1. 1

Dissolve 20. 0 g (0. 1 mole) of oxydianiline in 50 ml of dimethylformamide (DMF). Add this solution slowly (from a pressure relieved dropping funnel) to 29. 6 g (0. 2 mole) of phthalic anhydride in 400 ml of refluxing toluene in a three-necked, round botton flask equipped with mechanical stirrer, thermometer, Dean-Stark trap, and reflux condenser. Reflux this mixture until water stops collecting in the Dean-Stark trap. Collect the product on a sintered glass Buchner funnel and wash it with toluene and acetone. Dry in an oven at 110°C. The product was 70% of the theoretical yield.

Characterization of Product A. 1. 1

Melting Point: 289-291°C
Form: Tan crystals
Thermogram: See Figure A-1. 1

A. 1. 2 p, p' -Methylenediphenyldiphthalimide



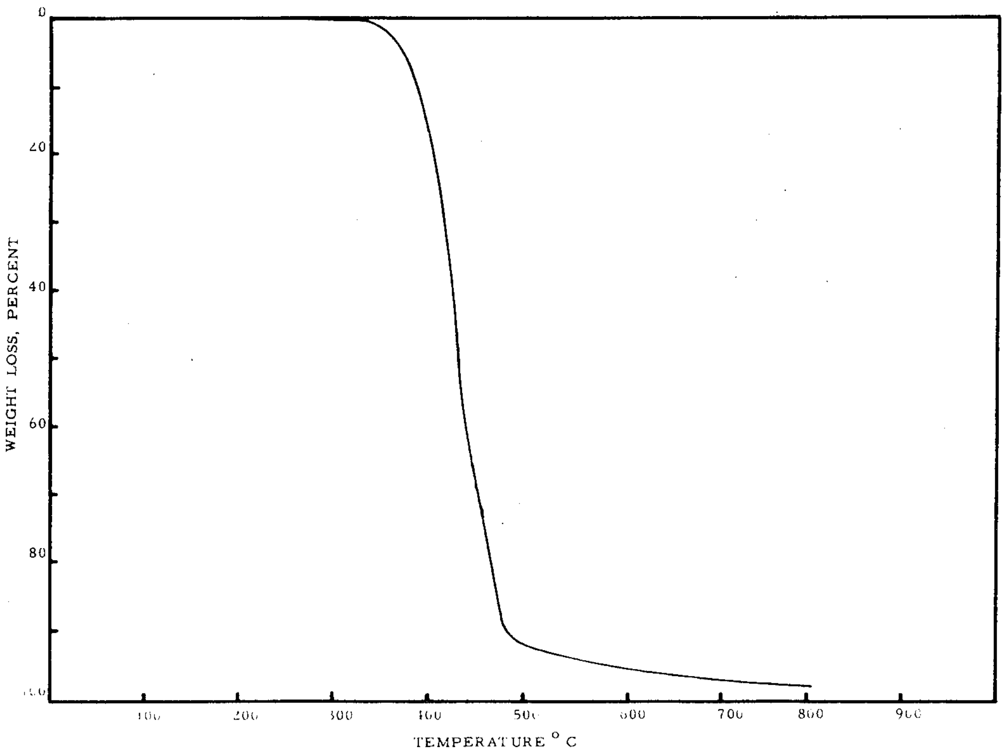


Figure A. 1. 1. Thermogram of p, p'-Oxydiphenyldiphthalimide
Environment: 1 atm N_2 Flow
Scan Rate: 3°C/Minute

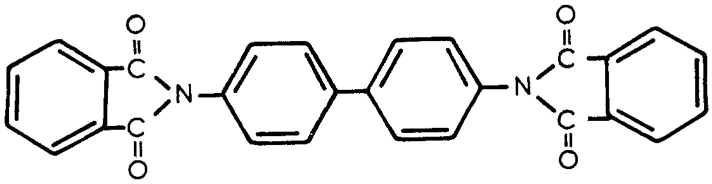
Procedure A. 1. 2

Dissolve 19. 8 g (0. 1 mole) of methylene dianiline in 20 ml of DMF and add this solution to 29. 6 g (0. 2 mole) of phthalic anhydride in 200 ml of refluxing toluene. Use the equipment described in Procedure A. 1. 1. Continue the refluxing until water stops collecting in the Dean-Stark trap. Collect the product from the hot solution on a sintered glass Buchner funnel and wash with fresh toluene and acetone. Dry in an oven at 110°C. The product was 82% of theoretical yield.

Characterization of Product A. 1. 2

Melting Point: Greater than 300°C
Form: Yellow crystals
Thermogram: See Figure A. 1. 2.

A. 1. 3 p, p'-Biphenyldiphthalimide



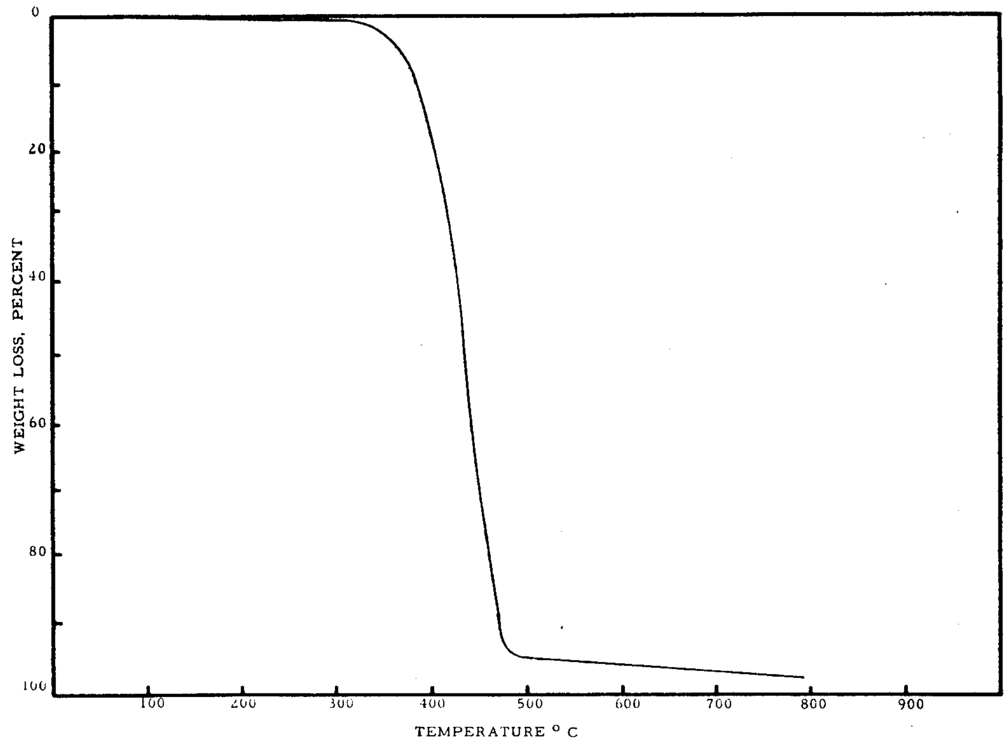


Figure A. 1. 2. Thermogram of p, p'-Methylenediphenyl-diphthalimide
Environment: 1 atm N_2 Flow
Scan Rate: 3° C/Minute

Procedure A. 1. 3

Dissolve 18.4 g (0.1 mole) of benzidine in 50 ml of dimethylformamide and add the solution to a refluxing solution of 29.6 g (0.2 mole) of phthalic anhydride in 500 ml of toluene. Use the equipment described in Procedure A. 1. 1. Refluxing is continued until water stops collecting in the Dean-Stark trap. Collect the product on a sintered glass Buchner funnel and wash it with toluene and acetone. Dry the product in an oven at 110° C. The product was 83% of theoretical yield.

Characterization of Product A. 1. 3

Melting Point: Greater than 300° C

Form: Yellow crystals

Thermogram: See Figure A. 1. 3.

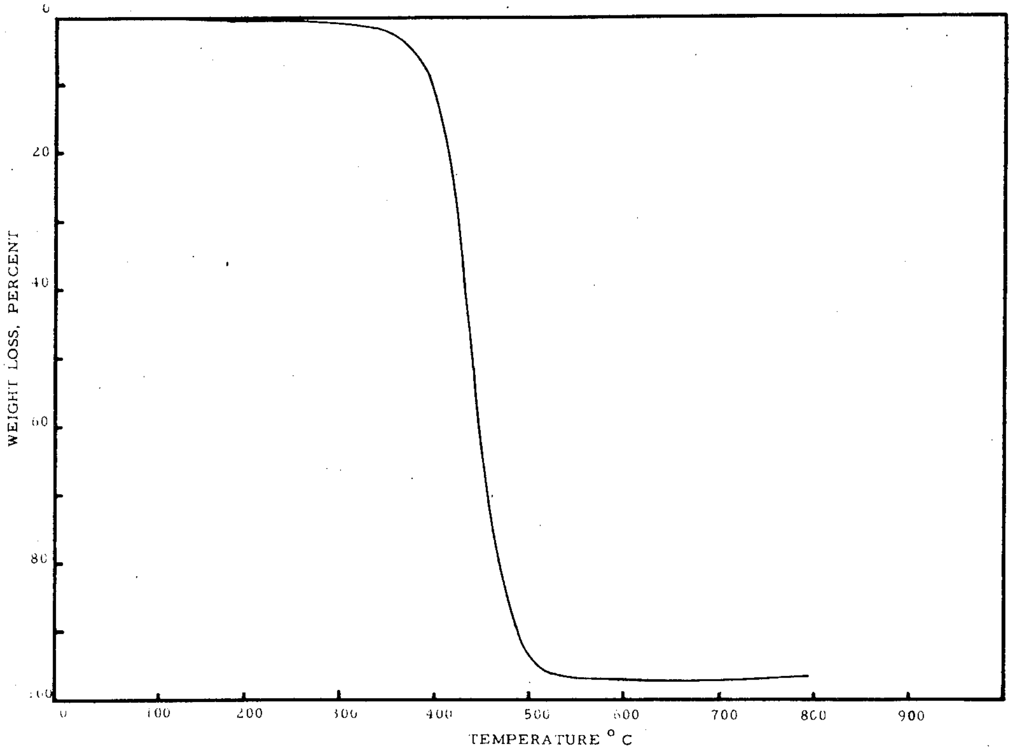
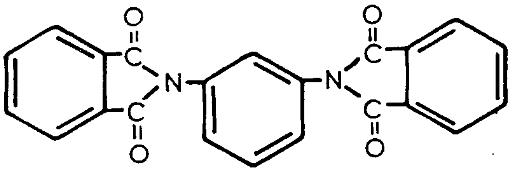


Figure A. 1. 3. Thermogram of p, p'-Biphenyldiphthalimide
Environment: 1 atm N_2 Flow
Scan Rate: 3°C/Minute

A. 1. 4 m-Phenylenediphthalimide



Procedure A. 1. 4

Dissolve 10. 8 g (0. 1 mole) of m-phenylene diamine in 10 ml of dimethylformamide and add it slowly to 29. 6 g (0. 2 mole) of phthalic anhydride in 100 ml of refluxing toluene. Use the equipment described in Procedure A. 1. 1. Reflux this mixture until water stops collecting in the Dean-Stark trap. Collect the product from the hot solution on a sintered glass Buchner funnel and wash with fresh toluene and acetone. Dry in an oven at 110°C. The product was 87% of theoretical yield.

Characterization of Product A. 1. 4

Melting Point: Greater than 300°C

Form: White Crystals

Thermogram: See Figure A. 1.4.

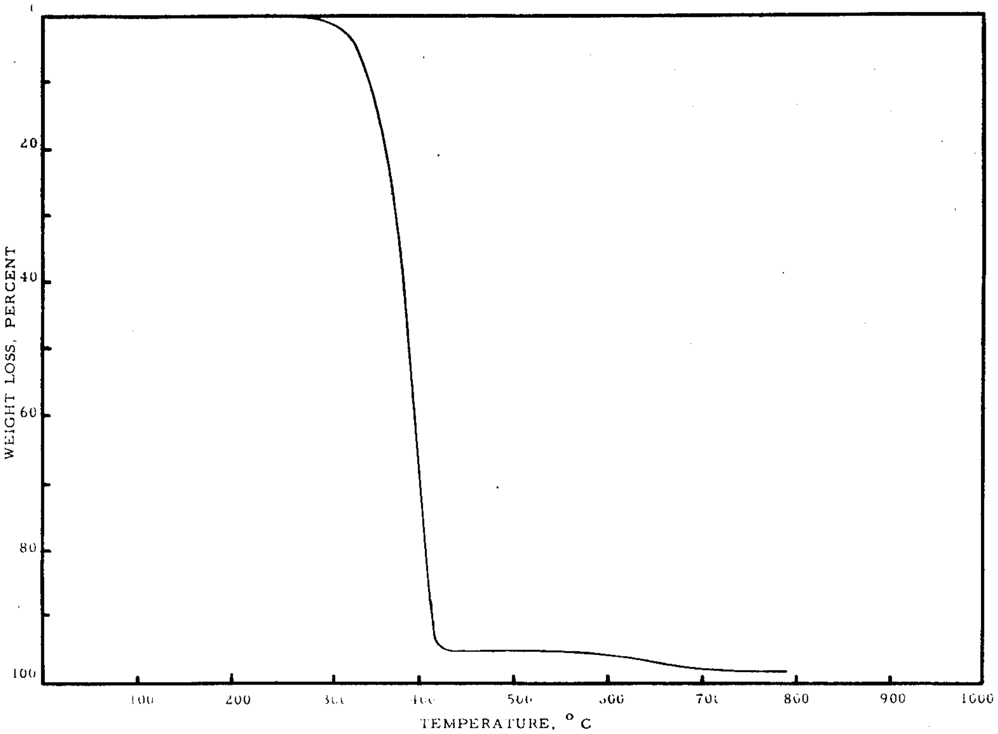
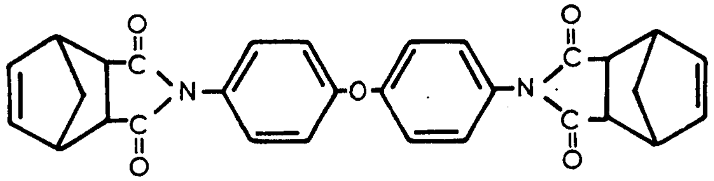


Figure A. 1. 4. Thermogram of m-Phenylenediphthalimide
Environment: 1 atm N_2 Flow
Scan Rate: 3°C/Minute

A. 1. 5 p, p'-Oxydiphenyl-bis(3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalimide



Procedure A. 1. 5

Dissolve 60. 0 g (0. 3 mole) of oxydianiline in 150 ml of dimethyl formamide and add slowly to 98. 4 g (0. 6 mole) of nadic anhydride in 400 ml of refluxing toluene. Use the equipment described in Procedure A. 1. 1. Reflux for 20 hours or until the water stops collecting in the Dean-Stark trap. Collect the product from the hot solution on a sintered glass Buchner funnel and wash with toluene and acetone. Dry in an oven at 110°C. The product was 83% of theoretical yield.

Characterization of Product A. 1. 5

Melting Point: 260-265°C

Form: Brown crystals

Thermogram: See Figure A. 1. 5.

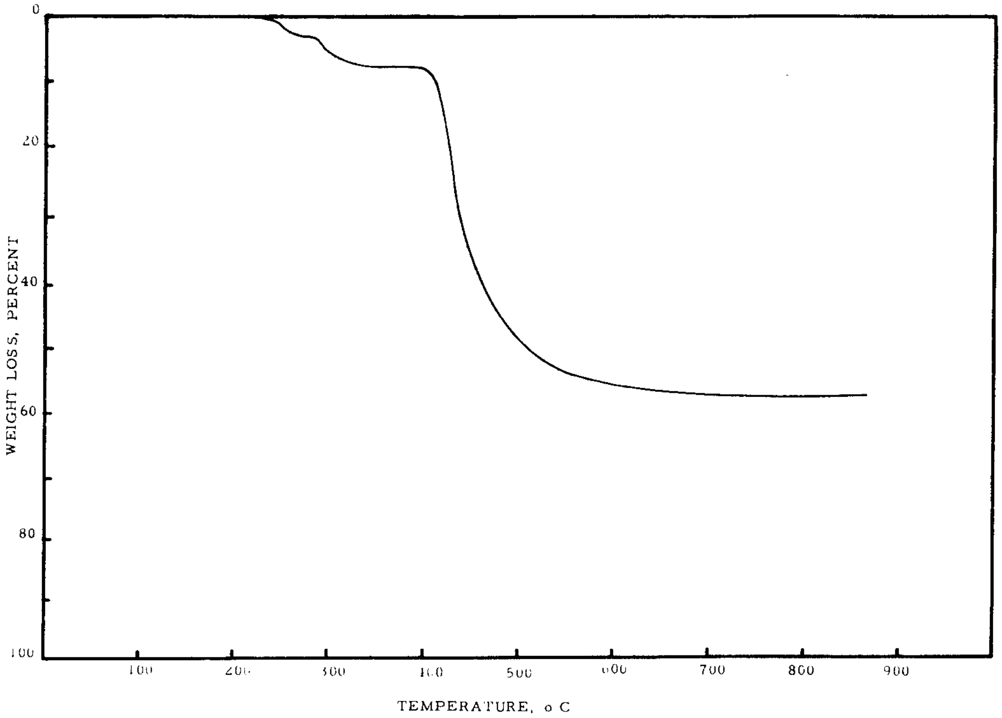
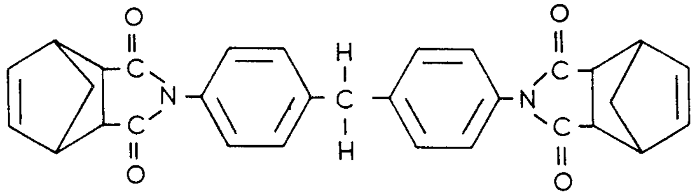


Figure A. 1. 5. Thermogram of p, p'-Oxydiphenyl-bis(3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalimide)
Environment: 1 atm N_2 Flow
Scan Rate: 3°C/Minute

A. 1. 6 p, p'-Methylenediphenyl-bis(3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalimide)



Procedure and Characterization of A. 1. 6 are given in Reference 2, A. 8, p. 74.

Thermogram: See Figure A. 1. 6.

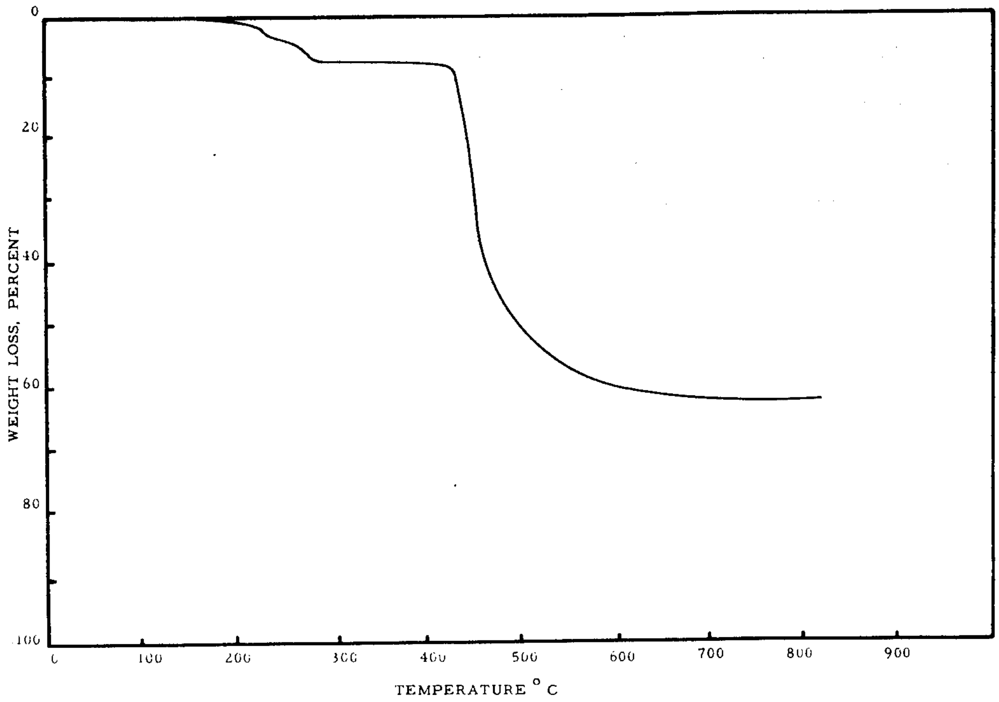
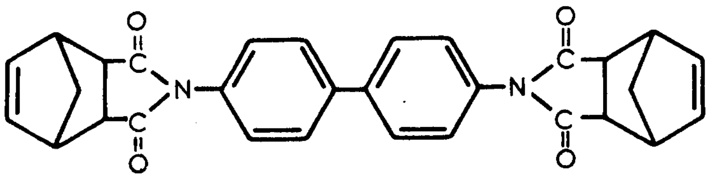


Figure A. 1. 6. Thermogram of p, p'-Methylenediphenyl-bis(3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalimide)
Environment: 1 atm N_2 Flow
Scan Rate: 3°C/Minute

A. 1. 7 p, p'-Biphenyl-bis(3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalimide



Procedure A. 1. 7

Dissolve 55. 2 g (0. 3 mole) of benzidine in 150 ml of dimethyl formamide and add it slowly to 98. 4 g (0. 6 mole) of nadic anhydride dissolved in 400 ml of refluxing toluene. Use the equipment described in Procedure A. 1. 1. Reflux this mixture for 20 hours. The water produced is collected in the Dean -Stark trap. At the end of the refluxing period, collect the solid product from the hot solution by filtering on a sintered glass Buchner funnel. Wash the product with fresh toluene and acetone. Dry in oven at 110°C. The product was 86% of theoretical yield.

Characterization of Product A. 1. 7

Melting Point: 286-290°C

Form: Tan crystals

Thermogram: See Figure A. 1. 7.

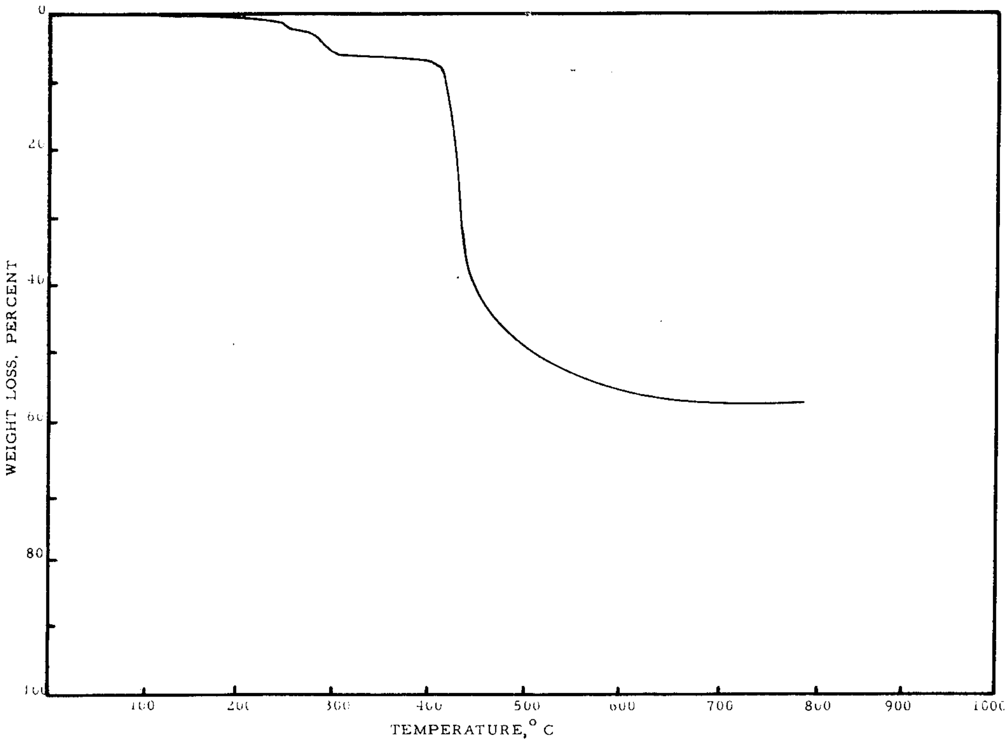
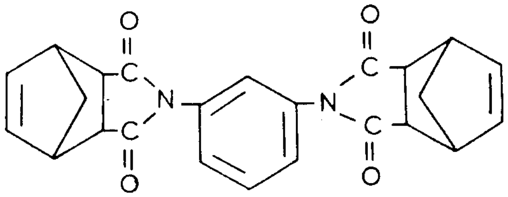


Figure A. 1. 7. Thermogram of p, p'-Biphenyl-bis(3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalimide)
Environment: 1 atm N_2 Flow
Scan Rate: 3°C/Minute

A. 1. 8 m-Phenylene-bis(3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalimide)



Procedure and Characterization of A. 1. 8 are given in Reference 2, A. 9, p. 75.

Thermogram: See Figure A. 1. 8.

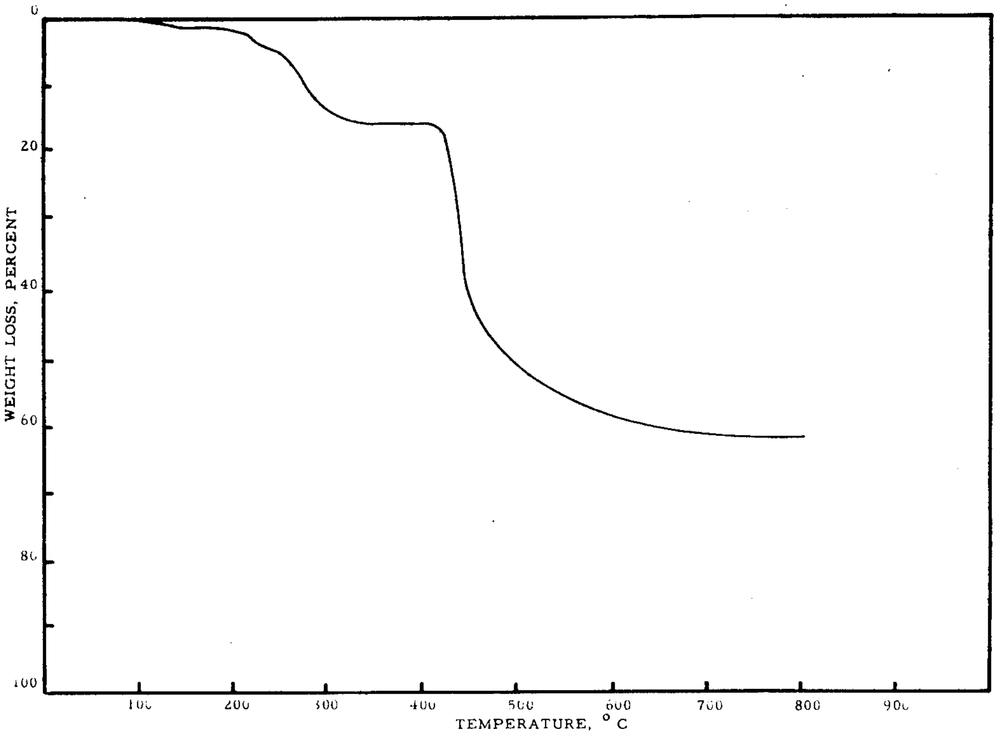
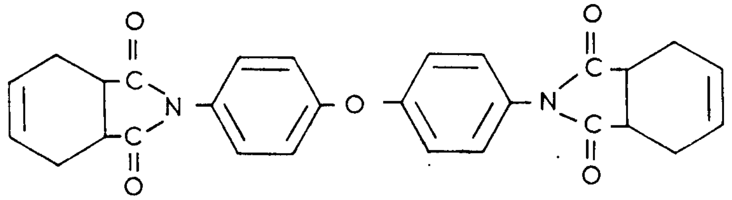


Figure A. 1. 8. Thermogram of m-Phenylene-bis(3, 6-endo-methylene-1, 2, 3, 6-tetrahydrophthalimide)
Environment: 1 atm N_2 Flow
Scan Rate: $3^{o}C$/Minute

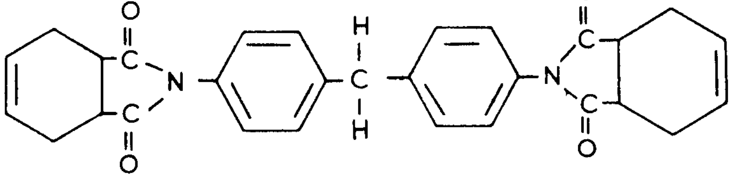
A. 1. 9 p, p'-Oxydiphenyl-bis(1, 2, 3, 6-tetrahydrophthalimide)



Procedure and Characterization of A. 1. 9 are given in Reference 2. A. 5, p. 70.

Thermogram: See Figure A. 1. 9

A. 1. 10 p, p'Methylenediphenyl-bis(1, 2, 3, 6-tetrahydrophthalimide)



Procedure and Characterization of A. 1. 10 are given in Reference 2, A. 3, p. 61.

Thermogram: See Figure A. 1. 10.

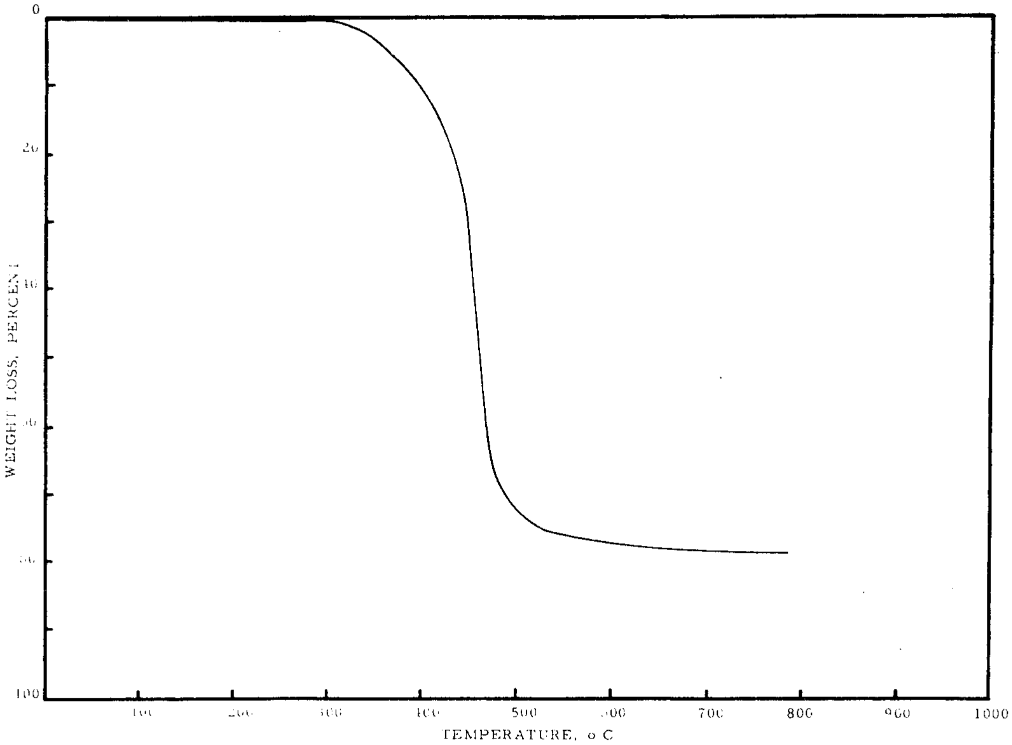
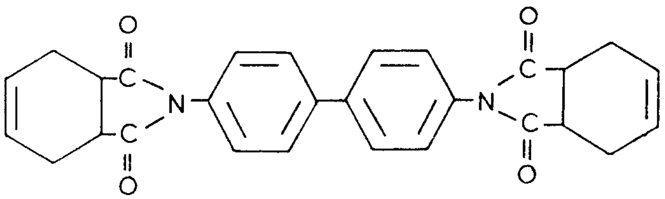


Figure A. 1. 9. Thermogram of p, p'-Oxydiphenyl-bis(1, 2, 3, 6-tetrahydrophthalimide)
Environment: 1 atm N_2 Flow
Scan Rate: 3°C/Minute

A. 1. 11 p, p'-Biphenyl-bis(1, 2, 3, 6-tetrahydrophthalimide)



Procedure and Characterization of A. 1. 11 are given in Reference 2, A. 4, p. 67.

Thermogram: See Figure A. 1. 11

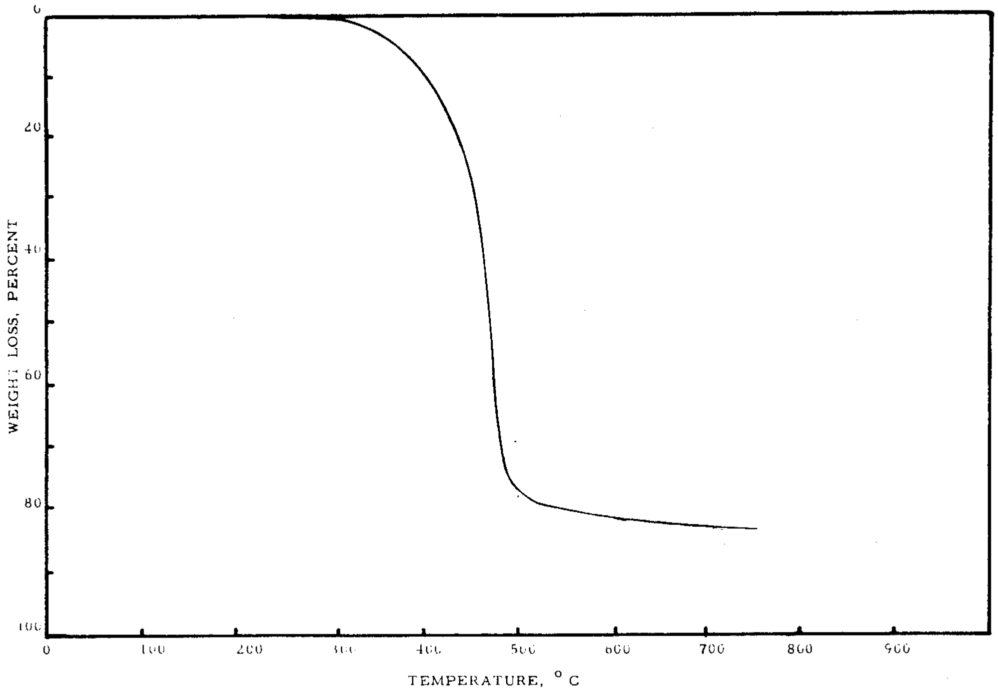


Figure A. 1. 10. Thermogram of p, p'-Methylenediphenyl-bis (1, 2, 3, 6-tetrahydrophthalimide)
Environment: 1 atm N_2 Flow
Scan Rate: 3°C/Minute

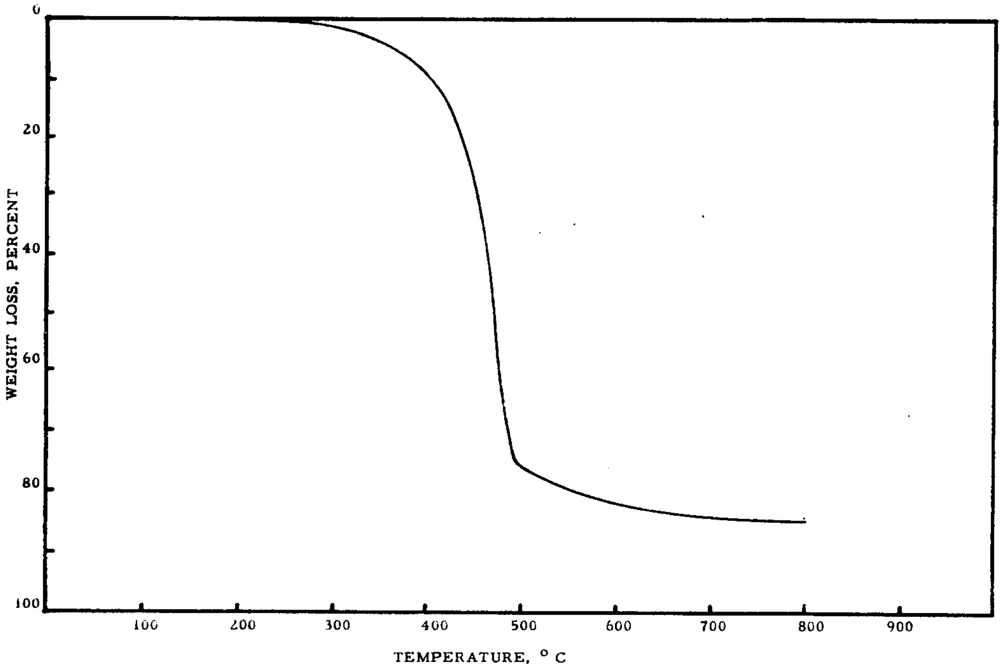
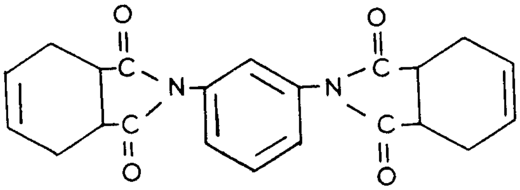


Figure A. 1. 11. Thermogram of p, p'-Biphenyl-bis(1, 2, 3, 6-tetrahydrophthalimide)
Environment: 1 atm N_2 Flow
Scan Rate: 3°C/Minute

A. 1. 12 m-Phenylene-bis(1, 2, 3, 6-tetrahydrophthalimide)



Procedure and Characterization of A. 1. 12 are given in Reference 2, A. 1, p. 63.

Thermogram: See Figure A. 1. 12.

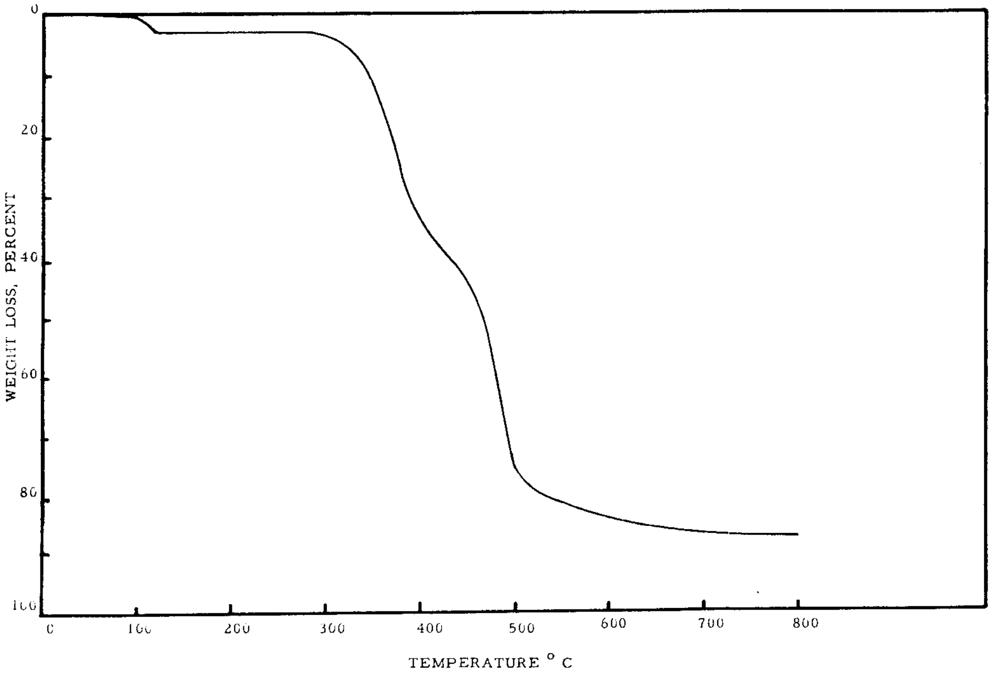
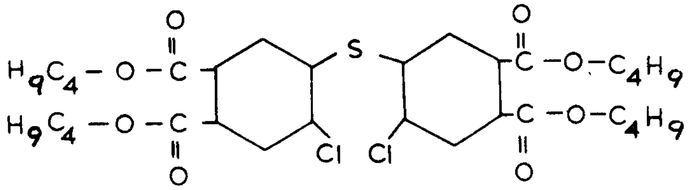


Figure A. 1. 12. Thermogram of m-Phenylene-bis(1, 2, 3, 6-tetrahydrophthalimide)
Environment: 1 atm N_2 Flow
Scan Rate: $3^{o}C$/Minute

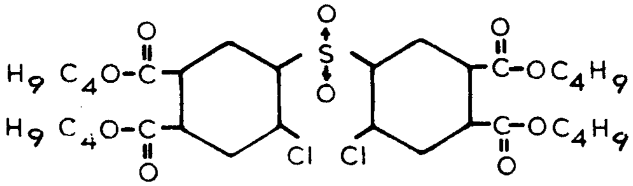
A. 2 PREPARATION OF A-TYPE PRECURSORS

A. 2. 1 Bis(6-chloro-3, 4-di-n-butyl carboxycyclohexyl) Sulfide



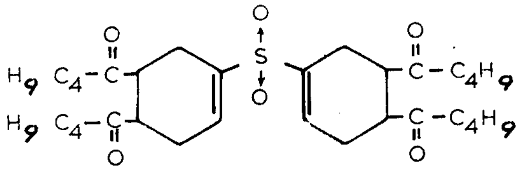
Preparation and Characterization of A. 2. 1 are given in Reference 2, A. 12, p. 79.

A. 2. 2 Bis(6-chloro-3, 4-di-n-butyl carboxycyclohexyl) Sulfone



Preparation and Characterization of A. 2. 2 are given in Reference 2, A. 13, p. 83.

A. 2. 3 Bis(3, 4 -di-n-butyl carboxy-2, 3, 4, 5-tetrahydrophthalic) Sulfone



Procedure A. 2. 3

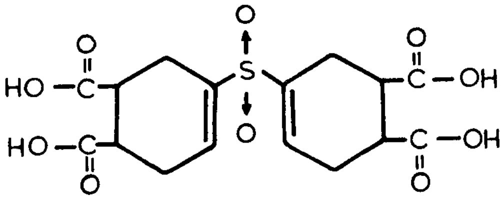
To 255 g (0. 36 mole) of bis(6-chloro-3, 4-di-n-butyl carboxycyclohexyl) sulfone prepared in A. 2. 2, add 202 g (2. 0 mole) of anhydrous triethylamine. Reflux this solution for 24 hours and then cool. Dissolve the resulting oil in ethyl ether and filter to remove the crystalline precipitate. Wash the ether solution with water, dilute HCl, and water again to remove any remaining amine. Dry the ether solution over drierite and strip. The product was 56% of theoretical yield.

Characterization of Product A. 2. 3

Melting Point: Liquid at room temperature

Form: Viscous yellow oil.

A. 2. 4 Bis(3, 4-dicarboxylic acid-2, 3, 4, 5-tetrahydrophthalic) Sulfone



Procedure A. 2. 4

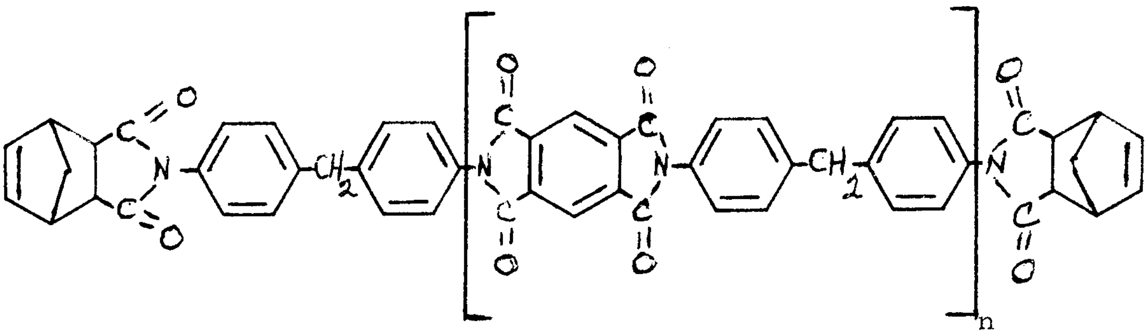
To 126. 8 g (0. 208 mole) of bis(3, 4-di-n-butyl carboxy-2, 3, 4, 5-tetrahydrophthalic) sulfone prepared in A. 2. 3, add 200 ml of glacial acetic acid, 100 ml of H_20 and 1 gram of p-toluene sulfonic acid. Reflux this solution slowly for 24 hours. The theoretical amount of butyl acetate is recovered in this time. Drown the reaction mixture in 1 liter of water and filter. Treat the filtrate twice with Norit A decolorizing carbon and finally strip to dryness. The product was 83% of theoretical yield.

Characterization of Product A. 2. 4

Melting Point: 100-110°C

Form: White crystals

A. 2. 5 Group I A-Type Polyimide Prepolymer (MNP)



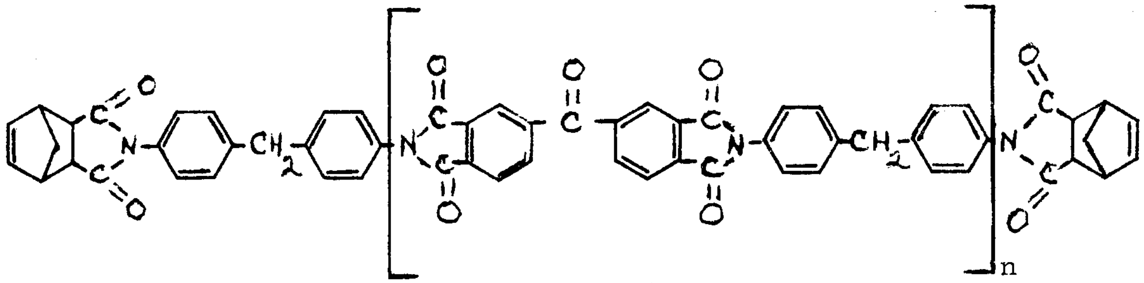
Procedure A.2.5

Pyromellitic dianhydride, 4,4'-methylene dianiline, and 3,6-endomethylene-1,2,3,6-tetrahydrophthalic anhydride were formulated and allowed to react in an appropriate solvent. Approximately 30% of the prepolymer product was soluble in the reaction liquor. The remainder precipitated from solution.

Characterization of Insoluble Product A.2.5

Melting Point: > 300°C
Form: Yellow-brown powder

A.2.6 Group II A-Type Polyimide Prepolymer (MNB)



Procedure A.2.6

3,3',4,4'-Benzophenone tetracarboxylic acid dianhydride, 4,4'-methylene dianiline, and 3,6-endomethylene-1,2,3,6-tetrahydrophthalic anhydride were formulated and allowed to react in an appropriate solvent. At the conclusion of the reaction period 65% of the material was soluble in the reaction solvent and 35% precipitated. The soluble material was isolated by treating the reaction liquor with water.

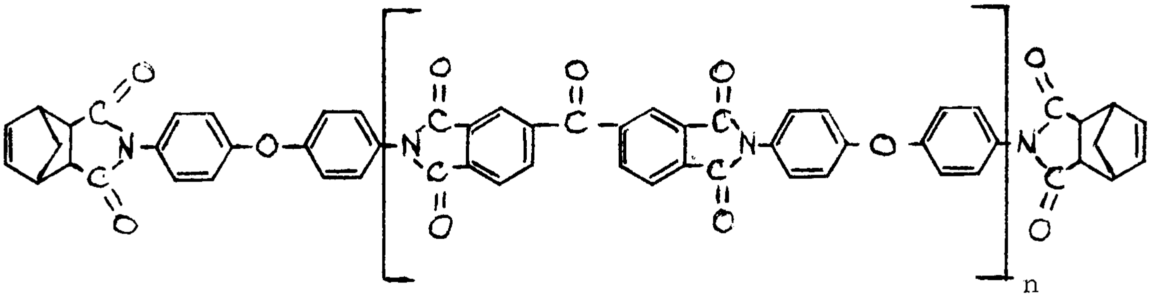
Characterization of Soluble Product A.2.6

Melting Point: 150°C
Form: Yellow Powder

Characterization of Insoluble Product A.2.6

Melting Point: > 300°C
Form: Yellow Powder

A.2.7 Group II A-Type Polyimide Prepolymer (ONB)



3,3',4,4'-Benzophenone tetracarboxylic acid dianhydride, 4,4'-oxydianiline, and 3,6-endomethylene-1,2,3,6-tetrahydrophthalic anhydride were formulated and allowed to react in an appropriate solvent. 80% of theoretical material was recovered, of which 30% was soluble and 70% insoluble.

Characterization of Soluble Product A.2.7

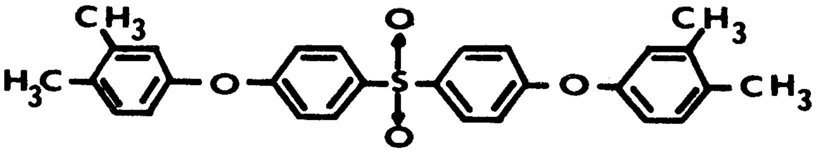
Melting Point: 175°C
Form: Greenish-yellow powder

Characterization of Insoluble Product A.2.7

Melting Point: 300°C
Form: Greenish-yellow powder

A.3 PREPARATION OF B-TYPE PRECURSORS

A.3.1 Bis(3,4-dimethylphenoxyphenyl) Sulfone



Procedure A.3.1

Bis(p-chlorophenyl) sulfone was dissolved in dimethylsulfoxide and chlorobenzene. To this solution was added sodium 3,4-dimethylphenoxide.

After the reaction was completed, the hot solution was poured into iced water with stirring. The white solid formed was washed with cold distilled water and filtered. The white solid was dried and then recrystallized twice from 2-propanol. Yield = 79.9%.

Characterization of Product A.3.1

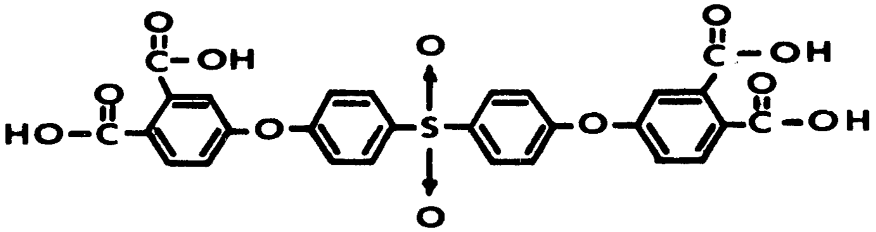
Melting Point: 129-130°C

Analysis: Calculated for

$(C_{28}H_{26}O_4S)$: C, 73.33%; H, 5.72%; Cl, 0.00%

Found: C, 72.93%; H, 5.61%; Cl, 0.51%

A.3.2 Bis(3,4-dicarboxyphenoxyphenyl) Sulfone



Procedure A.3.2

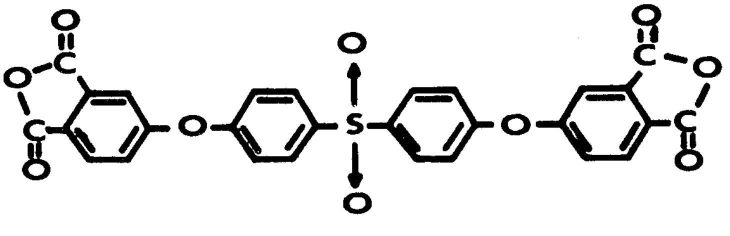
Bis(3,4-dimethylphenoxyphenyl) sulfone was dissolved in a solution of pyridine and water and oxidized with potassium permanganate using a specially developed procedure. A white precipitate product was collected, recrystallized, washed and air dried. The yield was 31% of the theoretical amount of bis(3,4-dicarboxyphenoxyphenyl) sulfone.

Characterization of Product A.3.2

Melting Point: 172°C

Form: Tan powder

A.3.3 Bis(3,4-dicarboxyphenoxyphenyl) Sulfone Dianhydride



Procedure A.3.3

Bis(3,4-dicarboxyphenoxyphenyl) sulfone was dissolved in acetic anhydride. The solution was heated to boiling, boiled five minutes, and then allowed to cool. Yellow needles crystallized from the solution. The needles were collected and dried under vacuum at 115°C for one hour. The yield was 70% of the theoretical amount of bis(3,4-dicarboxyphenoxyphenyl) sulfone dianhydride.

Characterization of Product A.3.3

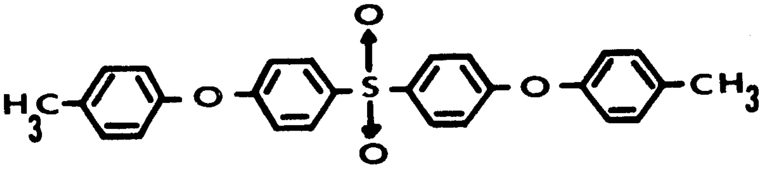
Melting Point: 253-254°C

Analysis: Calculated for

($C_{28}H_{14}O_{10}S$): C, 61.99%; H, 2.60%: S, 5.91%

Found: C, 61.56%; H, 2.84%; S, 5.36%

A.3.4 Bis(4-methylphenoxyphenyl) Sulfone



Procedure A.3.4

Bis(p-chlorophenyl) sulfone was dissolved in a solution of dimethylsulfoxide and chlorobenzene. Sodium p-methylphenoxide was added and the solution was heated. After the reaction was completed, the solution was cooled to room temperature, poured into a beaker containing water and stirred. The crude product was collected by filtration and recrystallized twice. After drying the crystals under vacuum, bis(4-methylphenoxyphenyl) sulfone was isolated in a 63% yield.

Characterization of Product A.3.4

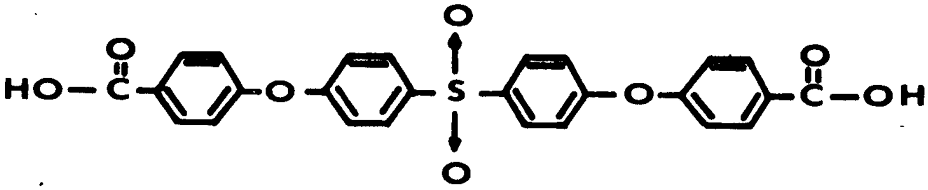
Melting Point: 129-140°C

Analysis: Calculated for

($C_{26}H_{22}O_4S$): C, 72.54%; H, 5.15%; Cl 0.00%

Found: C, 72.15%; H, 5.15%; Cl 0.00%

A.3.5 Bis(4-carboxyphenoxyphenyl) Sulfone



Procedure A.3.5

The precursor, bis(4-methylphenoxyphenyl) sulfone, was dissolved in a solution containing pyridine and water and was oxidized with potassium permanganate using a specially developed procedure. A white precipitate product was collected, recrystallized, washed and air dried. The yield was 42% of the theoretical amount of bis(4-carboxyphenoxyphenyl) sulfone.

Characterization of Product A.3.5

Melting Point: 300-302°C

Analysis: Calculated for

($C_{26}H_{18}O_8S$): C, 63.66%; H, 3.71%

Found: C, 63.82%; H, 3.93%

APPENDIX B
RESIN OPTIMIZATION STUDIES

This appendix provides detailed information generated in studies aimed at optimizing the neat candidate resin systems described in Section 3. Specific experimental studies are described here for:

- Poly(cyclized 1,2-polybutadiene) tolyl urethane,
- Polyalkaline earth acrylates, and
- Polyimide resins.

B.1 POLY(CYCLIZED 1,2-POLYBUTADIENE) TOLYL URETHANE

Prior art, reported for increasing the char yields of hydrocarbon elastomers, has employed the addition of both metal acetonyl acetonates and tributyl phosphate in equal portions of 10 phr* base polymer resin. A screening test matrix was established employing ferric and zinc acetonyl acetonates, nickel sulfate and tributyl phosphate. Nickel sulfate has been shown to be a useful substitute for nickel acetonyl acetonate for the purpose. The results of these tests, together with the weight loss at specific temperatures as obtained by thermogravimetric analysis are presented in Table B.I.

From these studies, it is seen that a modest improvement in char yield was effected with 0.5 phr zinc acetonyl acetate and 10 phr tributyl phosphate individually, but this increase was considerably below that required for use as an ablative resin. The other additives, both in combination and alone, in varying concentrations, did not increase the char yield and in some cases were detrimental to the cure of CPBU.

B.2 POLYALKALINE EARTH ACRYLATES

The following two approaches were investigated to improve processing characteristics so that high density specimens could be prepared thereby improving their ablative performance characteristics:

- Polycalcium acrylate-acrylic acid mixtures
- Polymerization of calcium acrylate during molding.

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*phr = parts per hundred resin

TABLE B.I

DEHYDROGENATION STUDIES ON CYCLIZED POLYBUTADIENE URETHANE (CPBU)

Specimen	Additive	Amount phr	Temperature at Percent Weight Loss, °C*		
			25%	50%	75%
1	None	0.0	420	430	440
2	Zinc acetonyl acetonate	10.0	-	No cure	-
3	Zinc acetonyl acetonate	0.5	450	470	480
4	Ferric acetonyl acetonate	10.0	-	No cure	-
5	Ferric acetonyl acetonate	0.5	390	410	420
6	Nickel sulfate	10.0	-	No cure	-
7	Tributyl phosphate	10.0	430	470	480
8	Zinc acetonyl acetonate/ Tributyl phosphate	10.0	-	No cure	-
9	Ferric acetonyl acetonate/ Tributyl phosphate	10.0	-	No cure	-
10	Nickel sulfate/ Tributyl phosphate	10.0	-	No cure	-

* Results of thermogravimetric analyses
Environment: 25 μ vacuum

The first approach utilized monomeric acrylic acid which could not only act as a binder for the finely divided polycalcium acrylate polymer, but also interact with it by interchange of the calcium ions. The mixture of approximately 10% by weight of acrylic acid (plus a small amount tert-butyl-perbenzoate) with the polycalcium acrylate polymer was pressed at a variety of times, temperatures and pressures. Solid, machinable specimens were produced by several differing processes, however, excessive spalling occurred on all specimens during FLOX/methane PEET evaluation (see Section 3.8 for details).

The second approach attempted to maximize the properties of the polycalcium acrylate and involved the polymerization of calcium acrylate monomer in the mold during pressing. Calcium acrylate monomer is a solid and was prepared for molding by ball-milling to a fine powder, mixing with a small amount of tert-butyl-perbenzoate, charging to the mold, and pressing. As in the preceding attempt, a variety of times, temperatures, and pressures were used to produce solid, machinable specimens suitable for PEET evaluation. Again, the FLOX/methane environment of PEET caused excessive spalling and weight loss.

In summary, a large effort has been carried out to optimize the polycalcium acrylate system for scale-up. Testing in FLOX/methane environments did not provide ablative results suitable for carrying the effort further.

B.3 POLYIMIDE RESINS

Attempts were undertaken to prepare neat polyimide resins to determine the ablative performance characteristics independent of reinforcement. The polyimide resin investigated was Monsanto Chemical Company's Skybond 700. Processing investigations conducted by TRW indicated that Skybond 700 could be handled by fabrication procedures similar to that used for polyamide-imides.

Unreinforced specimens for PEET evaluation were made by coating a piece of mold released aluminum foil with a thin film of the Skybond 700 varnish. The film was then "B-staged" for one hour at 450°F in an oven.

The rigid film was stripped off the foil and ball-milled for eight hours to provide a powdered molding compound. Six moldings were prepared by the process developed for polyamide-imide resins described in Reference 2.

APPENDIX C

PROPELLANT EXHAUST ENVIRONMENT TEST METHODOLOGY

C.1 GENERAL DESCRIPTION

The Propellant Exhaust Environment Test (PEET) permits evaluation of the resistance of materials to exhaust species of advanced propellant combinations such as F_2-H_2, FLOX-H_2, and FLOX-CH_4. All of the ablative composites evaluated in this report were fired with FLOX/CH_4 flame. This apparatus is designed to provide the chemical and thermal environment of rocket exhaust on a very small scale; e.g., the operational mass flow rate of FLOX is in the order of 0.06 g/sec (0.0013 lb/sec.). The complete operation of the PEET apparatus (maintaining proper flow rates of oxidizer and fuel, surface reaction temperature measurements and the testing of each ablative composite) is controlled from outside of the test cell.

PEET was performed using a system similar to that described in the Interim Report (Ref. 2). During this report period the following changes were made:

- The torch system was changed to fire vertically downward.
- The specimens were mounted in a graphite block, which was capable of movement and kinematic locking so that the specimens could be changed remotely after 30-second exposures.

These modifications permitted the following testing advantages:

- Assurance of a uniform flame on the specimen surface.
- Ability to measure the surface temperature by 2-color pyrometry during the test.
- Assurance that each specimen was located in the identical geometric configuration with respect to the torch tip.
- Improved safety of operation.
- Reduced overall testing time.

Before each PEET operation a calibration of the flowmeters is performed on the system, and a complete dry run experimental set-up is performed to insure that all parts in the system are functioning properly and test specimens are aligned. Figure C.1 shows the experimental set-up

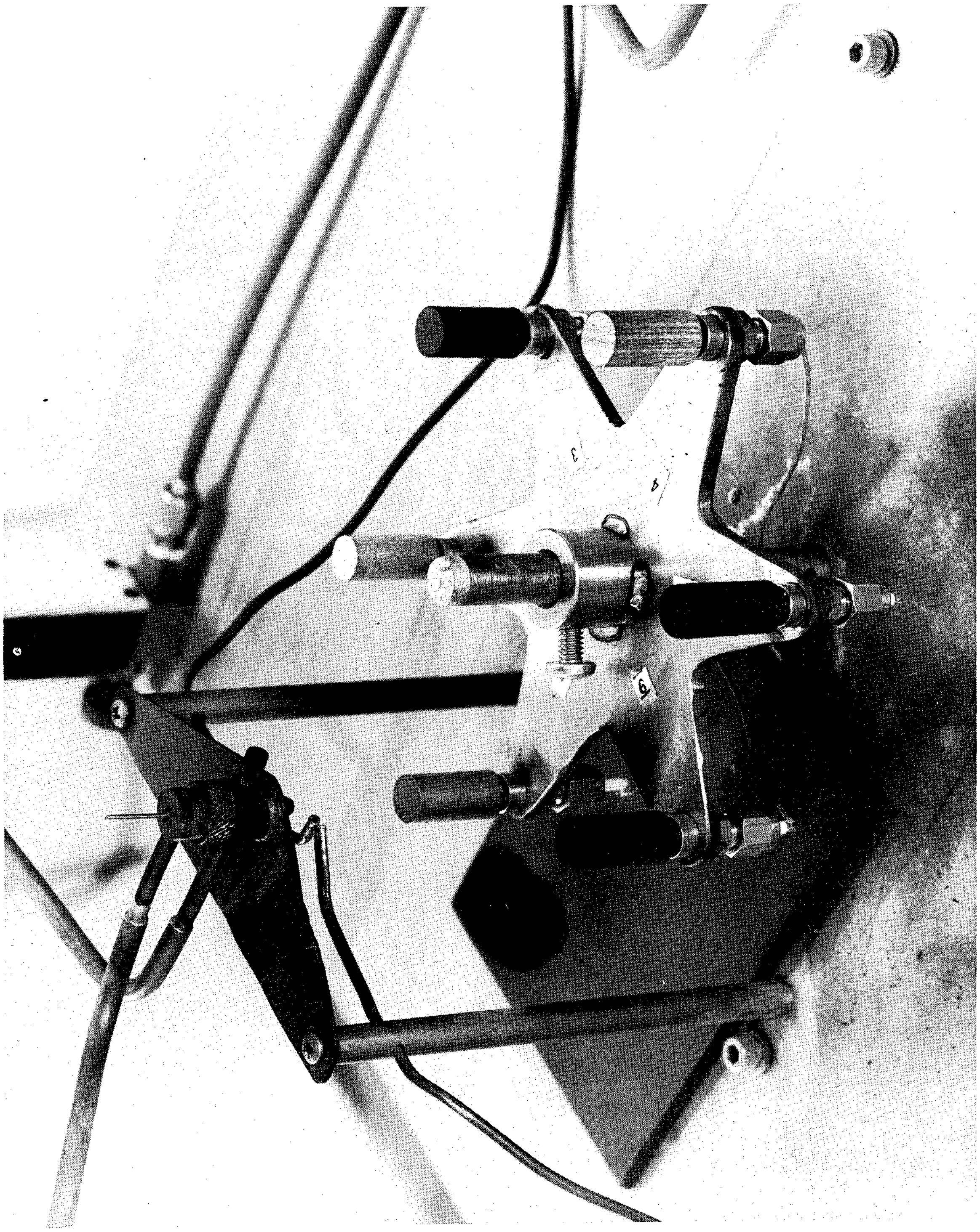

Figure C.1 PEET Experimental Set-Up Using Standard Specimen Size for the evaluation of the ablative composites using the large test specimens. Each composite is so aligned that the torch tip is 1-1/4-inch from the face of the composite. Also shown is the copper calorimeter which is used to measure the heat flux of the FLOX/CH_4 flame during the evaluation of the ablative composite series.

The experimental set-up for the testing of the small candidate ablative composites (0.25-inch diameter x 0.75-inch long) is shown in Figure C.2. In the smaller size specimen test, the heat flux was higher and it was not possible to obtain backwall temperature measurements. The specimen diameter was too small to drill the hole necessary for thermocouple embedment.

C.2 STANDARD THERMAL FLUX MEASUREMENTS (PEET)

In order to make meaningful comparisons of the ablative performance of candidate resin matrices in both fluorine/hydrogen and FLOX/methane combustion environments and to relate the performance with other thermal environments on the same, it is necessary to conduct tests at known thermal fluxes. Since it was decided to make the temperatures of the two flames as close as possible, it follows that the thermal flux of the two flames would not necessarily be identical.

The measurements of the thermal flux of the fluorine/hydrogen and FLOX/methane propellant combinations were obtained using a well defined copper heat sink having identical dimensions as the normal PEET target samples. The heat sink was mounted on the same holder used by the PEET samples. A thermocouple was installed within the target near the exposed surface. In this manner, the maximum temperature of the copper heat sink could be obtained during exposure to the fluorine-containing flames. The output of the thermocouple was fed into a Bausch and Lomb Model No. VOM5 recorder.

The standard flux measurements procedure was as follows:

The recorder was calibrated, the target was installed in the PEET assembly holder and the torch was initiated

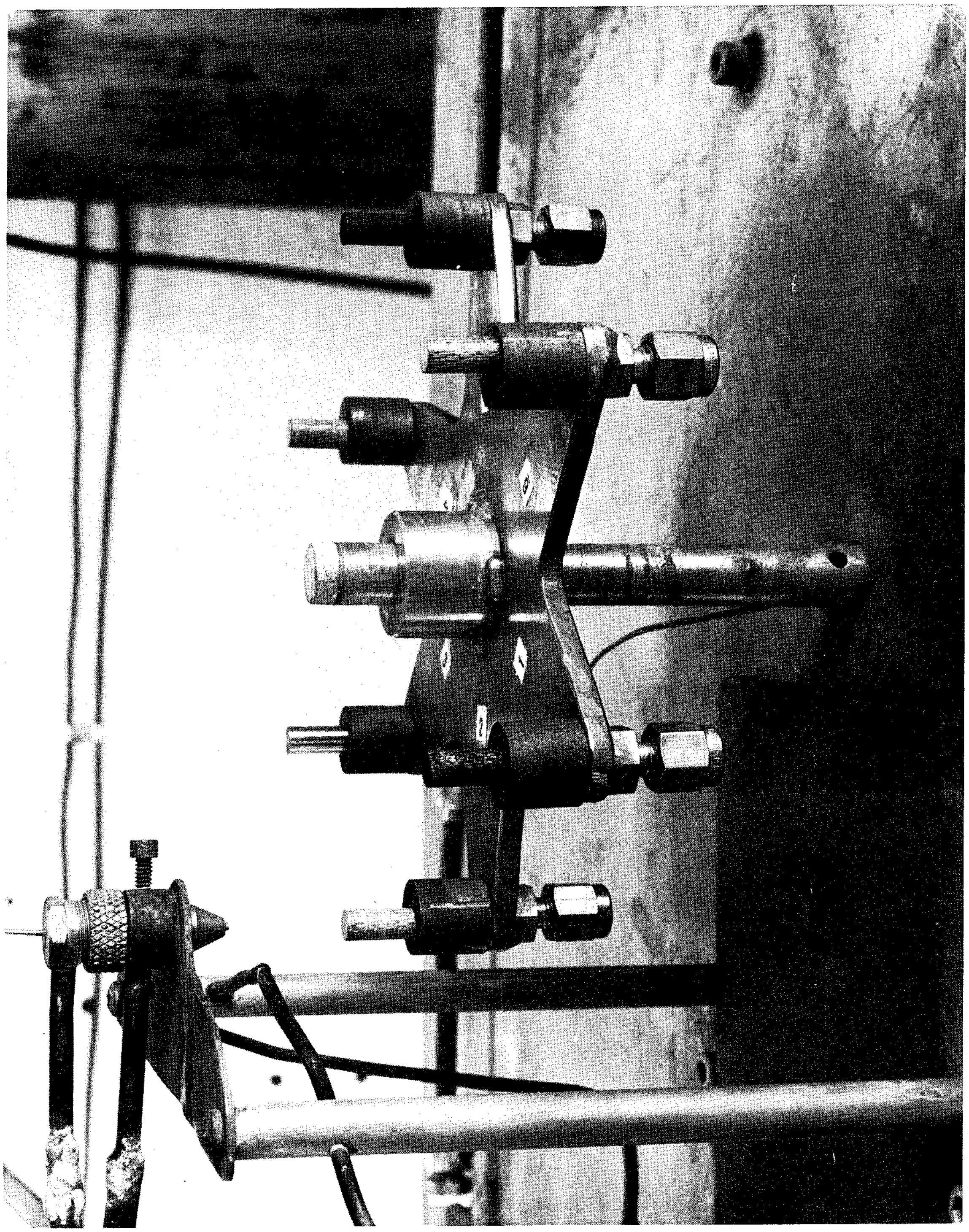

Figure C.2 PEET Experimental Set-Up Using Reduced Specimen Size using the standard **PEET** procedure (Ref. 2). These standard thermal flux measurements were performed at maximum flame temperatures for the fluorine/hydrogen and FLOX/methane propellant combination (volume mixture ratios of 1.08 and 2.44 respectively). Each test measurement was performed for a 10 second duration. Figures C.3 and C.4 show the recorded thermocouple vs. time measurements obtained for fluorine/hydrogen torch and FLOX/methane torch. The thermal flux of the fluorine/hydrogen torch assembly was calculated directly from the rate of temperature rise and the weight and heat capacity

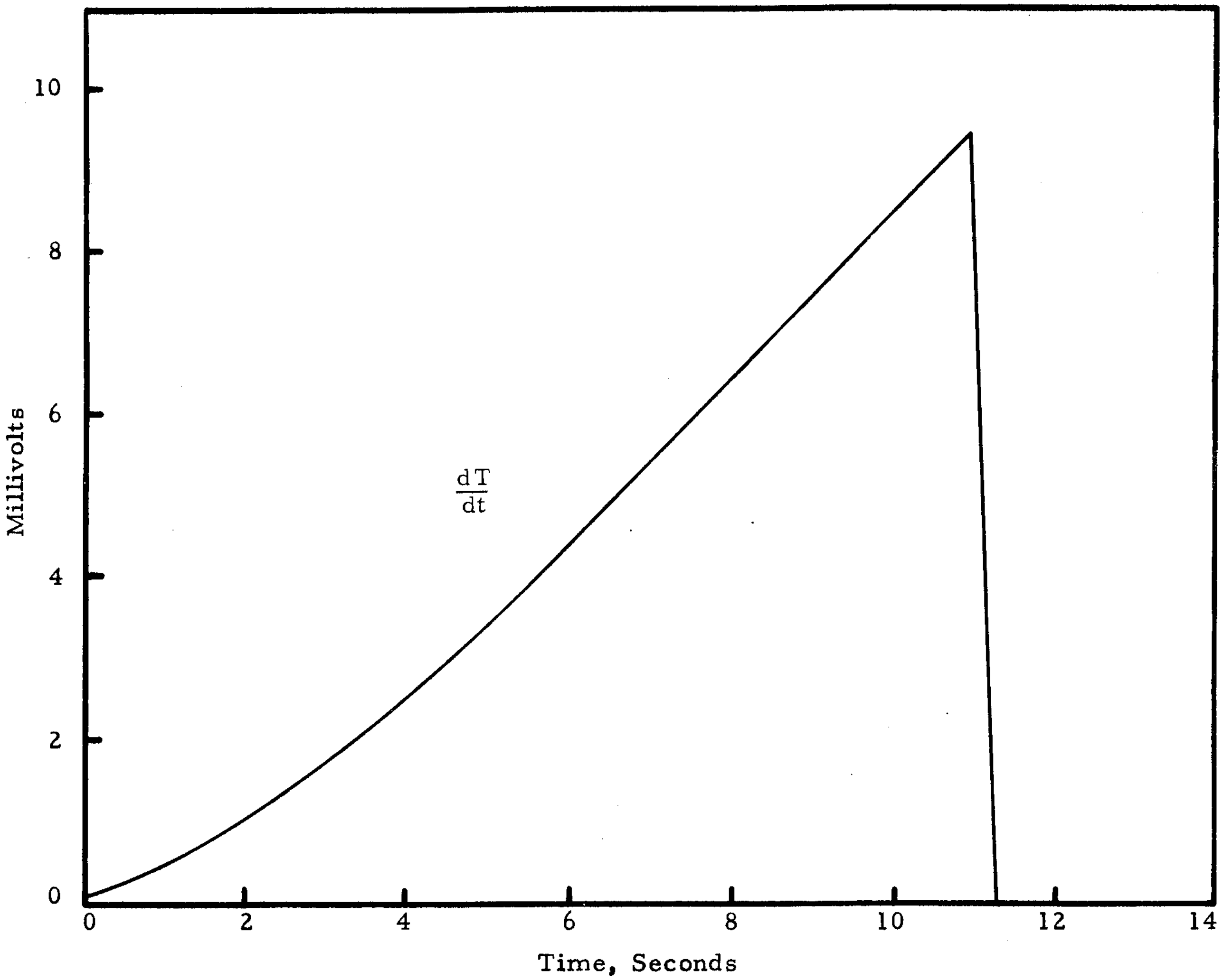

Figure C.3 Thermocouple Output vs. Time for F_2/H_2 Thermal Flux Measurements

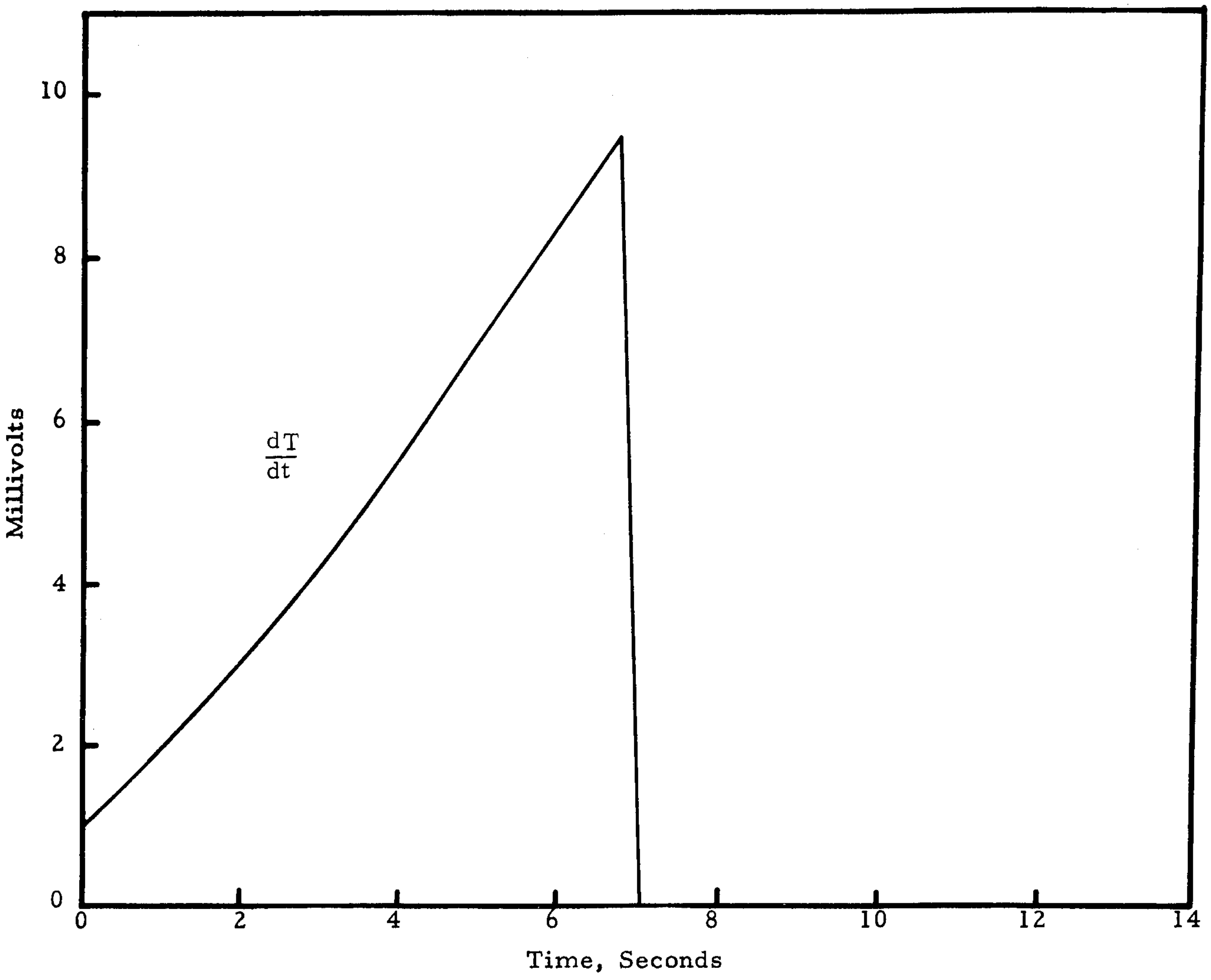

Figure C.4 Thermocouple Output vs. Time for FLOX/CH_4 Thermal Flux Measurement

of the heat sink. The average thermal flux of the F_2/H_2 PEET obtained at a volume ratio of 1.08 at a total flow of 5.916 liters/min., and at a temperature rise of 30.1 °F/sec., was 119.3 BTU/ft^2-sec. The average thermal flux of the FLOX/CH_4 PEET obtained at a volume ratio of 2.44, at a total flow of 5.31 liters/min., and at a temperature rise of 38.08 °F/sec., was 150.3 BTU/ft^2 - sec.

From these standard thermal flux measurements, it can be seen that direct comparison of the erosion test data obtained from ablative resin matrices tested with fluorine/hydrogen and FLOX/methane torches is not possible because of differences in the thermal fluxes of the two systems. The apparatus is amenable to direct comparison by decreasing the thermal flux of the FLOX/methane system by decreasing the total flow yet maintaining the same volume ratio. Table C.I gives flowrate data for the individual gases used on the PEET assembly. Figures C.5 and C.6 show plots of the calculated flame temperature vs. volume mixture ratio for the fluorine/hydrogen and FLOX/methane propellant systems, respectively. Table C.II shows the results of a series of FLOX/methane thermochemical performance calculations obtained by using the TRW AP2A Propellant Computer Program on 82.5% F_2 FLOX as a function of the FLOX/methane volume mixture ratio.

TABLE C.I

FLOW RATES FOR FLOX, F_2, H_2, CH_4

Flowmeter Reading mm	FLOX cc/sec	F_2 cc/sec	H_2 cc/sec	CH_4 cc/sec
10	3.67	3.67	15.5	10.0
20	15.0	15.0	33.3	16.7
30	22.0	22.0	51.5	24.5
40	28.4	28.4	68.3	31.5
50	34.7	34.7	83.7	38.3
60	40.4	40.4	103.0	45.7
70	46.0	46.0	121.5	53.3
80	51.6	51.6	138.3	60.5

Volume Ratio $V_R = \frac{FLOX}{CH_4} = 62.8/25.7 = 2.44$ (3985°K) Maximum Flame Temperature

Volume Ratio $V_R = F_2/H_2 = 51.6/47.0 = 1.09$ (3990°K) Maximum Flame Temperature

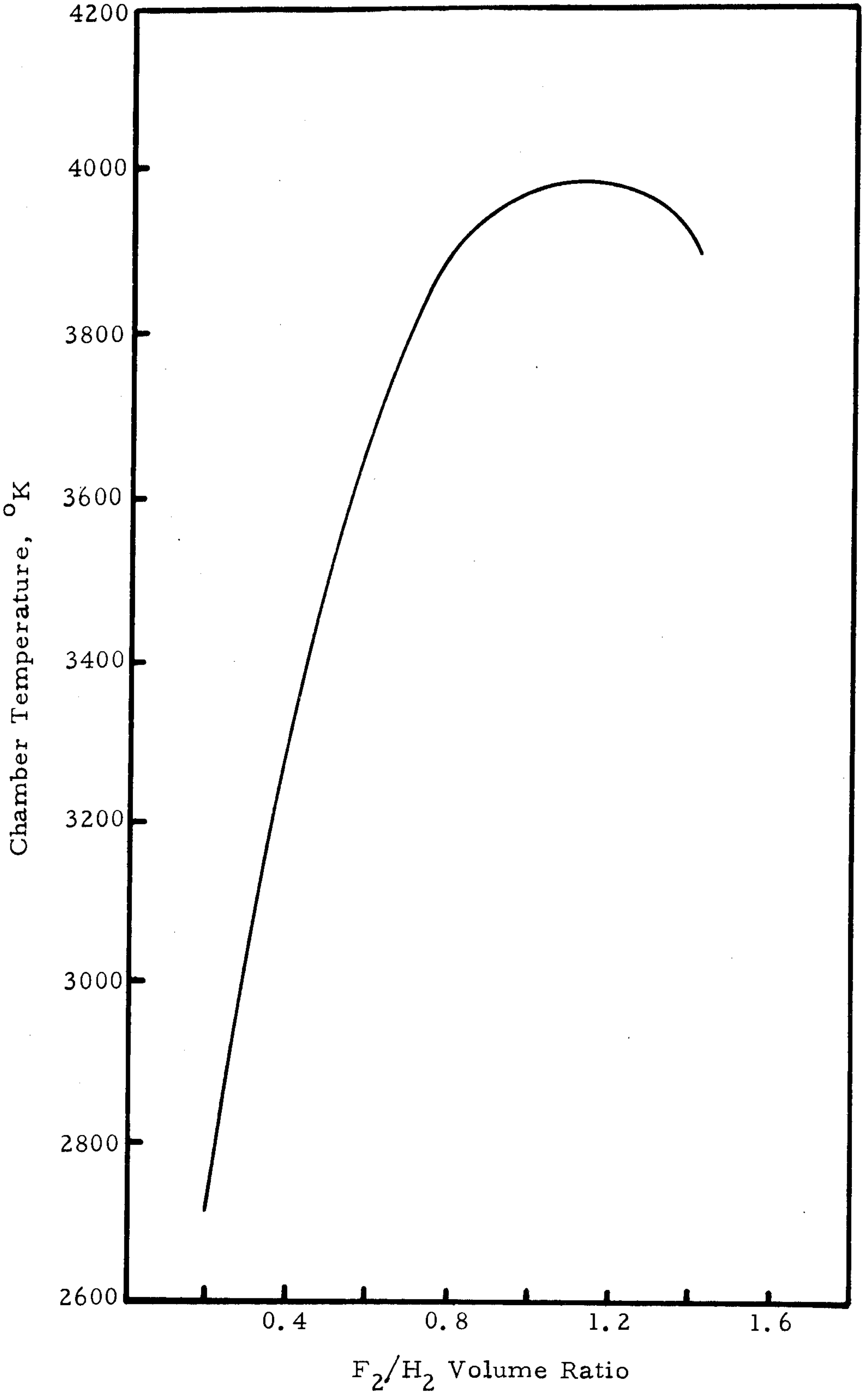

Figure C.5 F_2/H_2 Flame Temperature as a Function of Volume Mixture Ratio

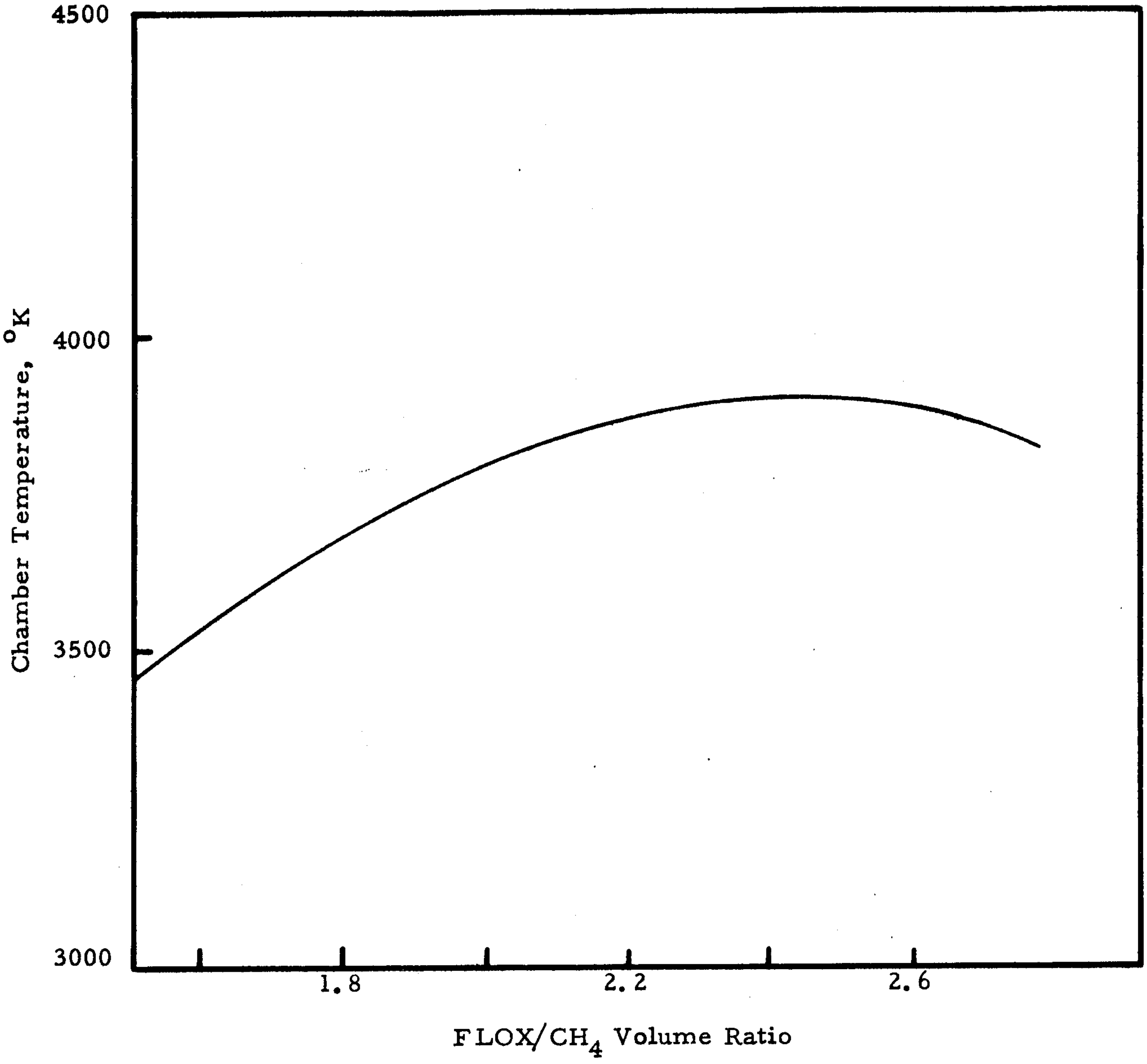

Figure C.6 FLOX/CH_4 Flame Temperature as a Function of Volume Mixture Ratio

TABLE C.II

FLOX-METHANE FLAME COMPOSITION AND TEMPERATURE AS A FUNCTION OF VOLUME COMPOSITION

Volume Ratio $FLOX/CH_4$	Principal Species, Mole Fraction					Total	Flame Temperature, ^oK
	F	H	HF	CO	H_2		
2.24	0.133	0.139	0.54	0.170	0.012	0.994	3864
2.32	0.151	0.134	0.530	0.168	0.010	0.993	3887
2.41	0.162	0.124	0.529	0.164	0.009	0.988	3886
2.49	0.172	0.112	0.528	0.163	0.008	0.983	3883
2.51	0.176	0.112	0.527	0.163	0.007	0.985	3882
2.53	0.178	0.109	0.527	0.161	0.007	0.984	3881
2.57	0.183	0.104	0.526	0.161	0.006	0.980	3878
2.65	0.193	0.096	0.525	0.158	0.005	0.978	3871

APPENDIX D
EXPLORATORY LAMINATE PROCESSING STUDIES

This appendix describes the results of exploratory laminate processing studies employing A-type polyimide, B-type polybenzimidazole, B-type polyimide, and commercial polybenzimidazoles.

D.1 A-TYPE POLYIMIDE

Laminates were prepared from MNB A-type Group NB prepolymer (See Section 2.1.2) by dissolving the soluble fraction and dispersing the insoluble fraction in 1-methyl-2-pyrrolidinone solvent. Both Style 181E glass cloth with an acrylosilane finish and low alkalinity carbon cloth were coated with the impregnation solution. The impregnated cloth was air dried, (60 minutes at 350°F), cut into 4-inch x 6-inch sections and stacked between steel plates. The stacked sections were laminated in a press preheated to 315°C (600°F) under 1000 psig for approximately 30 minutes. The Barcol hardnesses of the resulting laminates ranged between 70 and 80. The laminates were hard, tough and free of cracks and voids. The laminates had a resin content of 30 to 40%. The laminates were sawed into 1-inch x 4-inch test specimens and flexural strengths and modulus values were obtained at both room temperature and at 315°C. Three different formulations of the A-type Group NB prepolymers were employed (varying only in the relative amounts of high and low molecular weight components) with the glass cloth. The glass reinforced 75% high molecular weight and the carbon cloth reinforced 30% high molecular weight A-type Group NB polyimide composites were aged in air for 100 hours at 315°C. The flexural properties of the aged composites were also determined.

Table D.I lists the results of the flexural property tests of the A-type Group NB polyimide composites. From Table D.I is is seen that the flexural strengths and modulus values increase as a function of the high molecular weight prepolymer content. The flexural strength of 75% high molecular weight formulation of 91,200 psig and flexural modulus of 5.25×10^6 psig are outstanding values for polyimides. Discussions with Air Force Materials Laboratory personnel revealed that these properties are significantly higher than other exploratory polyimides. The high temperature properties are considerably higher than other state of the art polyimide compositions.

TABLE D.I
FLEXURAL PROPERTIES OF A-TYPE GROUP NB POLYIMIDE COMPOSITES

Reinforcement	Temperature of Test °C	Polyimide High Molecular Weight Fraction	Flexural Strength 10^3 psig	Flexural Modulus 10^6 psig
Style 181 E Glass Cloth	25	10	70.6	3.8
		30	78.4	4.5
		75	91.7	5.4
		75	90.7	5.1
	315	30	69.5	4.0
		30	66.2	4.0
		75[a]	50.6	4.1
		75[a]	46.1	4.2
Low Alkalinity Carbon Cloth CCA-1(1641)	25	30	44.2	2.2
	315	30	30.5	1.4

[a] Specimens aged at 315°C for 100 hours prior to test

The fact that these materials were prepared in a total press time of 30 minutes without the need of a post cure shows that a significant breakthrough in processing polyimides composite structures has been attained in this program. It is clear that the A-type Group NB polymers developed under this program offer improved properties and ease in processing permitting the preparation of advanced ablative materials.

D. 2 B-TYPE POLYBENZIMIDAZOLE

A study was undertaken to develop polymer synthesis conditions and to determine the effect of resin concentration on the impregnation of glass fabric reinforcement. In this study, equal molar amounts of bis(4-carboxyphenoxyphenyl) sulfone and diaminobenzidine were condensed under three different sets of synthesis conditions. In the synthesis of the polybenzimidazole polymer, three different processing steps were employed. The first consisted of polymerization to form the amic-acid precursor by refluxing for 45 minutes at approximately 290°C (maintaining all products of reaction in the solution) followed by heating at atmospheric pressure for 20 minutes at approximately 290°C (to remove the most volatile byproducts). Finally, ring closure was accomplished and the last traces of volatile matter in the polymerization solution were removed by heating under vacuum at approximately 320°C. In the studies described below, the duration of vacuum heating (ring closure) was the only variable investigated, namely, 30, 45 and 60 minutes duration. Solutions of resin were prepared by dissolving in dimethylacetamide solvent at 10, 20 and 30% w/w concentration. Style 181 S glass fabric was immersed in the impregnating solution and the excess impregnation solution was allowed to drain freely, the impregnated glass reinforcement was dried at 50°C for 60 minutes and the amount of resin retained on the fabric was determined. Table D. II shows the resin retention on the glass reinforcement as a function of resin content of the impregnating solution and polymer synthesis conditions.

The data in Table D. II show that resin retention on glass fabric is affected mainly by the concentration of polymer solution and is relatively independent of the polymer preparative procedure in the limits given. The information provides the basis for preparing suitable B-type PBI varnishes as glass fabric coating solutions.

TABLE D.II

PBI RESIN RETENTION AS A FUNCTION OF IMPREGNATING SOLUTION COMPOSITION

Polymer Synthesis Conditions[a] Duration of Vacuum Heating, min.	Resin Content of the Solution % w/w	Resin Retention on 181-S Glass Fabric % w/w
30	10	5.9
45	10	6.7
60	10	6.0
30	20	16.5
45	20	15.3
60	20	13.1
30	30	30.6
45	30	31.0
60	30	27.2

[a] Refluxed at 290°C for 45 minutes (polymerization),heated at atmospheric pressure at 290°C for 20 minutes (byproduct removal), followed by vacuum heating (ring closure) at 320°C for specified duration.

A coating solution was prepared from polybenzimidazole polymer and Style 181-E glass fabric was used to make a prepreg fabric having a resin content of 31-33%. The prepreg was dried at 100°C for 60 minutes, cut into small sections and stacked to a desired 8-ply thickness and then laminated using the following conditions:

Temperature:	600°F
Pressure:	500 psi
Duration:	2 minutes at contact pressure followed by 3 hours at 500 psi
Post Cure:	Under nitrogen in stepwise fashion, 24 hours at 600°F, 25 hours at 650°F, 24 hours at 700°F, 6 hours at 750°F, 6 hours at 800°F, and finally, 6 hours at 850°F.

The Barcol hardness of the laminate prior to post cure was found to be 42 to 50. After the 750°F post cure, the Barcol hardness had increased to 61 to 63. After the full post cure, the Barcol hardness was identical to that after the 750°F post cure (61-63). The maintenance of a constant

Barcol value above 750°F indicated that the laminate possesses extremely good thermal stability on completion of the curing reaction of the resin. A photomicrographic examination of the finished laminate showed good compaction and a low number of voids. It was possible to machine and saw the finished laminate without any special handling or tooling requirements. The overall quality of the initial polybenzimidazole laminate demonstrates the promise of the B-type polymer system.

D.3 B-TYPE POLYIMIDE

Using the polybenzimidazole results as guidelines, B-type polyimide laminating conditions were investigated. Processing conditions were examined with respect to temperature, pressure, dwell and cure time. The laminating conditions selected from these studies and physical properties of the initial B-type polyimide laminates are shown in Table D.III. Two of the three laminates were hard and tough. (Sample 2842-101 delaminated). Some voids are visible in Samples 2842-102 and 7379-1. (See Figure D.I).

TABLE D.III

SUMMARY OF B-TYPE POLYIMIDE LAMINATE PROCESSING CONDITIONS AND PROPERTY CHARACTERISTICS

	Specimen Number		
	2842-101	2842-102	7379-1
<u>Processing Condition</u>			
Resin Reaction Temperature, °C	138	164	152
Laminating Temperature, °C	310	316	316
Dwell Time, min.	5	4	3
Total Press Time, min.	30	60	60
Applied Pressure, psi	250	370	370
Post Cure at 288°C, hours	41	17	17
<u>Property Characteristics</u>			
Hardness before Post Cure, Barcol	55	67	67
Hardness after Post Cure, Barcol	58	67	67
Resin Content, % w/w	---	15	15
Density, g/ml	---	1.9500	1.9498

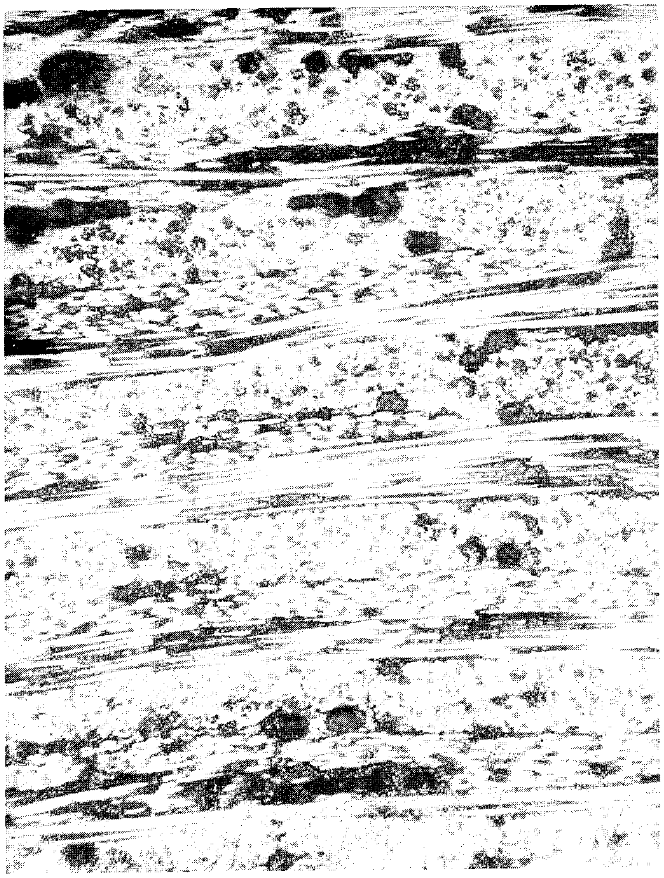

Figure D.1 B-Type Polyimide Laminate, Specimen 2842-102 (100X)

The prepregs for these laminates contained about 28 to 30% w/w resin, yet the finished laminate had a resin content of only 15% w/w indicating excessive flow. Additional laminate studies described in Appendix E established conditions condusive to the growth of high molecular weight soluble polyimide intermediates to reduce the resin flow.

D.4 COMMERCIAL POLYBENZIMIDAZOLE

An impregnated fiber glass fabric utilizing polybenzimidazole resin was purchased from the Narmco Materials Division of Whittaker Corporation. This material known as Imidite 2803 is a commercially available polymer with excellent physical properties for long term exposure to 600°F and for short time applications as high as 1200°F. The material is exceptionally chemically inert being unaffected by most acids, bases, and oils. According to the supplier's literature, the laminated material provides the highest interlaminar shear properties at temperatures up to 900°F of any known organic material. The Imidite 2803 gives off ammonia and water as condensation products during cure. An earlier version of this material, Imidite 2801, was a similar product but phenol and water were given off during cure of the resin. Approximately 12% volatile matter is lost during the cure.

Since this product was more readily available in a fabric form than as neat resin, laminating studies were conducted prior to investigating the neat resin properties early in this project.

Considerable difficulties were encountered in molding the polybenzimidazole system. Problems centered around either excessive or insufficient resin flow during molding. A number of different molding and B-staging cycles were used without success. Those laminates which were produced exhibited high porosity and very poor physical strength. The supplier was contacted on several occasions and latest recommendations were that an autoclave cure be utilized. The processing difficulties experienced detracted from the use of this material in preparing composites from experimental brittle fibers. Consequently, rather than commit further effort to optimization of the processing of polybenzimidazole, a molded laminate specimen was procured from Narmco for evaluation in the FLOX/methane Propellant Exhaust Environment Test (PEET) to ascertain the merit of this resin system.

APPENDIX E

DETAILED COMPOSITE PROCESSING INVESTIGATIONS

This Appendix provides detailed descriptions of composite processing investigations conducted in this project for the preparation of candidate ablative composites from commercial and TRW synthesized resin systems. Specifically, details are given for the methods used to prepare 1) silica and graphite reinforced Monsanto Skybond 700, Amoco's AI-11 polyamide-imide and Evercoat Chemical ECX-135 biphenol phenolics, 2) silica, graphite, tungsten and titanium diboride reinforced A-type polyimide, 3) silica and graphite reinforced B-type polyimide and polybenzimidazole, and 4) titanium diboride reinforced phenolic resin.

E. 1 PREPARATION OF COMPOSITES FROM COMMERCIAL RESIN SYSTEMS

Commercial resin systems evaluated by TRW Systems were molded with graphite and silica reinforcements. These resins include Monsanto's Skybond 700 modified polyimide, Amoco's AI-11 polyamide-imide and Evercoat Chemical ECX-137 biphenol phenolic. Exploratory lamination studies were also conducted with polybenzimidazole resin prepregs initially in lieu of commercial laminates. Because it was not desired for TRW to develop state-of-the-art processing technology, these studies were terminated when silica and graphite reinforced materials were finally obtained from the Narmco Division of Whittaker Corporation.

A number of different impregnating and laminating procedures have been used for the molding work done at TRW Systems. Details on the generation of this processing art were presented in the Interim Report (Reference 2). Table E-I shows the impregnating parameters selected for preparation of laminates from the commercial prepreg varnishes.

Several experimental procedures were used to prepare laminates from Skybond 700. The most successful method used is outlined below.

- Cut preimpregnated fabric into 3-inch by 4-inch rectangles and stack as high as needed for final laminate thickness.

TABLE E-I
IMPREGNATING PARAMETERS FOR VARIOUS RESIN SYSTEMS

Resin System	Resin Content Impregnating Solution, % w/w	Spacer Bar Setting Inches	B-Staging		Resin Content Impregnated Fabric, %, w/w
			Time, Min.	Temperature, °F	
Amoco AI-11	41.5	0.040	60	350	39.8
Polyamide-Imide	41.5	0.032	60	350	29.6
Skybond 700	64	0.037	60	350	41.5
Amide-Imide	64	0.025			30.7
ECX-137 Biphenol phenolic	49	None*	20	225	35.0

*No squeeze bars were used. Excess resin was allowed to flow back into resin pan.

- Maintain stacked plies at 500°F and 100 psig for two hours and "bump" every 15 minutes.
- Increase temperature to 550°F and maintain for one hour while "bumping" from 100 psig every 15 minutes.
- Increase temperature to 600°F and increase pressure to 1000 psig and cure for 120 minutes.

Processing conditions used to prepare laminates from Amoco AI-11 polyamide-imide were in accordance with a previously developed procedure based on the manufacturers' recommendations (Reference 2). The successful method utilized is outlined below:

- Cut impregnated fabric into 3-inch x 4-inch rectangles and stack as high as needed for final laminate thickness.
- Maintain stacked plies for 35 minutes in press at pressures up to 1500 psi and temperatures up to 500°F, all with frequent bumping of the press.
- Post cure the laminate for a total of 16 hours in steps from 390°F to 575°F.

In general, some slippage was encountered near the middle of the stack of laminate plies, however, satisfactory laminates were produced. A photomicrograph of a typical composite is shown in Figure E-1. As seen, a great number of voids are visible which nearly obscure the regions of silica fiber running perpendicular to the plane of the photograph. During machining of this laminate into PEET size specimens, several specimens were destroyed from gross delamination and fracture. However, it was possible to prepare specimens suitable for PEET evaluation.

The most successful molding procedure for ECX-137 biphenol material was as follows:

- Cut preimpregnated fabric into 3-inch x 4-inch rectangles and stack as high as needed for final laminate thickness.
- Maintain stacked plies at 220°F and 100 psig for 30 minutes and "bump" every five minutes.

Figure E-1. AMOCO AI-11 Amide-Imide-Silica Laminate (60X)

- Raise temperature to 325°F and increase pressure to 1000 psig. Hold for one hour.
- Cool laminate under pressure to 200°F and remove from press.

Laminates made with the above procedure had relatively high specific gravities (1.76) and a moderate amount of flow occurred during molding. Both procedures given above were successfully utilized for molding 5/8-inch thick laminates.

E.2 PREPARATION OF SILICA REINFORCED A-TYPE POLYIMIDE COMPOSITES

Initial laminate processing studies conducted with the A-type polyimide resin system were discussed in Appendix D. Further processing studies were conducted to optimize the A-type polyimide processing technology to prepare reproducible 0.50-inch to 1.0-inch thick composites of silica and graphite reinforced specimens. The optimization investigations were initially performed on Style 181E glass fabric rather than with silica because of its ready availability and lower cost.

Initial mechanical property results obtained with the TRW A-type polyimide/E-glass laminates (Appendix D Page 104) showed that the flexural strength and modulus values were a function of the ratio of soluble to insoluble prepolymer fractions used. An exploratory study was undertaken to determine the optimum ratio consistent with usable processing conditions and high mechanical strengths. For the methylene dianiline-3, 6-endomethylene-1, 2, 3, 6-tetrahydrophthalic anhydride-3, 3', 4, 4'-benzophenone tetracarboxylic acid dianhydride system (MNB), the ratio was determined to be 70/30% w/w for the insoluble/soluble prepolymer fraction. In this study ease of processing was evaluated visually by observing relative flow, gel-time, uniformity, and final appearance. Flexural strengths were measured by standard ASTM methods for laminates on 1-inch x 4-inch x 0. 125-inch specimens. The best overall results were obtained with the 70/30 prepolymer ratio noted above by simply stacking preimpregnated Style 181E glass fabric and pressing at 600°F for a period of 30 minutes. This combination provided specimens with very high mechanical properties at room temperature. Typical flexural properties of these composites are presented in Table E-II. These data clearly show that laminates having flexural strengths above 90, 000 psi and modulus values of over 4, 000, 000 psi are readily obtained. The highest flexural properties obtained for a single laminate (Resin Batch 2) were 112, 000 psi and 6, 000, 000 psi, respectively.

Silica (Refrasil) reinforced composites of the 70/30 ratio TRW A-type polyimide resin were investigated to prepare a laminate suitable for ablative performance (PEET) evaluation. The first attempt at preparation of a laminate from the 70/30 MNB resin formulation thicker than 0. 125-inches was successful. Impregnation of the Refrasil cloth was accomplished using the dip, squeeze and air dry (at 350°F for 60 minutes) method. The impregnated material was cut into approximately 4-inch x 5-inch patterns and stacked 40 plies high. The molding cycle was regulated using visual observations of resin flow, gel-time and uniformity

TABLE E-II

FLEXURAL PROPERTIES OF A-TYPE POLYIMIDE COMPOSITES

Resin Batch[a]	Laminate[b]	Replication	Average Flexural Properties[c]	
			Strength 10^3 psi	Modulus 10^6 psi
1	1	2	97.0	5.2
2	1	2	108.0	5.8
3	1	2	95.9	5.3
4	1	2	92.3	4.2
	2	2	103.7	4.7
	3	1	93.5	5.5
	4	1	90.3	4.2
	5	1	83.3	4.2

a. 70/30 MNB formulation

b. Style 181E-glass, I-545 finish, approx. 26% w/w resin

c. At 77°F, crosshead speed 0.05 inch/min

relative to the previous studies as operational guidelines. The applied mechanical pressure was increased slowly to 1000 psi as the temperature advanced to 600°F. This heating was accomplished by conduction from 600°F preheated platens. Press cure was one hour at 600°F from the beginning of application of 1000 psi on the composite. No post cure was used. A section of the 1-inch thick laminate prepared using this procedure is shown in Figure E-2. Figure E-3 shows a typical photomicrograph of composites prepared in this manner, and the complete absence of resin rich areas, shrinkage, cracks and microvoids. The resulting product machined readily which facilitated the preparation of 0.50-inch diameter 1.00-inch long cylindrical specimens for PEET evaluation.

A different A-type polyimide formulation was prepared using pyromellitic dianhydride in place of the 3,3',4,4'-benzophenone tetracarboxylic

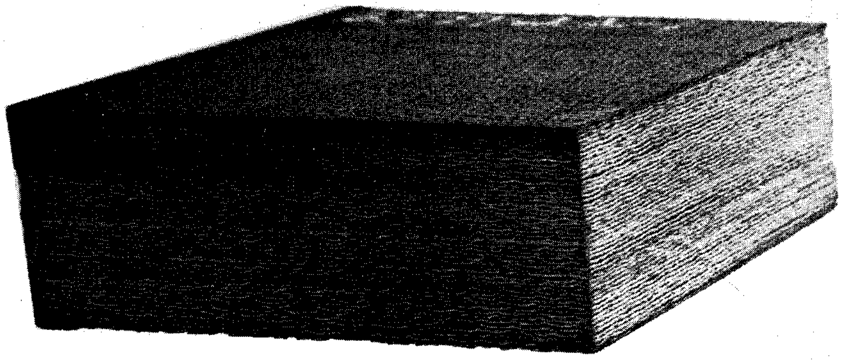

Figure E-2. Photograph of Silica Reinforced 70/30 MNB Resin (3 x 3 x 1 inch section from 4 x 5 x 1 inch laminate)

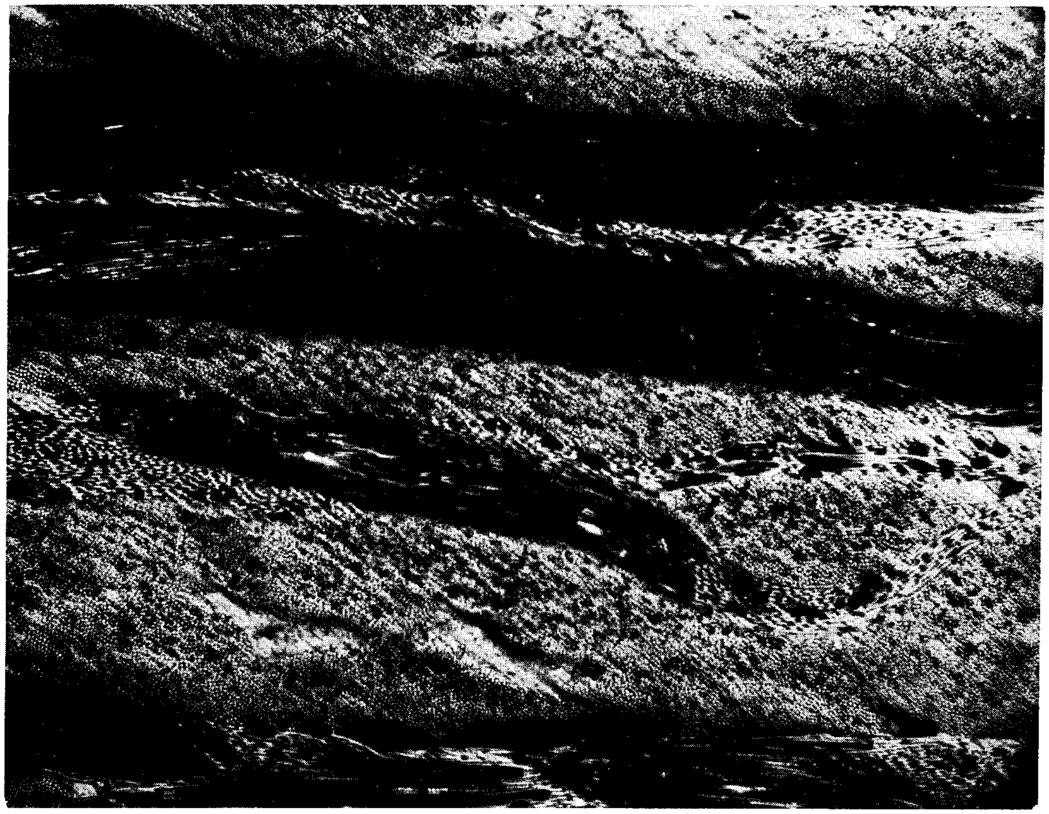

Figure E-3. Photomicrograph of MNB A-Type Polyimide Silica Laminate 21.9% Resin, 60X Magnification acid dianhydride. It has been often stated that pyromellitic dianhydride has improved thermal stability because it is fully aromatic and does not contain the labile carbonyl group present in 3, 3', 4, 4'-benzophenone tetracarboxylic acid dianhydride. In the preparation of this new prepolymer (called MNP) having an average molecular weight of 1000 g/mol, it was found that the ratio of insoluble to soluble fractions was 64/36, thus permitting good utilization of all materials produced when used in the 70/30 mixture ratio. In order to impregnate the Refrasil fabric, a hot bath of the polyimide fractions in 1-methyl-2-pyrrolidinone solvent was prepared. The resultant dispersion-solution had a definite thixotropic character which had not previously been evident with the MNB preparations and which promises to be of great interest for future work with applications for this material. Impregnation of the Refrasil fabric and the subsequent drying was accomplished identically to the MNB material procedure described earlier. A laminate approximately 4-inch x 5-inch and 40 plies thick was manufactured in the press. The press temperature and pressure was gradually raised to 600°F and 1000 psi and the laminate was cured under these conditions for 1 hour with no post cure.

A photomicrograph of this laminate is shown in Figure E-4 which displays an unusually even distribution of resin and fibers with no apparent resin rich areas, cracks or microvoids. The resin content of this laminate was 24.9% w/w. Machining of the laminate into standard PEET specimens 0.50-inch diameter by 1.0-inch long presented no problems and an excellent surface finish was obtained.

E.3 PREPARATION OF GRAPHITE REINFORCED A-TYPE POLYIMIDES

Graphite fabric reinforcement of the TRW A-type polyimide was accomplished with the MNP resin system. The MNP was selected because of its availability and the preliminary results obtained from the evaluation of the ablative characteristics of Refrasil fabric reinforced MNB and MNP systems which indicated negligible differences between the two resin systems. The manufacture of laminates was accomplished by precoating the fabric with furfural (used in laminating art to assist resin coating of graphite fabric), and drying the coated fabric at 250°F for 60 minutes.

Figure E-4. Photomicrograph of MNP A-Type Polyimide Silica Laminate 24.9% Resin, 60 X Magnification

The A-type polyimide was then staged on the fabric by the usual slurry method. The dried prepregs were stacked into a mold. The prepregged plies were laminated at 600°F and 1000 psi applied pressure for a period of 30 minutes. The resulting laminate was a porous-appearing product.

E.4 PREPARATION OF GRAPHITE FABRIC REINFORCED POLYIMIDE-AMIDE

Graphite fabric reinforcement of polyimide-amide was accomplished using Amoco's AI-11 polyimide-amide in accordance with previously developed processing conditions which were based on manufacturers' recommendations (See Appendix E.1) and utilization of HITCO G-1550 graphite fabric. The polyimide-amide was coated from a 50/50 V/V mixture of acetone and N,N-dimethylacetamide onto the graphite fabric using the dip and hand squeezed procedure. The preimpregnated fabric was dried to the B-stage condition in a 300°F oven.

Patterns of the prepared materials were cut approximately 4-inch x 5-inch and stacked ready for the press 50 plies high. A laminated block was obtained by curing the material in a press as follows:

> The material was loaded into the press at a temperature of 500°F and a pressure of 600 psi was applied. Frequent "bumping" was employed over a period of four hours.

Cooling of the laminate to room temperature was achieved under pressure. The resultant laminate had a good, uniform appearance consistent with standard production laminates being manufactured with this material although several slipped plies existed. The laminate machined readily and standard PEET-size specimens were prepared for subsequent testing.

E.5 PREPARATION OF TUNGSTEN REINFORCED A-TYPE POLYIMIDE

Considerable problems were encountered in the processing of tungsten wire with TRW A-type polyimides because the wire did not appear to be a good adherend for the A and B-stage A-type polyimides. In addition, tungsten is quite malleable, hence, straight short fibers of this reinforcement are difficult to obtain. It was apparent that the processing studies performed with the tungsten wire would be applicable for future work to be performed with the titanium diboride fibers only in the area of coating large diameters (e.g., 3 to 4 mil fibers).

A successful approach for preparing straight impregnated fibers (ready to mold into PEET test specimens) consisted of a wind and coating procedure. This was accomplished by winding the tungsten wire around two pins set approximately 2-inches apart. These fibers were wound into a band approximately 0.5-inch wide and one layer thick and then the A-type MNB polyimide solution/dispersion was brushed onto the wire strands. Successive layers of wire were wound by the same technique until sufficient material was prepared to mold a PEET specimen. Tape was bound around the strands and the material was removed from the winding jig. The resin was B-staged in this configuration and the impregnated wire was then cut to length ready for molding. The impregnated wire was then assembled into the mold and pressed at 600°F under 1000 psi for 30 minutes. The product obtained looked quite good, however, considerable difficulty was encountered in its machining because of the malleability of the tungsten. Figure E-5 shows the results of machining

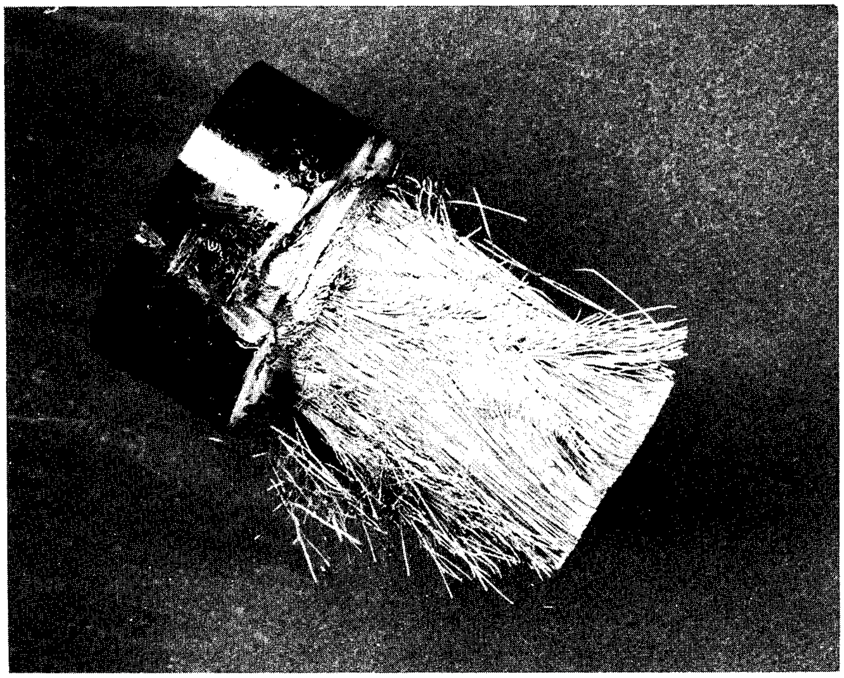

Figure E-5. Tungsten A-Type Polyimide Plug Machined by Standard Techniques

this plug by standard techniques. In order to obtain satisfactory PEET specimens of the requisite dimension, it was necessary to machine the tungsten polyimide plug by electron discharge milling (Elox). Considerable time was required to mill the laminate by this technique to the desired PEET specimen dimensions. Figure E-6 shows an electron discharge milled A-type polyimide PEET specimen.

E.6 PREPARATION OF TUNGSTEN REINFORCED POLYIMIDE-AMIDE

Tungsten reinforcement of polyimide-amide was accomplished using a process similar to that employed for the A-type polyimide, namely, impregnation of wound tungsten wire with the Amoco AI-11 varnish. The resin was B-staged in this configuration and the impregnated wire was cut to lengths ready for molding. Molding was accomplished at 500°F and a pressure of 600 psi. Frequent "bumping" was employed during the four-hour curing period. The tungsten composite was machined by electron discharge milling into PEET specimen dimensions.

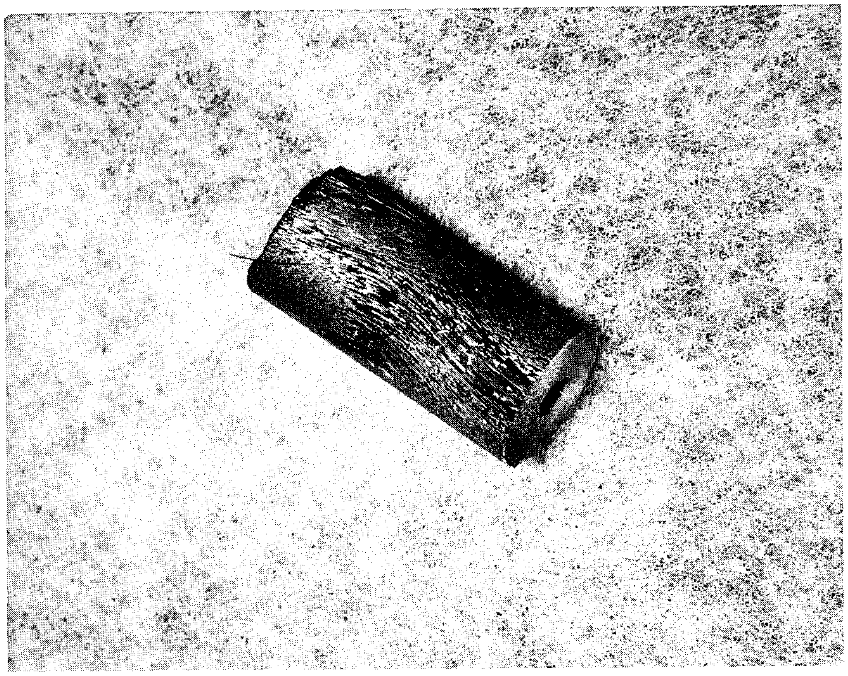

Figure E-6. PEET Specimen Tungsten Reinforced A-Type Polyimide Prepared by Electron Discharge Milling

E.7 PREPARATION OF TITANIUM DIBORIDE REINFORCED A-TYPE POLYIMIDE RESIN

As mentioned in Section 4.2 a limitation in the availability of titanium diboride fabric necessitated the reduction of ablative performance evaluation (PEET) specimen size. As a result, new cylindrical molds were prepared having a cavity of 0.32-inch diameter by 1.0-inch long. The PEET specimens fabricated from this mold could be machined readily to dimensions of 0.25-inch x 0.75-inch long. The method employed to prepare the titanium diboride reinforced A-type polyimide is given below:

> Titanium diboride filaments are grouped together in bundles of 30. The bundle is impregnated with the amic acid version of the condensation product of methylene dianiline, benzophenone dianhydride and nadic anhydride (MNB), in a continuous fashion by pulling it through a circular Teflon die maintained in a resin varnish solution. The impregnated bundle is dried

for four minutes at 400°F to remove solvent and imidize the resin. Because the fibers are not of a continuous nature, the process is quite slow thus requiring "re-threading" of the impregnation and drying device for each 4.6-foot long bundle of fibers. The bundle is cut to size and then molded for 60 minutes at 600°F with an applied pressure of 1000 psi.

A total of five specimens were molded and all exhibited good visual appearance as shown in Figure E-7. The specimens were machined with a diamond grinding wheel to the required PEET specimen dimensions without difficulty and, after polishing, photomicrographs were taken which showed excellent fiber consolidation and fiber wetting with a complete absence of voids (See Figure E-8).

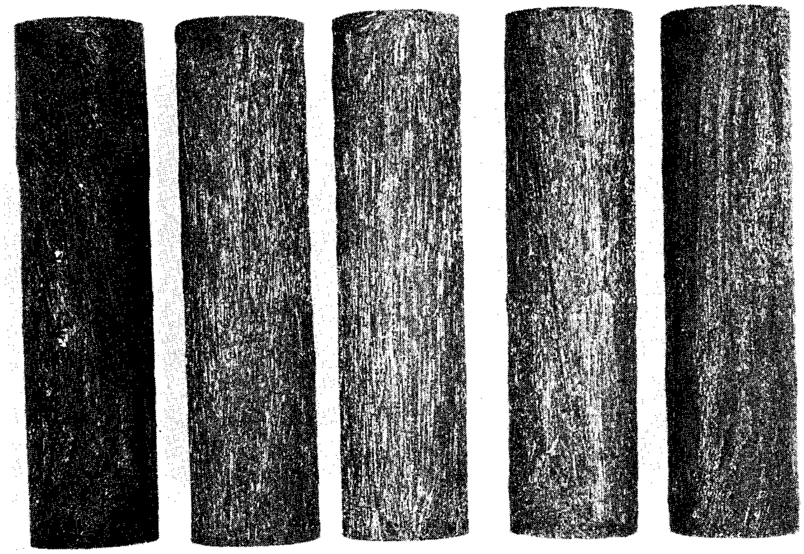

Figure E-7. Titanium Diboride Reinforced A-Type Polyimide Composite PEET Specimens - Magnification 2-1/2X

E.8 PREPARATION OF TITANIUM DIBORIDE REINFORCED PHENOLIC COMPOSITES

Titanium diboride reinforced phenolic composites were prepared using processing techniques considered to be state-of-the-art for preparation of phenolic resin composites. Titanium diboride fibers were impregnated with SC 1008 phenolic resin and B-staged for 20 minutes approximately at 300°F. These fibers were subsequently molded at 350°F for 60 minutes at 300 psi in the same mold as described earlier for the

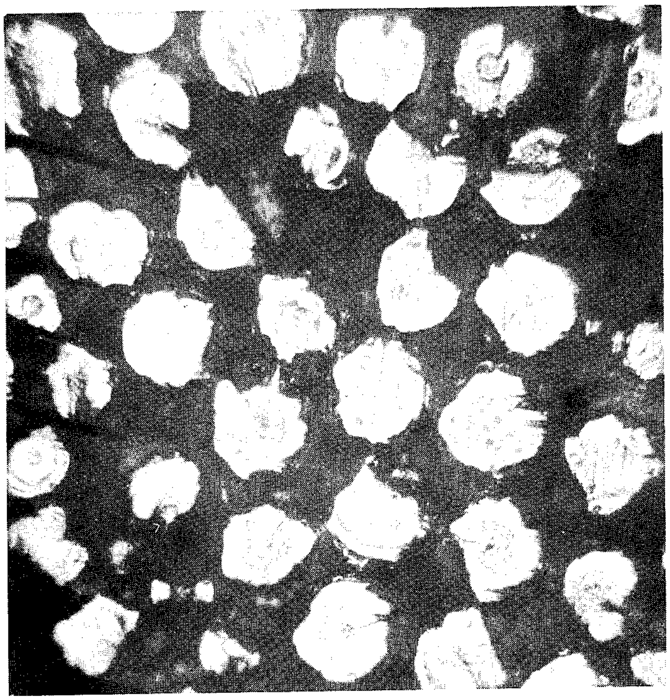

Figure E-8. Photomicrograph of Titanium Diboride of A-Type Polyimide Composite - Magnification 200X

A-type polyimide moldings. Post cure was accomplished as follows: 24 hours at 300°F, 24 hours at 350°F, 24 hours at 500°F and 24 hours at 600°F. The resultant two moldings were machined into 0.25-inch diameter by 0.75-inch long PEET specimens and one end of the specimens was polished. In spite of using standard phenolic resin "bumping" techniques, both of the moldings appeared to have numerous voids (See Figure E-9) and were, in general, poorer appearing in comparison with the titanium diboride reinforced A-type polyimide moldings.

Figure E-9. Comparison of Titanium Diboride Reinforced Specimens. On the left is the phenolic matrix and on the right A-type matrix

E.9 PREPARATION OF REINFORCED B-TYPE POLYBENZIMIDAZOLE RESIN

Laminates were prepared with a high silica reinforcement (Refrasil C-100-48) from the B-type polybenzimidazole system. Impregnation of the reinforcement was achieved using the hand dip and squeeze bar method and with an oven drying cycle of 60 minutes at 212°F. Molding of the prepreg material into a 4-inch x 4-inch x 5/8-inch thick laminate was achieve with a press cycle of 24 hours at 600°F at 400 psi and with a subsequent post cure in an air circulating oven for 24 hours at 600°F. The laminate was then sealed in a stainless steel cannister and continuously purged wit argon during a further post cure cycle of 24 hours each at 650°F and 700° and 6 hours each at 750°F, 800°F and 850°F. The resulting B-type polybenzimidazole laminate was of excellent appearance and had a calculated void content of ~5% v/v. It is interesting to note that it is extremely difficult, if not impossible, to prepare laminates this thick (0.625-inch) from state of the art polybenzimidazole resin systems.

Three small size PEET specimens (0.25-inch diameter, 0.75-inch long) were machined from the block and one piece of laminate approximately 5/8-inch x 5/8-inch x 2-inch long was then submitted to a further two-hour post cure at 950°F under an argon purge. Two additional PEET specimens were machined from the further post cured block and were of excellent appearance.

E.10 PREPARATION OF REINFORCED B-TYPE POLYIMIDE RESIN

The B-type polyimide system was used to prepare laminates consisting of high silica (Refrasil C-100-48), graphite (Hitco G1550) and carbon (Hitco CCA-1) reinforcements. The procedure used for preparation of each of the laminates was identical and is described below.

> The reinforcement was impregnated with B-type resin by the standard hand dip and squeeze bar method and the system was B-staged for one hour at 204°F in an air circulating oven to provide a prepreg having a total volatile content of about 4%. All prepregs were stored in a dry atmosphere (desiccator) prior to molding. The prepreg was cut to the desired shape and stacked to the desired height. The stacked plies were debulked in a press at 350°F with contact pressure (approximately 20 psi maximum) and were frequently bumped to remove volatiles during the 16-hour debulking cycle. After debulking, the laminates were sealed in an aluminum alloy foil bag and using a continuous nitrogen purge were molded in a press at 100 psi for two hours each at 450°F, 550°F and 600°F. The laminates were cooled to room temperature under pressure and then post cured for seven hours at 600°F under a nitrogen blanket.

The laminates consisting of the high silica and graphite reinforcements were both machined into the small size PEET specimens (0.25-inch diameter - 0.75-inch long) and were of good appearance. During machining of the carbon reinforced laminate, complete delamination occurred and subsequently necessitated discontinuance of tests with this composite. A section of the high silica reinforced B-type polyimide laminate was post cured for two hours at 950°F under an argon purge. PEET specimens were machined successfully from this composite.

APPENDIX F

RAW DATA FOR COMPOSITE MATERIALS AND STATISTICAL EVALUATION

This appendix presents the ablative performance raw data obtained during the FLOX/methane PEET evaluation of candidate composite ablative materials and comparative composite materials. The data obtained using the 1.27 volume mixture ratio of FLOX/methane is presented in Table F.I. The data obtained using the 2.44 volume mixture ratio of FLOX/methane is shown in Table F.II.

In addition to the depth of removal, weight loss, and backwall temperature parameters described in Section 4.3 , pretest specific gravities, the post firing dimensions measured perpendicular and parallel to the reinforcement plies, and post firing observations are also recorded in Tables F.I and F.II.

Evaluation of the raw data obtained from the 1.27 FLOX/methane volume mixture ratio experiments revealed that an insufficient number of tests were conducted to permit meaningful statistical interpretation. Consequently, detailed treatment of the 1.27 FLOX/methane volume mixture ratio data was not performed.

A summary of the depth of removal, weight loss and backwall temperature parameters reported for the raw data obtained with the 2.44 mixture ratio is presented in Table F.III. From this table, averages and standard deviations are reported together with pooled standard deviations for each of the three parameters. Utilization of the pooled standard deviations for the three parameters in the manner outlined in Reference 5 (a combination of u- and t- test operations) provided a means to eliminate "wild" data obtained in small sample groups. This technique provided the basis for elimination of specific data values shown in Table F.IV.

Upon elimination of the "wild" data, revised mean and pooled standard deviations were calculated and these results are reported in Table XI (Section 4.3). The identical statistical technique was used to reject "wild" data in the raw data obtained for the 1.27 FLOX/methane mixture ratio. From these studies, it was ascertained that for a single measurement of depth of removal, weight loss and backwall temperature, the pooled standard deviation (or repeatability) is 0.0158 inch, 0.046 g and 10.8°C respectively.

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TABLE F.I

FLOX/METHANE PEET EVALUATION OF FABRIC REINFORCED ABLATIVE COMPOSITES, RAW DATA VOLUME MIXTURE RATIO 1.27

Supplier	Material Designation	Resin Type	Specific Gravity	Weight Loss, g	Depth of Removal, Inch	Post Firing Diameter, Inch Perpendicular to Plies/ Parallel to Plies	Backwall Temperature, °C	Remarks
Carbon Fiber Reinforced								
Coast Manufacturing Company	4C1036	Phenolic	1.54	0.77	0.163	0.517/0.501	490	No Delaminations.
	4C1036-1	Phenolic	1.54	0.56	0.065	0.517/0.502	314	Several very minor delaminations.
	4C1636-1	Phenolic	1.47	0.46	0.114	0.507/0.502	374	Several very minor delaminations.
American Reinforced Plastics	259PHC	Phenolic	1.54	0.54	0.164	0.505/0.485	184	Several very minor delaminations.
	218PHC	Phenolic	1.50	0.46	0.142	0.507/0.509	378	Several minor delaminations.
Fiberite Corporation	MX4926	Phenolic	1.49	0.41	0.097	0.543/0.497	390	Several minor delaminations.
	MXC51	Phenolic	1.50	0.27	0.048	0.497/0.493	367	No delaminations.
W. S. Polymeric Corporation	85592	Phenolic	1.54	0.57	0.057	0.505/0.500	276	One very minor delamination.
Western Backing Company	WB8217	Phenolic	1.37	0.53	0.096	0.545/0.501	241	
Graphite Fabric Reinforced								
Coast Manufacturing Company	4G3036	Phenolic	1.49	0.50	0.108	0.517/0.505	488	No delaminations.
American Reinforced Plastics	185PHGR	Phenolic	1.58	0.52	0.88	0.525/0.496	503	No delaminations.
	185PHGRL	Phenolic	1.46	0.34			492	
Fiberite Corporation	MX4500	Phenolic	1.51	0.40	0.128	0.512/0.502	602	No delaminations.
U. S. Polymeric Corporation	X5441	Phenolic	1.44	0.60	0.111	0.504/0.482	266	No delaminations.
	FM5064	USP39	1.49	0.67	0.140	0.514/0.498	192	
Western Backing Company	WB8207	Phenolic	1.49	0.36			307	One very minor delamination.
	WB8249	Phenolic	1.52	0.48	0.094	0.512/0.497	457	
Narmco	4824	PBI[a]	1.34	0.09	0.081	0.512/0.499	426	No delaminations.
	4824	PBI	1.34	0.53				
	4824	PBI	1.34	0.57				
	4824	PBI	1.34	0.36				
	4824	PBI	1.34	0.35				
Silica Fiber Reinforced								
American Reinforced	307PHS	Phenolic	1.95	0.32	0.159	0.500/0.484	172	

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	4824	PBI	1.34	0.53				
	4824	PBI	1.34	0.57				
	4824	PBI	1.34	0.36				
	4824	PBI	1.34	0.35				
<u>Silica Fiber Reinforced</u>								
American Reinforced Plastics	307PHS	Phenolic	1.95	0.32	0.159	0.500/0.484	172	
	307PHS	Phenolic	1.99	0.38			150	
Fiberite Corporation	MXS-51	Phenolic	1.88	0.46	0.209	0.531/0.512		Several slight delaminations.
	MXS-51	Phenolic		0.82				
	MXS-51	Phenolic		0.46				
	MX2600	Phenolic	1.80	0.47	0.177	0.520/0.505		Two major delaminations; several minor delaminations.
	MX2600	Phenolic	1.78	0.46	0.117	0.505/0.493	171	Several minor delaminations.
Western Backing Company	WB2230	Phenolic	1.57	0.26	0.205	0.513/0.487	135	No delaminations.
TRW Systems	RS28	Skybond 700[b]	1.69	0.47	0.145	0.509/0.488	161	No delaminations.
	RS44	Skybond 700	1.55	0.48	0.229	0.493/0.485		Several minor delaminations.
	RS44	Skybond 700	1.70	0.23	0.100	0.495/0.487	180	Several minor delaminations.
	RS46	Skybond 700	1.55	0.33	0.118	0.521/0.515	152	No delaminations.
	RS46	Skybond 700	1.60	0.32	0.187	0.518/0.516		No delaminations.
	RS29	AI-11[c]	1.59	0.64	0.286	0.542/0.498		Several delaminations; pronounced swelling-fired end.
	RS45	AI-11[c]	1.76	0.44	0.199	0.570/0.574		Several minor delaminations; pronounced swelling-fired end; resin exuding from laminate.
	RS45	AI-11	1.82	0.29	0.083	0.507/0.498	248	Same as above.
	RS47	AI-11	1.72	0.45	0.187	0.534/0.496		One major, several minor delaminations; pronounced swelling-fired end; resin exuding from laminate.
	RS47	AI-11	1.72	0.26	0.037	0.563/0.504	248	One major delamination; pronounced swelling-fired end; resin exuding from laminate.
<u>$Mg(OH)_2$ Fiber Reinforced</u>								
Western Backing Company	WBC5217	Phenolic	2.03	0.46	0.121	0.512/0.504	135	Several minor delaminations.

a. Narmco's Polybenzimidazole Resin.
b. Monsanto's Skybond 700 Polyimide Resin.
c. Amoco's AI-11 Amide-imide Resin.

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TABLE F. II

FLOX/METHANE PEET EVALUATION OF FABRIC REINFORCED ABLATIVE COMPOSITES, RAW DATA VOLUME MIXTURE RATIO 2.44

Series	Supplier	Material Designation	Resin Type	Specific Gravity	Weight Loss, g	Depth of Removal, Inch	Post Firing Diameter, Inch Perpendicular to Plies/ Parallel to Plies	Backwall Temperature, °C	Remarks
	<u>Carbon Fiber Reinforced</u>								
2	Coast Manufacturing Company	4C1036	Phenolic	1.54	0.37	0.119	0.524/0.499	247	Several very minor delaminations.
		4C1036	Phenolic	1.57	0.36	0.135	0.527/0.505	249	Several very minor delaminations.
9		4C1036-1	Phenolic	1.45	0.45	0.114	0.502/0.495	295	No delaminations.
		4C1036-1	Phenolic	1.44	0.50	0.128	0.500/0.490	319	No delaminations.
		4C1036-1	Phenolic	1.43	0.45	0.133	0.503/0.493	340	No delaminations.
3	American Reinforced Plastics	259PHC	Phenolic	1.51	0.51	0.104	0.508/0.501	204	Several minor delaminations.
		259PHC	Phenolic	1.52	0.39	0.089	0.507/0.500	161	Several delaminations.
		259PHC	Phenolic	1.53	0.34	0.120	0.505/0.498	202	Several minor delaminations.
4		218PHC	Phenolic	1.35	0.34	0.123	0.499/0.504	254	Several very minor delaminations.
		218PHC	Phenolic	1.45	0.25	0.090	0.501/0.509	319	No delaminations.
		218PHC	Phenolic	1.45	0.29	0.123	0.504/0.510	258	Several very minor delaminations.
7		MX4926	Phenolic	1.54	0.39	0.139	0.554/0.504	295	Two major delaminations.
		MX4926	Phenolic	1.53	0.40	0.120	0.545/0.502	308	One major, several minor delaminations.
		MX4926	Phenolic	1.51	0.39	0.103	0.558/0.500	259	Three major delaminations.
8	Fiberite Corporation	MXC-51	Phenolic	1.43	0.47	0.067	0.517/0.502	295	No delaminations.
		MXC-51	Phenolic	1.42	0.41	0.112	0.515/0.501	336	No delaminations.
		MXC-51	Phenolic	1.45	0.41	0.108	0.516/0.502	302	No delaminations.
30	U. S. Polymeric Corporation	85592	Phenolic	1.54	0.45	0.092	0.501/0.496	307	No delaminations.
		85592	Phenolic	1.53	0.36	0.089	0.511/0.500	283	One minor delamination.
52		M-4032	Skybond 700[a]	1.47	0.49	0.133	0.504/0.503		Several minor delaminations.
		M-4032	Skybond 700	1.48	0.47	0.145	0.505/0.503	331	One major delamination.
		M-4032	Skybond 700	1.47	0.44	0.146	0.506/0.505	273	One major delamination.
22	Western Backing Company	WB8217	Phenolic	1.50	0.40	0.145	0.531/0.509	319	One major, several minor delaminations.
		WB8217	Phenolic	1.54	0.44	0.106	0.532/0.507	322	Two major, several minor delaminations.
		WB8217	Phenolic	1.52	0.36	0.115	0.537/0.509	307	Three major, several

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	Corporation	85592	Phenolic	1.53	0.36	0.089	0.511/0.500	283	One minor delamination.
52		M-4032	Skybond 700[a]	1.47	0.49	0.133	0.504/0.503		Several minor delaminations.
		M-4032	Skybond 700	1.48	0.47	0.145	0.505/0.503	331	One major delamination.
		M-4032	Skybond 700	1.47	0.44	0.146	0.506/0.505	273	One major delamination.
22	Western Backing Company	WB8217	Phenolic	1.50	0.40	0.145	0.531/0.509	319	One major, several minor delaminations.
		WB8217	Phenolic	1.54	0.44	0.106	0.532/0.507	322	Two major, several minor delaminations.
		WB8217	Phenolic	1.52	0.36	0.115	0.537/0.509	307	Three major, several minor delaminations.
51	Narmco	X-5-96	Phenolic	1.47	0.39	0.136	0.504/0.503	155	No delaminations.
		X-5-96	Phenolic	1.48	0.33	0.100	0.505/0.503	145	No delaminations.
		X-5-96	Phenolic	1.47	0.43	0.144	0.506/0.505	177	No delaminations.
	Graphite Fiber Reinforced								
1	Coast Manufacturing Company	4G3036	Phenolic	1.52	0.37	0.123	0.529/0.499	485	No delaminations.
		4G3036	Phenolic	1.46	0.41	0.125	0.524/0.502	445	
		4G3036	Phenolic	1.51	0.44	0.110	0.528/0.505	485	No delaminations.
38	American Reinforced Plastics	185PHGRL		1.48	0.43	0.089	0.514/0.503	662	No delaminations.
		185PHGRL		1.47	0.55	0.152	0.510/0.497	668	No delaminations.
		185PHGRL		1.47	0.43	0.141	0.512/0.499	603	
5	Fiberite Corporation	MX4500	Phenolic	1.51	0.24	0.138	0.511/0.503	570	No delaminations.
16	U. S. Polymeric Corporation	X5441	Phenolic	1.45	0.44	0.128	0.495/0.500	476	No delaminations.
		X5441	Phenolic	1.44	0.40	0.092	0.493/0.499	487	No delaminations.
17		FM5064	USP39	1.49	0.44	0.114	0.512/0.498	532	No delaminations.
		FM5064	USP39	1.50	0.47	0.122	0.502/0.501	532	No delaminations.
53		M-4033	Skybond 700	1.25	0.47	0.146	0.503/0.505	442	No delaminations.
		M-4033	Skybond 700	1.30	0.49	0.142	0.501/0.502	440	No delaminations.
		M-4033	Skybond 700	1.29	0.48	0.148	0.503/0.507	484	No delaminations.
20	Western Backing Company	WB8207	Phenolic	1.48	0.43	0.111	0.512/0.503	471	One major delamination.
		WB8207	Phenolic	1.49	0.52	0.132	0.515/0.504	513	One major, several minor delaminations.
		WB8207	Phenolic	1.50	0.51	0.134	0.512/0.504	532	One major, several minor delaminations.
23		WB8249	Phenolic	1.55	0.37	0.106	0.525/0.498	662	One major delamination.
		WB8249	Phenolic	1.53	0.24	0.114	0.526/0.499	621	One major delamination.
37	Narmco	4824	PBI[b]	1.33	0.06	0.179	0.510/0.497	579	No delaminations.
		4824	PBI	1.33	0.16	1.111	0.508/0.499	532	No delaminations.
		4824	PBI	1.34	0.14	0.113	0.503/0.499	544	No delaminations.

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TABLE F. II (CONTINUED)

Series	Supplier	Material Designation	Resin Type	Specific Gravity	Weight Loss, g	Depth of Removal, Inch	Post Firing Diameter, Inch Perpendicular to Plies/ Parallel to Plies	Backwall Temperature, °C	Remarks
	Silica Fiber Reinforced								
54	Coast Manufacturing Company	4S4136-1A	Phenolic	1.74	0.33	0.151	0.520/0.481	154	No delaminations.
		4S4136-1A	Phenolic	1.78	0.33	0.188	0.513/0.480	145	No delaminations.
		4S4136-1A	Phenolic	1.73	0.33	0.206	0.509/0.476	145	No delaminations.
55		4S4136-1B	Phenolic	1.71	0.35	0.186	0.524/0.481	139	No delaminations.
		4S4136-1B	Phenolic	1.88	0.69	0.192	0.513/0.479	145	No delaminations.
		4S4136-1B	Phenolic	1.80	0.30	0.194	0.531/0.487	142	No delaminations.
	Fiberite Corporation	MXS-51	Phenolic	1.95	0.44	0.225	0.550/0.509		One major, several minor delaminations.
		MXS-51	Phenolic	1.90	0.47	0.225	0.543/0.510	154	Two major, several minor delaminations.
		MXS-51	Phenolic	1.90	0.47	0.230	0.540/0.504	157	Two major, several minor delaminations.
56	Coast Manufacturing Company	4S4133-X	Phenolic	1.86	0.66	0.234	0.530/0.500	150	No delaminations, pronounced ovality-fired end.
		4S4133-X	Phenolic	1.87	0.59	0.218	0.525/0.500	107	
		4S4133-X	Phenolic	1.85	0.77	0.232	0.512/0.504	151	No delaminations, pronounced ovality-fired end.
41	Fiberite Corporation	MX2600	Phenolic	1.80	0.50	0.267	0.515/0.502	145	Several minor delaminations.
		MX2600	Phenolic	1.83	0.50	0.184	0.535/0.503	99	Several minor delaminations.
63	Narmco	4850	PBI[b]	1.65	0.35	0.200	0.522/0.505	162	No delaminations.
		4850	PBI	1.63	0.44	0.225	0.523/0.507	170	No delaminations.
		4850	PBI	1.60	0.47	0.239	0.521/0.503	190	No delaminations.
61	TRW Systems	RS-61	Biphenol[c] ECX137	1.47	0.37	0.229	0.503/0.491	139	
		RS-61	Biphenol ECX137	1.49	0.54	0.218	0.510/0.492	132	No delaminations.
		RS-61	Biphenol ECX137	1.47 1.47	0.33 0.33	0.193 0.193	0.505/0.495 0.505/0.495	142 142	No delaminations. No delaminations
62		RS-62	Biphenol ECX137	1.75	0.33	0.178	0.525/0.499	110	No delaminations.
		RS-62	Biphenol ECX137	1.75	0.34	0.177	0.532/0.499	112	No delaminations.
		RS-62	Biphenol ECX137	1.73	0.38	0.131	0.523/0.496	112	No delaminations.
		RS-62	Biphenol ECX137	1.73	0.35	0.111	0.511/0.503	96	No delaminations.
44		RS-47	Skybond 700[a]	1.61	0.56	0.184	0.506/0.495		Several minor delaminations.
60		RS-60	Skybond 700	1.63	0.40	0.234	0.502/0.487	136	No delaminations.
		RS-60	Skybond 700	1.63	0.35	0.216	0.507/0.490	142	No delaminations.
		RS-60	Skybond 700	1.63	0.46	0.220	0.509/0.507		No delaminations.
	Silica/Cellulose[d] Fiber Reinforced								
57	Western Backing	AVC-RS/2223	Phenolic	1.54	0.67	0.136	0.499/0.500	78	Minor cracks in

②

		RS-62	Biphenol ECX137	1.73	0.38	0.131	0.523/0.496	112	No delaminations.
		RS-62	Biphenol ECX137	1.73	0.35	0.111	0.511/0.503	96	No delaminations.
44		RS-47	Skybond 700[a]	1.61	0.56	0.184	0.506/0.495		Several minor delaminations.
60		RS-60	Skybond 700	1.63	0.40	0.234	0.502/0.487	136	No delaminations.
		RS-60	Skybond 700	1.63	0.35	0.216	0.507/0.490	142	No delaminations.
		RS-60	Skybond 700	1.63	0.46	0.220	0.509/0.507		No delaminations.
	Silica/Cellulose[d] Fiber Reinforced								
57	Western Backing Company	AVC-RS/2223	Phenolic	1.54	0.67	0.136	0.499/0.500	78	Minor cracks in charred portion.
		AVC-RS/2223	Phenolic	1.54	0.67	0.238	0.499/0.500	88	Minor cracks in charred portion.
		AVC-RS/2223	Phenolic	1.54	0.77	0.207	0.499/0.500	64	Minor cracks in charred portion.
	Silica/Carbon[e] Fiber Reinforced								
58	Western Backing Company	AVC-CS/2223	Phenolic	1.63	0.61	0.145	0.499/0.501	182	Minor cracks in charred portion.
		AVC-CS/2223	Phenolic	1.58	0.68	0.212	0.501/0.500	180	Minor cracks in charred portion.
		AVC-CS/2223	Phenolic	1.59	0.52	0.122	0.501/0.500	170	Minor cracks in charred portion.

[a] Monsanto's Skybond 700 Polyimide Resin.

[b] Narmco's Polybenzimidazole Resin.

[c] Evercoat Chemical's Biphenol Phenolic.

[d] Food Machinery Corporation's Silica/Cellulose Fabric.

[e] Food Machinery Corporation's Silica/Carbon Fabric.

TABLE F. III

Summary of PEET Evaluation Raw Data Mixture Ratio 2.44

Series	Number of Tests	Depth of Removal × 10^3, in.		Weight Loss × 10^2, g		Backwall Temperature, °C	
		Average	Standard Deviation	Average	Standard Deviation	Average	Standard Deviation
Carbon Fiber Reinforced Phenolic							
2	2	127	11.3	37	0.7	248	1.4
9	3	125	9.3	48	2.9	318	13.7
3	3	104	15.6	41	8.8	189	24.2
4	3	112	26.9	29	4.5	277	32.7
7	3	120	16.9	40	0.7	287	25.4
8	3	96	23.8	43	3.5	311	22.3
30	2	91	2.0	41	6.4	295	18.4
22	3	122	17.0	40	4.0	316	7.9
51	3	126	23.4	38	5.1	159	16.4
Pooled Data	25	114	17.5	44	4.8	263	21.0
Carbon Fiber Reinforced "Stiff" Polymers							
52[a]	3	141	7.3	41	2.5	302[d]	41.0
Graphite Reinforced Phenolic							
1	3	119	8.2	40	5.0	472	23.6
38	3	127	32.6	47	6.9	644	36.0
5	1	138	-	24	-	570	-
16	2	110	25.4	42	2.8	481	7.8
17	2	118	6.0	45	2.0	532	0.0
20	3	126	12.8	49	4.9	505	31.2
23	2	110	5.7	31	9.1	642	0.7
Pooled Data	16	121	19.1	42	5.7	546	25.2
Graphite Reinforced "Stiff" Polymers							
53[a]	3	145	3.0	48	1.0	455	31.8
37[b]	3	134	30.6	12	5.3	552	17.6
Pooled Data	6						
Silica Reinforced Phenolics							
54	3	182	28.0	33	0.0	148	5.4
55	3	191	4.2	52	21.3	142	3.0
6	3	227	2.9	46	1.7	156[d]	2.1
56	3	228	4.8	67	9.1	136	11.6
41	2	225	58.6	50	0.0	122	7.6
Pooled Data	14	209	23.8	50	10.9	141	7.1
Silica Reinforced "Stiff" Polymers							
63[b]	3	221	19.8	42	6.3	174	14.4
44[a]	1	[illegible]	-	56	-	-	-
60[a]	3	22	9.5	40	5.5	139[d]	4.2
Pooled Data	7						
61[c]	3	213	18.5	41	11.2	138	5.1
62[c]	4	149	33.4	35	2.2	108	7.7
Silica/Cellulose Fiber Reinforced Phenolics							
57	3	194	52.3	70	5.8	77	12.0
Silica/Carbon Fiber Reinforced Phenolics							
58	3	160	46.8	60	8.0	177	6.6
Grand Pooled Standard Deviation							
	53		23.8	53	6.7	50	19.3

a. Skybond 700 polyimide
b. Polybenzimidazole
c. Biphenol
d. Average of only 2 data points

TABLE F. IV

IDENTIFICATION OF REJECTED "WILD" DATA IN FLOX/METHANE 2.44 MIXTURE RATIO PEET RESULTS

Depth of Removal		Weight Loss		Backwall Temperature	
Test Series	Datum	Test Series	Datum	Test Series	Datum
4	2	3	1	4	2
8	1	38	2	1	2
51	2	55	2	53	3
38	1	61	2	20	1
37	1			56	2
41	2			63	2
57	1				
58	3				

Raw test data obtained from PEET measurements of candidate silica, graphite and tungsten reinforced phenolic, A-type polyimide and polyamide-imide resins are listed in Table F. V. Because there was no clear cut trends for a basis to reject any individual data points, the summarized data presented in Table XV, Section 5.1 were obtained by averaging the entire population of each resin-reinforcement class.

Raw test data obtained from PEET of reduced size Refrasil, graphite and titanium diboride reinforced phenolic, A-type and B-type resin systems are listed in Table F. VI. These data are summarized in Table XVI, Section 5.2 without the rejection of any individual data points.

①

TABLE F.V

FLOX/METHANE PEET EVALUATION OF FABRIC REINFORCED ABLATIVE COMPOSITES[a]

Reinforcement/Resin		Weight Loss g	Temperature, °C Surface	Temperature, °C Backwall	Specimen Diameter Pre Test/Post Test inch	Depth of Removal inch	Remarks
Silica	Phenolic (MX 2600)	0.52	2230	68	0.496/0.511	0.224	Several minor delaminations. Cracks along surface on all specimens
		0.54	2150	49	0.497/0.503	0.223	
	Phenolic (MXS-51)	0.54	2130	47	0.491/0.500	0.257	Several minor delaminations, cracks-1/4-inch along exposed surface
		0.51	2125	49	0.485/0.496	0.225	
		0.70^{b}	2180	47	0.488/0.506	0.249	
		0.70^{b}	2210	64	0.502/0.513	0.236	
		0.68^{b}	2200	52	0.488/0.512	0.210	
		0.54^{c}	2250	49	0.499/0.505	0.213	
		0.55^{c}	2250	49	0.500/0.515	0.217	
		0.52^{c}	2250	51	0.500/0.508	0.221	
	Type A-II Polyimide No post cure	0.49^{b}	2370	57	0.505/0.509	0.187	No delaminations. Carbon buildup on side of exposed surface
		0.49^{b}	2340	45	0.500/0.503	0.205	
		0.55^{b}	2470	69	0.500/0.502	0.229	
	600°F, 1 hr. Post cure	0.59	2160	54	0.501/0.500	0.233	
		0.58	2160	42	0.500/0.501	0.231	
		0.55	2205	40	0.495/0.497	0.246	
	Polyamide-imide	0.56^{c}	2450	57	0.498/0.502	0.279	No delamination. Black carbon buildup on side of exposed surface. Resin could be seen spalling from sample during exposure
		0.55^{c}	2410	71	0.502/0.516	0.224	
		0.52^{c}	2300	64	0.499/0.506	0.249	
		0.54^{b}	2370	69	0.495/0.492	0.254	
	Phenolic (MX 4500)	0.44	2000	319	0.499/0.510	0.119	No delaminations. Exposed surface porous after firing
		0.45	2010	426	0.501/0.512	0.118	
		0.46	1985	391	0.502/0.512	0.127	
		0.40^{b}	1880	465	0.497/0.507	0.084	
		0.43^{b}	1880	438	0.502/0.514	0.106	
		0.43^{b}	1940	449	0.505/0.515	0.102	
		0.44^{b}	1970	488	0.501/0.509	0.135	
		0.44^{b}	2020	466	0.502/0.519	0.154	
		0.45^{b}	1980	427	0.501/0.509	0.182	

②

Graphite	Phenolic (MX 4500)	0.44 0.45 0.46	2000 2010 1985	319 426 391	0.499/0.510 0.501/0.512 0.502/0.512	0.119 0.118 0.127	No delaminations. Exposed surface porous after firing
		0.40[b] 0.43[b] 0.43[b] 0.44[b] 0.44[b] 0.45[b]	1880 1880 1940 1970 2020 1980	465 438 449 488 466 427	0.497/0.507 0.502/0.514 0.505/0.515 0.501/0.509 0.502/0.519 0.501/0.509	0.084 0.106 0.102 0.135 0.154 0.182	
	Type A-II Polyimide	0.76 0.83 0.82	2315 2320 2325	258 293 300	0.500/0.557 0.488/0.553 0.496/0.557	0.145 0.163	Delaminations; considerable swelling; carbon deposited on side of specimens
	Polyamide-imide	0.64	----	---	0.505/-----	-----	Specimen split in half during test (after 3 seconds); no measurements were taken; specimen completely deteriorated during test
		0.72[b] 0.69[b]	2260 2250	--- ---	0.500/ 0.495/	----- -----	All specimens were severely damaged during combustion. Sample split into several sections. Thermocouple exposed to hot flame. No backwall data obtained
Tungsten	Type A-I Polyimide	2.29	2345	—	0.505/-----	-----	Specimen totally deteriorated in test. Flame engulfed sample after 3 seconds; weight loss corresponds to consumption of resin
	Polyamide-imide	1.71	2500	---	0.502/-----	-----	Specimen totally deteriorated in test, split in half after 3 seconds; we weight loss corresponds to resin consumption

[a] Average Heat Flux = 165 BTU/ft^2-sec except where noted; 30-second test duration

[b] Average Heat Flux = 169 BTU/ft^2-sec

[c] Average Heat Flux = 175 BTU/ft^2-sec

TABLE F.VI

FLOX/METHANE PEET EVALUATION[a] OF CANDIDATE ABLATIVE COMPOSITES

Reinforcement	Resin Type	Weight Loss g	Depth of Erosion, in.	Surface[b] Temp. °C	Remarks
Refrasil	Phenolic (Fiberite MX2600)	0.197 0.232 0.205 0.260	0.148 0.160 0.151	2280 2350 2390 2420	Numerous cracks along side of exposed surface; white residue on exposed surface and along side; char depth along side of combusted face extended down to the embedded portion of specimens.
	A-Type Polyimide	0.212 0.237 0.216	0.139 0.149 0.161	2590 2460 >2760	Numerous cracks along side of exposed surface; white residue on exposed surface; carbon buildup along side of exposed surface which extended down to the embedded portion of the specimen completely engulfed by flame.
	B-Type Polyimide post cured at 850°F	0.175 0.173 0.194	0.141 0.130 0.135	>2760 >2760 2390	No cracks along side of exposed surface; combusted face changed to oval shape indicating flow of resin; white residue on exposed surface.
	B-Type Polyimide post cured at 950°F	0.182 0.175 0.179	0.179 0.164 0.170	>2760 2620 >2760	No cracks along side of exposed surface. White residue on exposed surface. Erosion pattern indicate considerable flowing of resin. Combusted face formed oval shape.
	B-Type Polybenzimidazole post cured at 850°F	0.172 0.190 0.157 0.158	0.145 0.130 0.138 0.140	2640 >2760 2650 >2760	No cracks along side of exposed surface; white residue on exposed surface; char depth center around combusted face. No residue buildup along side of exposed surface.
	B-Type Polybenzimidazole post cured at 950°F	0.170 0.156	0.143 0.144	2480 2450 2570	No cracks along side of exposed surface; char region confined to vicinity of exposed surface. No residue buildup along side of exposed surface.

[a] Samples (0.25-inch diameter by 0.75-inch long) exposed to 20-second FLOX-Methane combustion environment parallel to reinforcement. Specimen located 1.25-inch from torch tip. Test conditions MR 2.44 FLOX (82.5% w/w F_2, 17.5% w/w O_2)/Methane; Thermal Flux 217.5 BTU/ft^2-sec.

[b] Surface reaction temperatures measured by Coloratio Pyrometer. Temperature range 1650 to 2760°C.

TABLE F.VI

FLOX/METHANE PEET EVALUATION[a] OF CANDIDATE ABLATIVE COMPOSITES (CONTINUED)

Reinforcement	Resin Type	Weight Loss g	Depth of Erosion,	Surface[b] Temp. °C	Remarks
Graphite	Phenolic (Fiberite MX4500)	0.132	0.106	2250	No cracks along side of exposed surface; exposed surface very porous. No cracks or swelling on exposed surface.
		0.141	0.108	2270	
		0.130	0.101	2220	
		0.133	0.108	2320	
		0.139	0.115	2120	
		0.141	0.128	2090	
		0.137	0.121	2130	
	A-Type Polyimide	0.241	----	2320	Most specimens delaminated during testing; considerable swelling of the specimen which did not delaminate. Exposed surface very porous.
		0.179	0.116	2380	
		0.246	----	2480	
		0.243	----	2520	
		0.249	0.146	2250	
	B-Type Polyimide	0.224	0.173	2490	Considerable swelling and residue building along side of exposed surface; exposed surface very porous. Each specimen completely engulfed by flame.
		0.231	0.186	2360	
	Polybenzimidazole post cured at 850°F	0.164	----	2160	No crack along side of exposed surface; combusted face very porous.
		0.150	0.123	2250	
		0.102	0.106	2210	
	Polybenzimidazole post cured at 950°F	0.141	0.137	1680	No cracks long side of exposed surface; combusted face porous after firing. No char residue buildup along side of exposed face.
		0.142	0.130	2200	
		0.136	0.139	2230	
		0.122	0.141	2120	
		0.123	0.140	2240	
Titanium Diboride	Phenolic (SC-1008)	0.264	0.116	>2760	Numerous cracks along side of specimen. Sparks emitted during firing; uneven erosion pattern, considerable build-up along side of exposed face.
		0.361	----	>2760	
	A-Type Polyimide	0.230	0.109	>2760	Considerable residue build-up along exposed surface; considerable swelling and longitudinal cracks on all specimens. Cracks extend down to embedded portion of specimen. Green and white residue along side and on exposed surface.
		0.269	0.141	>2760	
		0.228	0.114	>2760	
		0.221	0.080	>2760	
		0.287	0.113	>2760	

[a] Samples (0.25-inch diameter by 0.75-inch long) exposed to 20-second FLOX-CH_4 combustion environment parallel to reinforcement. Specimen located 1.25-inch from torch tip. Test conditions MR 2.44 FLOX (82.5 wt% F_2, 17.5 wt% O_2) Methane; Thermal Flux 217.5 BTU/ft^2-sec.

[b] Surface reaction temperatures measured by Coloratio Pyrometer. Temperature range 1650 to 2760°C.

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