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MODIFIED COMPOSITE MATERIALS WORKSHOP

Dennis L. Dicus, Compiler

JULY 1978

National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23665

MODIFIED COMPOSITE MATERIALS

WORKSHOP

(Held at Langley Research Center, Hampton, Virginia,
March 23-24, 1978)

DENNIS L. DICUS, Compiler

JULY 1978

PREFACE

A hazard which results from accidental release of graphite fibers from composite materials has been identified. The risk resulting from this hazard is being evaluated. In the meantime, NASA has initiated a program to explore alternate materials which eliminate the hazard or reduce the risk. On March 23 and 24, 1978, NASA Langley Research Center sponsored a Modified Composite Materials Workshop. This workshop was intended to display the NASA program on alternate materials and to solicit new ideas for other alternate materials.

Working groups were organized to consider six topics: epoxy modifications, epoxy replacement, fiber modifications, fiber coatings and new fibers, hybrids, and fiber release testing. Because of the time required to develop a new material and acquire a design data base, most of the workers concluded that a modified composite material would require about four to five years of development and testing before it could be applied to aircraft structures. However, the Hybrid Working Group considered that some hybrid composites which reduce the risk of accidental fiber release might be put into service over the near term. The Fiber Release Testing Working Group recommended a coordinated effort to define a suitable laboratory test. That group did not have sufficient time to give careful consideration to the problems of large scale outdoor testing to prove the performance at full scale of proposed alternate materials. Most groups expressed a desire for further interaction with NASA in their technology areas in the future to monitor progress.

Hampton, Virginia
July 11, 1978

General Chairman

Willam A. Brooks, Jr. - NASA Langley Research Center

Administrative Chairman

Dennis L. Dicus - NASA Langley Research Center

Program Co-Chairmen

Robert T. Swann - NASA Langley Research Center
Norman J. Johnston - NASA Langley Research Center

Working Group Chairmen

E. Bruce Belason - AVCO Specialty Materials Division
Russell J. Diefendorf - Rensselaer Polytechnic Institute
James Economy - IBM Research Laboratory
Billy F. Landrum - Ciba-Geigy Corporation
James Noland - American Cyanamid Company
Karl M. Prewo - United Technologies Research Center

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INTRODUCTION

Graphite fibers in an epoxy matrix provide a composite material having high strength and stiffness relative to its weight. Because low weight is such an important consideration in aircraft structures, NASA has undertaken a variety of activities intended to resolve problems involved in applying these composite materials to aircraft structures. NASA activities include laboratory studies, as well as major projects to get flight experience with composites in secondary and primary structures on commercial aircraft. However, because of their low density, small diameter, and high electrical conductivity, graphite fibers raise issues beyond those normally considered in structural design.

Since graphite fibers are electrical conductors, they can cause short circuits, equipment malfunctions, or possibly fires if they get into electrical equipment. Furthermore, because of their low density and small diameter, graphite fibers can remain airborne for considerable time, and hence can be transported from the scene of an accident to the site of electrical or electronic equipment[1,2]. NASA has underway a project to study, and if possible, to quantify the risk associated with this electrical hazard. While no definitive results from this risk assessment study will be available for some time, NASA has initiated exploratory investigations of alternate materials which can reduce electrical hazards and yet retain or enhance currently available graphite fiber composites properties.

On March 22 and 23, 1978, NASA Langley Research Center held a workshop to display the current program on alternate materials, to solicit approaches other than those being investigated, and to stimulate further thinking about possible materials solutions to eliminate a possible electrical hazard. At the workshop, a brief overview of the risk assessment activity was provided. This overview was not intended to be complete or definitive, nor was the workshop intended to address risk issues except from the point of view of alternate materials which would tend to reduce risk. After the risk overview, Langley, Lewis, and Ames Research Centers presented summaries of programs and plans to explore alternate materials. Following these summaries, test methods currently used to study accidental graphite fiber release were outlined. After the discussion of test methods, attendees divided into six working groups.

The workshop had working groups on epoxy modifications, epoxy replacement, fiber modifications, fiber coatings and new fibers, hybrids, and fiber release testing. These working groups began with prepared presentations in their topic areas. Then they considered a set of issues that had been defined in advance. After further deliberations, the working groups prepared reports, guided by a recommended format, which were presented to all attendees. For each working group, two NASA employees were assigned as reporters, and they provided summaries of the activities of the groups.

The purpose of this document is to provide to attendees and other interested persons as much information as is likely to be useful and can be readily compiled. No text is available for any of the presentations. The information contained in this document includes copies of vugraphs used in presenting NASA programs, vugraphs summarizing working group findings, and NASA reporters' accounts of working group activities. Also included are an attendance list, and issues directed to each group. While care has been exercised in compiling this information, editing has been minimal and the source of the information should be consulted before taking further action. Furthermore, the reporter's accounts of the working group proceedings reflect the reporter's view of a dynamic process, and the opinions expressed may not reflect the considered judgement of the individuals involved or of their sponsoring institutions.

1. A Report of Observed Effects on Electrical Systems of Airborne Carbon/Graphite Fibers. NASA TM 78652, 1978.

2. Intergovernmental Committee, Compilers: Carbon Fiber Study. NASA TM 78718, 1978.

AGENDA

MODIFIED COMPOSITE MATERIALS WORKSHOP

March 23-24, 1978
NASA-Langley Research Center
Hampton, Virginia

Thursday, March 23

8:00 a.m.	Registration	
8:30	Welcome	Richard R. Heldenfels NASA-Langley
	Workshop Expectations	William A. Brooks, Jr. NASA-Langley
	Potential Graphite Fiber Problems	Vernon L. Bell NASA-Langley
	Review of NASA-Langley Materials Modification Program	
	Overview	Robert T. Swann NASA-Langley
	Improved High Modulus Fibers	R. J. Diefendorf Rensselaer Polytechnic Institute
	Graphite Fibers with High Electrical Resistivity	F. Lincoln Vogel Un. of Pennsylvania
	Silicon Carbide, Boron, and Glass Coated Graphite Fibers	Francis Galasso United Technologies Research Center
	Boron Carbide and Silicon Carbide Coated Graphite Fibers	Raymond Suplinskas AVCO Corporation
	Boron Nitride, Silicon Carbide and Silicone Coated Graphite Fibers	Herbert F. Volk Union Carbide Corporation
10:35-10:50	BREAK	
10:50	Review of NASA-Ames Materials Modification Program	
	An Approach to the Development of Fire Resistant Composites	John A. Parker NASA-Ames
	Preliminary Test Results of the Fiber Release Characteristics of Baseline Graphite Epoxy Composites Compared with New Char Forming Analogs	Joseph Mansfield NASA-Ames
	Review of NASA-Lewis Materials Modification Program	Tito T. Serafini NASA-Lewis

12:10-[illegible]0 [illegible] - LUNCH - NASA Cafeteria (B-1213) Private Dining Room

1:10 p.m.	Fiber Release Testing Facilities and Results	Vernon L. Bell NASA-Langley
1:40	Charge to Working Groups	
1:50	Working Groups Convene (6 concurrent meetings)	
	I. Graphite Fiber Modification R. J. Diefendorf, Chairman Rensselaer Polytechnic Institute	STAGE
	II. Graphite Fiber Coating and Alternative Fibers James Economy, Chairman IBM Research Laboratory	HAMPTON ROOM
	III. Epoxy Resin Modifications James Noland, Chairman American Cyanamid Company	SUN LOUNGE
	IV. Epoxy Resin Replacements B. F. Landrum, Chairman Ciba-Geigy Corporation	MAIN LOUNGE
	V. Hybrid Composites Karl Prewo, Chairman United Technologies Research Center	WYTHE ROOM
	VI. Fiber Release Simulation Testing E. Bruce Belason, Chairman AVCO Corporation	LANGLEY ROOM
2:00-3:00	Coffee or Soft Drinks will be available in Main Lounge	
5:00	Working Groups Recess Buses depart for Holiday Inn	
6:00	Buses depart Holiday Inn for Sam's Seafood Restaurant	
6:15	Cash Bar Social	
7:00	Dinner	

Friday, March 24

8:00 a.m.	Working Groups Reconvene
9:45	BREAK
10:00	Reassemble for Working Group Reports
12:30 p.m	Closing Remarks
12:45	Buses depart for Patrick Henry International Airport and Holiday Inn

WORKSHOP EXPECTATIONS

WILLIAM A. BROOKS, JR.
MARCH 23, 1978

MODIFIED COMPOSITE MATERIALS WORKSHOP
NASA LANGLEY RESEARCH CENTER
MARCH 23-24, 1978

OBJECTIVES

- DISPLAY NASA PROGRAM ON MATERIALS MODIFICATIONS TO ALLEVIATE POTENTIAL ELECTRICAL PROBLEMS WITH GRAPHITE FIBER COMPOSITES

- SOLICIT POSSIBLE SOLUTIONS TO THIS PROBLEM FROM THE COMPOSITE MATERIALS COMMUNITY

- INITIATE A MORE GENERAL INVOLVEMENT OF THE COMPOSITES MATERIALS COMMUNITY IN APPROPRIATE ACTIVITIES

MODIFIED COMPOSITE MATERIALS WORKSHOP
NASA LANGLEY RESEARCH CENTER
MARCH 23-24, 1978

PARTICIPATION

	INVITATIONS	ACCEPTANCES
INDIVIDUALS (POLYMERS, FIBERS, FIRE TESTING)	149	111
COMMERCIAL COMPANIES	65	51
UNIVERSITIES	10	6
GOVERNMENT INSTALLATIONS	26	21

POTENTIAL GRAPHITE FIBER PROBLEMS

V. L. BELL
3/23/78

GRAPHITE COMPOSITES

- IMPORTANT LIGHTWEIGHT STRUCTURAL MATERIAL
- USED CURRENTLY IN AEROSPACE, SPORTING GOODS
- RAPID GROWTH PROJECTED
  - AEROSPACE: 1 MILLION LBS. (1990)
  - AUTOMOTIVE: 1 BILLION LBS. (1990)
  - CONSUMER PRODUCTS: 1 MILLION LBS. (1990)
- MADE UP OF LIGHT GRAPHITE FIBERS IN POLYMER MATRIX

USES OF CF COMPOSITES ON COMMERCIAL AIRCRAFT

PRESENT

SPOILERS: 28 B-737's WITH 4 SPOILERS = 13 LBS. CF/PLANE
RUDDERS: 7 DC-10's = 30 LBS. CF/PLANE
FLOORS: 25 B-747's WITH CF/EPOXY FLOORS

FUTURE

SECONDARY STRUCTURE

DC-10 RUDDER	40 LBS. CF
727 ELEVATOR	130 LBS. CF
L-1011 AILERON	70 LBS. CF

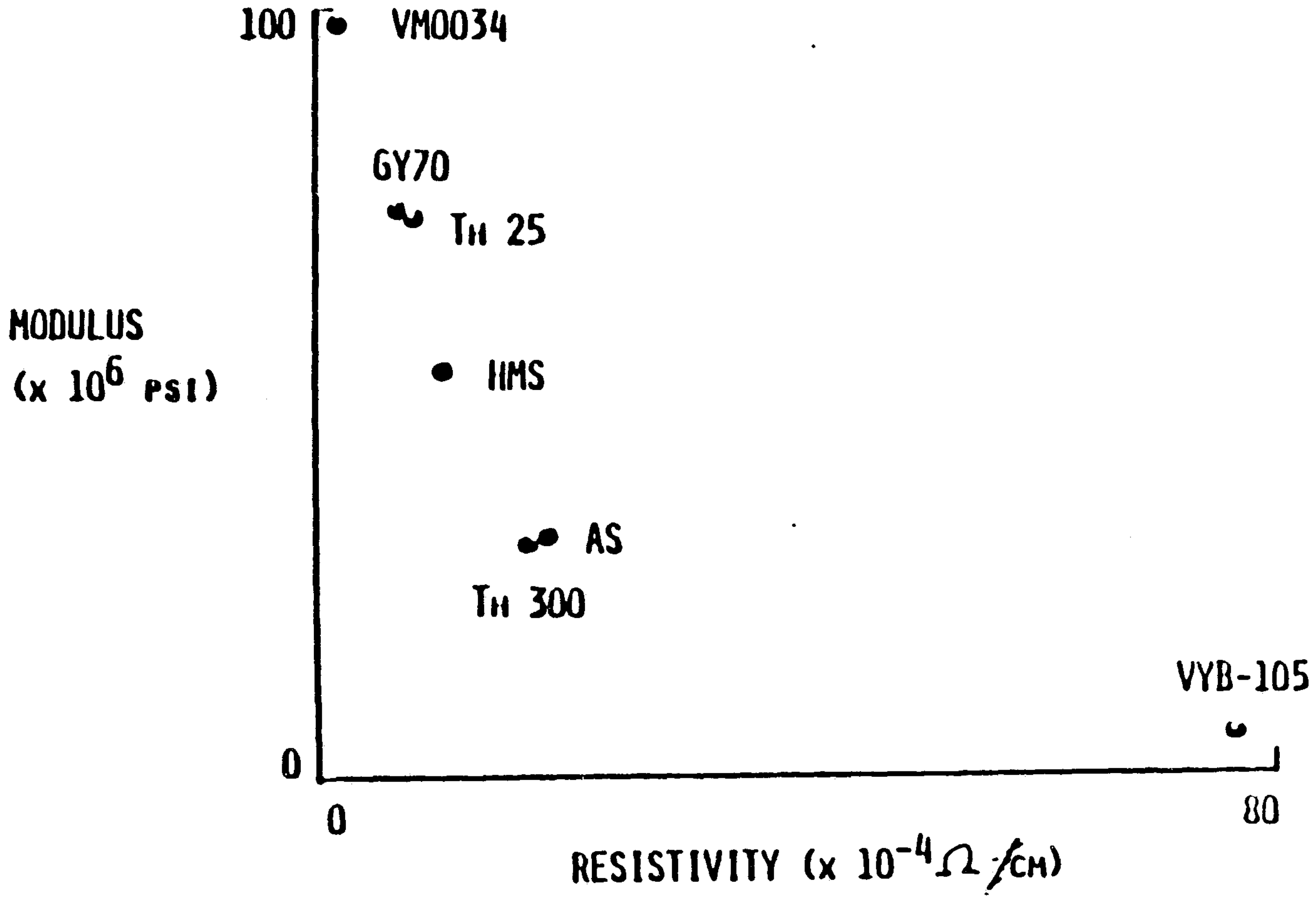
PRIMARY STRUCTURE

737 HORIZONTAL STABILIZER	125 LBS. CF
DC-10 VERTICAL FIN	700 LBS. CF
L-1011 VERTICAL FIN	700 LBS. CF

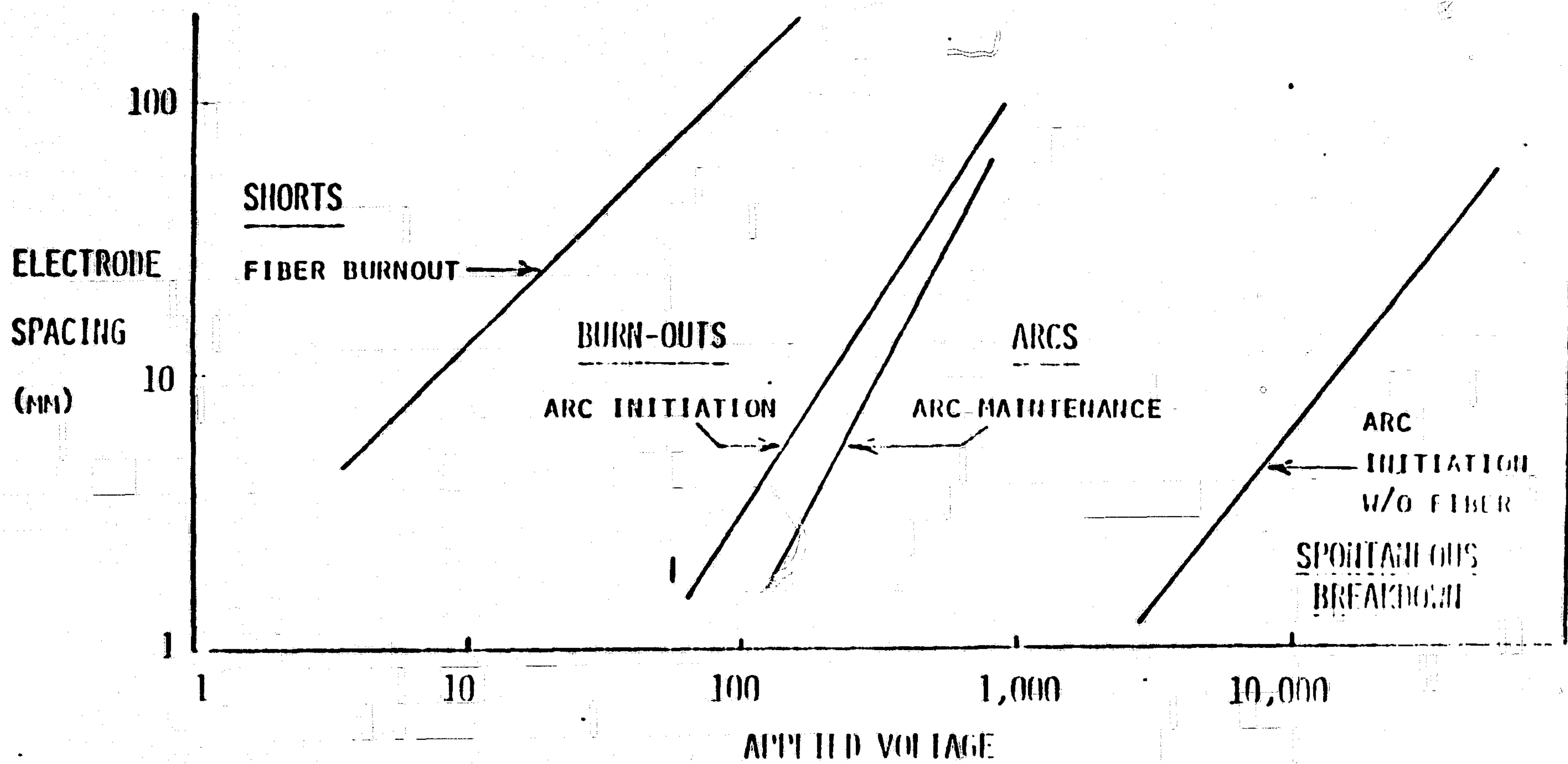
CHARACTERISTICS OF GRAPHITE FIBERS

- HIGH MODULUS (∼50 X 10^6 PSI)
- DIAMETER (∼8 MICRONS)
- FALL RATE (∼2 CM/SEC)
- RESISTIVITY (∼1000 Ω - CM)
- FIBER BURNOUT 0.5 TO 1 WATT/CM (∼10 TO 30 MA)
- CONTACT VOLTAGE DROP (∼2 TO 5 VOLTS)

EFFECT OF MODULUS ON RESISTIVITY



SUMMARY OF ELECTRICAL EFFECTS WITH GRAPHITE FIBER



TYPES OF ACCIDENTAL RELEASE

● CRASH AND FIRE

o INDUSTRIAL OPERATIONS

o SCRAP/WASTE DISPOSAL

o INCINERATION OF USED PRODUCTS

o TESTING

RISK ANALYSIS FOR GRAPHITE STRUCTURES

OBJECTIVES

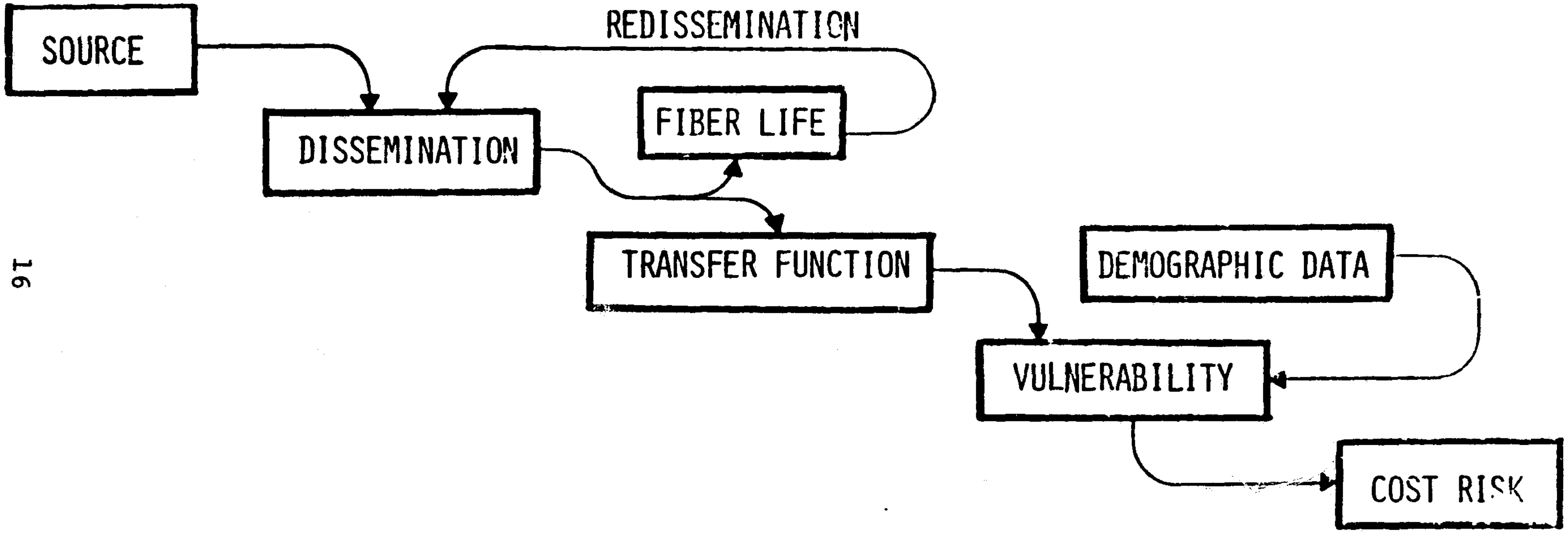
SHORT TERM

- ESTABLISH LEVEL OF CONFIDENCE IN METHODS AND RESULTS
- QUANTIFY NEAR TERM RISK OF GRAPHITE FIBER ON CURRENT CIVIL AIRCRAFT

LONG TERM

- QUANTIFY RISKS ASSOCIATED WITH ACCIDENTAL RELEASE OF GRAPHITE FIBERS FROM AERONAUTICAL USES OF COMPOSITES IN THE FUTURE
- QUANTIFY REDUCTION IN RISKS ASSOCIATED WITH USE OF MODIFIED MATERIALS

RISK ANALYSIS FLOW



SOURCE PARAMETERS

AIRCRAFT ACCIDENT AND FIRE STATISTICS

AIRCRAFT ACCIDENT AND FIRE LOCATIONS

FIRE ENERGY CONTENT AND RATE

FIRE FIGHTING EFFECTS

QUANTITY AND LENGTHS RELEASED

ORIGINAL PAGE IS
OF POOR QUALITY

DISSEMINATION PARAMETERS

- Atmospherics
  - Stability
  - Wind
  - Inversion height
  - Weather
- Fall Velocity of Fiber
  - Length dependence
- Local Effects
  - Fire plume
  - Turbulence, vortices
  - Buildings, trees
- Life and reentrainment

TRANSFER FUNCTION PARAMETERS

PARAMETERS:
- FIBER LENGTH
- FIBER FALL VELOCITY
- LOCAL VELOCITY
- SEASON (DOORS, WINDOWS, CANOPIES)
- CASE OPENING AREA

REQUIRED FOR: BUILDINGS, ROOMS, AIRCRAFT, EQUIPMENT RACKS, AIR CONDITIONING, FILTERS . . .

VULNERABILITY

USER CLASSIFICATIONS:

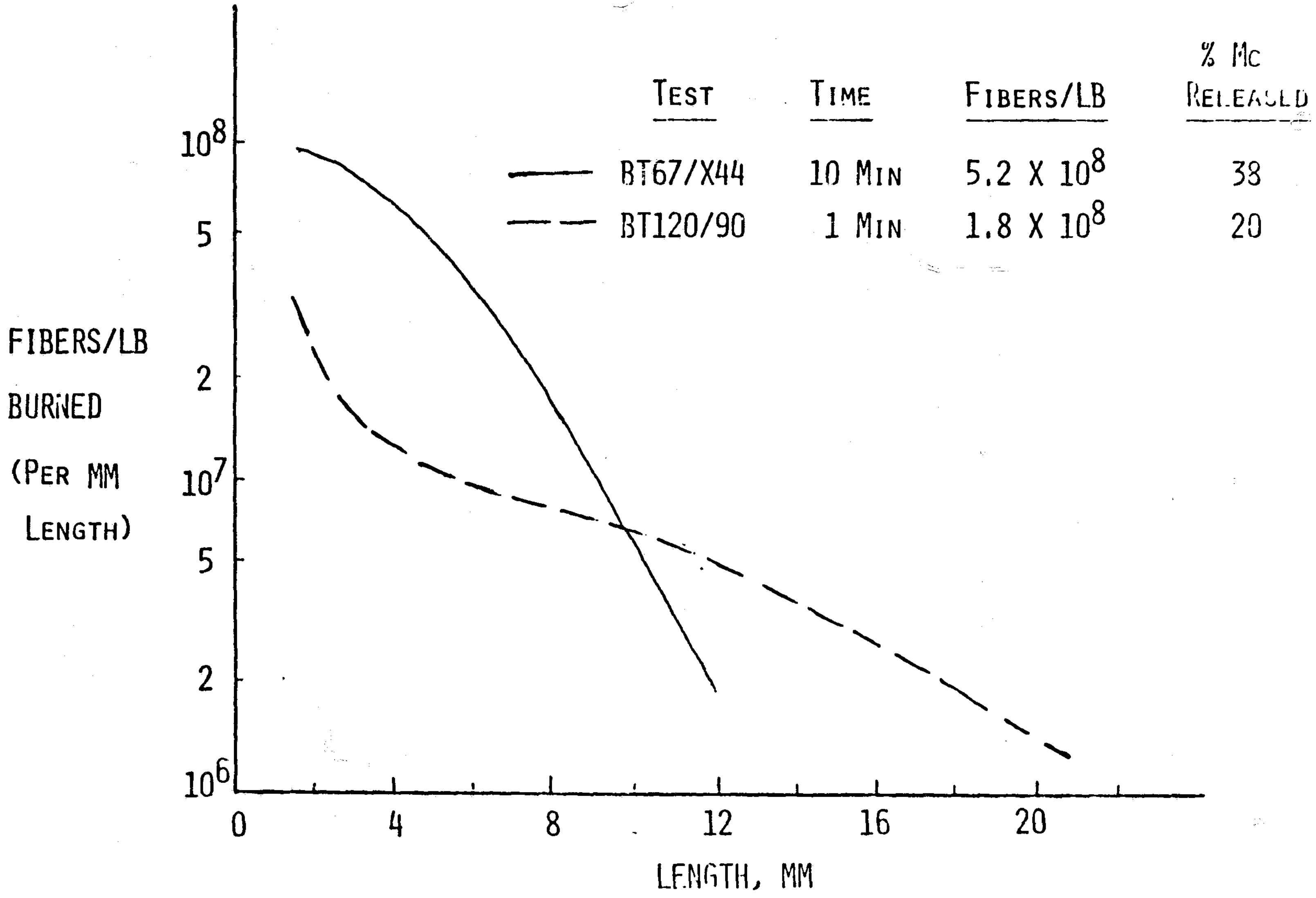
- HOME APPLIANCES
- COMMERCIAL
- MANUFACTURE
- PUBLIC SERVICE
  - POLICE, FIRE, COMMUNICATIONS
- AIRCRAFT

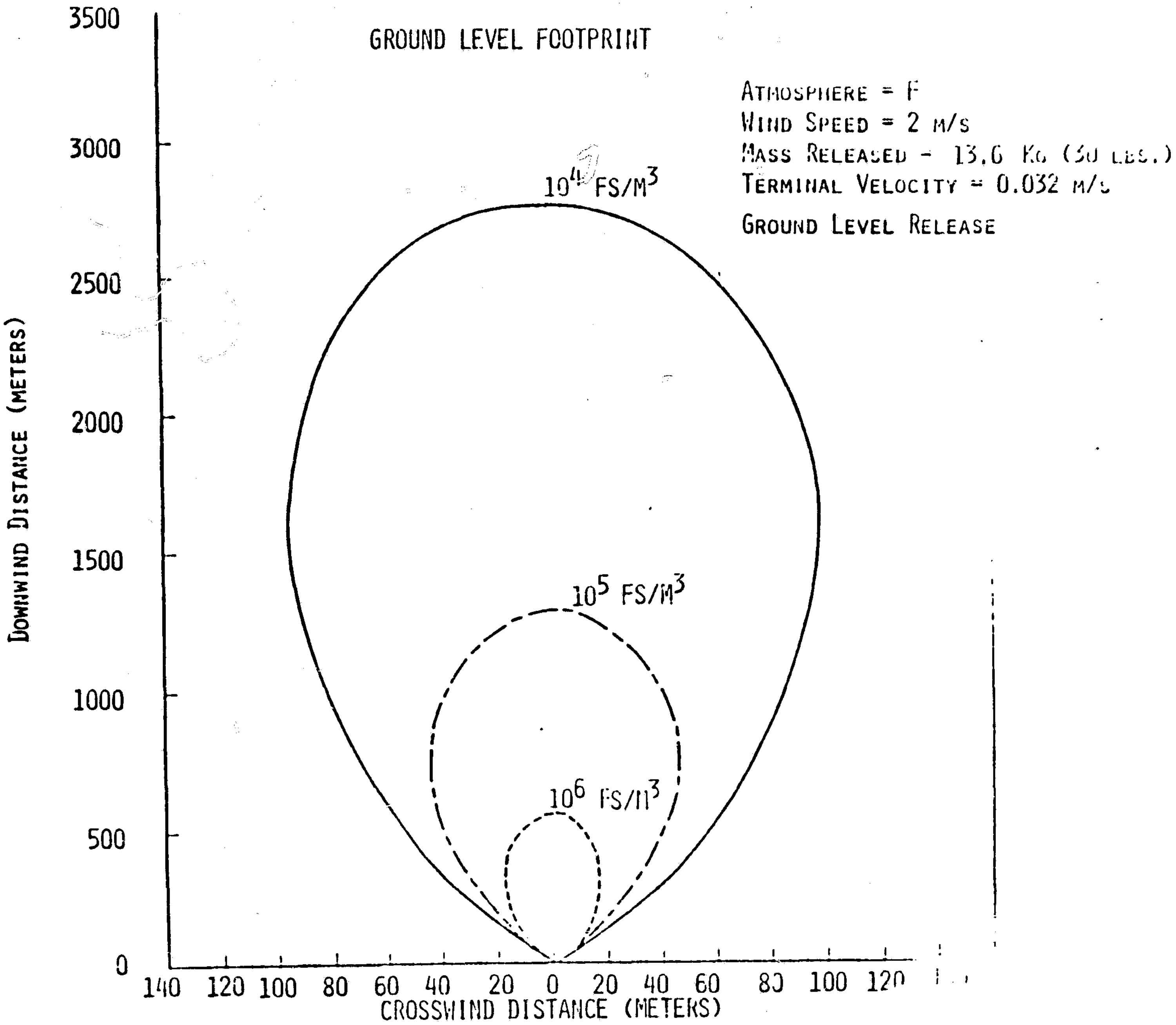
TYPE CLASSIFICATIONS:

- MOTORS
- AMPLIFIERS
- CONTROLLERS
- RADARS

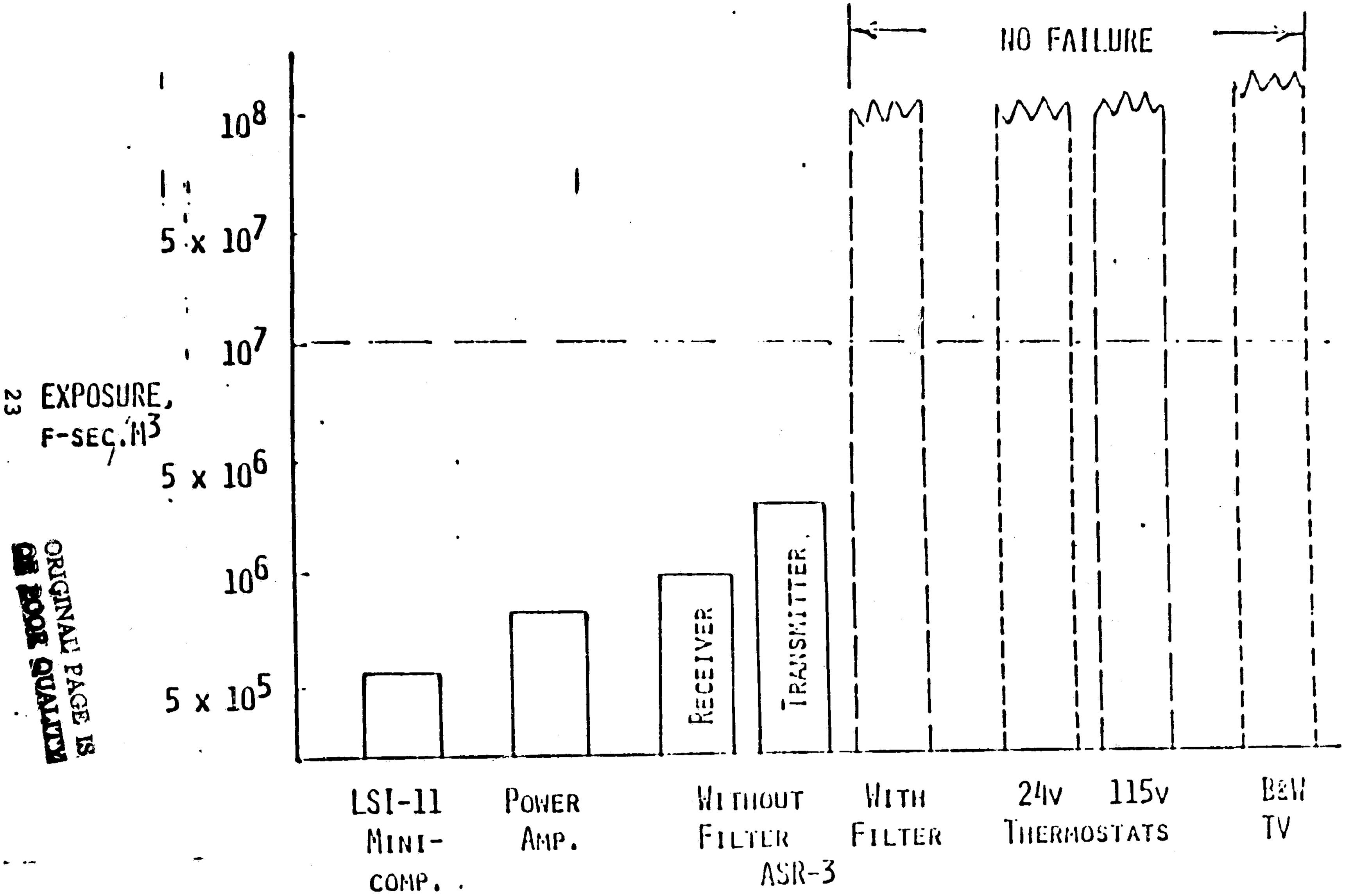
MATERIAL RELEASE CHARACTERISTICS

BURN AND EXPLODE CHAMBER TESTS




GROUND LEVEL FOOTPRINT
ATMOSPHERE = F
WIND SPEED = 2 M/S
MASS RELEASED = 13.6 KG (30 LBS.)
TERMINAL VELOCITY = 0.032 M/S
GROUND LEVEL RELEASE
10^4 FS/M^3
10^5 FS/M^3
10^6 FS/M^3
DOWNWIND DISTANCE (METERS)
3500
3000
2500
2000
1500
1000
500
0
140
120
100
80
60
40
20
0
20
40
60
80
100
120
CROSSWIND DISTANCE (METERS)

FAILURE EXPOSURE LEVELS FOR CIVILIAN EQUIPMENT



CONCLUSIONS

1. PRELIMINARY COMPUTATIONS INDICATE THE RISK IS NEITHER NEGLIGIBLE NOR OF HIGH MAGNITUDE, HOWEVER,

2. INSUFFICIENT DATA IS AVAILABLE TO ADEQUATELY COMPUTE THE MAGNITUDE OF THE RISK

3. FURTHER WORK IS REQUIRED:
    - A. TEST DATA IS REQUIRED ON SOURCES, TRANSFER FUNCTION AND VULNERABILITY
    - B. MODELLING FOR THESE FACTORS IS REQUIRED
    - C. METHODOLOGY FOR COMPUTING AND PREDICTING RISK NEEDS DEVELOPMENT

OVERVIEW

NASA LANGLEY MATERIALS MODIFICATION PROGRAM

ROBERT T. SWANN
MARCH 23, 1978

IMPROVED MATERIALS FOR STRUCTURAL COMPOSITES

LANGLEY RESEARCH CENTER PROGRAM

PRIMARY PROGRAM

- O FIBER MODIFICATIONS
  - RPI
  - U. PA - MERADCOM
- O FIBER COATINGS
  - UTRC
  - AVCO
  - UNION CARBIDE

SECONDARY PROGRAM

- O ALTERNATE FIBERS (BN)
  - SOURCE PENDING
- O HYBRIDS
- O RESIN MODIFICATIONS

IMPROVED MATERIALS FOR STRUCTURAL COMPOSITES

HYBRIDS AND RESIN MODIFICATIONS

OBJECTIVE: SCREEN HYDBRIDS AND RESIN MODIFICATIONS TO DETERMINE WHICH ONES REDUCE FIBER RELEASE

APPROACH: EVALUATE HYBRIDS

- 0 OUTER PLIES WITH S-GLASS AND E-GLASS FIBERS
- 0 OUTER PLIES WITH BORON FIBERS
- 0 METAL CLADDING
- 0 ADD SEALING GLASS

EVALUATE RESIN MODIFICATIONS

- 0 NCNS: EPOXY
- 0 XYLOK: EPOXY
- 0 SILICONE: EPOXY
- 0 HEXCEL 178 PI

IMPROVED MATERIALS FOR STRUCTURAL COMPOSITES

ALTERNATE FIBERS

OBJECTIVE: DEVELOP HIGH STRENGTH, HIGH MODULUS BORON NITRIDE FIBERS

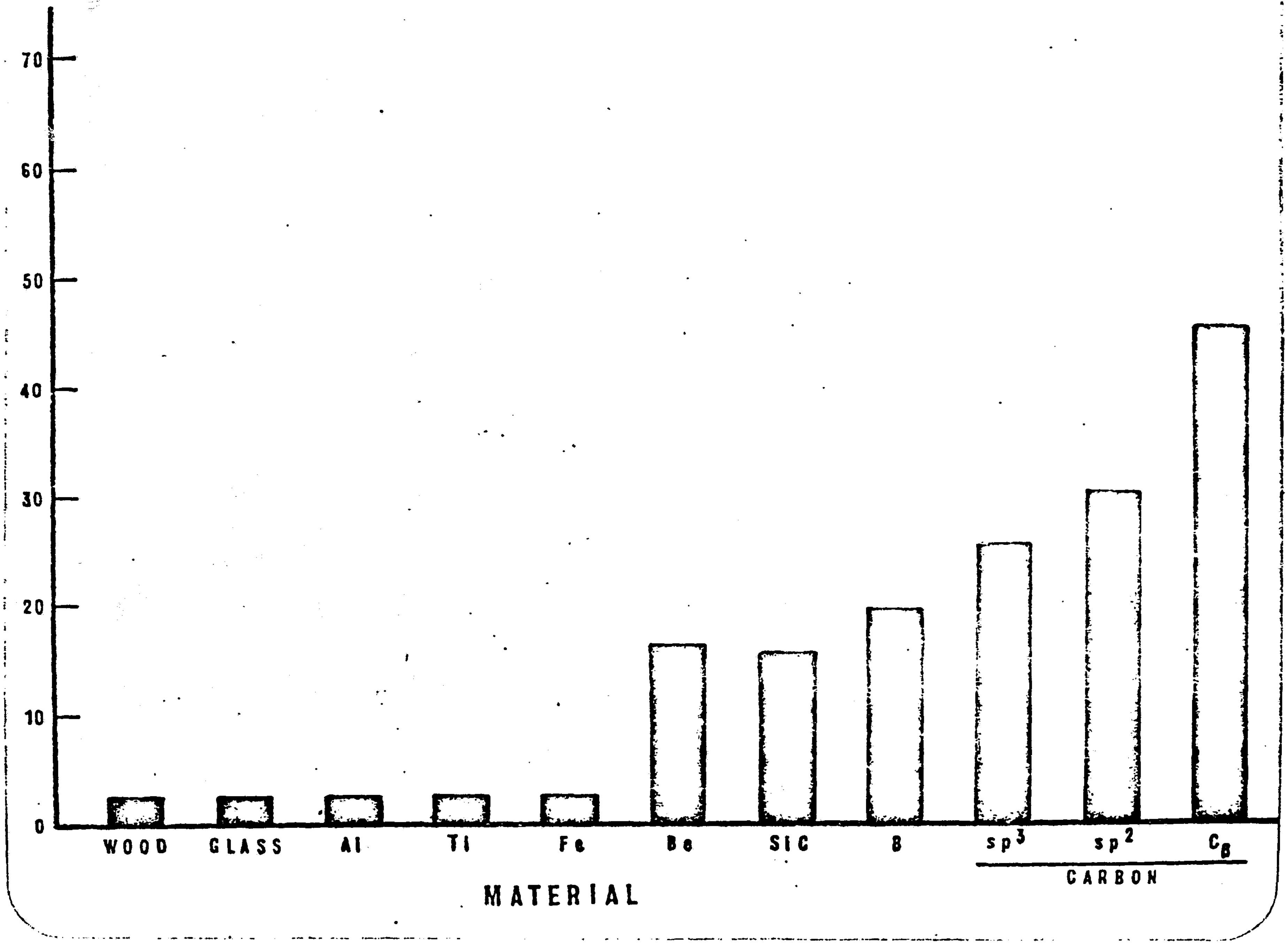
APPROACH:

- COOPERATE WITH NAVY TO EXTEND USAF-INITIATED DEVELOPMENT OF BN FIBERS
- DEVELOP TECHNICAL PLAN WHICH ADDRESSES CRITICAL PROBLEMS IDENTIFIED IN PRIOR WORK

IMPROVED HIGH MODULUS FIBER

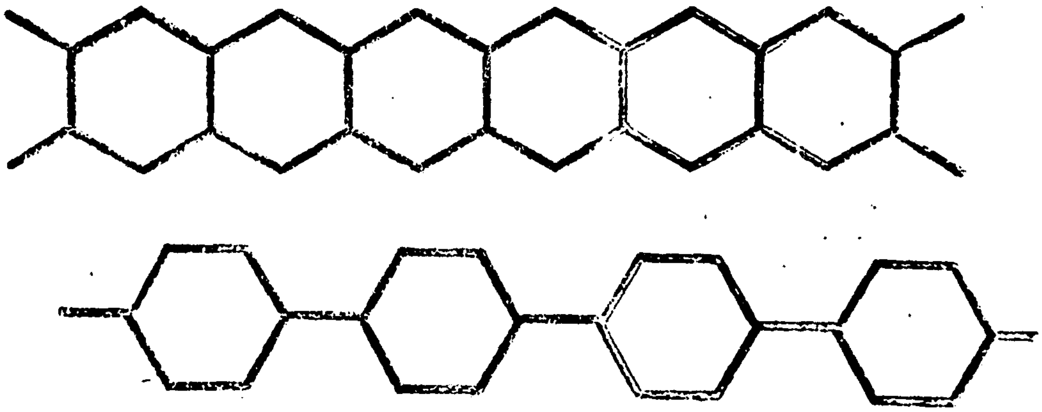
R. J. DIEFENDORF
RENSSELAER POLYTECHNIC INSTITUTE

MARCH 23, 1978



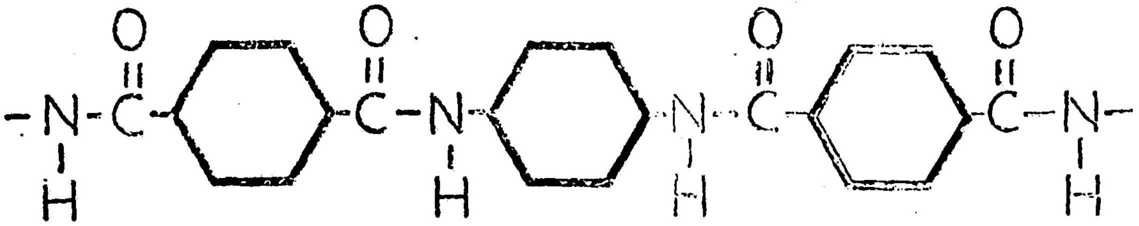
NASA LANGLEY RESEARCH CENTER

LADDER POLYMERS



1) M.P. TOO HIGH
2) INSOLUBLE

KEVLAR

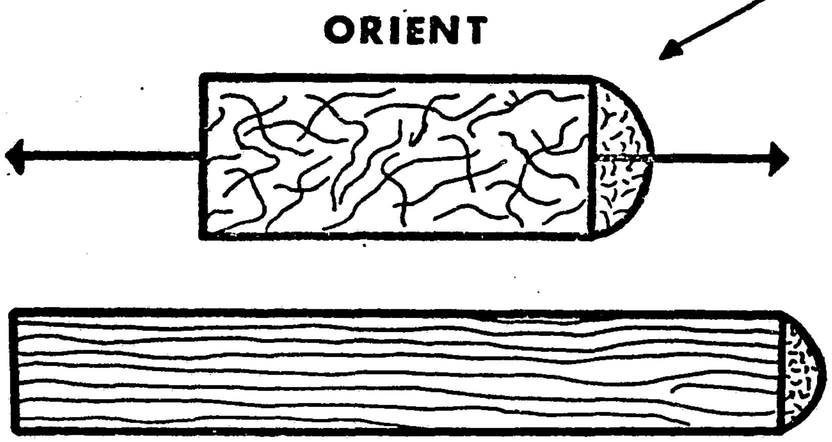


1) AMIDE GROUPS MAKE SOLUBLE

2) FORMS L.C.

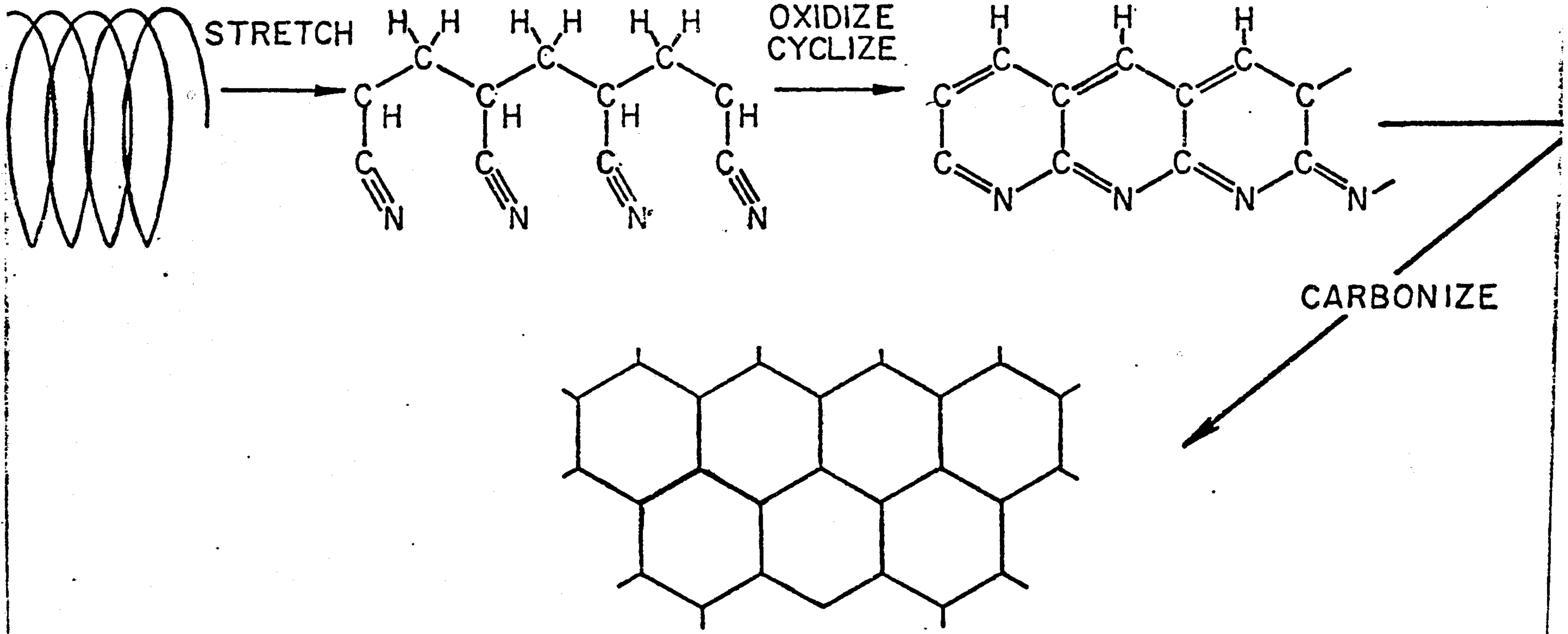
RAYON BASE FIBERS

FIBER → STABILIZE → CARBONIZE → GRAPHITIZE

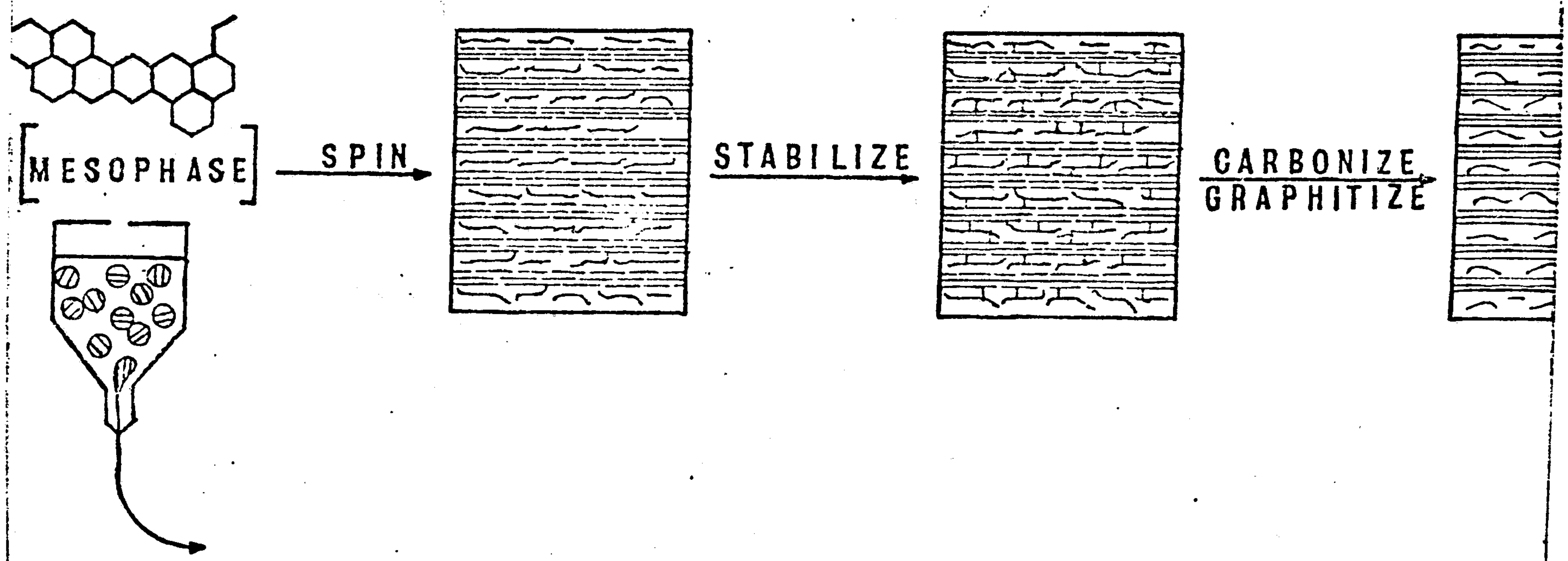


NO. 1

POLYACRYLONITRILE PROCESS



PITCH FIBERS 2

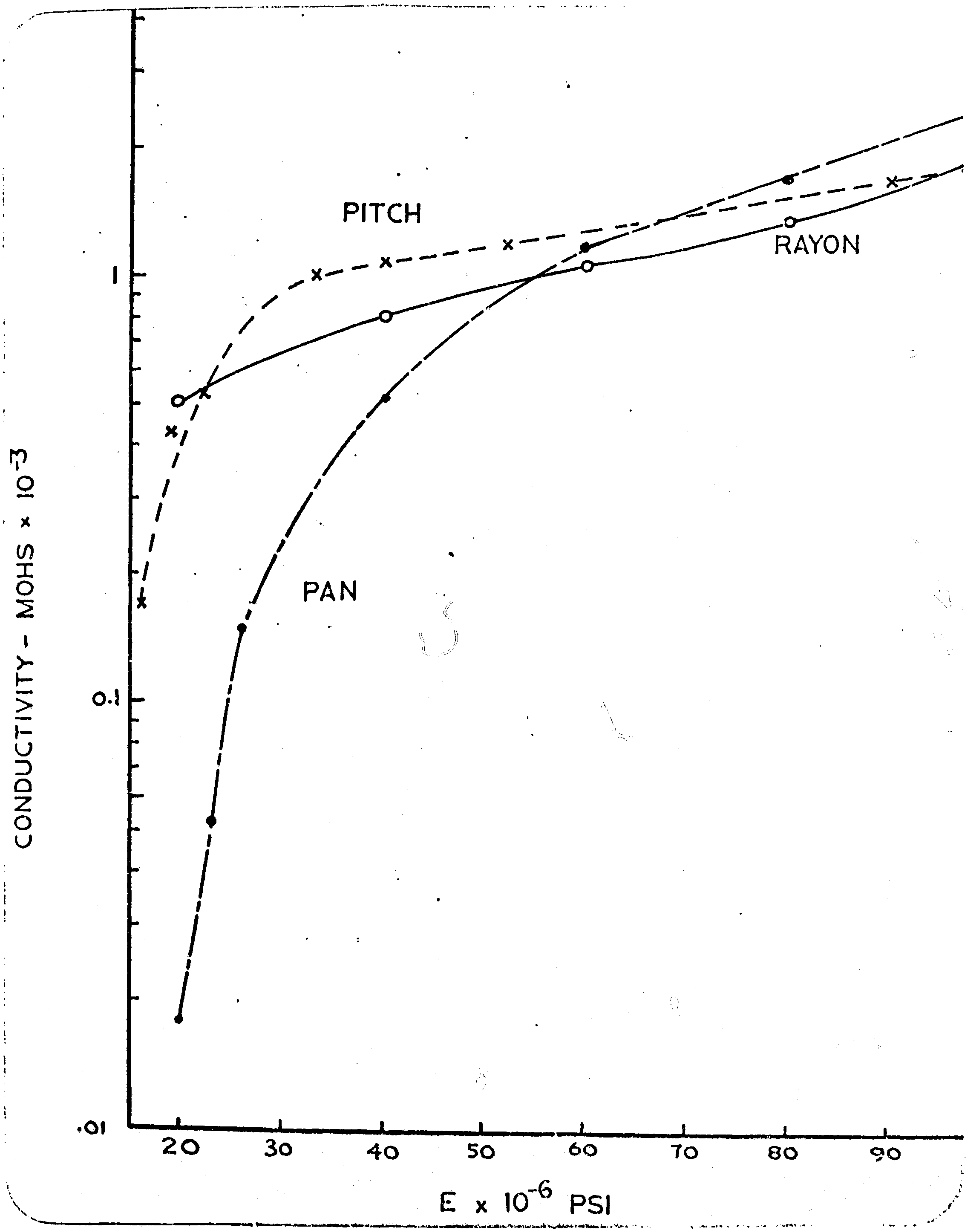


MESOPHASE

SPIN

STABILIZE

CARBONIZE
GRAPHITIZE



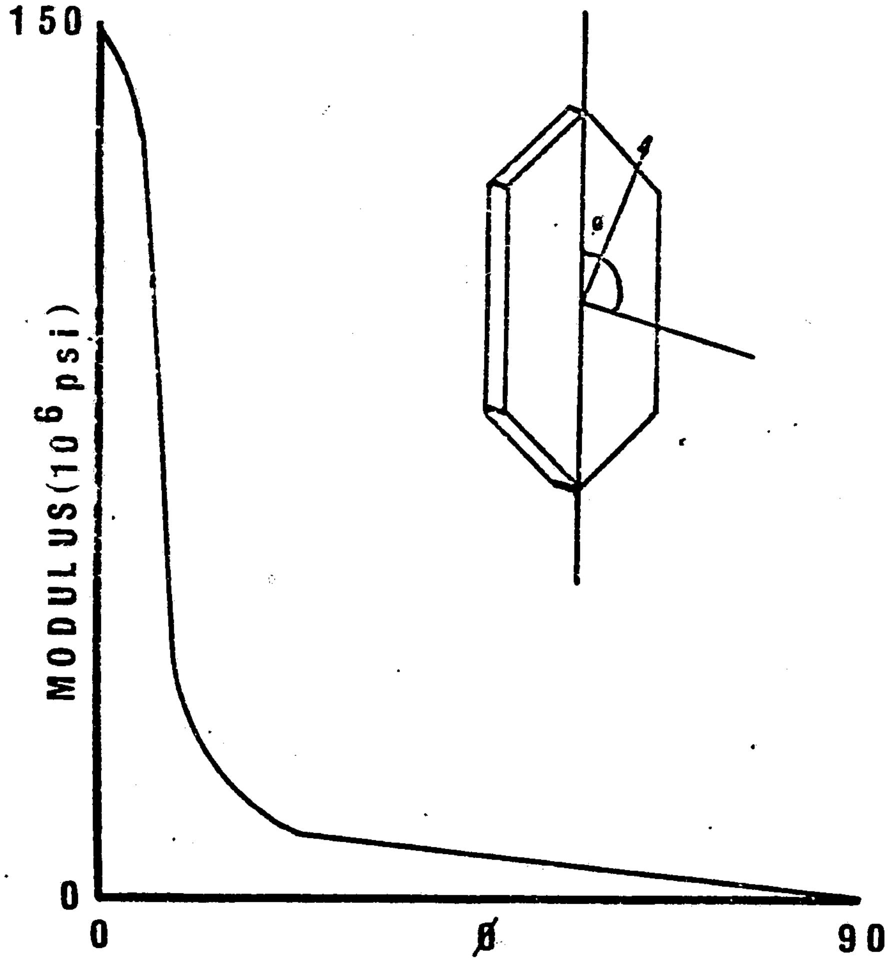
PITCH
RAYON
PAN
CONDUCTIVITY - MOHS × 10^{-3}
1
0.1
.01
20
30
40
50
60
70
80
90
E × 10^{-6} PSI

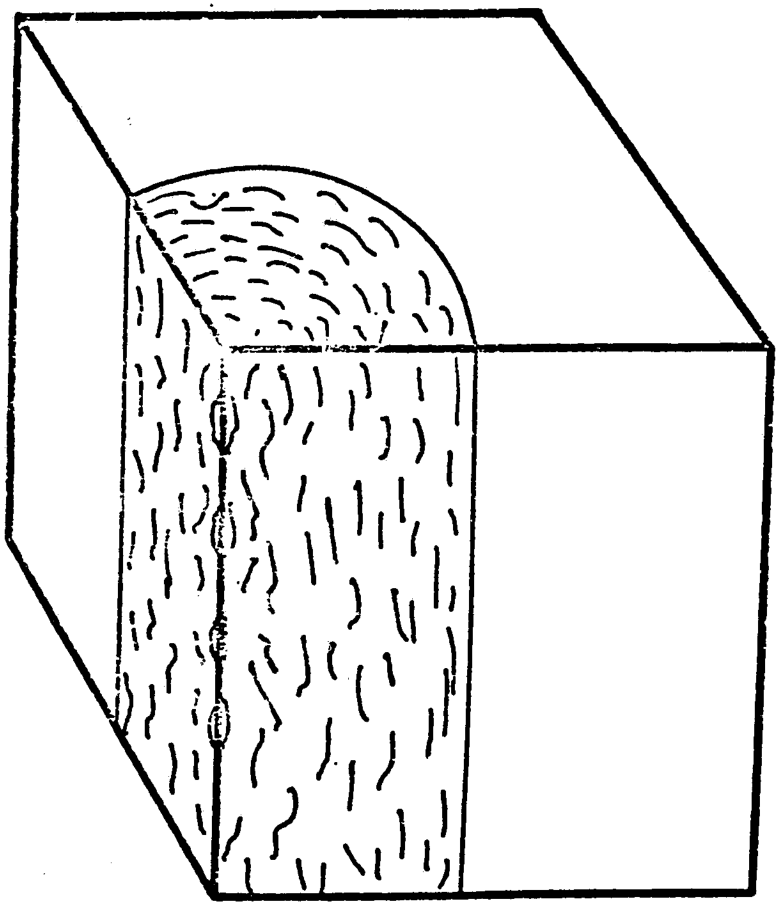
FIBER PROPERTIES

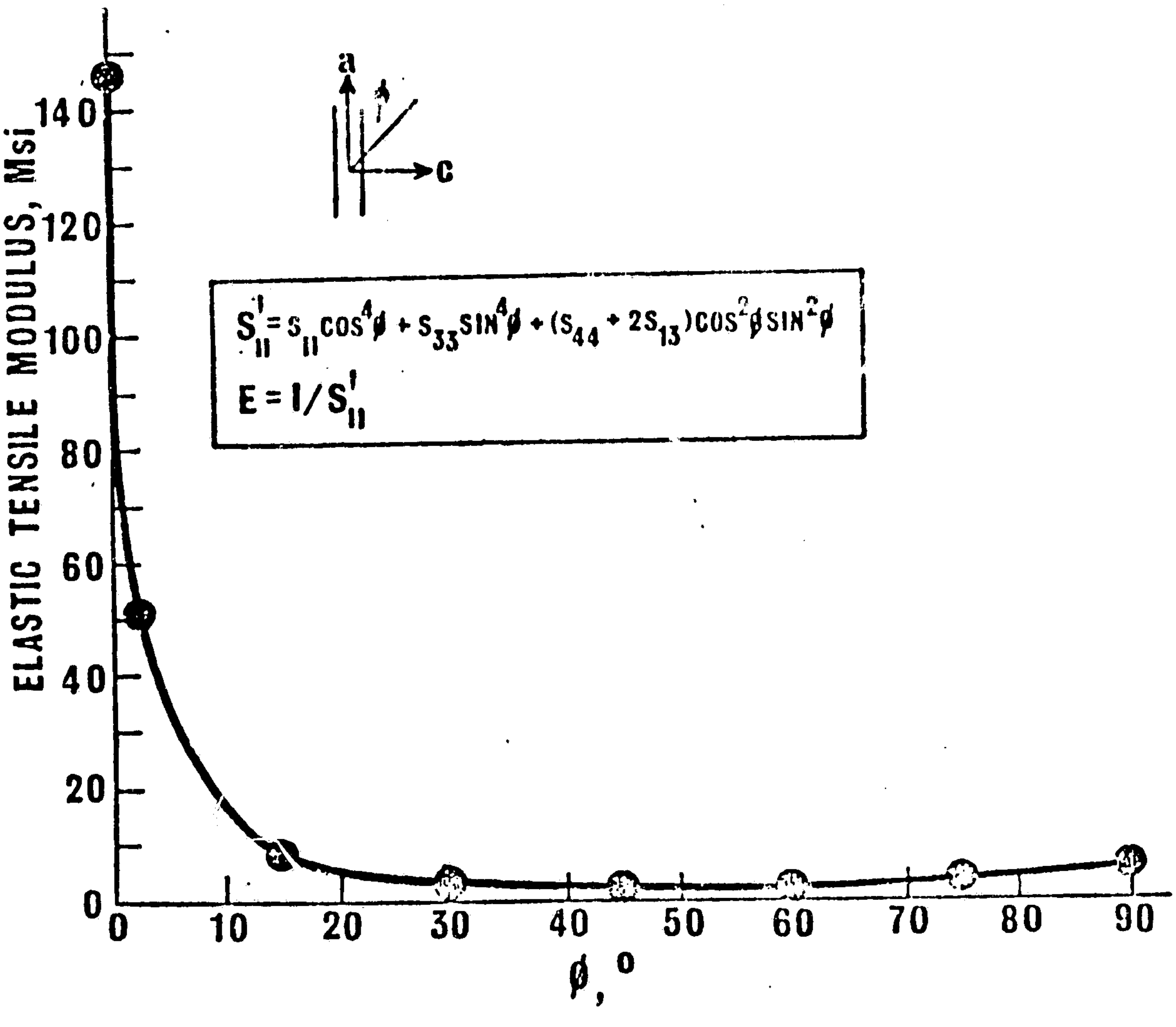
- PREFERRED ORIENTATION
- MICROSTRUCTURE
- ELASTIC CONSTANTS
- CRYSTALLITE SIZE

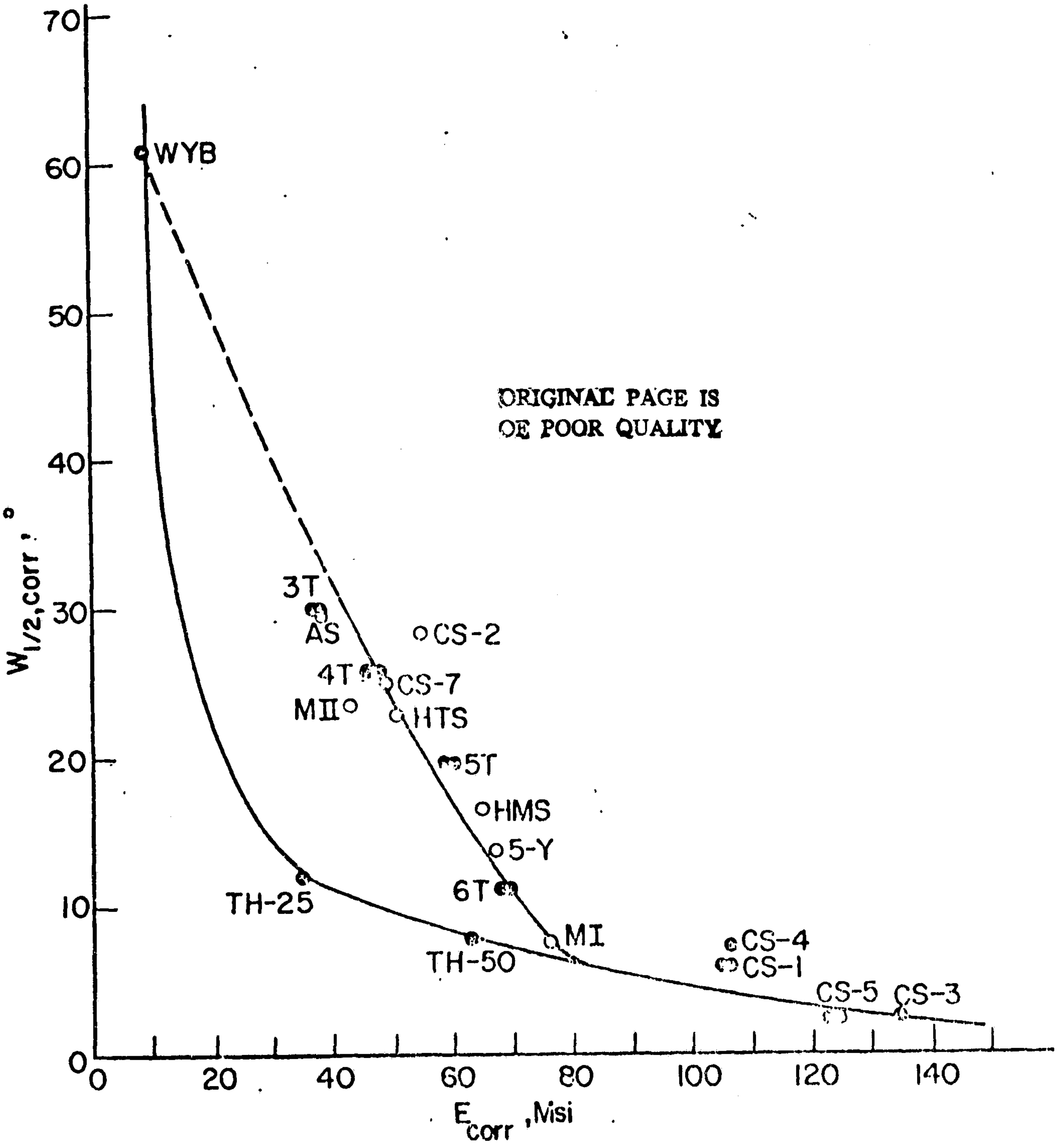
NO. ____________

FIBER PREFERRED ORIENTATION






a
c
$S'_{11} = S_{11}\cos^4\phi + S_{33}\sin^4\phi + (S_{44} + 2S_{13})\cos^2\phi\sin^2\phi$
$E = 1/S'_{11}$
ELASTIC TENSILE MODULUS, Msi
140
120
100
80
60
40
20
0
0
10
20
30
40
50
60
70
80
90
ϕ, °



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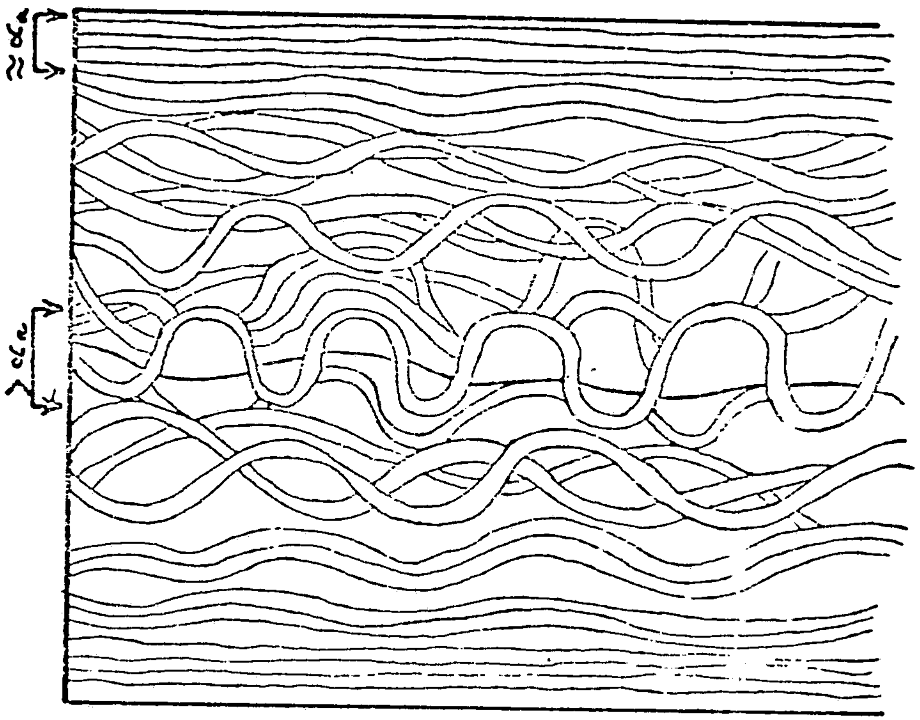
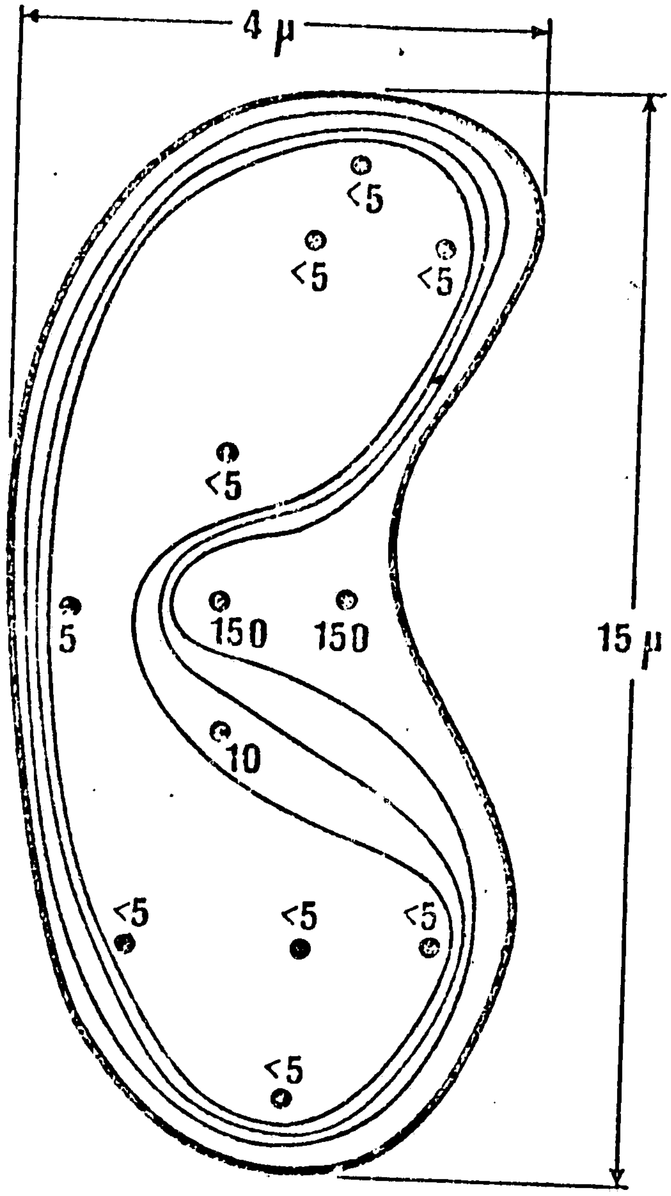
Index of Preferred Orientation, $W_{\frac{1}{2}}$ vs. Fiber Modulus

TOP





NUMBERS REPRESENT AXIAL MODULI VALUES (IN MSI) OVER THE CROSS SECTION OF THE FIBER.

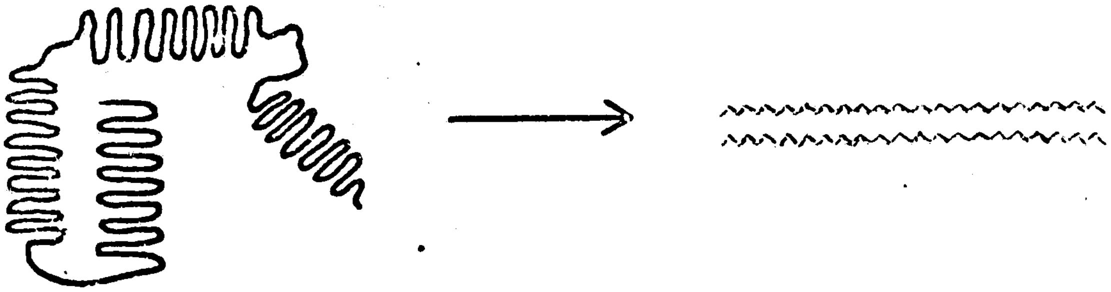
TOP

LOW TEMPERATURE DEFECTS

(WORK WITH PAN AND PITCH)

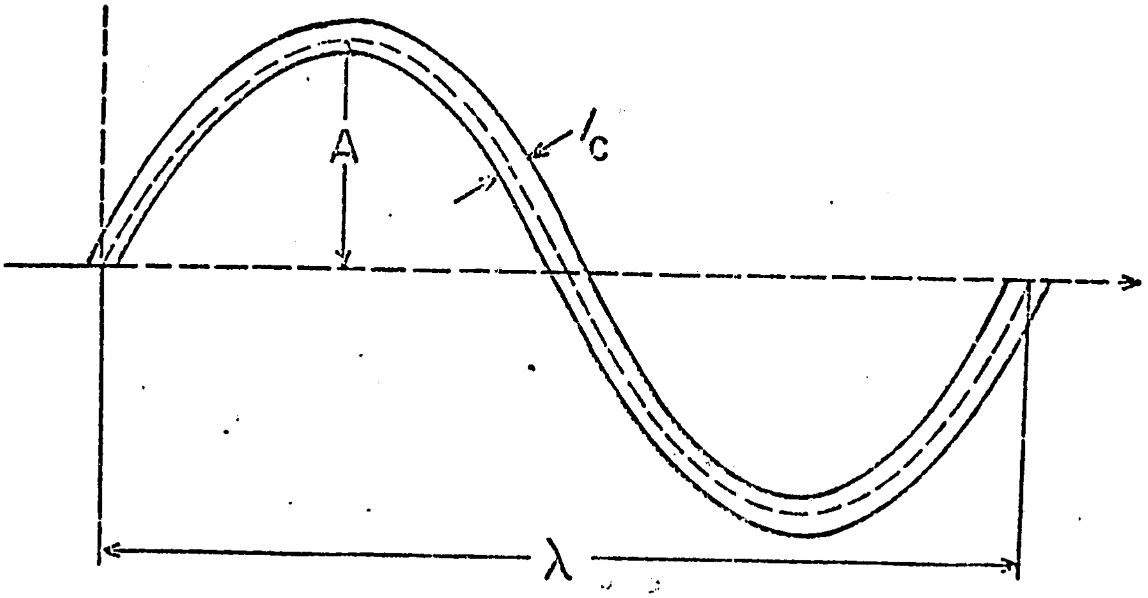
- ORIENTATION
- RELAXATION
  - OXIDATION
  - CARBONIZATION
- FIBRIL SIZE - L_A AND L_C

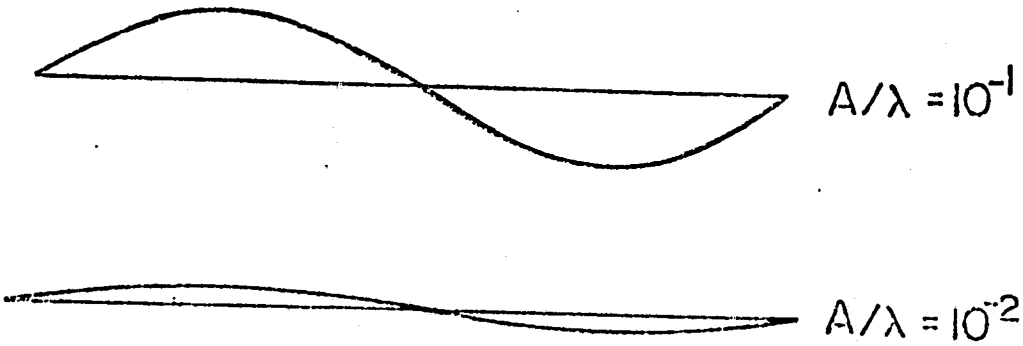
FULLY EXTENDED P.E.



1. HYDROSTATIC EXTRUSION
2. WARM DRAWING
3. L.C. MELT EXTRUSION ?

TOP


A
l_c
λ


$A/\lambda = 10^{-1}$
$A/\lambda = 10^{-2}$

RESISTIVITY

- LOW TEMPERATURE - DEFECTS
- NITROGEN TRAPS - PAN
- BORON/NITROGEN/CARBON SOLID SOLUTION
- INSULATING COATING -BN - SiC

PROPERTY	BN	C
MELTING POINT	2400°C (SUBL.)	3600°C (SUBL.)
THEOR. DENSITY	2.25	2.25
ELEC. RESIST. 25°C (OHM-CM)	$10^{13} - 10^{10}$	10^{-3}
THERM. EXP. COEF. 25°C $-\alpha_a$	1.8×10^{-6}	1.8×10^{-6}
THERM. EXP. COEF. 25°C $-\alpha_c$	45×10^{-5}	15×10^{-6}

ABSTRACT

Graphite Fibers with High Electrical Resistivity

BY: F.L. Vogel[+], Russell Eaton*, and W. David Lee*

Problems of arc over and circuit perturbation in electrical equipment have been traced to the presence of graphite fibers. A potential solution to this problem lies in increasing the electrical resistivity of the graphite fibers by several orders of magnitude. It is proposed herein that this may be accomplished by treating the fibers to form graphitic oxide. This treatment has the effect of inserting oxygen into the graphite lattice and increasing the resistivity considerably. The graphite layer planes remain largely unaffected and so the elastic modulus and tensile strength are predicted to be unchanged.

Supporting work in the literature will be reviewed.

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University of Pennsylvania
Philadelphia Pa., 19104

* Electrical Equipment Division
MERADCOM Fort Belvoir, Va. 22060

INTERSTITIAL COMPOUND APPROACH

CAN CONVERSION OF GRAPHITE FIBER TO GRAPHITE OXIDE (FLUORIDE) REDUCE ELECTRICAL CONDUCTIVITY SIGNIFICANTLY WITHOUT DEGRADING MECHANICAL PROPERTIES?

SYNTHESIS

COMPOSITIONS

STRUCTURES
  COVALENT BONDING = HIGH RESISTIVITY
  AROMATIC RINGS = HIGH STRENGTH AND MODULUS

ELECTRICAL RESISTIVITY

GRAPHITE OXIDE SYNTHESIS

GRAPHITE	+	HNO_3 AND/OR H_2SO_4	+	$KCLO_3$ $KMnO_4$ $K_2CR_2O_7$	=	GRAPHITE OXIDE

BRODIE, HOFFMAN, STAUDENMAIER

TIME CONSUMING, HAZARDOUS

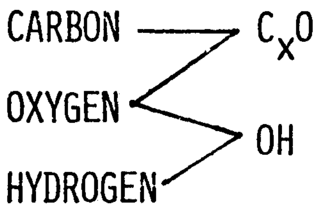
GRAPHITE	+	H_2SO_4	+	$NaNO_3$ $KMnO_4$	=	GRAPHITE OXIDE

HUMMERS AND OFFEMAN

RAPID REACTION - NO HAZARD

GRAPHITE OXIDE COMPOSITIONS

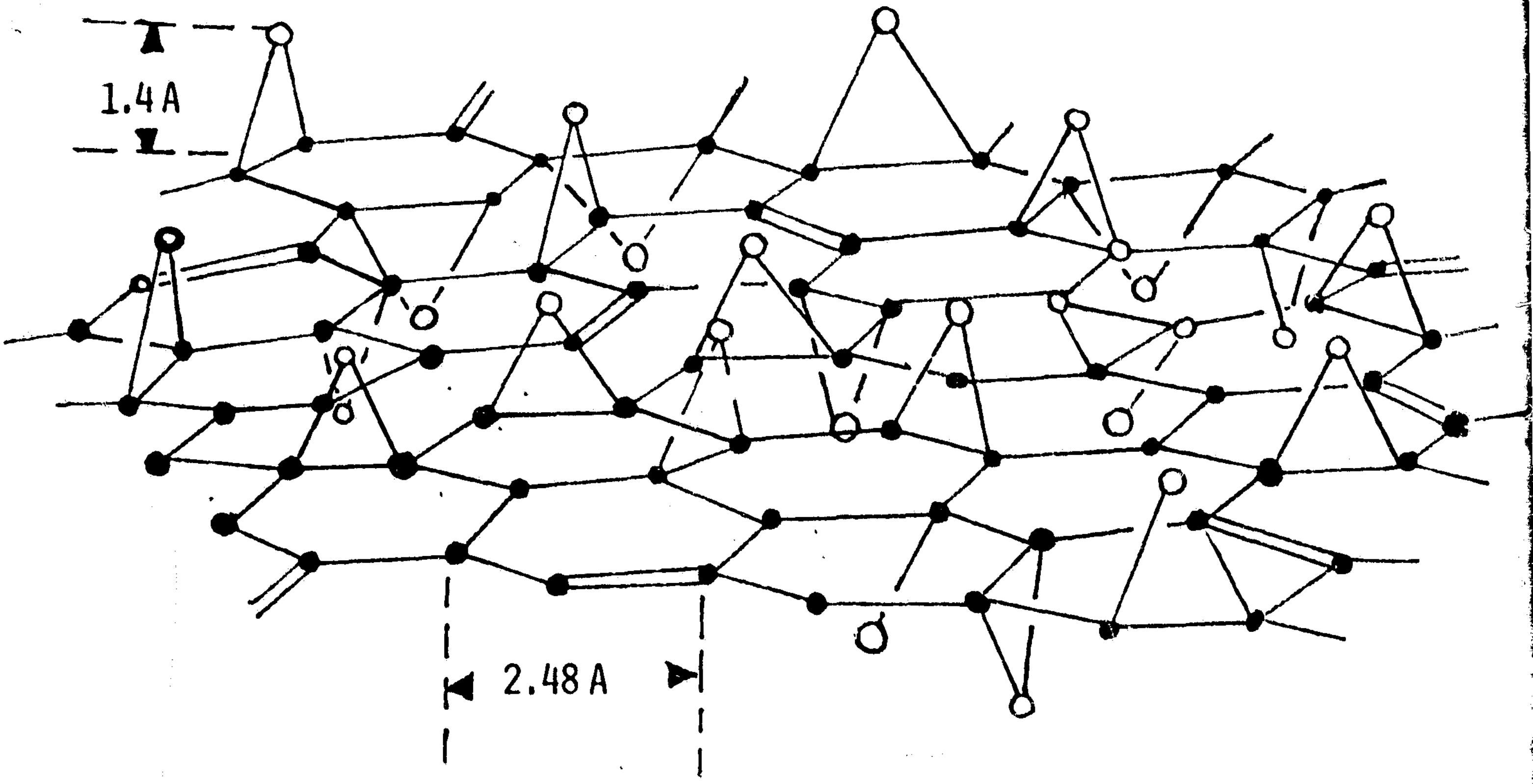
MIXTURES



$X > 1, = 2$ OR 3

$\frac{\text{CARBON}}{\text{OXYGEN}}$ RATIO	COLOR
16	BLACK
3	GREEN
2	YELLOW

GRAPHITE OXIDE STRUCTURE

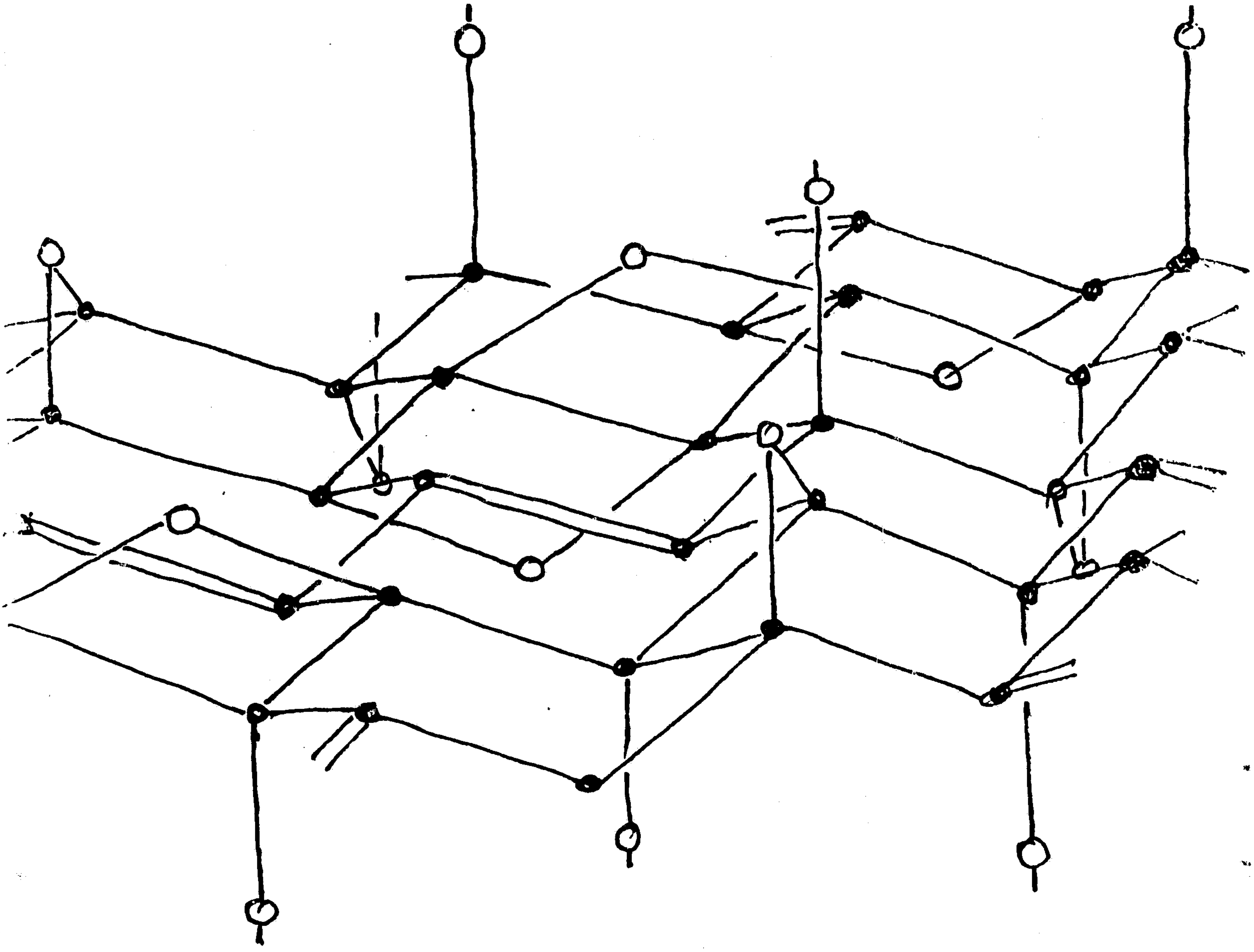


○ OXYGEN ATOM

● CARBON ATOM

FROM HOFFMAN, FRENZL, CSALAN

GRAPHITE OXIDE STRUCTURE



○ OXYGEN ATOM

● CARBON ATOM

FROM CLAUSS, PLASS, BOEHM, HOFFMAN

GRAPHITE OXIDE ELECTRICAL RESISTIVITY

$\frac{\text{CARBON}}{\text{OXYGEN}}$ RATIO	RESISTIVITY (DRY) OHM-CM
3.0	10^7
3.5	4,000
4.3	250
7.1	0.4
12	0.2
21	0.05
GRAPHITE	0.023

SILICON CARBIDE, BORON, AND GLASS COATED GRAPHITE FIBERS

FRANCIS GALASSO
UNITED TECHNOLOGIES RESEARCH CENTER

MARCH 23, 1978

Fibers	%Loss in weight (600°C) 1 Hour	%Loss in weight (600°C) 3 Hours	As received Modulus x 10^6 psi
Hercules HTS	14.8	100.0	37
Hercules HMS	9.4	39.5	51
Celanese DG102	3.7	36.1	77
Thornel 50	3.2	16.7	57
Thornel type P	5.3	21.1	60

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Fiber	%Loss in weight (550°C)		
	1 Hour	3 Hours	6 Hours
1 HMS	34.8	77.0	88.6
2 HMS	6.1	20.9	39.4
3 HMS	12.4	27.7	52.0
1 HTS	3.1	17.1	93.9
2 HTS	4.9	21.8	97.8
3 HTS	3.8	13.6	34.3
AS	78.3	–	–
T300	71.4	–	–

Graphite Fiber Coating Program

Molten glass	J. Bacon
Colloidal silica Dip coating Electrophoretic coating	S. Holmquist
Organo-silicon compounds Dip and conversion	D. Scola and H. Roth
CVD SiC	R. Veltri and F. Galasso
CVD B	R. Veltri and F. Galasso

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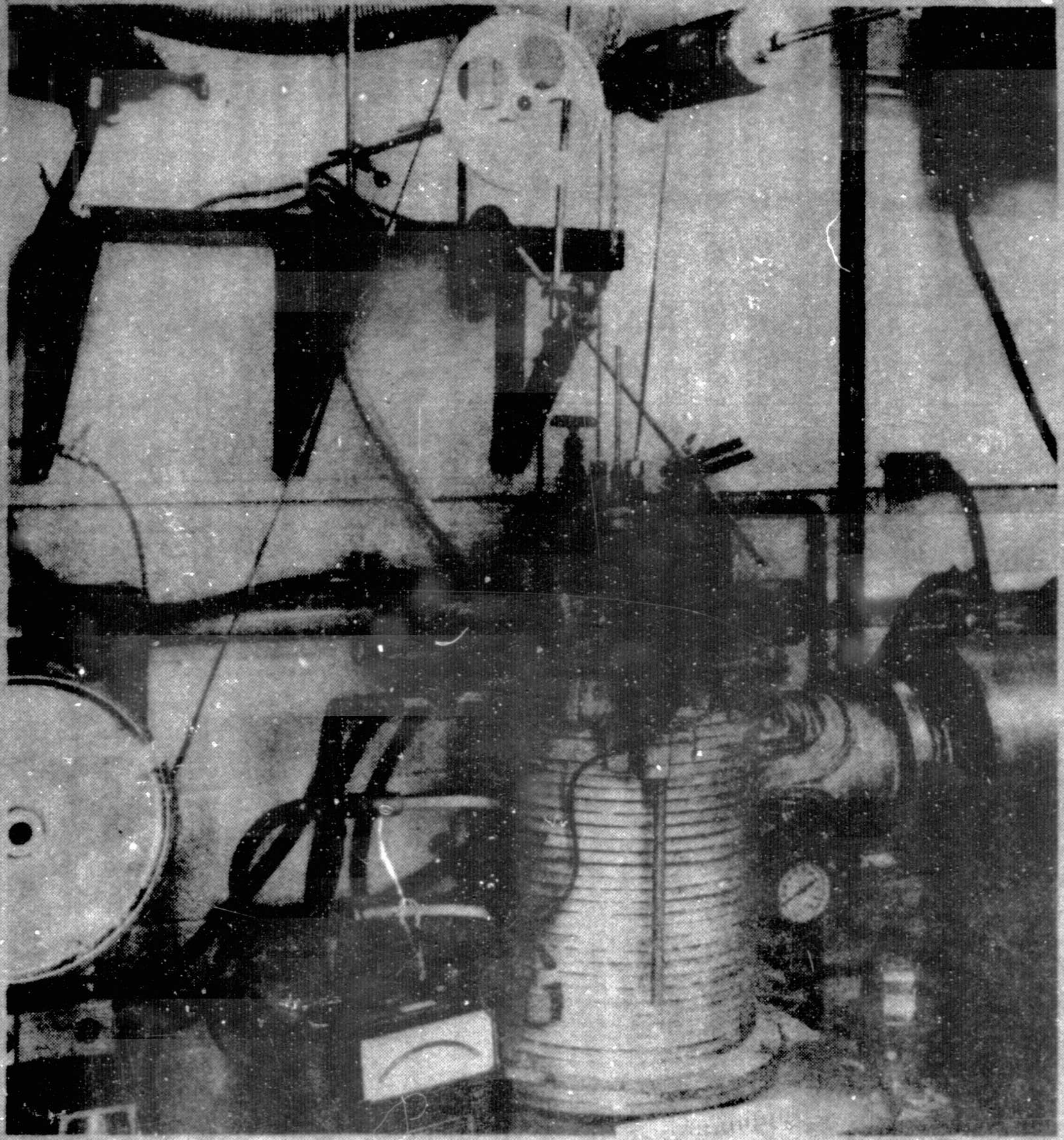
Material	Resistivity (ohm–cm)
SiC	$10^3 - 10^5$
B	7×10^3
B_4C	5×10^{-1}
TiC	10^{-4}
BN	10^{13}
Si_3N_4	10^{17}
SiO_2	10^{16}

Continuous Glass Coating Apparatus



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Graphite Fiber Drawn Through E-Glass

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Colloidal SiO_2

(30%)

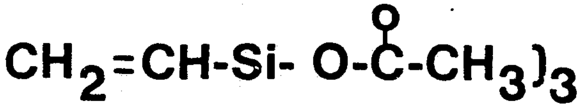
Dip Coating

Dilutions	Results
as received	Crusty coating (stiff)
1/2	
1/4	
1/9	Coating not observed
1/20	
1/50	
1/100	

Electrophoresis

Voltage	Results
10v	Coating with O_2 given off at electrode
5v	
3v	

Organo-Silicon Coatings and Thermal Conversion

Material deposited	Number of coats	EDAX analysis Si deposited/ Si background
$CH_3\text{-}Si\text{-}(OC_2H_5)_3$	1	Trace
(methyltriethoxysilane)	5	Trace
 $CH_2{=}CH\text{-}Si\text{-}\ O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3)_3$	1	230/100
(Vinyl triacetoxysilane)	5	1250/100
Silicone resin G.E. SR 355	1	Trace
	5	1100/100
Ethyl silicate prepolymer	1	675/100
	5	2250/100

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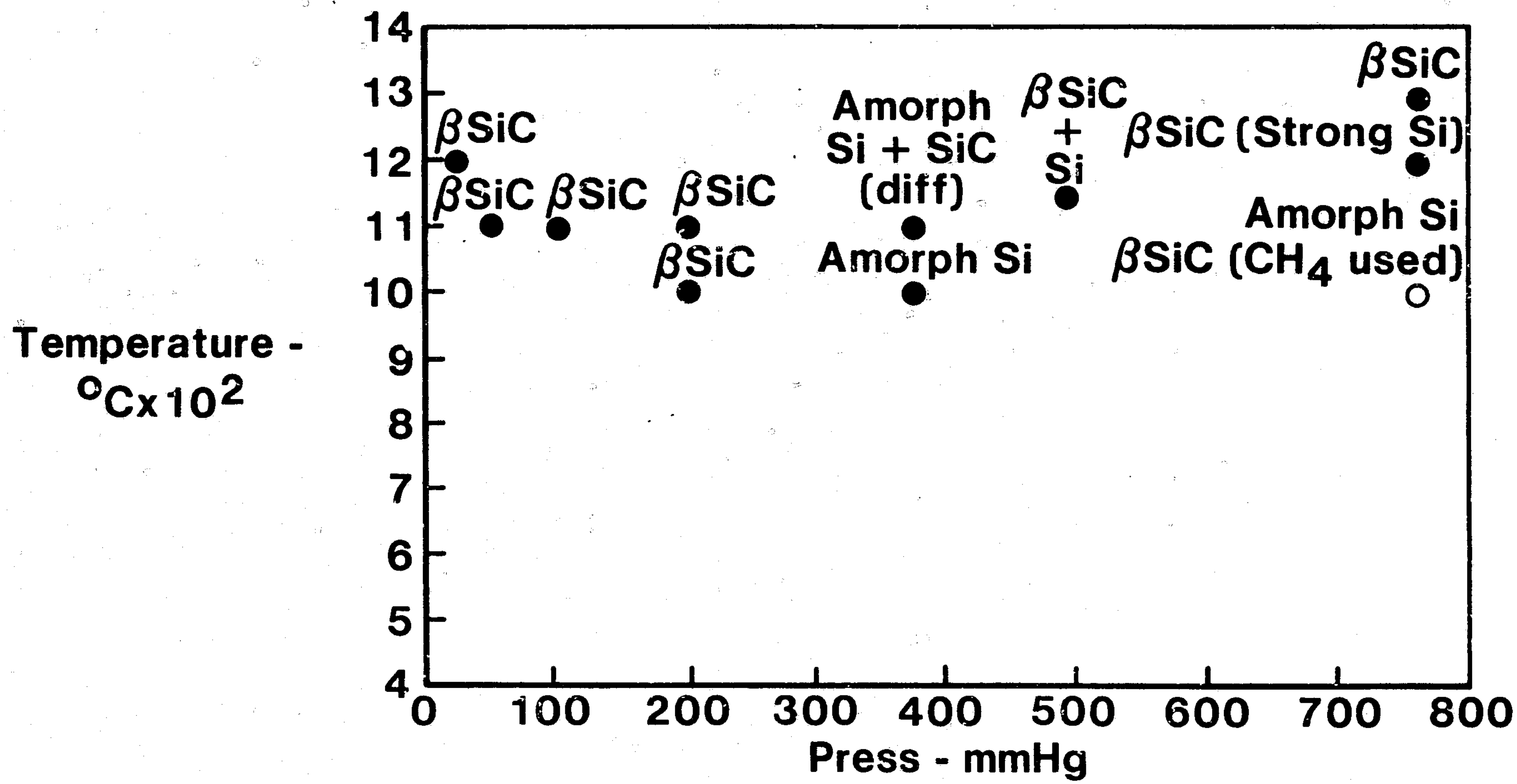
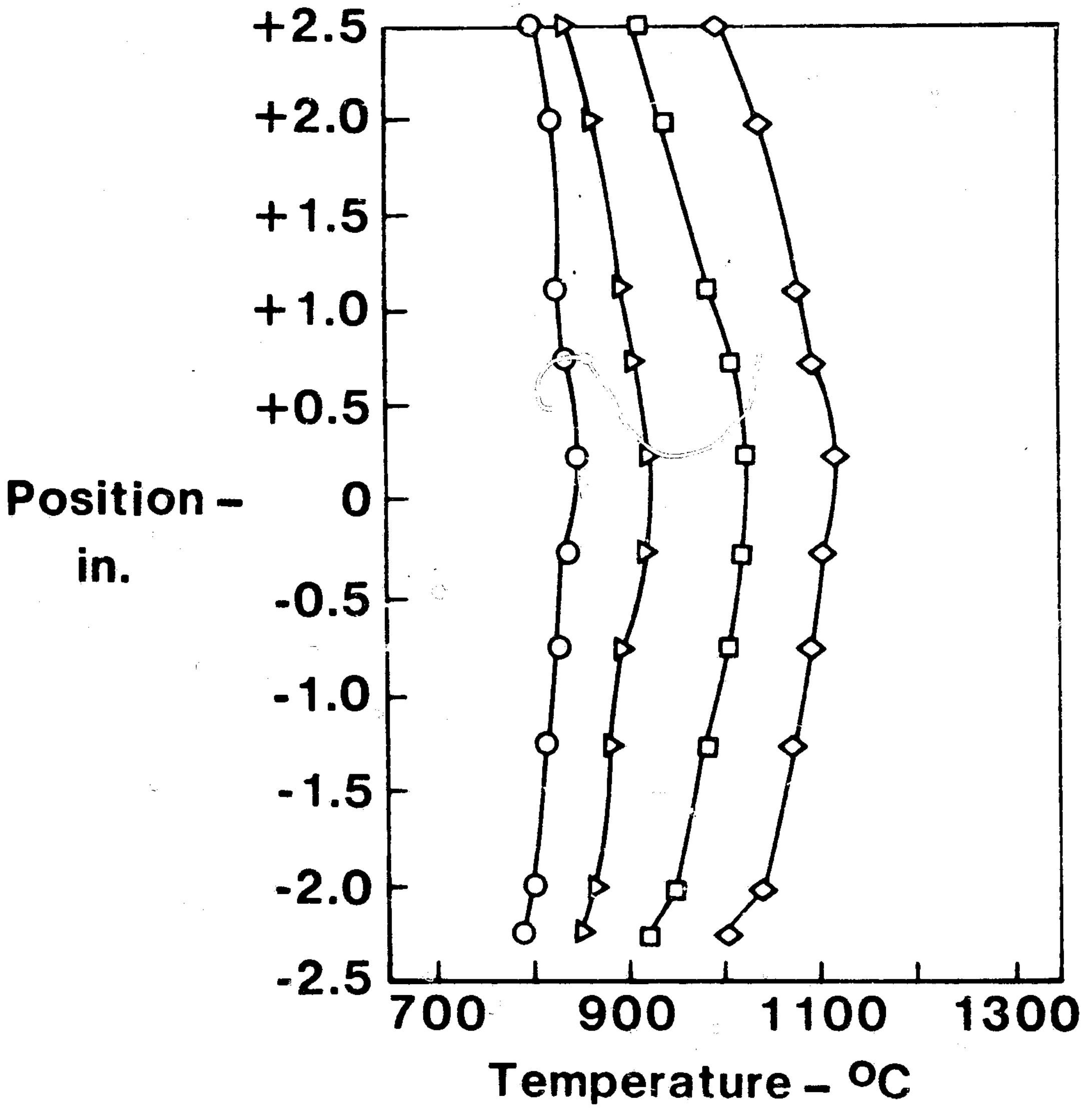
X-Ray Data for SiC Produced at Various Temperatures and Pressures



Thermal Profile in Reactor Zone for Four Power Levels



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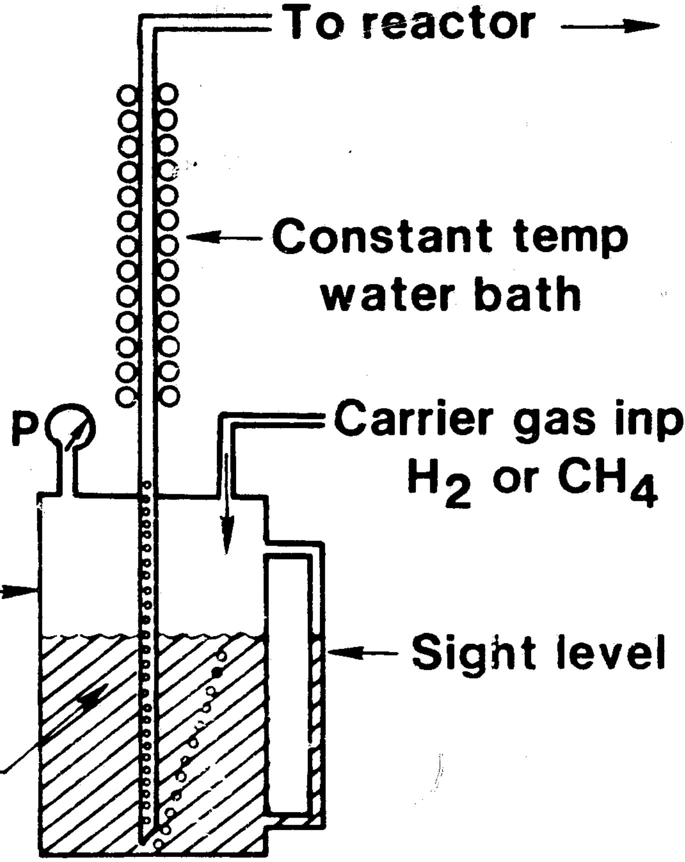
Silane Evaporator



To reactor →

Constant temp water bath

P

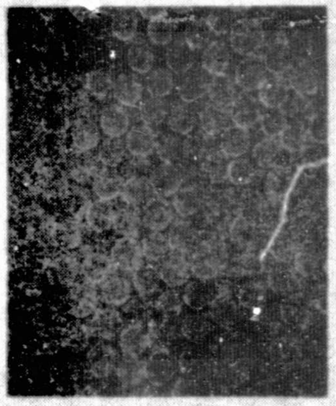
Carrier gas input H_2 or CH_4

Stainless steel tank

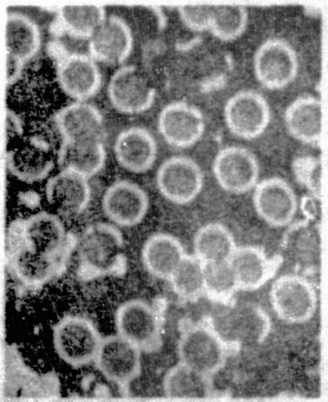
Sight level gage

Methyldichlorosilane CH_3SiHCl_2

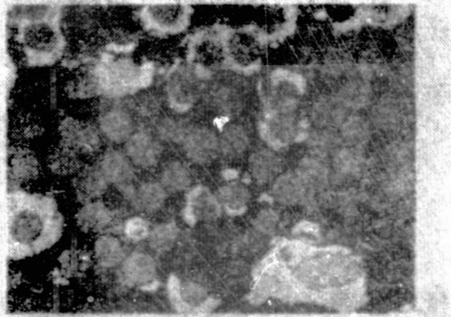
SiC on Graphite Fiber Static Run



A 1/4 in. into graphite susceptor



B 1 in. into graphite susceptor



C 1/2 in. over graphite susceptor

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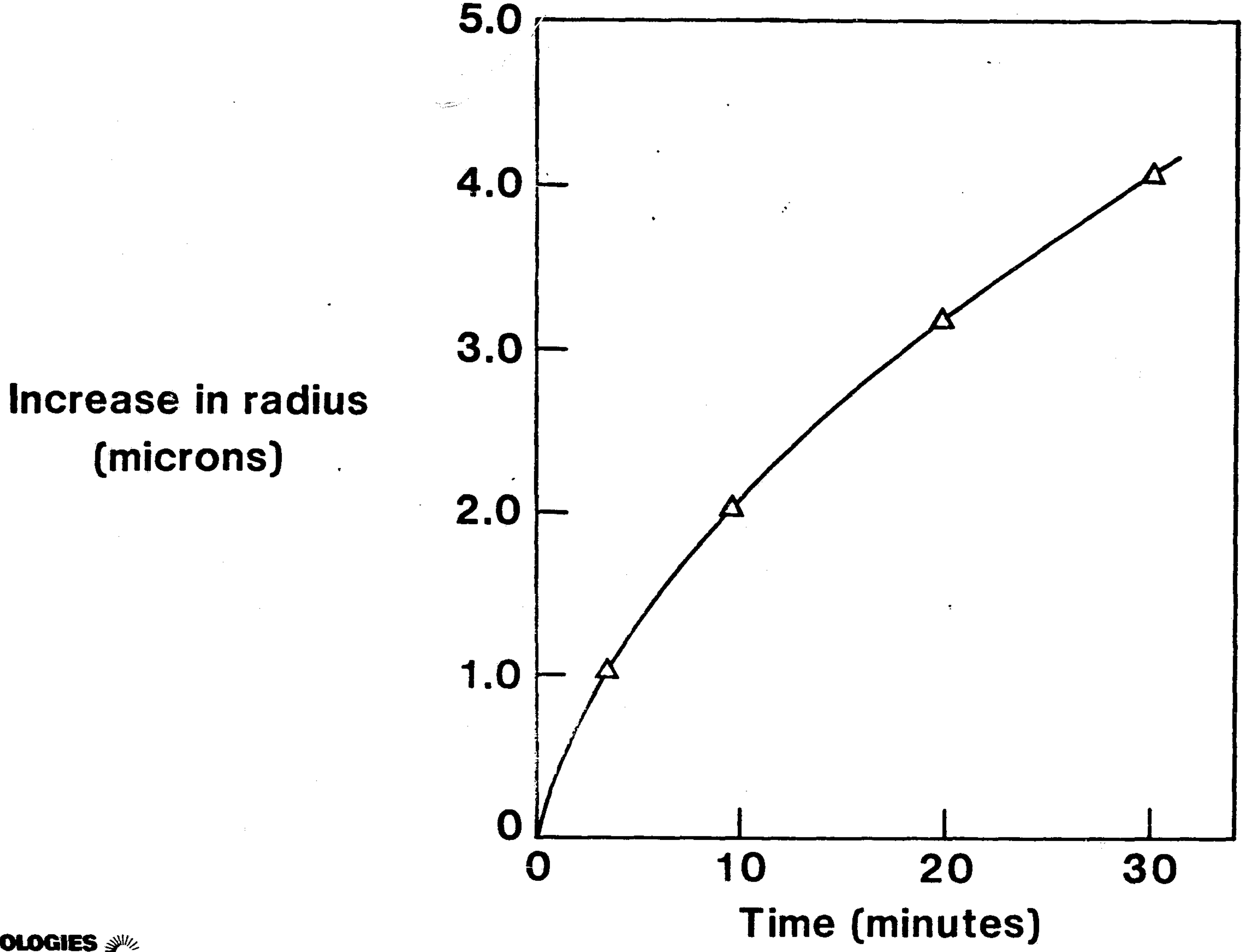
Deposition Rate

Temp 1050 °C Amospheric pressure Static runs



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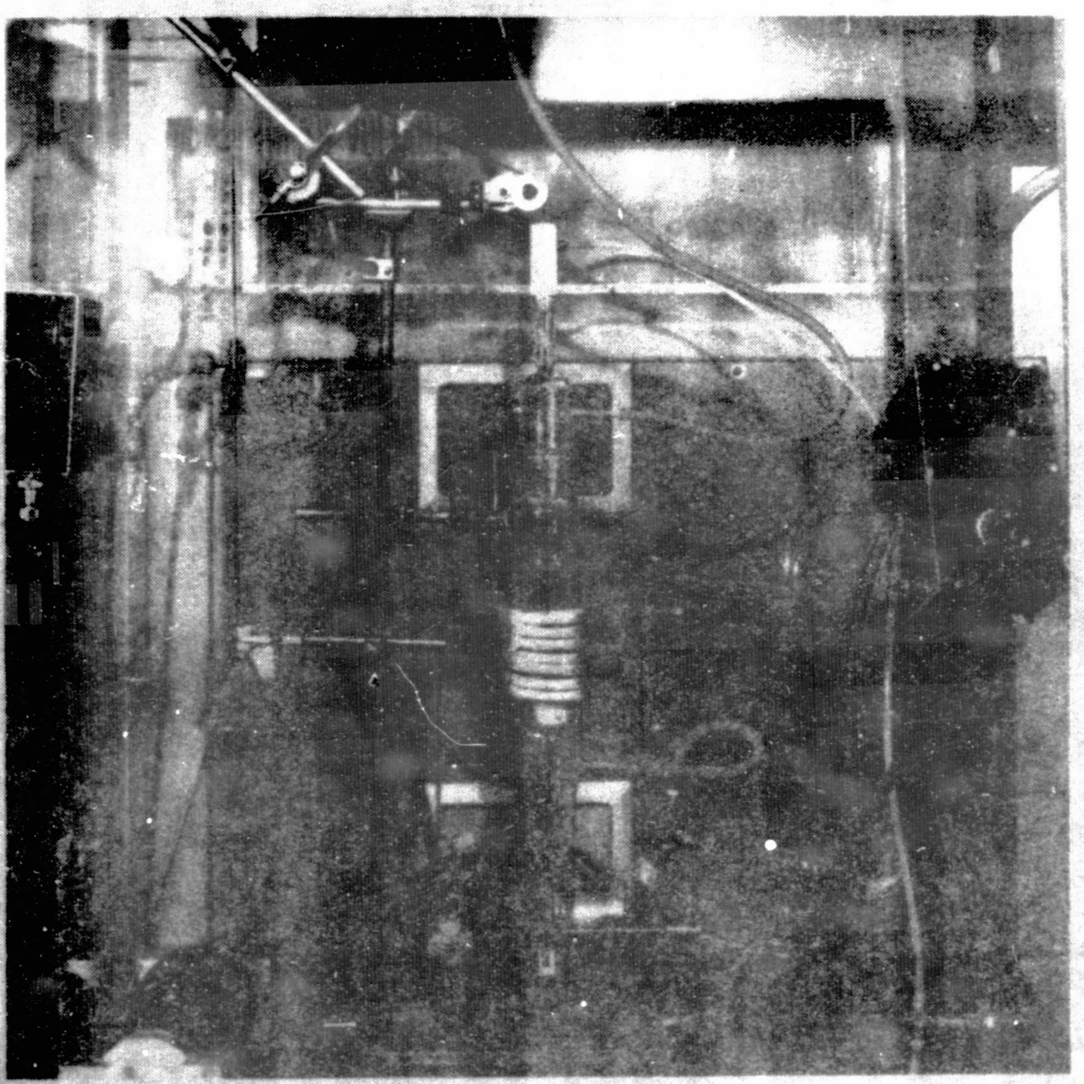
Chemical Vapor Deposition Apparatus



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78-01-8 78-03-132-1

BORON CARBIDE AND SILICON CARBIDE COATED GRAPHITE FIBERS

RAYMOND J. SUPLINSKAS

AVCO SPECIALTY MATERIALS DIVISION

MARCH 23, 1978

- COATING MATERIALS:

  SILICON CARBIDE

  BORON CARBIDE

- SUBSTRATE

  THORNEL 300

- COATING THICKNESS

  0.1 MICRON

BULK ELECTRICAL PROPERTIES

- RESISTIVITY

SILICON CARBIDE	~ 100 Ohm-cm
BORON CARBIDE	~ 1 Ohm-cm
GRAPHITE	$\sim 10^{-3}$ Ohm-cm

- SiC IS HI-TEMP. SEMICONDUCTOR

  BREAKDOWN VOLTAGE - 1100 VOLTS

  (1/4" SPECIMEN)

- OTHER PROPERTIES
    - REFRACTORY
    - DIFFUSION BARRIER
    - ENHANCED WETTING
- OXIDIZED COATINGS
    - SiO_2 - INSULATOR
    - B_2O_3 - FUSIBLE

- CVD PROCESS

$$4BCl_3 + CH_4 + 4\ H_2 \rightarrow B_4C + 12HCl$$

$$4BCl_3 + C + 6H_2 \rightarrow B_4C + 12HCl$$

$$(CH_3)\ \ Cl_3Si \rightarrow SiC + 3HCl$$

- RATE CONTROL VS. DIFFUSION CONTROL
- CVD PARAMETERS
  - TEMPERATURE
  - PLATING GAS COMPOSITION
  - FLOW GEOMETRY
  - RESIDENCE TIME

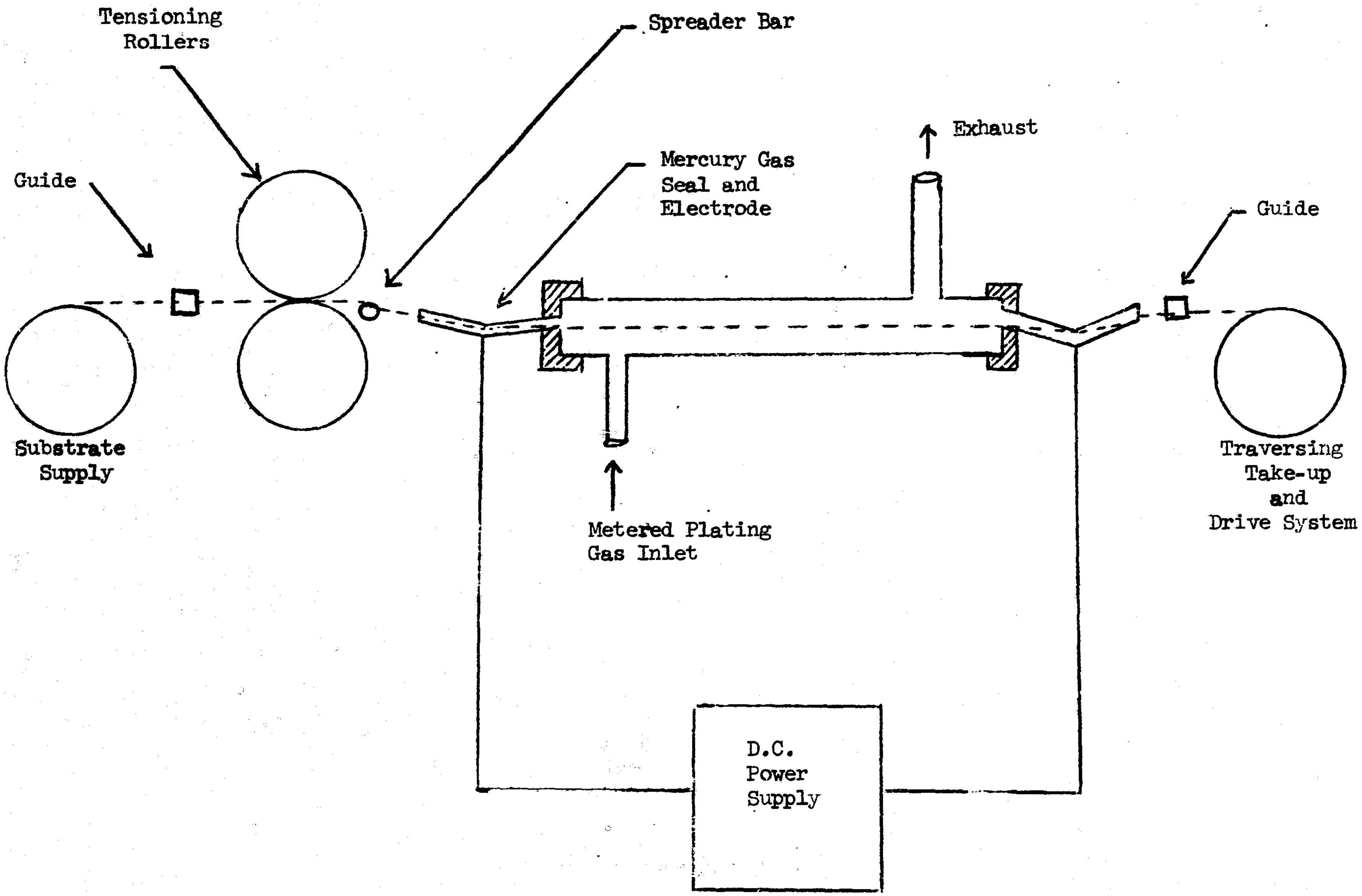


Figure 1. Sketch of CVD Reactor to Produce Carbide Coatings on Graphite

COATING CHARACTERIZATION

SEM

AUGER SPECTROSCOPY

TENSILE TESTS

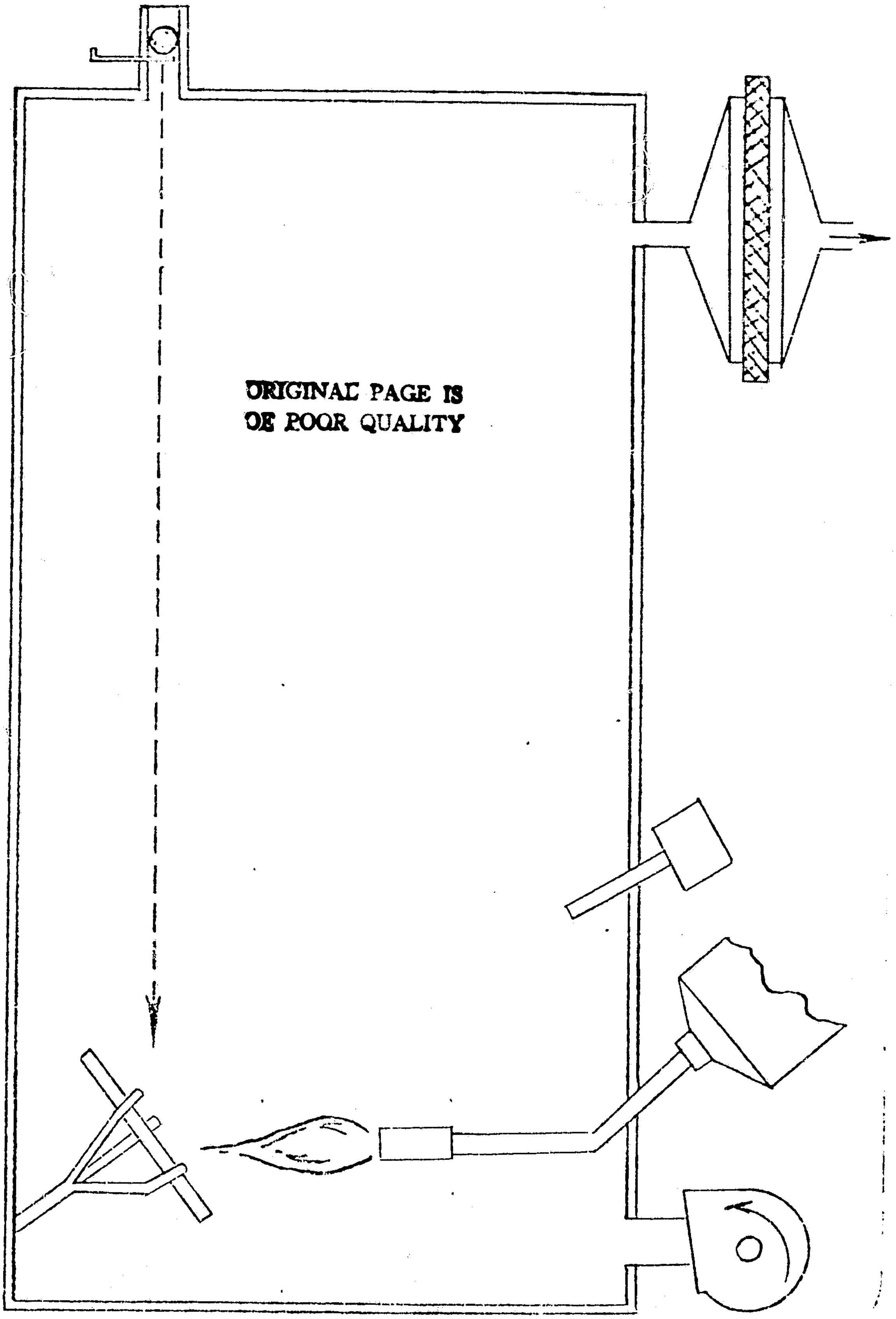
BORON NITRIDE, SILICON CARBIDE AND SILICONE COATED GRAPHITE FIBERS

HERBERT F. VOLK
UNION CARBIDE CORPORATION

MARCH 23, 1978

TECHNICAL TASKS

1. HIGH RESIDUE SILICON COATINGS.
2. BORON NITRIDE COATINGS.
3. SILICATE COATINGS.
4. SILICONE CARBIDE COATINGS.
5. BURN TEST CHAMBER.



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REVIEW OF NASA-AMES MATERIALS
MODIFICATION PROGRAM

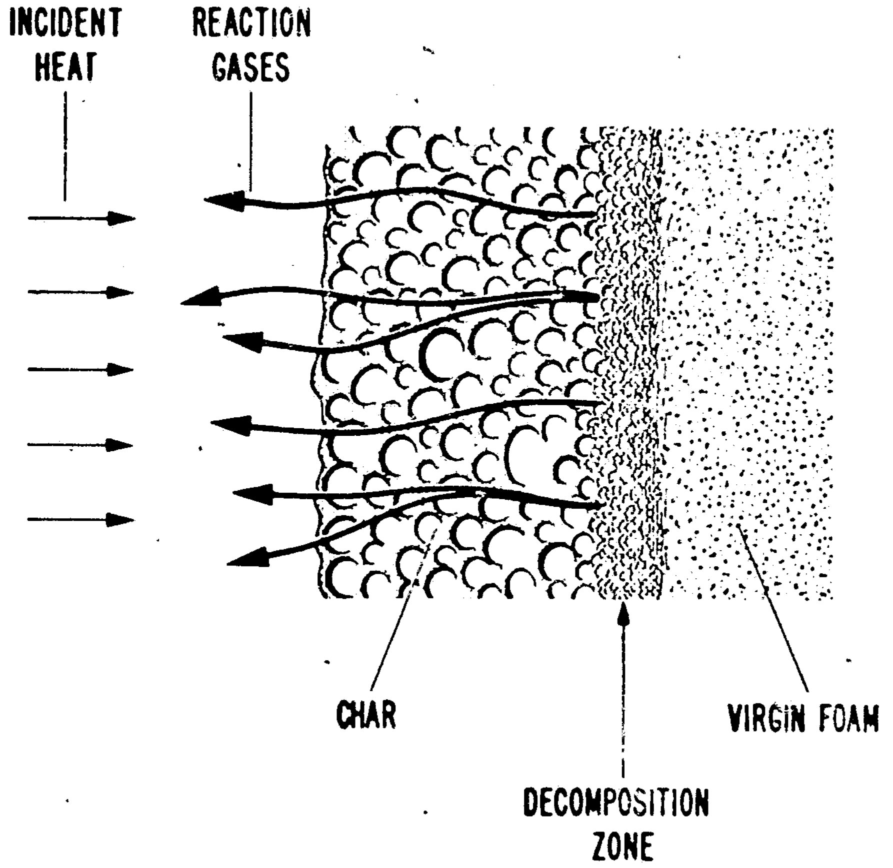
"AN APPROACH TO THE DEVELOPMENT OF FIRE RESISTANT COMPOSITES"

JOHN A. PARKER

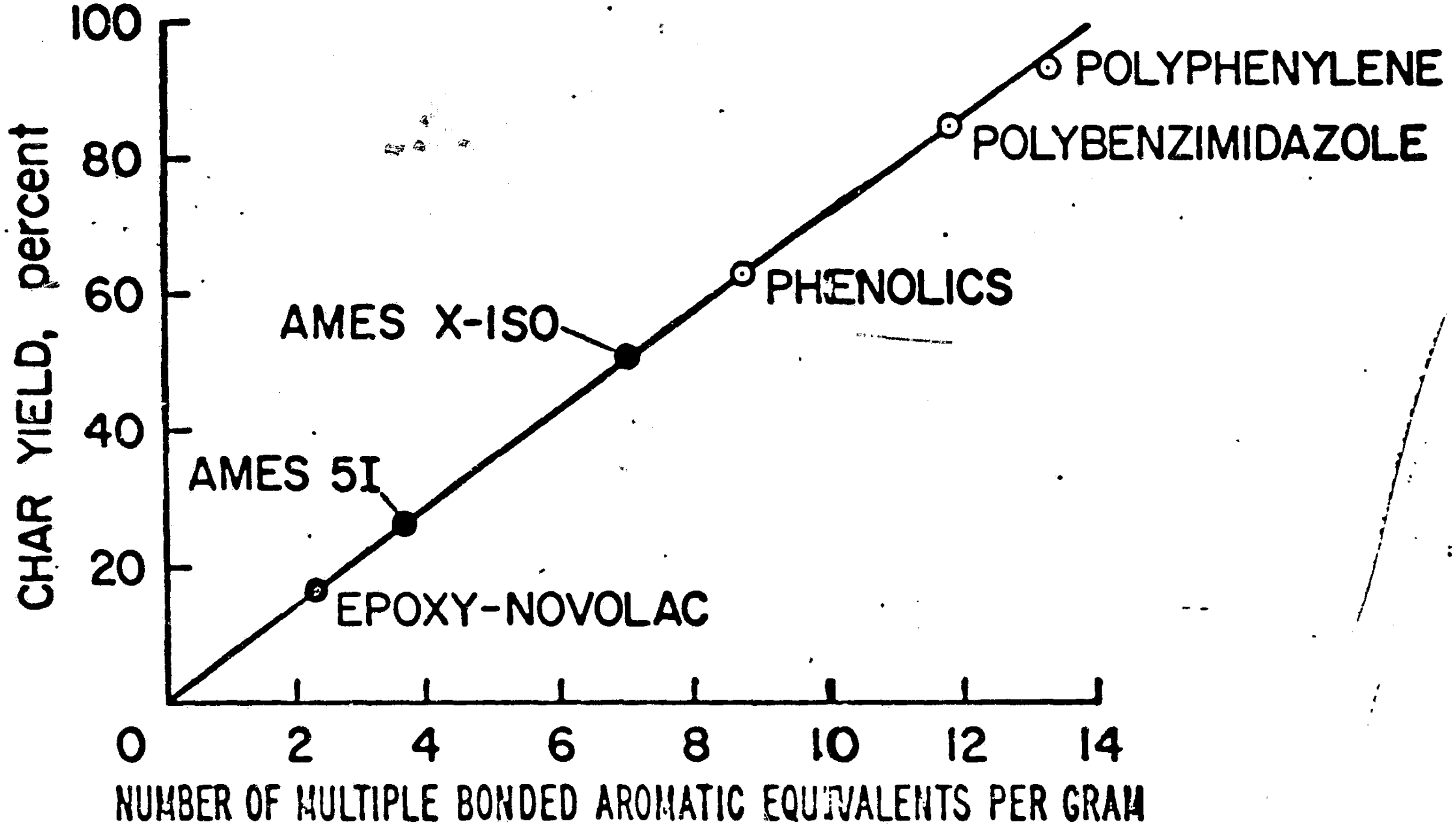
NASA AMES RESEARCH CENTER

MARCH 23, 1978

TYPICAL REACTION OF CHAR FORMING FOAMS DUE TO THERMAL LOADS



CORRELATION OF PRIMARY THERMOCHEMICAL CHAR YIELD WITH MOLECULAR STRUCTURE



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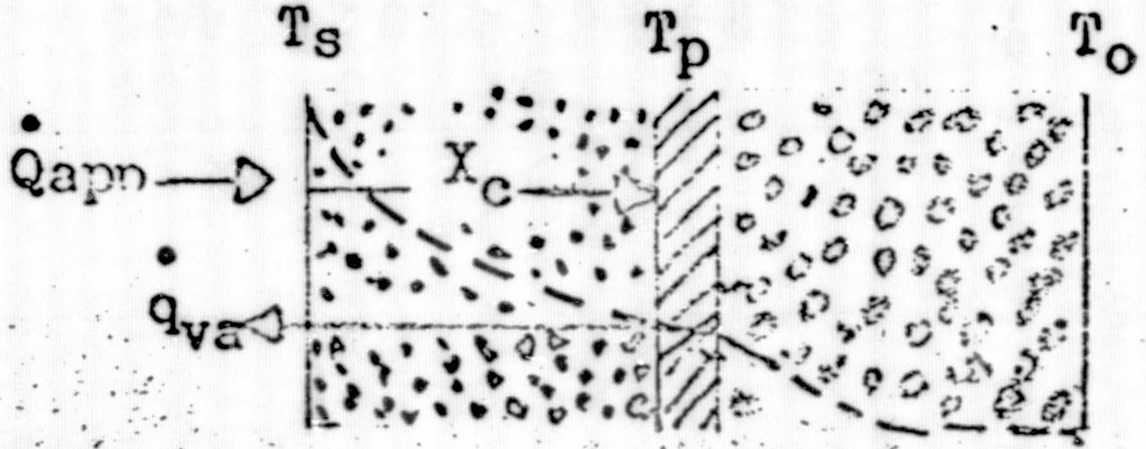


$$Y_c :: \int_0^t \mathring{X}_c \, dt :: \int_0^t \mathring{Q}app \, dt$$

$$\mathring{X}_c :: \frac{1}{\mathring{q}_{va}}$$

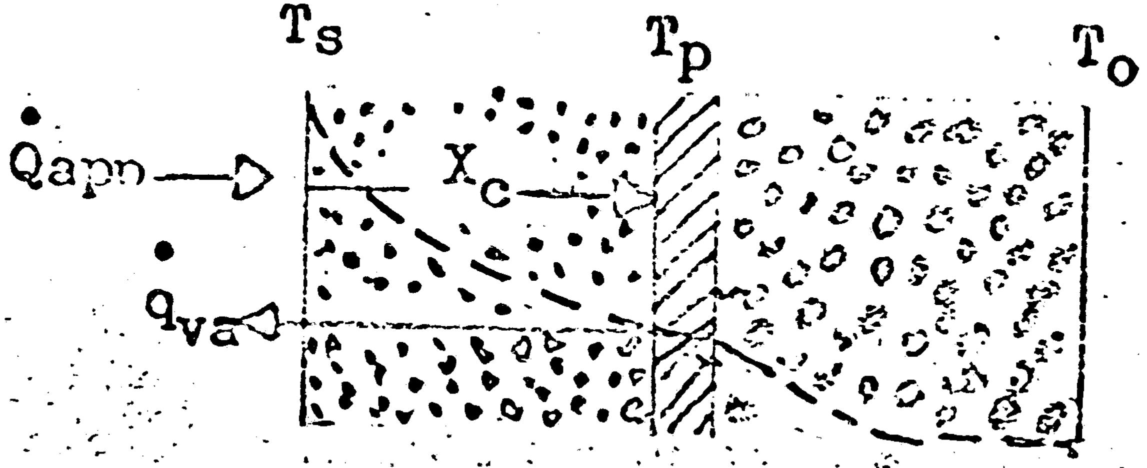
$$\therefore Y_c :: \frac{1}{q_{va}} \Big|_t$$

Administration

NASA

NAME ______________________________ NO. ________

✓ ③

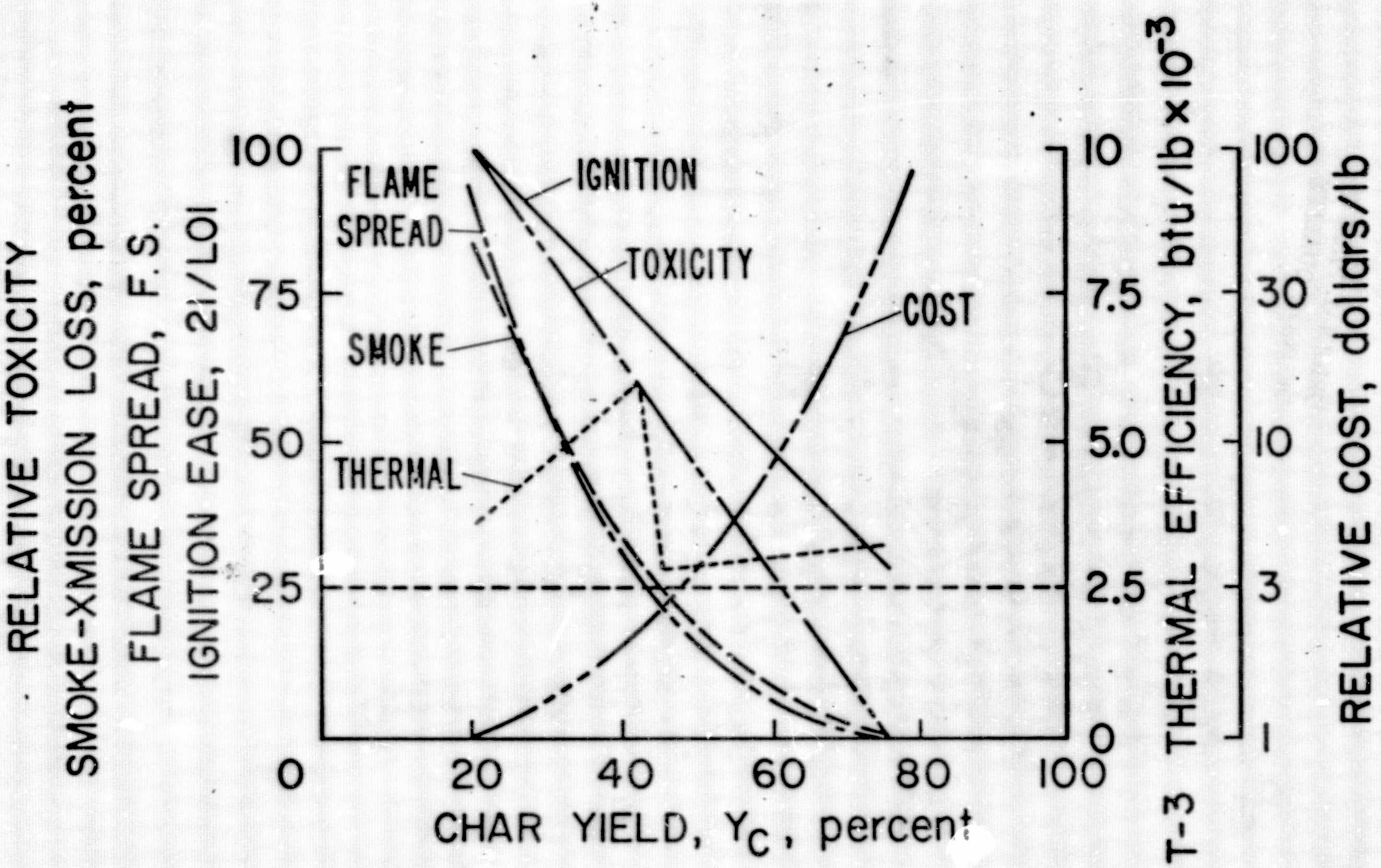


$$Y_c :: \int_0^t \dot{X}_c \, dt :: \int_0^t \dot{Q}_{app} \, dt$$

$$\dot{X}_c :: \frac{1}{\dot{q}_{va}}$$

$$Y_c :: \left. \frac{1}{q_{va}} \right|_t$$

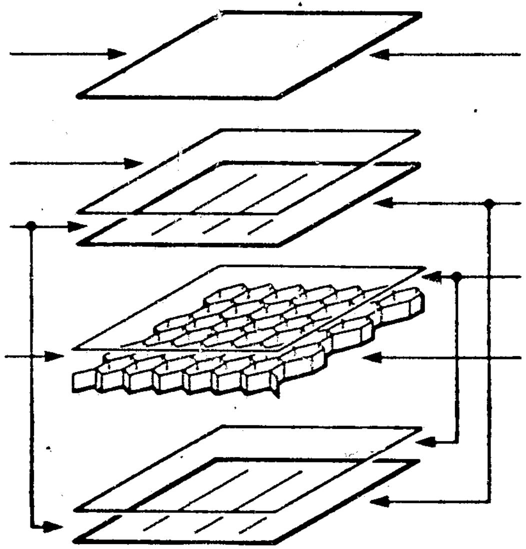
SUMMARY OF PROPERTIES OF CHAR FORMING FOAMED POLYMERS



R4

TOP VERTICAL

COMPOSITE CONFIGURATION OF AIRCRAFT INTERIOR PANELS



STATE-OF-THE-ART

POLYVINYL FLUORIDE FILM, 0.0025 cm WITH POLYMETHYL METHACRYLATE ADHESIVE UNDERNEATH

POLYVINYL FLUORIDE, 0.005 cm WITH DECORATIVE INK ON TOP

TWO PLIES, TYPE 181, AND TYPE 120 E GLASS EPOXY PREPEG

POLYAMIDE PAPER HONEYCOMB

ADVANCED

PHENOLPHTHALEIN POLYCARBONATE FILM, 0.005 cm WITH DECORATIVE INK ON TOP AND CHLORENDIC ANHYDRIDE-EPOXY ADHESIVE UNDERNEATH

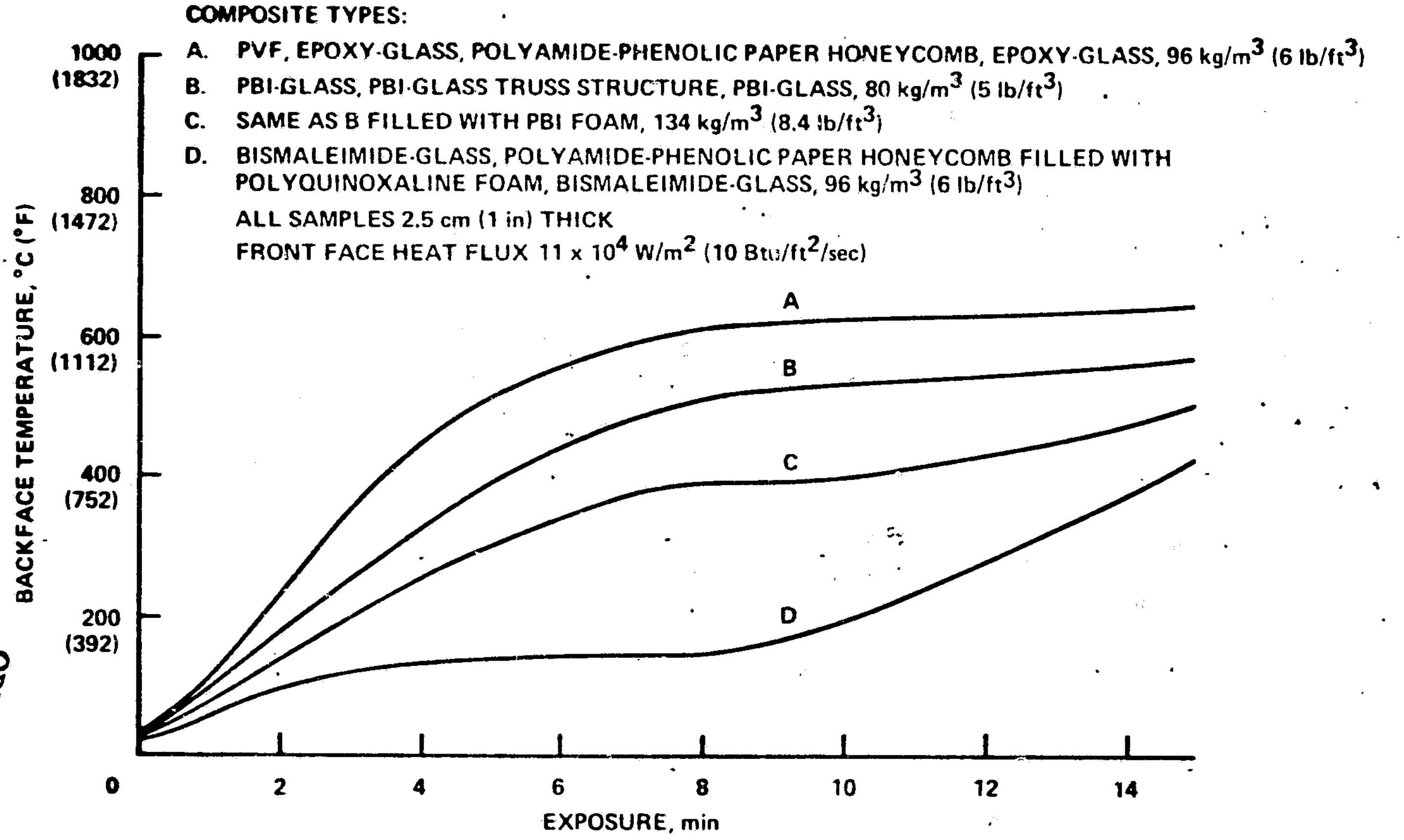
ONE PLY TYPE 181 E GLASS BISMALEIMIDE PREPEG

POLYAMIDE ADHESIVE

POLYQUINOXALINE FOAM IN POLYAMIDE HONEYCOMB

TOP VERTICAL

THERMAL DIFFUSIVITY



TOP VERTICAL

COMPARISON OF FLAMMABILITY PROPERTIES OF AIRCRAFT INTERIOR PANELS

● COMPOSITE PROPERTIES	PVF, EPOXY-GLASS POLYAMIDE HONEYCOMB, EPOXY-GLASS	PHENOL-POLYCARBONATE, BASMALEIMIDE-GLASS, POLYAMIDE HONEYCOMB FILLED WITH POLYQUINOXALINE FOAM, BISMALEIMIDE-GLASS
DENSITY (ASTM D 71)	96 kg/m^3	96 kg/m^3
FLATWISE TENSILE STRENGTH (ASTM C307), 24°C	0.02-0.05 N/m^2	–
FIRE ENDURANCE, NASA AMES T-3 THERMAL TEST FACILITY, TIME (min) TO REACH BACK-FACE TEMPERATURE OF 204°C, FRONT FACE HEAT FLUX 11 × 10^4 W/m^2	2	10
SMOKE DENSITY (NBS), Ds 4 min. SPECIFIC OPTICAL DENSITY	87	16
FAR 25.853, VERTICAL TEST METHOD STAND. 191, METHOD 5903	PASSES	PASSES
● COMPONENT SMOKE DENSITY MAXIMUM SPECIFIC OPTICAL DENSITY (NBS SMOKE CHAMBER)	POLIVINYL FLUORIDE 7 POLYAMIDE PHENOLIC PAPER 2 EPOXY RESIN 90 GLASS –	PHENOL-POLYCARBONATE 5 NOMEX PHENOLIC PAPER 2 BISMALEIMIDE RESIN 9 –
● COMPOSITE MATERIAL BALANCE % BY WEIGHT	POLYVINYL FLUORIDE 7.6 POLYAMIDE PHENOLIC PAPER 20.5 181, 120 GLASS 41.9 EPOXY RESIN 30.0	PHENOL POLYCARBONATE 5.0 POLYAMIDE PHENOLIC PAPER 20.5 181 GLASS 30.0 BISMALEIMIDE RESIN 30.0 POLYQUINOXALINE 14.5

TOP VERTICAL

STATUS OF NEW RESIN MATERIALS DEVELOPMENT

OBJECTIVE

To develop resins which provide enhanced fire resistance, and provide for minimal fiber release in graphite composites subjected to a fire and impact environment.

STATUS

1. High char yield resins with char yield (800°C, N_2) in excess of 50% such as phenolics and polyimides can, under post-crash fire simulation, almost totally eliminate conductive fiber release.
2. Currently available aromatic polymers such as phenolics and polyimides exhibit poorer fracture toughness than the currently used epoxy resins.
3. Currently used epoxy resins are also sensitive to photo-thermal oxidative degradation as well as weathering (humidity) resulting in a resin poor composite surface.

NEEDS

1. Development of new resins which provide both high char yield, fracture toughness and weathering resistance.
2. Development of hybrid composites and modified fibers.

STATUS OF NEW RESIN MATERIALS DEVELOPMENT

APPROACH Advanced Resin Development and Modifications

- a. Polystyryl Pyridene (PSP) - SNPE (RFP issued)
- b. Bismaleimide - Technochemie (RFP issued)
- c. Phenolics - Resins obtained from Ciba-Geigy, Fiberite, Narmco
- d. Other Resins - Benzyl - Weyerhauser; Epoxy Copolymers - New York Polytechnic Institute; HR-600 - Hughes (being procured)

2. Curing Agents for Resins
    - a. New curing agent to reduce voids and to provide optimum fracture-toughness characteristics in new resin-graphite composites
3. Hybrid Composites
    - a. Use of metallic coatings to provide oxidation resistance and fire protection
    - b. Use of intumescent coating to provide resistance to weathering and fire.
4. Fiber Modifications
    - a. Reduce fiber conductivity by heating fibers in various atmospheres (NO etc)
    - b. Evaluate other char forming mechanisms for resin-fiber combinations.

TOP VERTICAL

PROGRAM OBJECTIVE: COMPOSITE PRIMARY AIRCRAFT STRUCTURES

SPECIFIC OBJECTIVE: COMPOSITE WING

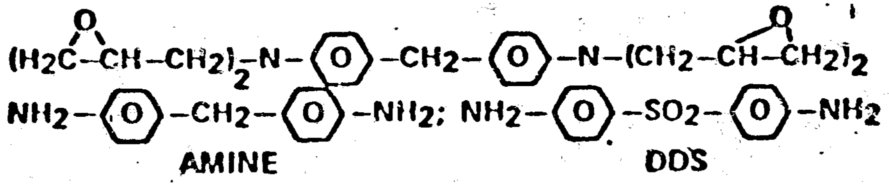
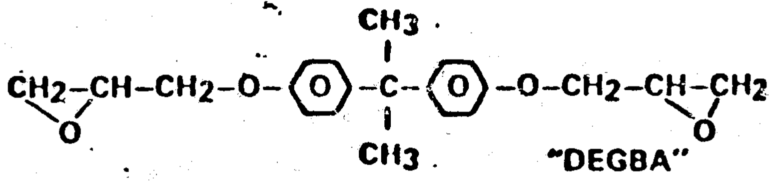
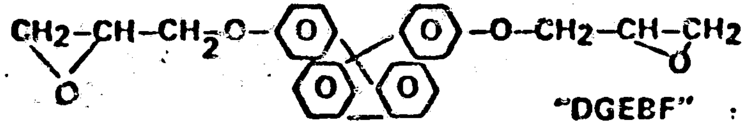
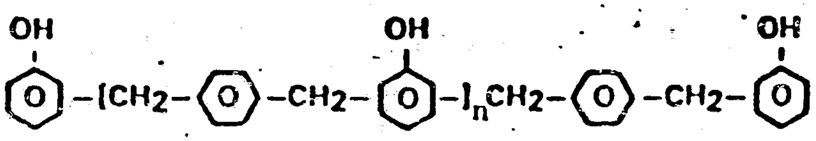
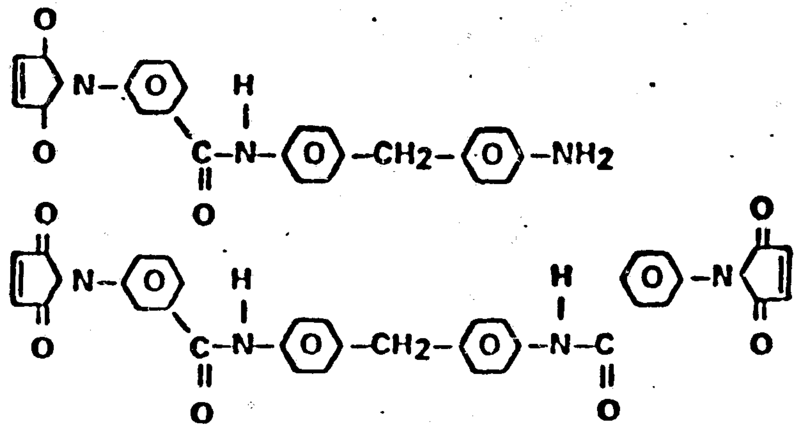
RTOP: EVALUATION AND DEVELOPMENT OF ADVANCED STRUCTURAL COMPOSITE MATERIALS (743-02-11)

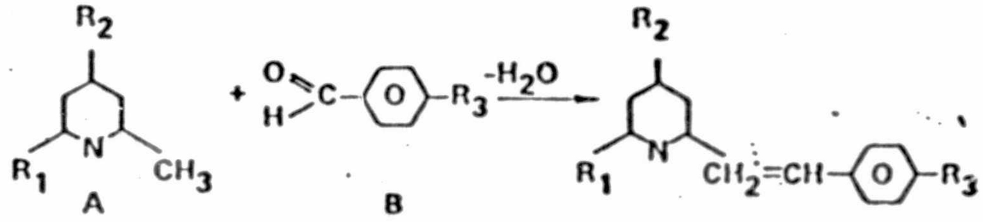
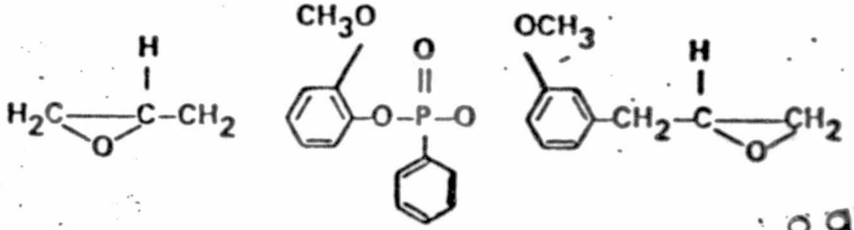
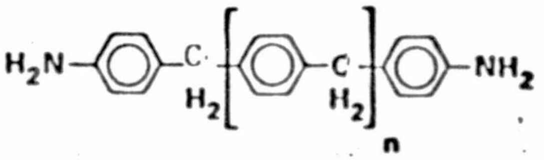
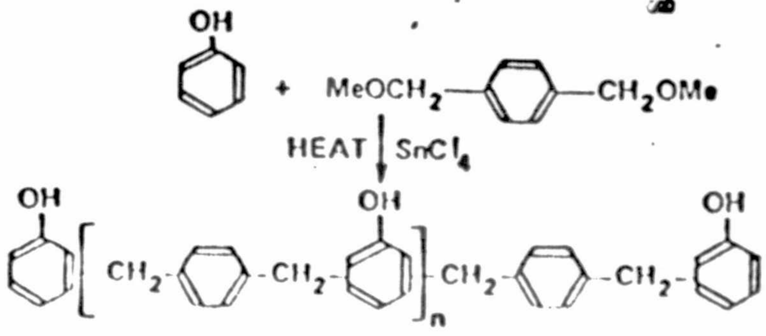
OBJECTIVES: TO SELECT, PREPARE AND EVALUATE RESIN/GRAPHITE FORMULATIONS WHICH ARE MORE FIRE RESISTANT THAN CURRENTLY AVAILABLE STATE OF THE ART EPOXY/GRAPHITE COMPOSITES.

TARGETS:

- EVALUATE ADVANCED RESIN SYSTEMS INCLUDING EPOXIES, NOVOLAC PHENOLICS, POLYIMIDES, PSP AND BISMALEIMIDE.
- EVALUATE THERMAL PROTECTION COATINGS.
- DETERMINE DEGRADATION OF MECHANICAL PROPERTIES UNDER THERMAL/FIRE LOAD IN STATE OF THE ART AND ADVANCED COMPOSITES.
- CHARACTERIZE PRODUCTS OF THERMAL/FIRE DEGRADATION.

RESIN MATRICES FOR COMPOSITES

RESIN/CURING AGENT	TYPICAL CHEMICAL STRUCTURE
EPOXY RESIN BASED ON METHYLENE DIANILINE CURED WITH AROMATIC AMINE OR 4,4' DIAMINO DIPHENYL SULPHONE (DDS) CIBA GEIGY MY 720; NARMCO 5208; FIBERITE 1034C	
EPOXY RESIN BASED ON DIGLYCIDYL ETHER OF BISPHENOL A (DGEBA) OR 9,9-BIS (4-HYDROXYPHENYL) FLUORENE (DGEBF) OR COPOLYMERS CURED WITH TRIMETHOXYBOROXINE (TMB) OR MDA OR DDS	 "DEGBA"  "DGEBF"
PHENOLIC NOVOLAC RESIN BASED ON CONDENSATION OF DIMETHOXY-P-XYLENE AND PHENOL CURED WITH HEXAMINE (XYLOK) CIBA GEIGY XYLOK 210	
POLYBISMALEIMIDE PREPOLYMER (TECHNOCHEMIE M751)	

RESIN CURING AGENT	TYPICAL CHEMICAL STRUCTURE
POLYSTYRYL PYRIDENE RESIN (SNPE-PSP 6030)	 MONOMER A/B, mole/mole: 0.936
BIS(4-GLYCIDYL-2-METHOXYPHENYL) PHENYLPHOSPHONATE EPOXY RESIN CURED WITH N,N-DIETHYLAMINOPROPYLAMINE (DEAPA) (HUGHES)	
POLYMETHYLENE POLYPHENYLAMINE (CIBA GEIGY NCNS-12M)	
BENZYL RESIN (WEYERHAUSER)	 PRE POLYMER + 2n + 2MeOH

SIGNIFICANT THERMOCHEMICAL PROCESS CHARACTERISTICS OF DIFFERENT TYPES OF COMPOSITE MATRIX RESINS ON THE FIRE ENVIRONMENT

A. THERMOCHEMICAL SCISSION (VAPOR PRODUCTION)

1. TEMPERATURE INDUCED CHAIN SCISSION
    - a. RANDON CHAIN FRAGMENTATION
    - b. SIDE CHAIN ELIMINATION
    - c. RADICAL UNZIPPING MONOMER PRODUCTION
2. THERMAL CROSS-LINKING PROCESSES (CHAR FORMATION)
    - a. THERMALLY INDUCED BIFUNCTIONAL REACTIONS OF CHAIN BEARING CHEMICAL GROUPS.
    - b. THERMAL CRACKING REACTIONS PRODUCING RADICAL SPECIES WHICH COMBINE TO FORM STABLE POLYCYCLIC AROMATIC MOEITIES.
    - c. AROMATIZATION INCLUDING CYCLIZATION/ DEHYDROGENATION.

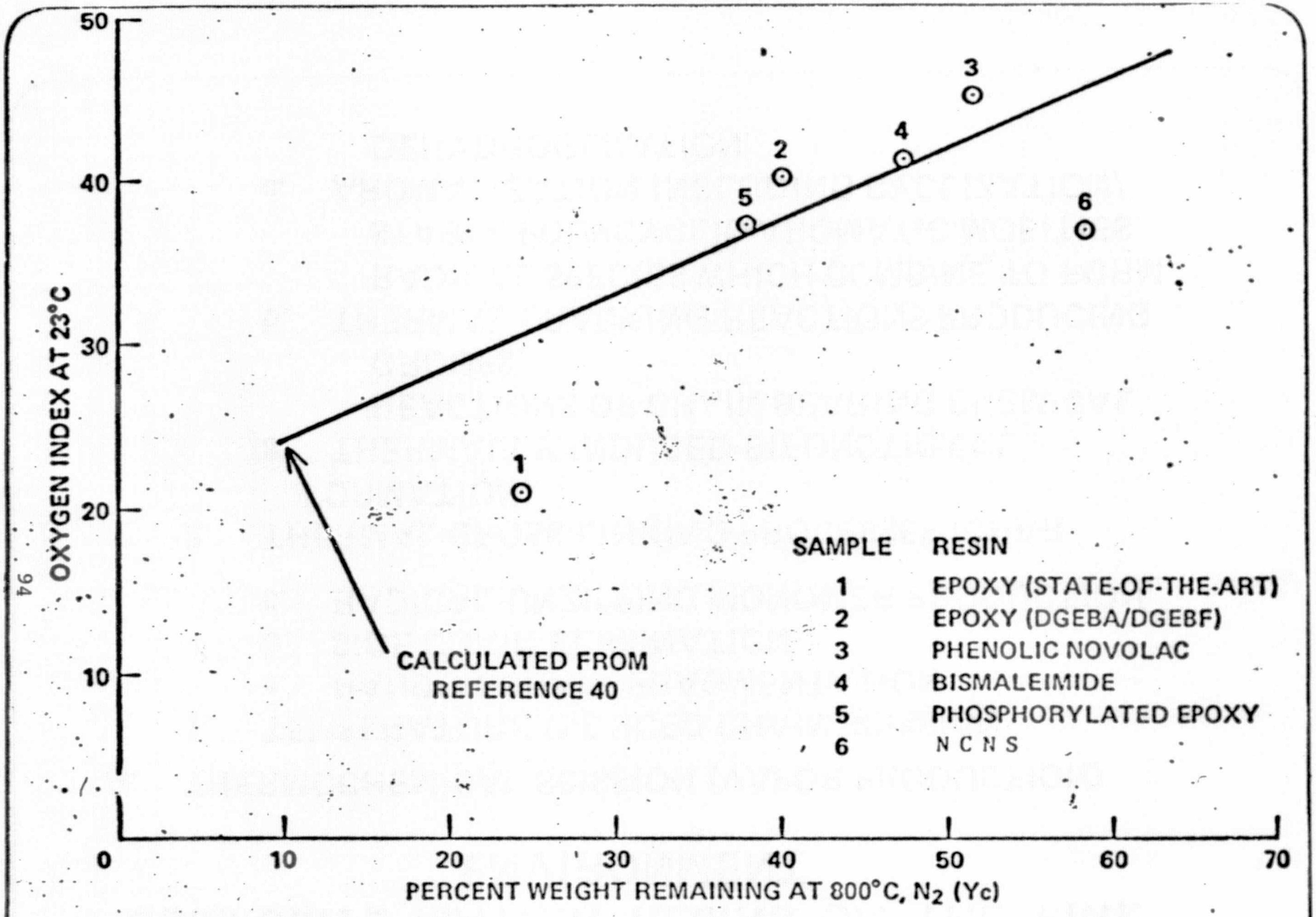
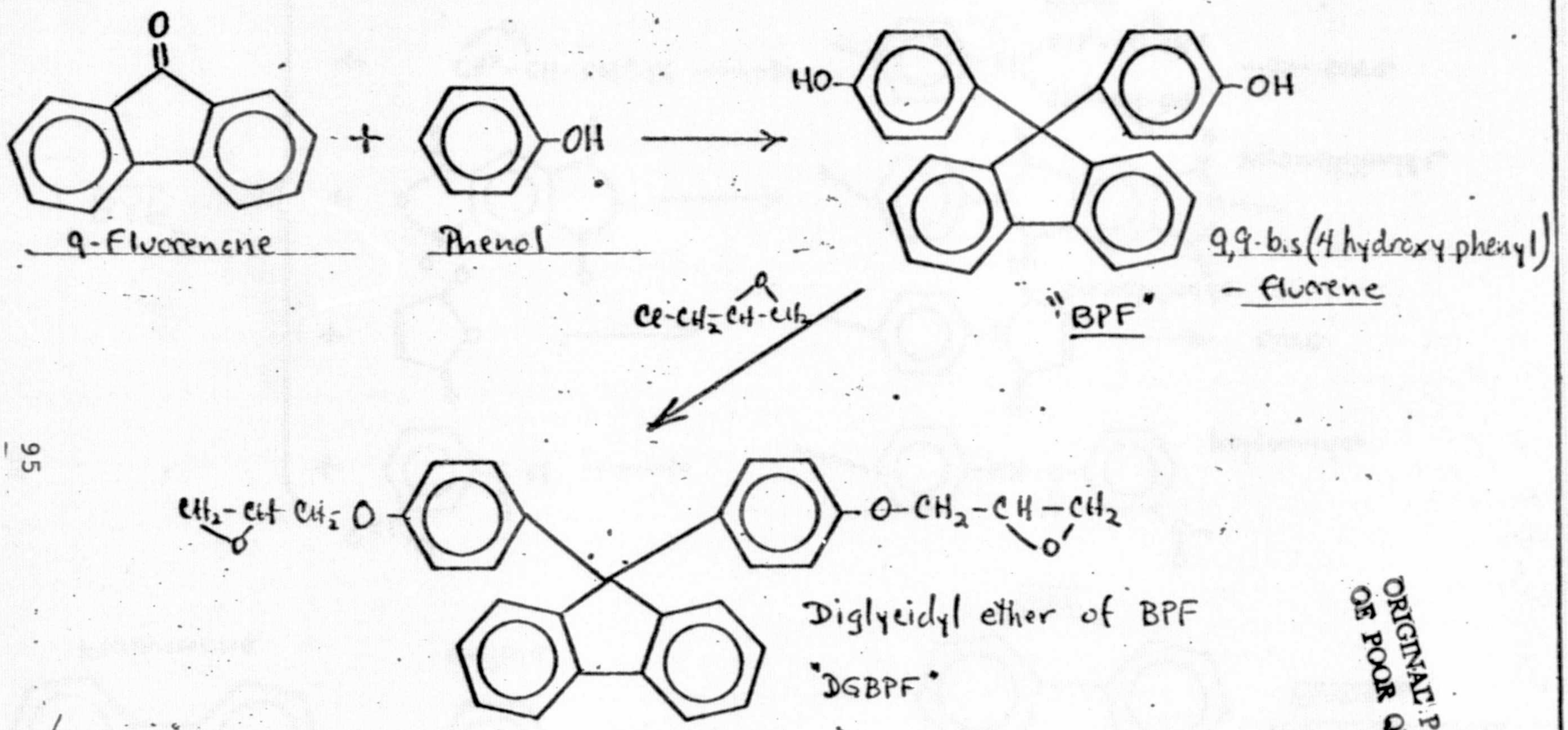


Figure 8 Effect of char yield of thermoset polymers on oxygen index.

TOP VERTICAL

CHEMISTRY OF NEW EPOXY RESINS

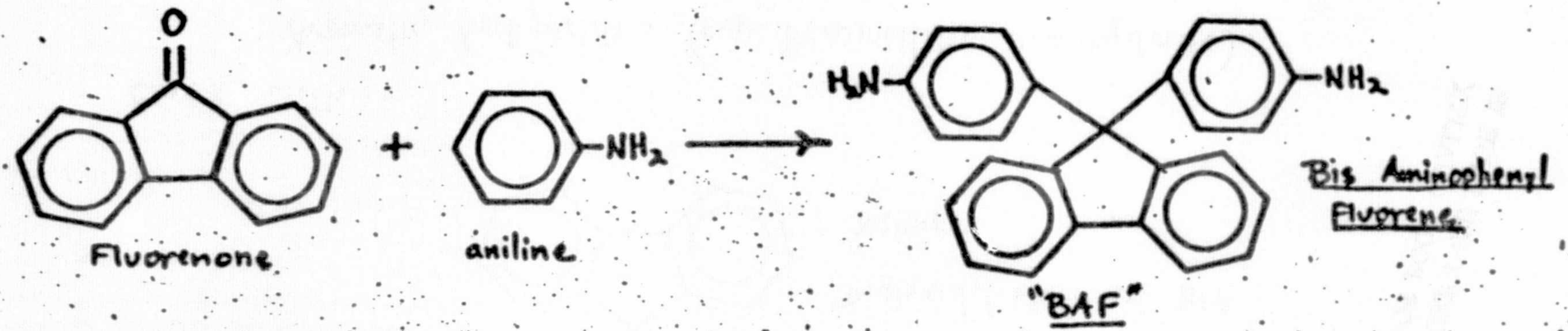


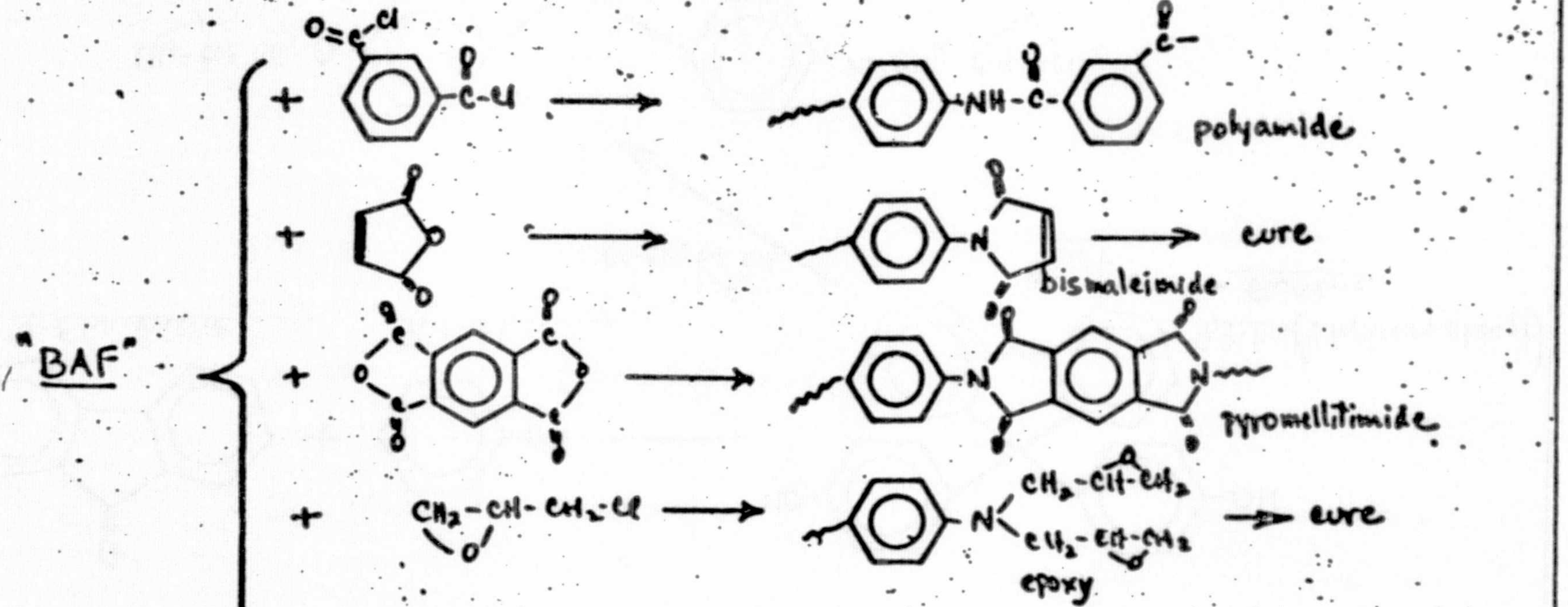
Cured with:

- Aromatic Anhydrides (e.g.: Pyromellitic Dianhydride)
- Aromatic Amines (e.g.: meta-Phenylene diamine, MDA)
- Catalytically: BF_3, Trimethoxy boroxine

NAME ______________________________ NO. ________

POLYMERS FROM "BAF"



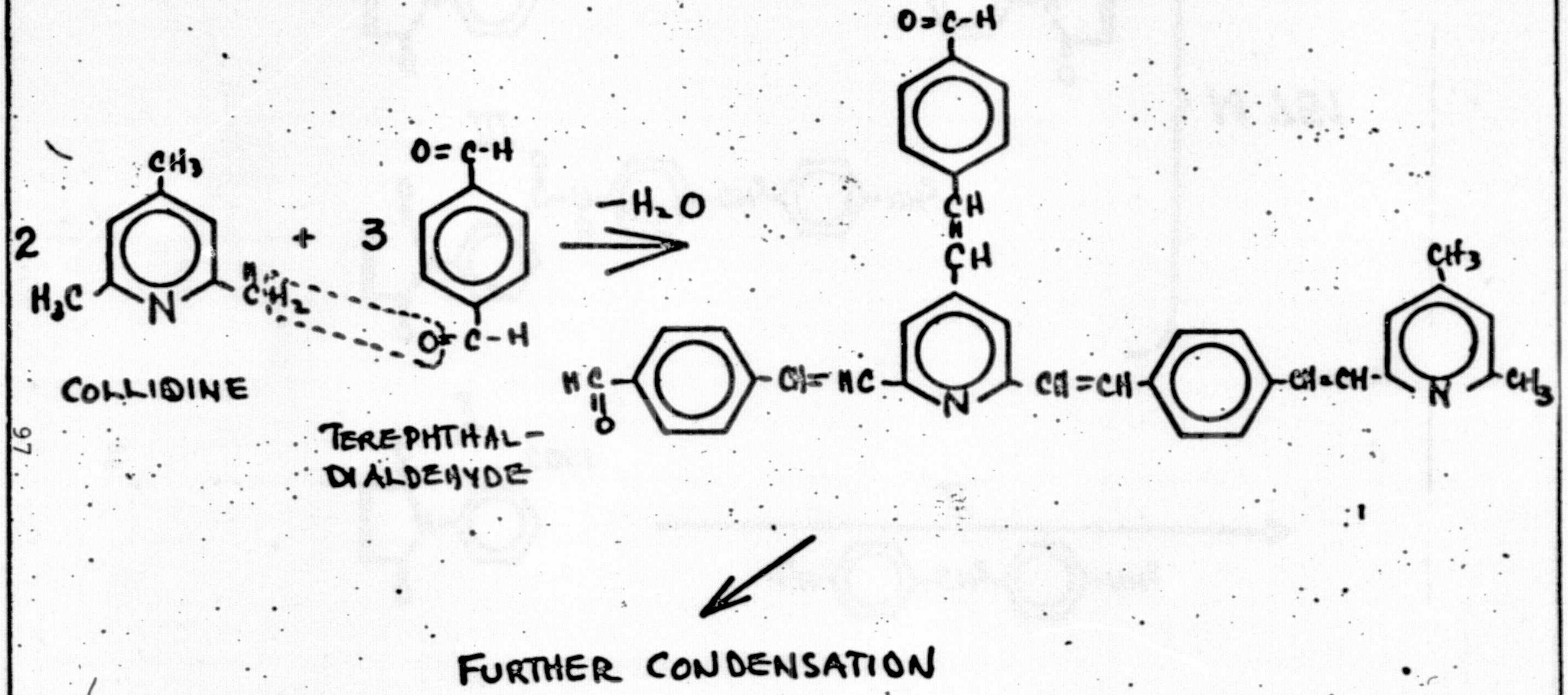


as curing agent for epoxy resins.

GMF, 1277

TOP VERTICAL

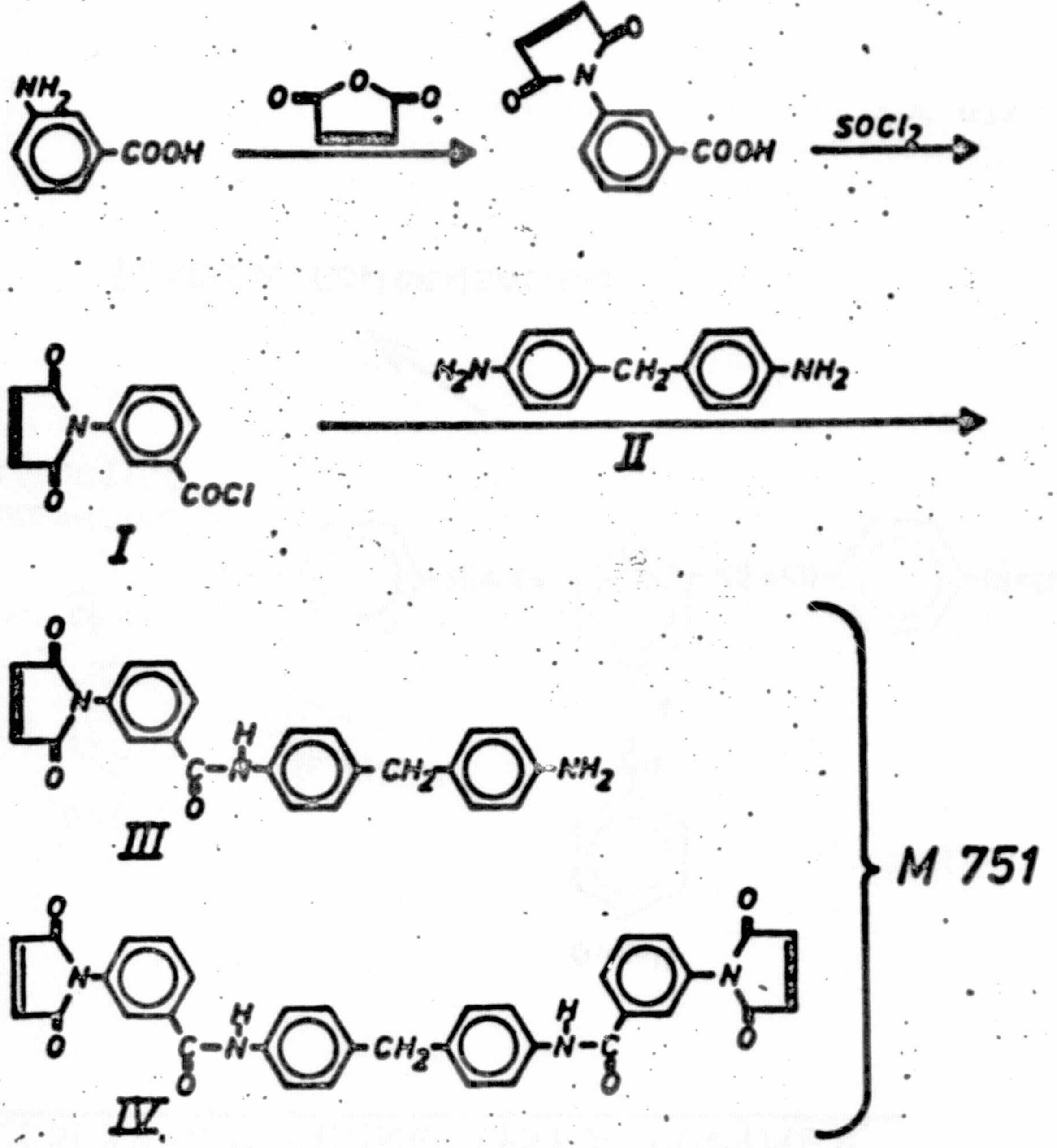
POLYSTYRYL PYRIDINE (PSP) POLYMER



GMP 11.77

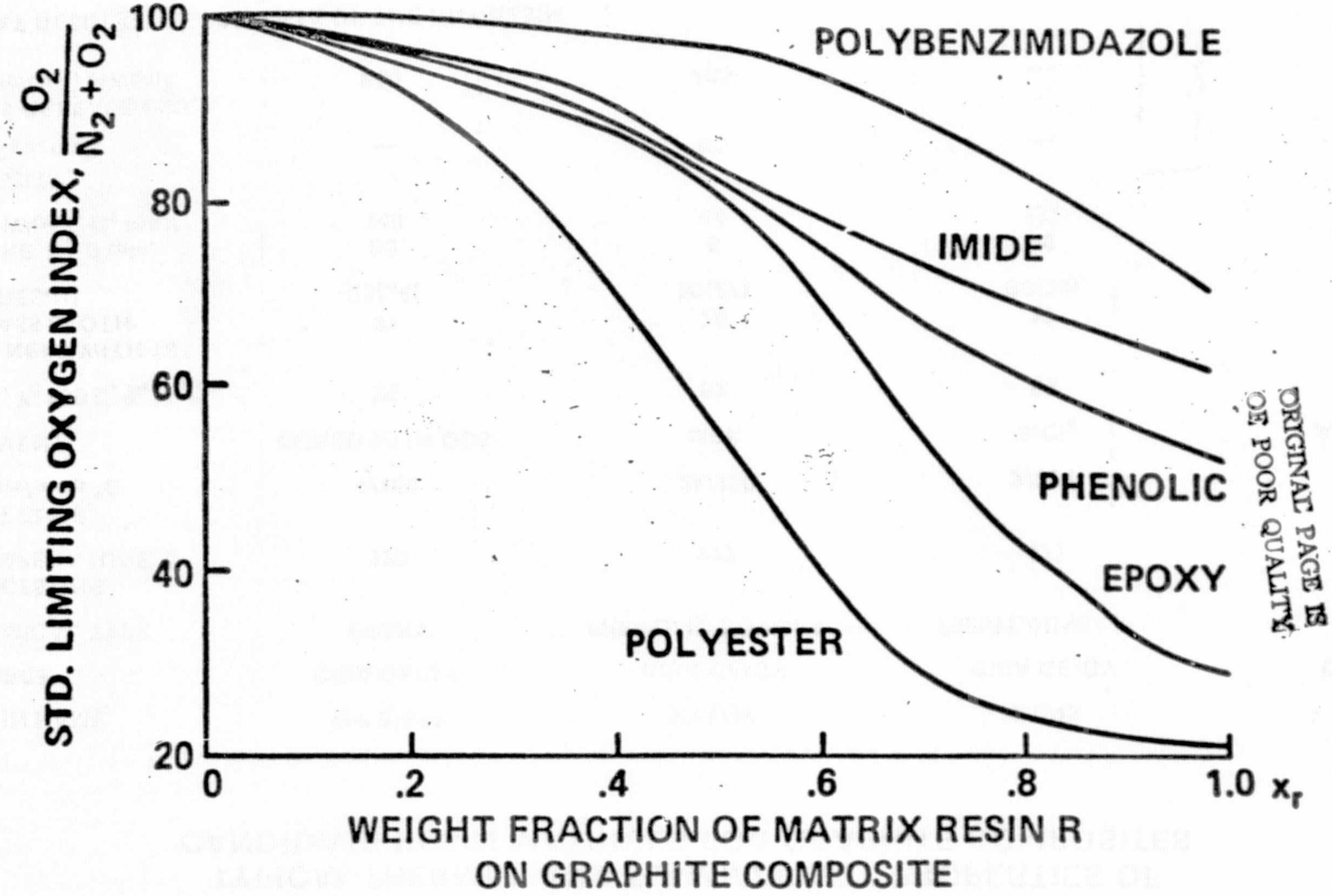
NAME ______________________ NO. ________

CHEMISTRY OF EUTECTIC BISMALEIMIDE



TOP VERTICAL

EFFECT OF MATRIX RESIN TYPE AND WEIGHT FRACTION ON THE STD. LIMITING OXYGEN INDEX OF GRAPHITE/RESIN COMPOSITES



TOP VERTICAL

NAME ______________________ NO. ____

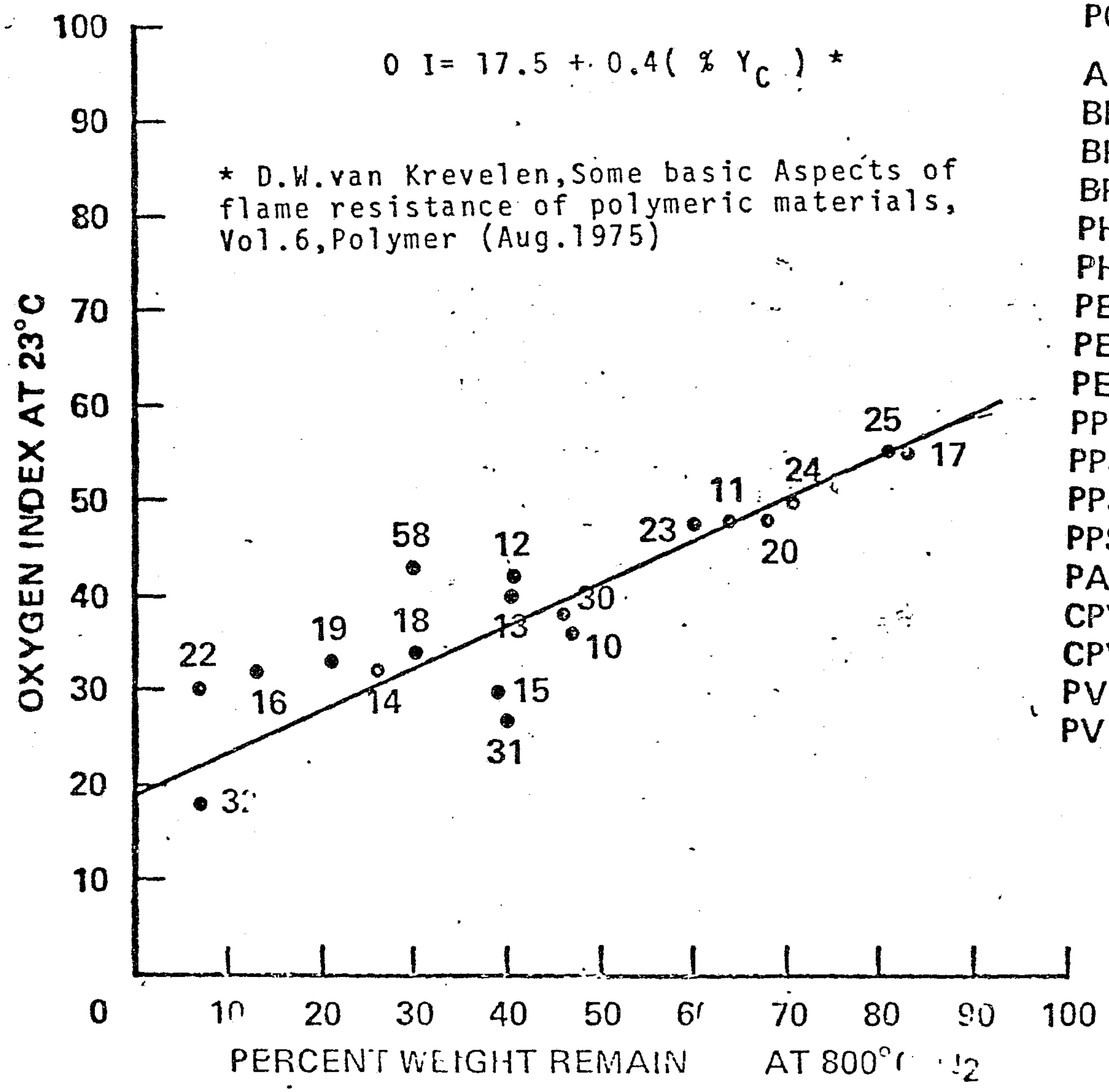
TYPICAL THERMAL AND FLAMMABILITY PROPERTIES OF CANDIDATE RESIN MATRICES FOR GRAPHITE COMPOSITES

RESIN NAME	MY 720**	XYLOK	NCNS	FURAN
SOURCE	CIBA GEIGY	CIBA GEIGY	CIBA GEIGY	QUAKER
CHEMICAL TYPE	EPOXY	PHENOLIC NOVOLAC	PHENYLAMINE	FURAN
PROCESSING TEMPERATURE, C	120	177	177	135
POST CURE, hours/temp °C	4/180	24/250	2/224	2/135
SOLVENT	CURED WITH DDS	MEK	$MeCl_2$	ACETONE
TGA, Y_c 850 C, %, N_2*	35	52	58	59
LOI, NEAT WITH 181 GLASS CLOTH (% RESIN)	21 23(34)	26 60(27)	27 90(29)	— 60(35)
SMOKE, D_s, 2 min. 2.5 W/cm², D_s MAX	80 140	6 44	89 172	0.8 75
TOXICITY, ALC_{50}, mg/l	—	61	—	—
HEAT RELEASE OSU, W-sec/cm², 5W/cm²	600	460	—	—

*NEAT RESIN **STATE-OF-THE-ART RESIN

DDS: DIAMINODIPHENYL SULPHONE

EFFECT OF CHAR YIELD OF THERMOPLASTIC POLYMERS ON OXYGEN INDEX


$O\ I = 17.5 + 0.4(\%\ Y_C)$ *

* D.W.van Krevelen, Some basic Aspects of flame resistance of polymeric materials, Vol.6, Polymer (Aug.1975)

POLYMER	NUMBER
ABS	18
BPAPC	14
BPAPC	19
BPFC-DMS	23
PH-BPAPC	30
PH-BPAPC	31
PES	12
PES	13
PES	22
PPO	16
PPS	11
PPS	20
PPS	24
PAS	15
CPVC	17
CPVC	25
PVF	32
PVF_2	58

TOP VERTICAL

TYPICAL THERMAL AND FLAMMABILTY PROPERTIES OF CANDIDATE RESIN MATRICES FOR GRAPHITE COMPOSITES

RESIN NAME	DGEBF/DGEBA**	BENZYL	K601	PSP 6030
SOURCE	POLYTECHNIC	WEYERHAUSER	RHODIA	SNPE/FRANCE
CHEMICAL TYPE	EPOXY	BENZYL	BISMALEIMIDE	POLYSTYRYL PYRIDINE
PROCESSING TEMPERATURE, C	135	150	182	250
POST CURE, hours/temp °C	3/135, 3/180	NONE	4/240	NONE
SOLVENT/CATALYST	TMB	WATER	NMP	NMP
TGA, Y_c 850 C, N_2, %*	40	61	47	—
LOI, NEAT AND WITH 181 GLASS CLOTH (% RESIN)	38	34 90(32)	26 46(30)	36 100(27)
SMOKE, D_s, 2 min. 2.5 W/cm², D_s MAX	—	8 34	1 80	1 33
TOXICITY, ALC_{50}, mg/l	—	119	—	130
HEAT RELEASE OSU, W-sec/cm², 5W/cm²	—	—	480	—

*NEAT RESIN

**50% mole of DGEBF

DGEBF: DIGLYCIDYL ETHER OF 9,9-BIS (4-HYDROXYPHENYL) FLUORENE
DGEBA: DIGLYCIDYL ETHER OF BISPHENOL A
TMB: TRIMETHOXYBOROXINE
NMP: N-METHYL PYROLIDONNE

TOP VERTICAL

"PRELIMINARY TEST RESULTS OF THE FIBER RELEASE CHARACTERISTICS OF BASELINE GRAPHITE EPOXY COMPOSITES COMPARED WITH NEW CHAR FORMING ANALOGS"

JOHN A. PARKER

NASA-AMES RESEARCH CENTER

MARCH 23, 1978

STATUS OF ENGINEERING AND TESTING OF COMPOSITE MATERIALS

OBJECTIVE To develop test methods to adequately simulate Crash-Fire (or Fire-Crash) scenarios, to test baseline and modified graphite composite materials, and to determine cost benefit and risk analysis of baseline and modified systems.

STATUS

1. Laboratory type screening device developed and undergoing initial tests and modifications.
2. Larger scale thermal-mechanical test facility being designed based upon postulated limits of typical crash and fire scenarios.
3. Proposals sought for fabrication and testing of variant composite systems.
4. Proposal being studied for cost benefit analysis model, applicable to variant composite systems.

APPROACH

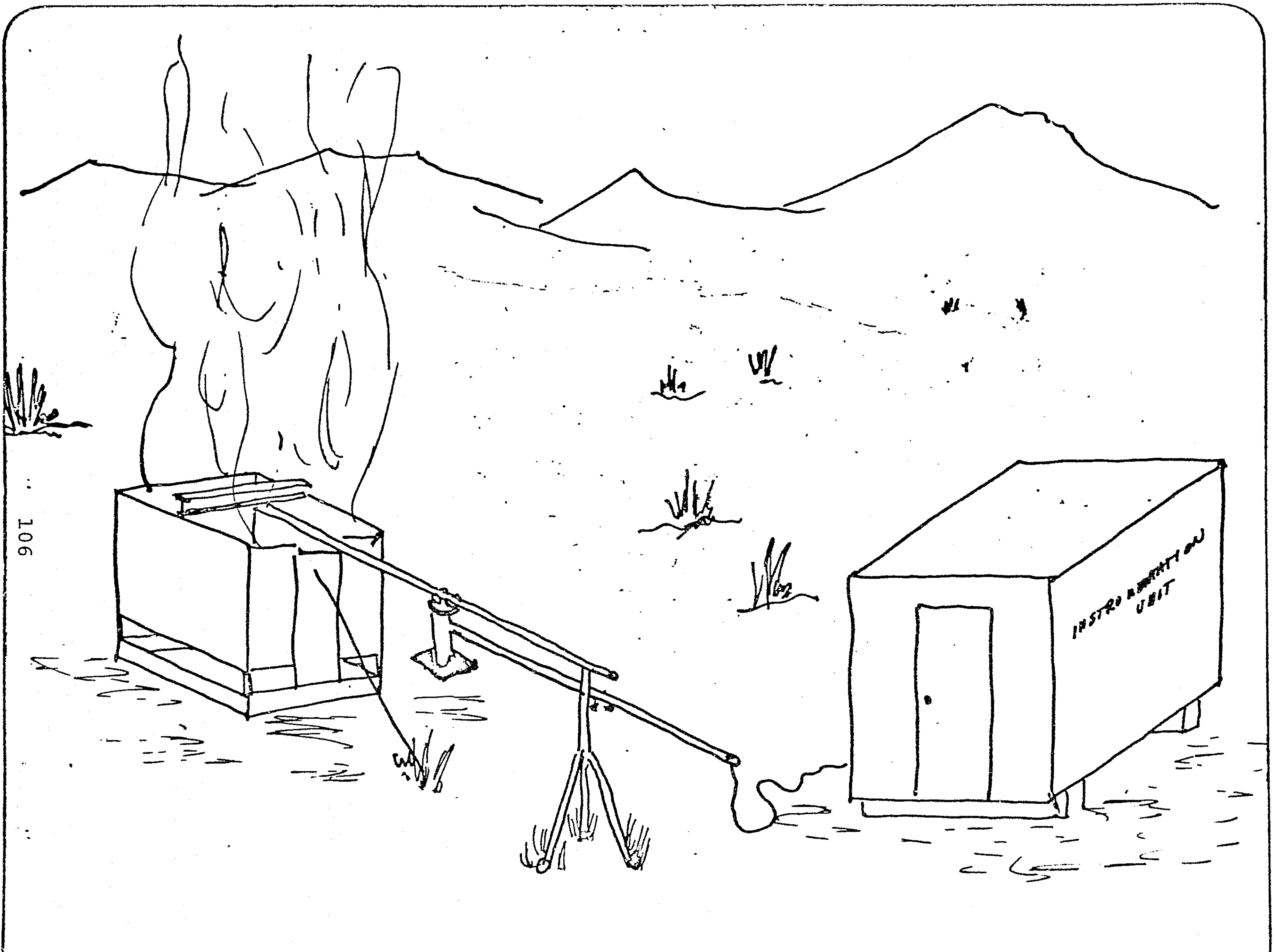
1. A screening type apparatus will be constructed based upon Charpy Impact testing machine and both direct burning and preheated composite samples. Expected data include: Breaking energy of baseline and degraded samples: weight loss and fiber release; Characteristics of broken sample, i.e., Critical fiber length, delamination and brittle resin failure; and residual strength of composite versus temperature.

TOP VERTICAL

2. Design and construction of larger scale test facility capable of variant: heat fluxes, bypass air flows, projectile impact, shock wave interactions, and fiber release classification due to fire, fire and impact, impact and fire, and fire and shock wave. Filtered output to provide for measurement of fiber release events.

3. Baseline and modified composite systems will be tested for mechanical properties, thermochemical properties, environmental properties, and response to thermal-mechanical shock.

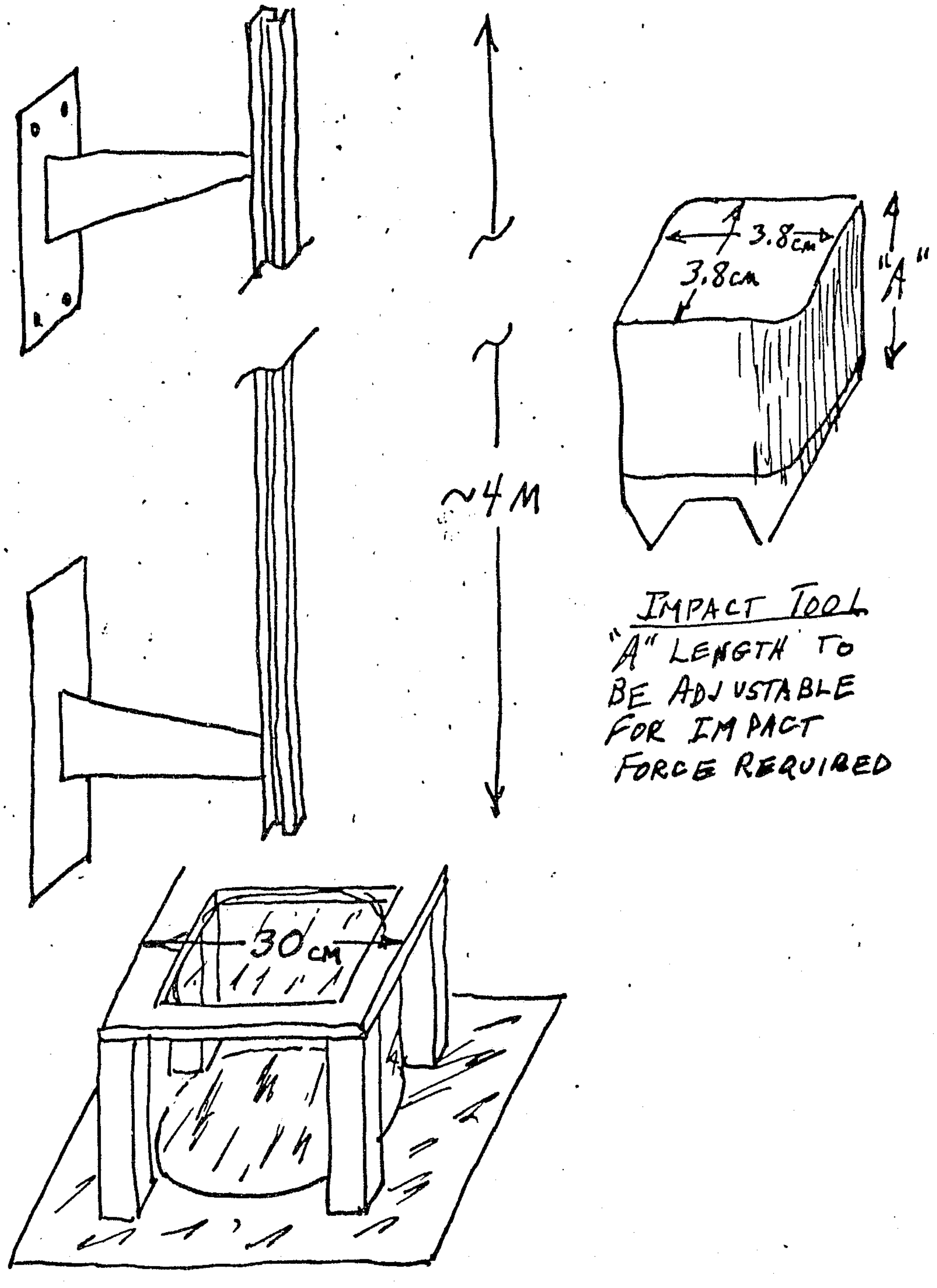
4. Cost benefit and risk analysis models will be developed so that results of tests of modified composites may be used to determine cost benefit analysis of variant systems.



POOL FIRE TEST FACILITY — NWC, CHINA LAKE, CA

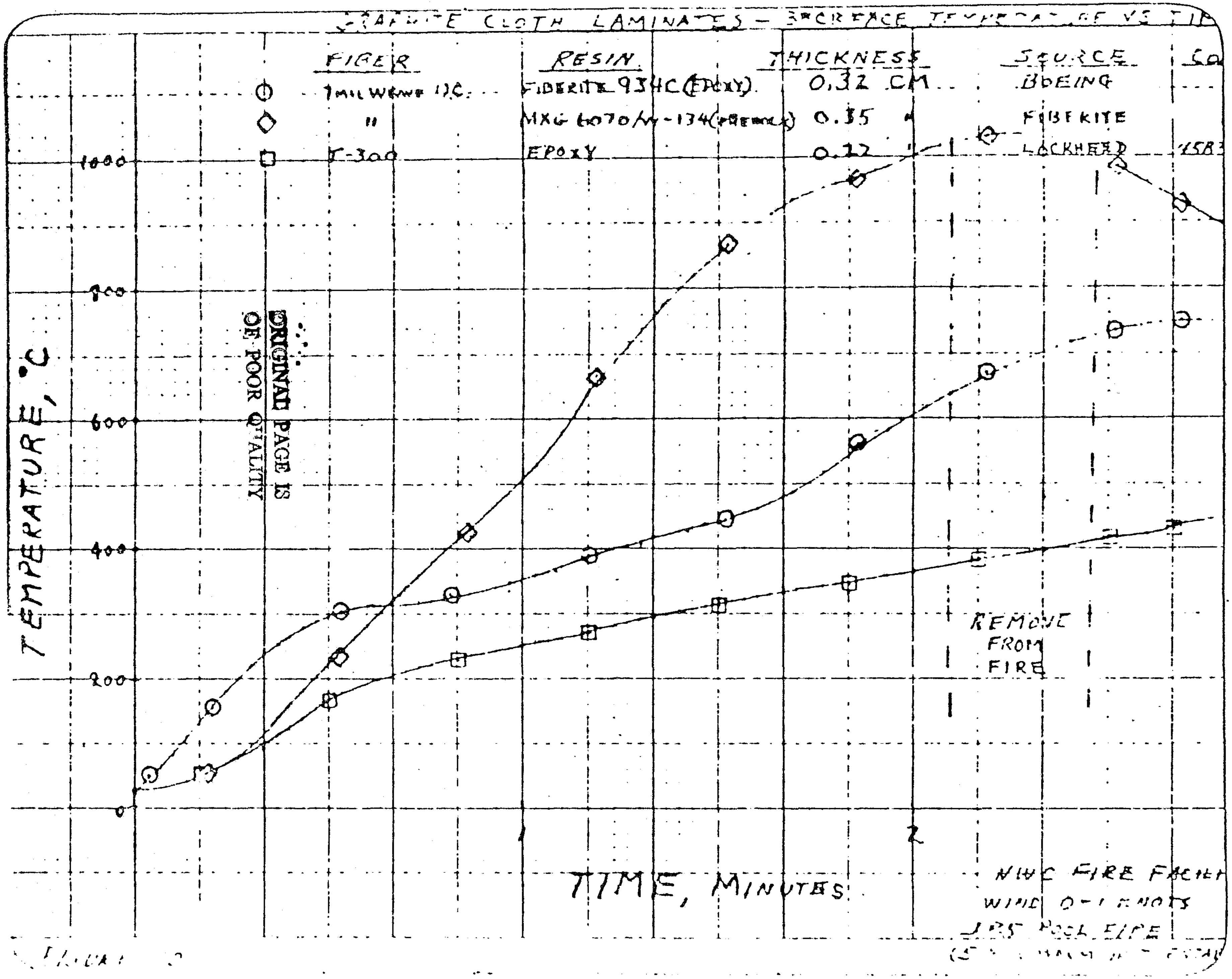
NO.

NAME



IMPACT TOOL
"A" LENGTH TO
BE ADJUSTABLE
FOR IMPACT
FORCE REQUIRED

DROP TESTING FIXTURE, CRPO, AMES RES. CTR.


GRAPHITE CLOTH LAMINATES – SURFACE TEMPERATURE VS TI
FIBER
RESIN
THICKNESS
SOURCE
SO
○ 1 MIL WEAVE 12C. FIBERITE 934C (EPOXY) 0.32 CM BOEING
◇ " MXG 6070/W-134 (PHENOLIC) 0.35 " FIBERITE
□ T-300 EPOXY 0.22 " LOCKHEED 1583
TEMPERATURE, °C
0
200
400
600
800
1000
TIME, MINUTES
1
2
REMOVE FROM FIRE
NWC FIRE FACILI
WIND 0-1 KNOTS
JP-5 POOL FIRE

FIGURE

DEMONSTRATED TECHNOLOGY

CHINA LAKE/AMES TESTS

- 0 POOL FIRE TEST FACILITY/POST-BURN IMPACT
- 0 BASELINE AND 8 MODIFICATION CONCEPTS

MATERIAL	FIBER RELEASE
GR/EP	HIGH
COATED GR/EP	MODERATE
GLASS FABRIC ON GR/EP	MODERATE
METAL COATED GR/EP	HIGH
POLYIMIDE	MODERATE
GLASS FABRIC ON GR/EP	MODERATE
GLASS FILLED PMR	MODERATE
GR/PHENOLIC	LOW
GR/IMIDE (HR 600)	LOW

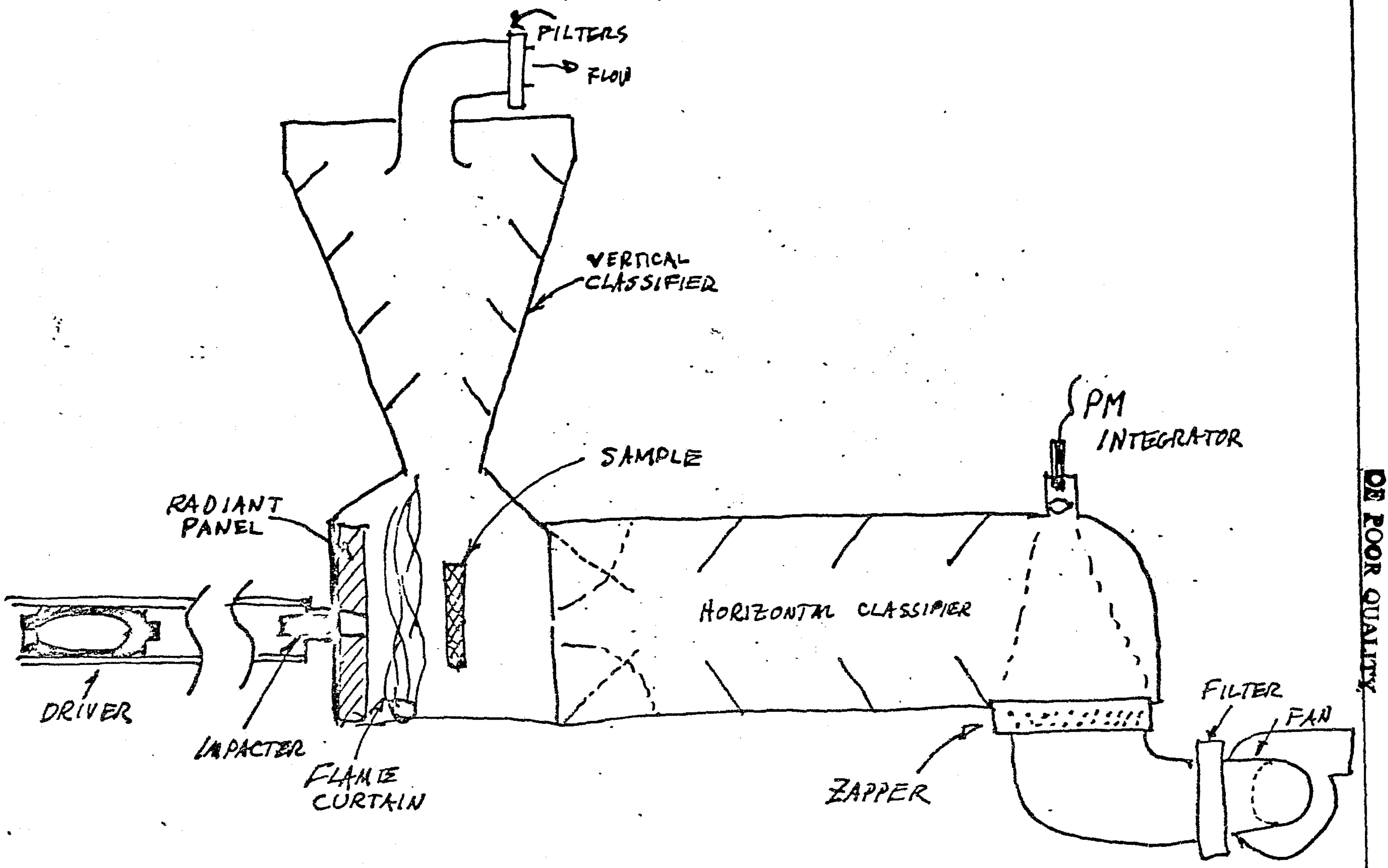
NSWC (DAHLGREN) TESTS

- 0 BURN + EXPLOSION TESTS SHOWED SIGNIFICANT FIBER RELEASE IN GR/PHENOLIC

TOP VERTICAL

COMPOSITE FIRE SIMULATION TESTING

	AIR VELOCITY KNOTS	FIRE WATTS/CM²	SPECIMEN LOADING	IMPULSE ΔForce & Δtime	PEAK PRESSURE (SHOCKS) PSI	PROJECTILE VELOCITY m/sec	PROJECTILE AREA	PROJECTILE SHAPE	DEBRIS CONTAINED	FACILITY LOCATION
I FIRES IN FLIGHT										
A - EFFECTS OF AIR VELOCITY ON DETERIORATION OF BURNING OR BURNT MATERIALS	10-300	8-15	YES	—	–	—	—	—	?	ARC NWC
B - DETERIORATION DURING CRASH IMPACT OF BURNING OR BURNT MATERIALS	0-30	8-15	yes	>100 Kts IMPACT	TBD	TBD	SMALL TO LARGE	BLUNT TO SHARP	YES	ARC
II FIRES ON GROUND										
A - DETERIORATION IN POOL FIRE CONDITIONS	0-30	1-15	yes	—	—	—	—	—	YES	ARC
B - DETERIORATION OF BURNING MATERIALS UNDER IMPULSIVE LOADS										
1 - LOW ORDER SHOCK WAVES! FUEL-AIR EXPLOSIONS; FUEL TANK RUPTURES, etc	0-30	1-15		Δt ~ Sec	UP TO 100	400	LARGE	BLUNT (SHOCK)	YES	ARC
2 - LOW ORDER PENETRATIONS RESULTING FROM FUEL/AIR EXPLOSIONS, etc.	0-30	1-15		Δt - ms to Secs	TBD	400	MED	BLUNT to SHARP	YES	ARC
3 - HIGHER ORDER SHOCK WAVES & PENETRATIONS FROM MUNITIONS DETONATIONS	0-30	1-15		Δt ~ ms	TBD	1000 to 3000	SMALL	SHARP	?	NWC
TEST DEVICE DESIRED CAPABILITIES FOR MOST GENERAL USAGE.	0-30	0-15	YES		150	0-500	VARY	VARY	YES	ARC



PROPOSED THERMAL-MECHANICAL SHOCK TEST FACILITY

FISH

STATUS OF MATERIALS MODIFICATION
PROGRAM IN THE CHEMICAL RESEARCH PROJECTS OFFICE

Ames Research Center - Feb. 24, 1978

I. Most probable conclusions (current opinion) concerning the fiber release threat from involvement of graphite epoxy resin systems in accidental commercial aircraft fires:

POSITIVE RESULTS

a. The fire dynamics and thermal-mechanical impact sequencing used to make initial threat assessment relative to (I) are probably invalid. The fire chemistry, impact energy and sequence is probably not related to real postcrash commercial aircraft fires.

b. Graphite structural composties with exceptional fire resistance and integrity may only be required in certain highly crash fire vulnerable areas of domestic aircraft.

c. High char yield resin binders (matrix resins) with anaerobic char yields of greater that 60% when used in structural graphite composites can completely accomodate the normal aircraft crash fire without loss of fibers and can also provide long time retention of structural integrity in in-flight fires.

d. Minor modifications of currently available graphite fiber systems may provide reduction of fiber conductivity to a degree that when combined with char forming resin systems may significantly reduce the threat without compromising mechanical properties.

STATUS OF MATERIALS MODIFICATION PROGRAM

Problematic Conclusions and Areas Requiring Intensive Effort

a. Graphite epoxy structural composites may have an additional fiber release problem due to combined thermal and photo-oxidation environmental effect. Various coatings may resolve this in the short term.

b. The use of high char yield resin systems may create minor processing and cost problems. Significant improvements in fracture toughness and impact strengths will have to be made before these resins can be safely used in structural applications.

c. The fiber release problem is primarily a polymer flammability and mechanical stability problem.

d. The effect of risk assessment on overall cost benefits for using graphite composites is confused by the lack of significant connection among crash fire scenario, crash-impact fire dynamics, crash fire fiber release and test simulation.

TOP VERTICAL

STATUS OF CONTRACT AND INTERFACE DEVELOPMENT WITH INDUSTRY AND UNIVERSITY ELEMENTS - Feb. 24, 1978

I. INDUSTRIAL INTERFACE

A. Materials and Process

1. Resins

   a. Hughes Aerospace Group, Culver city, CA (Dr. N. Bilow) High char yield, void free composites from HR-600 polyimides cured with 1,2 poly addition acetylenic termination. Briefing conducted. Obtained and tested composite samples. (Proposal being submitted)

   b. Hitco, Gardena, CA (Dr. George Lee) Prepreg and composite fabrication from new phenolic and benzyl resin systems. Supplied state-of-the-art test specimens. Investigation of high temperature interface coatings. (Proposal being submitted)

   c. Composites Horizons, Ontario, CA (Dr. Ira Petker) Processability and initial physical properties screening on new experimental resins - i.e., hot melt bismaleimide, epoxy resin systems based on fluorenone bisphenol derivatives and others (Proposal being submitted)

   d. Technochemie GMBH, Heidelberg, West Germany (Dr. H. Stenzenberger) Development of graphite - bismaleimide prepregs and composites based on hot melt bismaleimide resins. (Contract being negotiated)

e. SNPE, Paris, France (Dr. B. Melassine) Development of polystyryl pyridene resin (PSP 6030) for application to graphite composites (Contract being negotiated)

2. Fibers

a. Union Carbide, Parma, Ohio (Dr. B. H. Eckstein) Application of carbon fiber coatings with increased resistivity without significantly affecting composite performance or fabrication cost. (Discussions being held for a proposal)

b. Cellanese Research Division, Summit, New Jersey (Dr. J. Leal) Modification of graphite fibers by coating or "doping" with high resistance silica, glan, boron, metal carbides (Discussions for proposal; presentation to be made)

II. University Interface

University of Utah, Salt Lake City, Utah (Dr. A. Sosin) Study of the effects of optimum cure of resins on the thermochemical and flammability properties of epoxy and other advanced resins (Contract in final stages of negotiation).

Polytechnic Institute of New York, Brooklyn, New York (Dr. E. Pearce) Synthesis of modified epoxy resins and copolymers. (Grant proposal being discussed).

ENGINEERING TESTING AND MODELING

1. Econ, Inc., San Jose, California - Modeling and cost benefit analysis of various composites (Contract being negotiated)

2. Douglas Aircraft Company, Long Beach, California - Environmental testing of composite structures (Discussions only).

3. Lockheed Aircraft Company, Burbank, California - Aircraft fire testing of composite structures (Discussions only).

4. San Jose State University, San Jose, California - Design and computation of mechanical test devices for composites (Continuation of existing Grant).

5. University of California, Berkeley, California - Design and construction of crash fire test facility for graphite composites.

REVIEW OF NASA LEWIS
MATERIALS MODIFICATION PROGRAMS

TITO T. SERAFINI
NASA-LEWIS
3-23-78

NASA-LEWIS MATERIAL

MODIFICATION PROGRAM

OBJECTIVE: TO DEVELOP COMPOSITE MATERIALS WHICH HAVE THE DESIRABLE HIGH PERFORMANCE PROPERTIES OF POLYMER MATRIX/GRAPHITE FIBER COMPOSITES WHILE ELIMINATING THE HAZARD TO UNPROTECTED ELECTRICAL EQUIPMENT CAUSED BY GRAPHITE FIBER RELEASE IN FIRE RELATED ACCIDENTS.

MAJOR THRUSTS:

- DEVELOPMENT OF NEW AND/OR IMPROVED MATRIX RESINS
- IDENTIFICATION OF ALTERNATE FIBER MATERIALS
- DEVELOPMENT OF HYBRID COMPOSITES WHICH EXHIBIT IMPROVED RETENTION OF CONSTITUENT MATERIALS WHEN SUBJECTED TO SEVERE OXIDATIVE CONDITIONS.

LERC

TITLE: SYNTHESIS OF IMPROVED PHENOLIC RESINS

OBJECTIVE : TO SYNTHESIZE PROCESSABLE PHENOLIC RESINS FOR USE AS MATRIX RESINS IN HIGH PERFORMANCE FIBER REINFORCED COMPOSITES.

PERIOD OF PERFOMRANCE : 12 MONTH

STATUS : PROPOSALS DUE MARCH 26, 1973

LeRC

TITLE: SYNTHESIS OF IMPROVED POLYESTER RESINS

OBJECTIVE : TO SYNTHESIZE POLYESTER RESINS WITH IMPROVED CHAR FORMING CHARACTERISTICS.

PERIOD OF PERFORMANCE : 12 MONTH

STATUS : PROPOSALS DUE APRIL 6, 1978

TITLE: SILICONE COPOLYMERS FOR COMPOSITE MATRIX APPLICATIONS

OBJECTIVE : TO SYNTHESIZE COPOLYMERS INCORPORATING SILICONE RESINS WITH ENGINEERING RESINS TO PROVIDE MATRIX MATERIALS FOR ADVANCED FIBER COMPOSITES.

PERIOD OF PERFORMANCE : 12 MONTH

STATUS : PROPOSALS DUE APRIL 3, 1978

LERC

TITLE: SURVEY OF INORGANIC POLYMERS

OBJECTIVE : TO SURVEY THE LITERATURE PERTAINING TO INORGANIC POLYMERS AND TO IDENTIFY POLYMERS WITH HIGH POTENTIAL FOR USE AS MATRIX RESINS IN ADVANCED COMPOSITES.

PERIOD OF PERFORMANCE : 6 MONTH

STATUS : PROPOSALS ARE BEING EVALUATED

LeRC

TITLE : ULTRA-HIGH MODULUS ORGANIC FIBERS

OBJECTIVE : TO DEMONSTRATE THE LABORATORY SCALE PRODUCTION OF ORGANIC FIBERS HAVING TENSILE STRENGTHS AND MODULI IN THE RANGES OF 400 TO 450 KSI AND 25 TO 30 X 10^6 PSI, RESPECTIVELY.

PERIOD OF PERFORMANCE: 12 MONTH

STATUS : PROPOSALS DUE MARCH 29, 1978

TITLE : HYBRIDIZED POLYMER MATRIX COMPOSITES

OBJECTIVE: TO CONCEIVE, FABRICATE AND EVALUATE HYBRIDIZED POLYMER MATRIX COMPOSITES WHICH EXHIBIT IMPROVED CONSTITUENT MATERIALS' RETENTION CHARACTERISTICS WHEN SUBJECTED TO SEVERE OXIDATIVE ENVIRONMENTS.

PERIOD OF PERFORMANCE : 12 MONTH

STATUS : PROPOSALS DUE APRIL 3, 1978

LERC

PHTHALEIN PMR POLYIMIDES

OBJECTIVE : TO MINIMIZE THE LOSS OF CONSTITUENT MATERIALS FROM GRAPHITE FIBER/ PMR POLYIMIDE COMPOSITES SUBJECTED TO COMBUSTIVE ENVIRONMENTS BY INCREASING THE CHAR YIELD OF THE MATRIX RESIN.

APPROACH: PREPARE PHTHALEIN MODIFIED PMR POLYIMIDES

STATUS : NEW TASK, MONOMERS SYNTHESIS IN PROGRESS

PRINCIPAL INVESTIGATOR : W. ALSTON

LEVEL OF EFFORT : 0.2 MY

IMPROVED PHENOLIC RESINS

OBJECTIVE: TO SYNTHESIZE PHENOLIC RESINS HAVING IMPROVED PROCESSING CHARACTERISTICS

APPROACH : SYNTHESIS OF LOW MOLECULER WEIGHT PHENOLIC RESIN PRECURSORS HAVING PENDENT OLEFINIC GROUPS CAPABLE OF ADDITION - TYPE POLYMERIZATION

STATUS : NEW TASK - MATERIALS SELECTION IN PROGRESS

PRINCIPAL INVESTIGATOR : PETER DELVIGS

LEVEL OF EFFORT : 0.2 MAN-YEAR

CHAR FORMING EPOXY MATRIX RESINS

OBJECTIVE: TO MINIMIZE THE LOSS OF CONSTITUENT MATERIALS FROM GRAPHITE FIBER/ EPOXY COMPOSITES SUBJECTED TO COMBUSTIVE ENVIRONMENTS BY INCREASING THE CHAR YILED OF THE MATRIX RESIN.

APPROACHES : INVESTIGATE THE FOLLOWING FOR MODIFICATION OF EPOXY RESINS AND CURING AGENTS:

A. PHTHALEIN GROUPS
B. PHENOLIC RESINS (NOVOLACS)
C. PHOSPHATES AND PHOSPHATE ESTERS
D. IMIDES

STATUS : NEW TASK

PRINCIPAL INVESTIGATORS : W. ALSTON AND P. DELVIGS

LEVEL OF EFFORT : 0.4 MY

IMPROVED POLYESTERS

OBJECTIVE : TO SYNTHESIZE POLYESTER RESINS HAVING IMPROVED HEAT RESISTANCE AND CHAR - FORMING CAPABILITY

APPROACH: SYNTHESIS OF NEW VINYL - TYPE CURING AGENTS CONTAINING IMIDE OR QUINOXALINE STRUCTURES

STATUS : NEW TASK - MATERIALS SELECTION AND SYNTHESIS HAVE BEEN INITIATED

PRINCIPAL INVESTIGATOR : PETER DELVIGS

LEVEL OF EFFORT : 0.3 MAN-YEAR

LeRC

CHARACTERIZATION OF RESINS FOR GRAPHITE FIBER CONTAINMENT

OBJECTIVE: TO DETERMINE THE MODE AND EXTENT OF DEGRADATION OF CANDIDATE RESINS AND COMPOSITES.

TECHNICAL APPROACH: THE THERMAL AND OXIDATIVE DEGRADATION PRODUCTS EMITTED FROM CANDIDATE RESINS AND COMPOSITES ARE BEING INVESTIGATED USING PYROLYSIS-GC TECHNIQUES. THE AMOUNT OF CHAR RESIDUE ALSO WILL BE MEASURED.

PROGRAM STATUS: PROCEDURES ARE BEING ESTABLISHED. PRELIMINARY RESULTS ON PMR-15 RESINS HAVE BEEN OBTAINED.

PRINCIPAL INVESTIGATOR: R. E. GLUYAS

LEVEL OF EFFORT: 0.3 MY

LeRC

CHARACTERIZATION OF CHAR RESIDUES

OBJECTIVE: TO DETERMINE THE STRUCTURE AND COMPOSITION OF CHAR RESIDUES FROM CANDIDATE RESINS AND COMPOSITES.

TECHNICAL APPROACH: OPTICAL AND SCANNING ELECTRON MICROSCOPY WILL BE USED TO CHARACTERIZE CHAR RESIDUES. ALSO, THE ELEMENTAL COMPOSITION OF THE CHAR RESIDUES WILL BE ANALYZED.

PROGRAM STATUS: WORK BEING STARTED

PRINCIPAL INVESTIGATOR: R. E. GLUYAS

LEVEL OF EFFORT: 0.1 MY

THERMAL ANALYSIS OF IMPROVED MATRIX RESINS

OBJECTIVE: TO DETERMINE THE REACTIVITY, THERMAL STABILITY AND THERMAL-OXIDATIVE STABILITY OF ORGANIC AND INORGANIC POLYMER MATERIALS.

APPROACH: THERMAL ANALYSES (DSC, DTA, TGA) WILL BE CONDUCTED TO CHARACTERIZE THE THERMAL RESPONSE OF SELECTED POLYMER MATRIX MATERIALS. INITIAL ANALYSES WILL BE DIRECTED TOWARD:

(A) CHARACTERIZATION OF RESIN CURE.
(B) CHARACTERIZATION OF THERMAL DEGRADATION.
(C) CHARACTERIZATION OF THERMAL-OXIDATIVE STABILITY TO DEVELOP CRITERIA FOR RELATIVE STABILITY AND TO CORRELATE THESE ANALYTICAL TEST CRITERIA WITH LARGER SCALE COMBUSTION TESTS.

STATUS: TECHNICAL CAPABILITY ESTABLISHED; INSTRUMENTAL CAPABILITY TO BE EXPANDED; MATERIALS SELECTION IN PROGRESS.

PRINCIPAL INVESTIGATOR: RICHARD W. LAUVER

LEVEL OF EFFORT: 0.2 MY

LeRC

SPECTRAL CHARACTERIZATION OF HIGH PERFORMANCE MATRIX RESINS

OBJECTIVE: TO CHEMICALLY CHARACTERIZE SOLUBLE MONOMERS, PRECURSORS, AND OLIGOMERS OF ORGANIC AND INORGANIC POLYMER MATERIALS TO ELUCIDATE REACTIONS AND MECHANISMS CRITICAL TO THE PROCESSABILITY AND PERFORMANCE OF THE MATERIALS.

APPROACH: INSTRUMENTAL ANALYSES (NMR, IR, ESCA) WILL BE CONDUCTED TO CHARACTERIZE THE CHEMISTRY OF SELECTED POLYMER MATRIX MATERIALS. INITIAL ANALYSES WILL BE DIRECTED TOWARD:

(A) PURITY AND REACTIVITY OF MONOMERS AND PRECURSORS.
(B) IDENTIFICATION OF REACTION MECHANISMS AND SEQUENCE DISTRIBUTIONS IN SELECTED POLYMERS AND COPOLYMERS.
(C) IDENTIFICATION OF SOLUBLE OXIDATION PRODUCTS OF POLYMERS AND MODEL COMPOUNDS.

STATUS: TECHNICAL CAPABILITY ESTABLISHED; NEW HETERONUCLEAR NMR FACILITY CURRENTLY BEING INSTALLED; MATERIALS SELECTION IN PROGRESS.

PRINCIPAL INVESTIGATOR: RICHARD W. LAUVER

LEVEL OF EFFORT: 0.2 MY

LERC

STRUCTURAL CHARACTERIZATION OF RESINS AND COMPOSITES

OBJECTIVE: TO CHARACTERIZE NEW RESIN SYSTEMS, COMPOSITES AND COMPOSITE COATINGS BY FOURIER TRANSFORM INFRARED SPECTROSCOPY.

APPROACH: FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY WILL BE USED TO OBTAIN MOLECULAR STRUCTURAL INFORMATION ABOUT IMPROVED RESIN SYSTEMS, HYBRIDIZED POLYMER MATRICES, AND COMPOSITE COATINGS.

PRINCIPAL INVESTIGATOR: KATHERINE E. REED

LEVEL OF EFFORT: 0.2 MY

LERC

DYNAMIC MECHANICAL TESTING OF RESINS AND COMPOSITES

OBJECTIVE: TO EXAMINE THE DYNAMIC MECHANICAL PROPERTIES OF HYBRID COMPOSITES AND RESIN SYSTEMS.

APPROACH: DYNAMIC MECHANICAL ANALYSIS (DMA) WILL BE USED TO EXAMINE THE EFFECT OF MIXED RESIN AND OTHER HYBRID SYSTEMS ON THE TEMPERATURE-DEPENDENT FREQUENCY AND DAMPING CHARACTERISTICS OF THE COMPOSITE.

PRINCIPAL INVESTIGATOR: KATHERINE E. REED

LEVEL OF EFFORT: 0.1 MY

LeRC

HYBRIDIZED POLYMER MATRIX COMPOSITES

OBJECTIVE: TO FABRICATE AND EVALUATE HYBRIDIZED POLYMER MATRIX COMPOSITES WHICH EXHIBIT IMPROVED CONSTITUENT MATERIALS RETENTION CHARACTERISTICS WHEN SUBJECTED TO SEVERE OXIDATIVE ENVIRONMENTS.

APPROACH: FABRICATE AND CHARACTERIZE PMR POLYIMIDE AND EPOXY RESIN MATRIX COMPOSITES OF KEVLAR/SILICON CARBIDE, KEVLAR/ALUMINA AND KEVLAR/GRAPHITE FIBERS.

PRINCIPAL INVESTIGATORS: M. P. HANSON
K. J. BOWLES

LEVEL OF EFFORT: 1.1 MY

LeRC

POLYMER ADDITIVES FOR FIBER CONTAINMENT

OBJECTIVE: TO INVESTIGATE POLYMER BLENDS AND INORGANIC FILLERS FOR MINIMIZING LOSS OF CONSTITUENT MATERIALS FROM GRAPHITE FIBER COMPOSITES SUBJECTED TO COMBUSTION.

APPROACH: PMR POLYIMIDE, EPOXY AND POLYESTER RESINS BLENDED WITH VARIOUS COMMERCIALLY AVAILABLE SILICONE COMPOUNDS OR INORGANIC FILLERS WILL BE INVESTIGATED FOR:

1. COMPATIBILITY
2. CHAR FORMATION
3. PROCESSABILITY
4. FIBER CONTAINMENT
5. COMPOSITE PROPERTIES

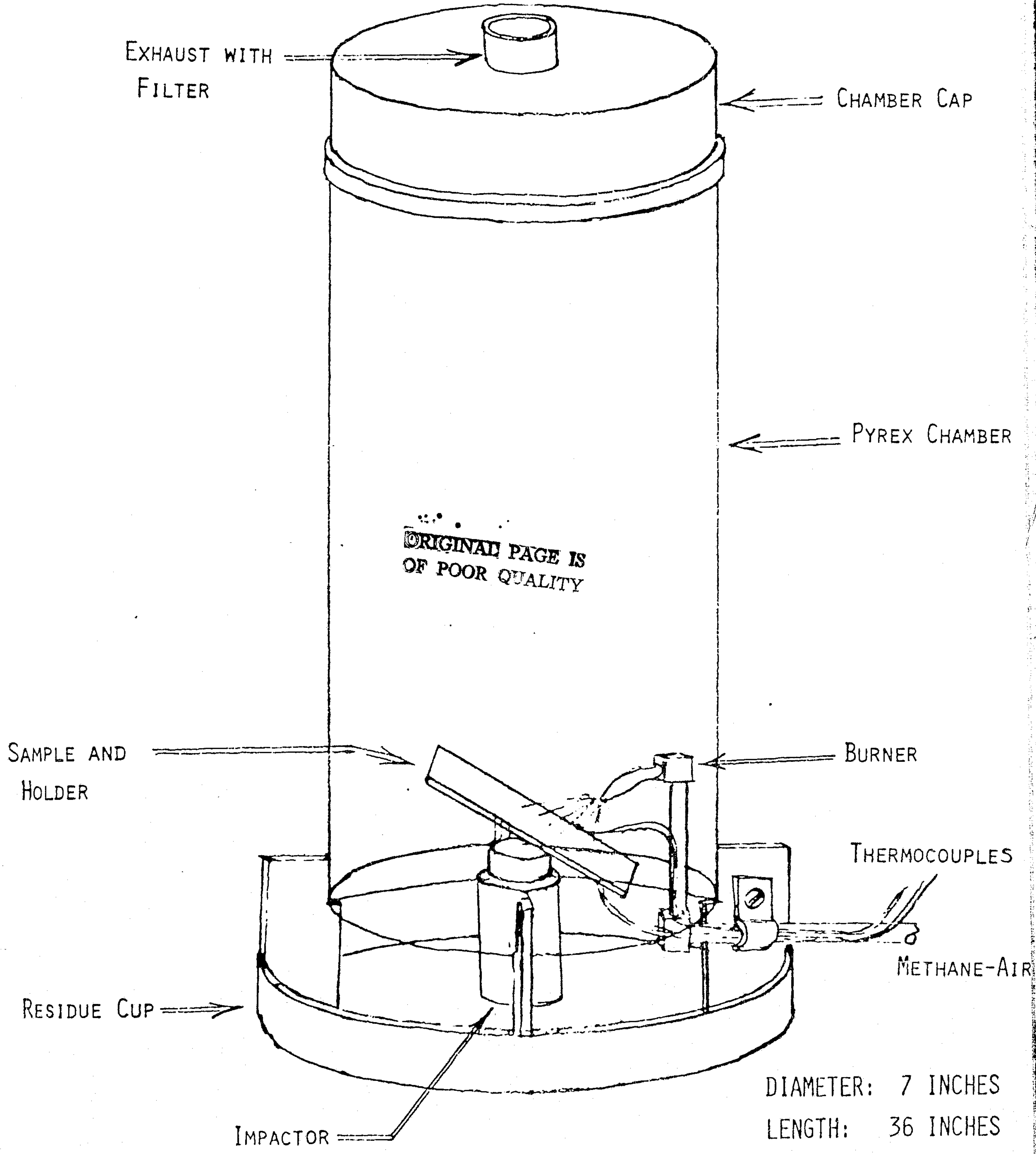
STATUS: WORK INITIATED

PRINCIPAL INVESTIGATOR: R. D. VANNUCCI

LEVEL OF EFFORT: 0.5 MY

LeRC

PRELIMINARY BURNING RIG



DIAMETER: 7 INCHES
LENGTH: 36 INCHES

BURNER RIG FEATURES

1. SAMPLE VISIBILITY
2. PARTICULATE COLLECTION
    - A) HEPA FILTER & RESIDUE CUP
    - B) SMOOTH INNER SURFACES
    - C) EASY DISASSEMBLY
3. LARGE AIR FLOW
    - A) DIRECT PARTICULATE MATTER TOWARD FILTER
    - B) COOL FLAME PRODUCTS
4. INSTRUMENTATION
    - A) GAS FLOW METERING
    - B) FLAME AND SAMPLE TEMPERATURE MEASUREMENT
    - C) CHAMBER AIR FLOW MEASUREMENT
    - D) FILTER PRESSURE DROP
5. IMPACTOR
    - A) SPRING DRIVEN PISTON
    - B) GAS DRIVEN PISTON
    - C) POSITIONED BELOW SAMPLE
6. HEAT FLOW - UP TO 20 $\frac{\text{BTU}}{\text{FT}^2\ \text{SEC}}$

SUMMARY OF LEWIS IN-HOUSE PROGRAMS

	LEVEL OF EFFORT IN FY 79 (MY)
RESIN SYNTHESIS	1.1
MATERIALS CHARACTERIZATION	1.1
HYBRIDIZED COMPOSITES	1.6
TOTAL	3.8

FIBER RELEASE TESTING FACILITIES AND RESULTS

V. L. BELL
MARCH 23, 1978

FIBER RELEASE TEST FACILITIES

PROBLEM: HOW TO DETERMINE AMOUNTS AND TYPES OF GRAPHITE FIBERS FROM CIVILIAN AIRCRAFT CRASH/FIRE SITUATIONS ?

EXPERIENCE: NO KNOWN CRASHES OF CIVILIAN AIRCRAFT WITH GRAPHITE COMPOSITE PARTS.

SEVERAL CRASHES OF MILITARY AIRCRAFT RELEASED FREE GRAPHITE FIBERS.

TEST LIMITATIONS: NATIONAL MORATORIUM ON OUTDOOR RELEASE OF GRAPHITE FIBERS EXCEPT UNDER RIGIDLY CONTROLLED CONDITIONS.

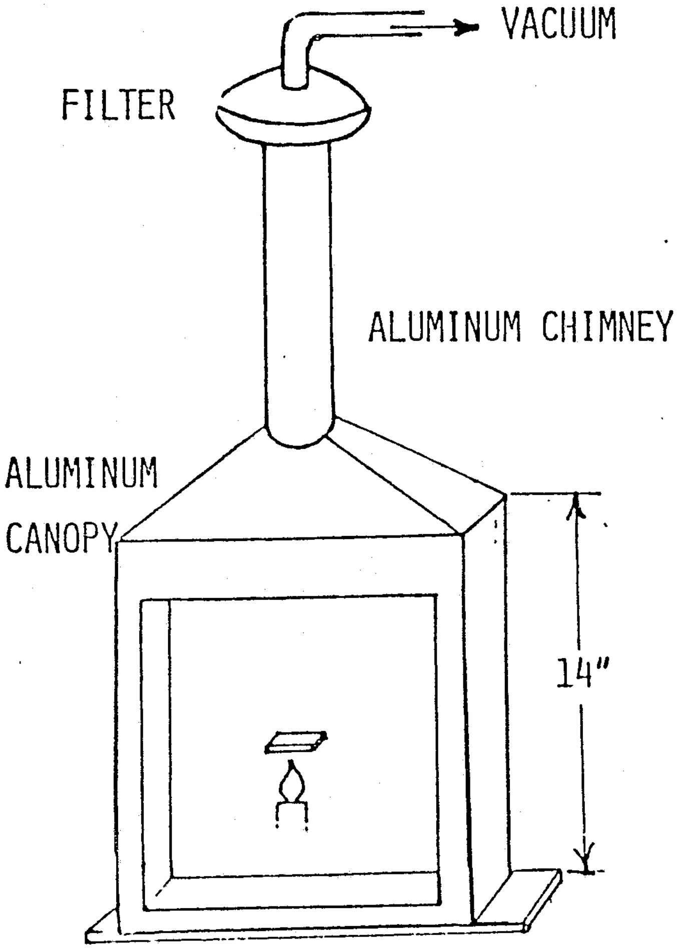
ACTIVE FIBER RELEASE TEST FACILITIES

- LABORATORY/EXPLORATORY - NAVAL RESEARCH LABORATORY
  (DR. J. P. REARDON)

- CHAMBER/INTERMEDIATE - NAVY - DAHLGREN, VIRGINIA
  (DR. K. R. MUSSELMAN)

- OUTDOOR/RANGE - TRW - AF - NAVY/CHINA LAKE
  (DR. PAUL LIEBERMAN)

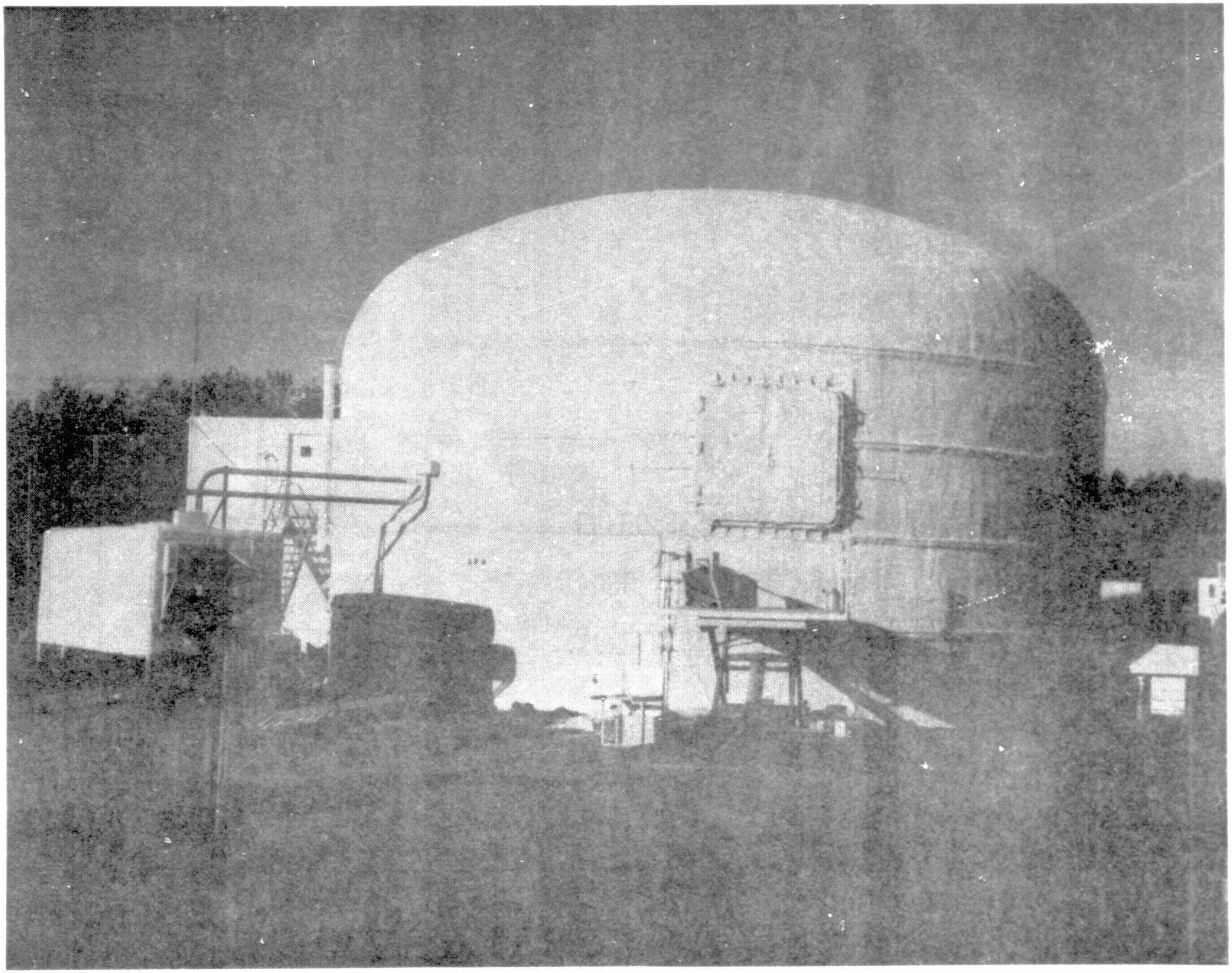
LABORATORY TESTING AT NAVAL RESEARCH LABORATORY

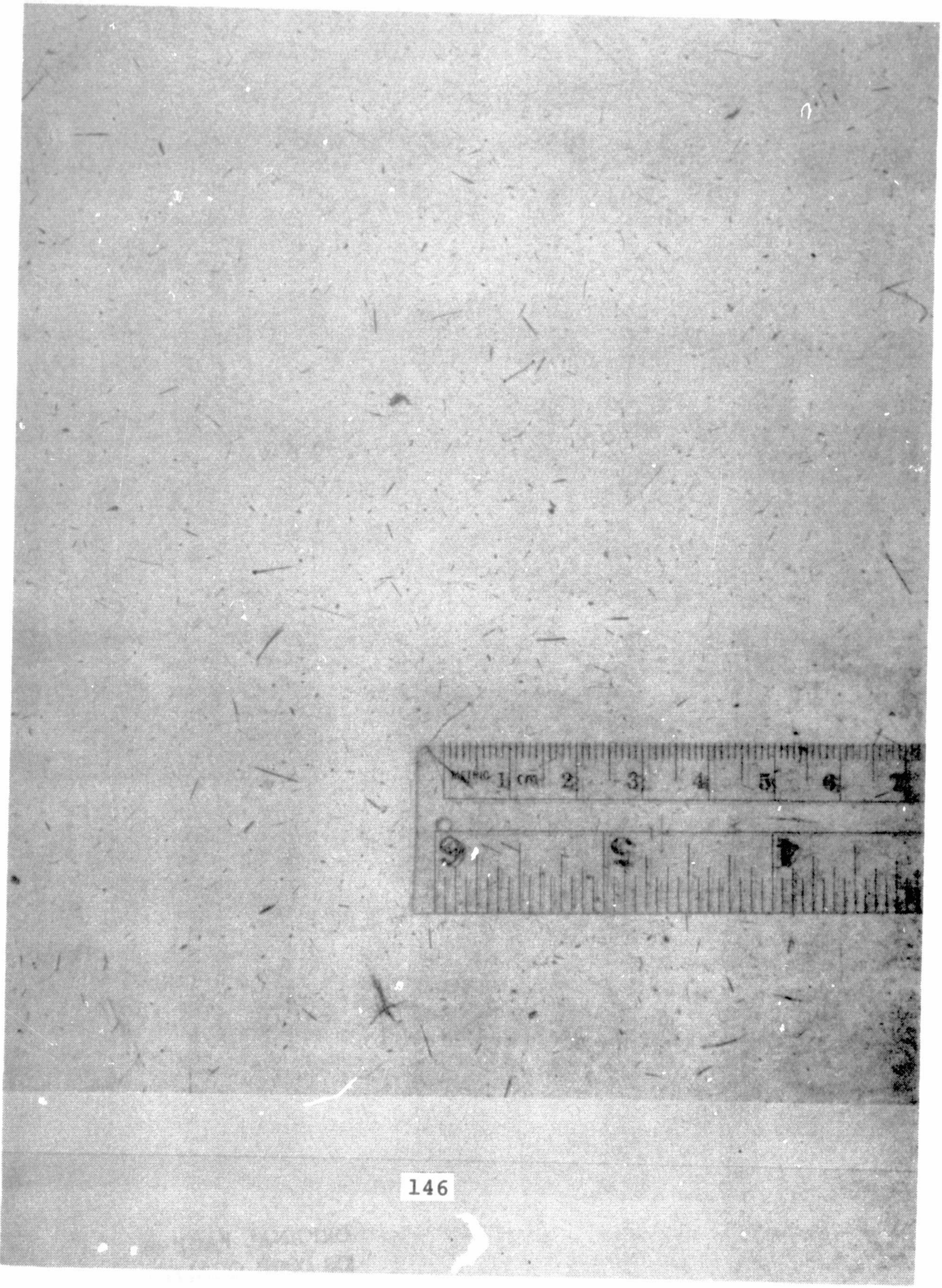


SAMPLE SIZE: 2" X 2" X 1/4"

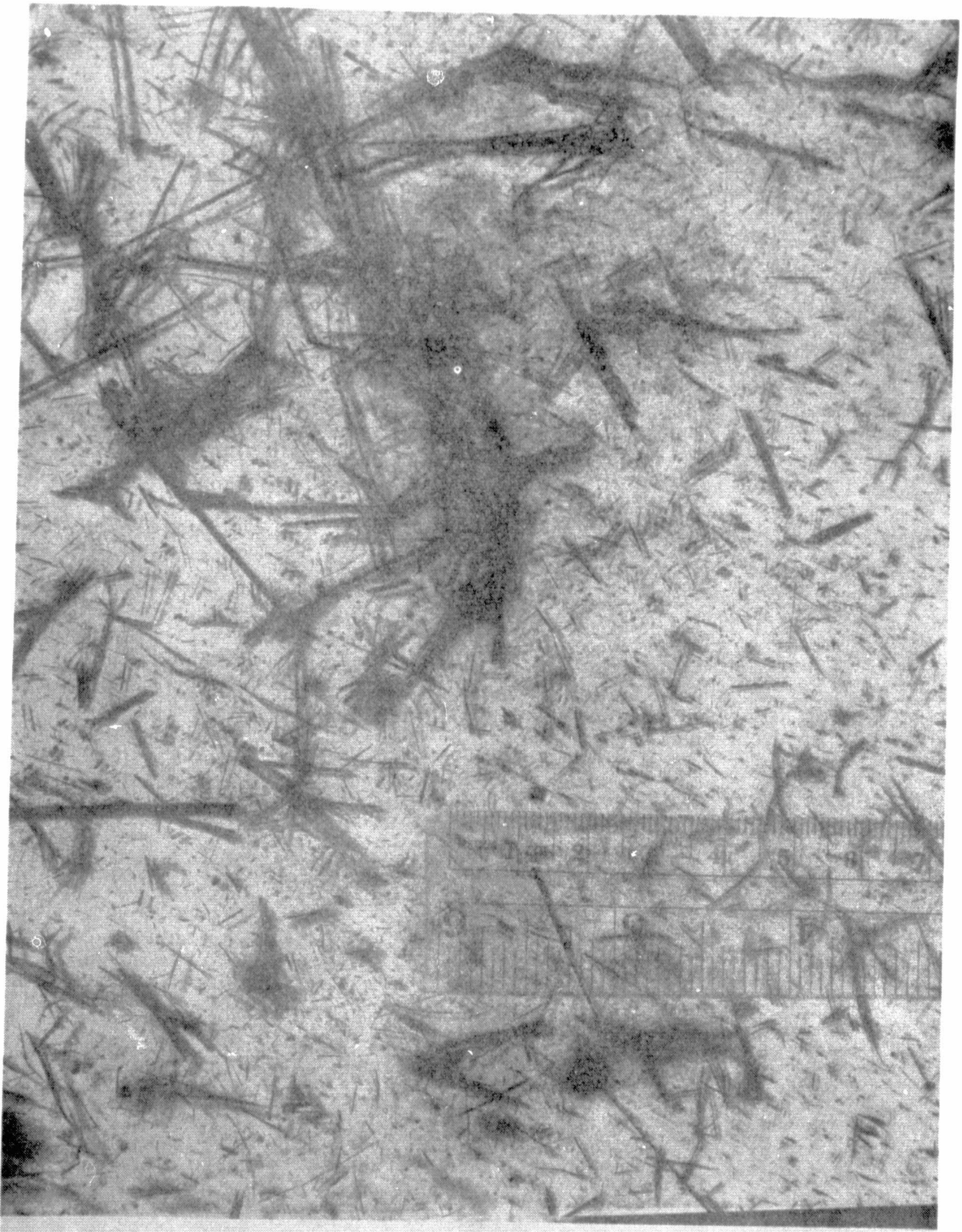
FUEL: PROPANE, JP-5

EFFECTS STUDIED: COMBUSTON TIME
FIBER RELEASE
SPONTANEOUS IGNITION TEMPERATURE
CHAR FORMATION
COMPOSITE CONSTRUCTION
ELECTRICAL PROPERTIES





METRIC 1 cm 2 3 4 5 6 7

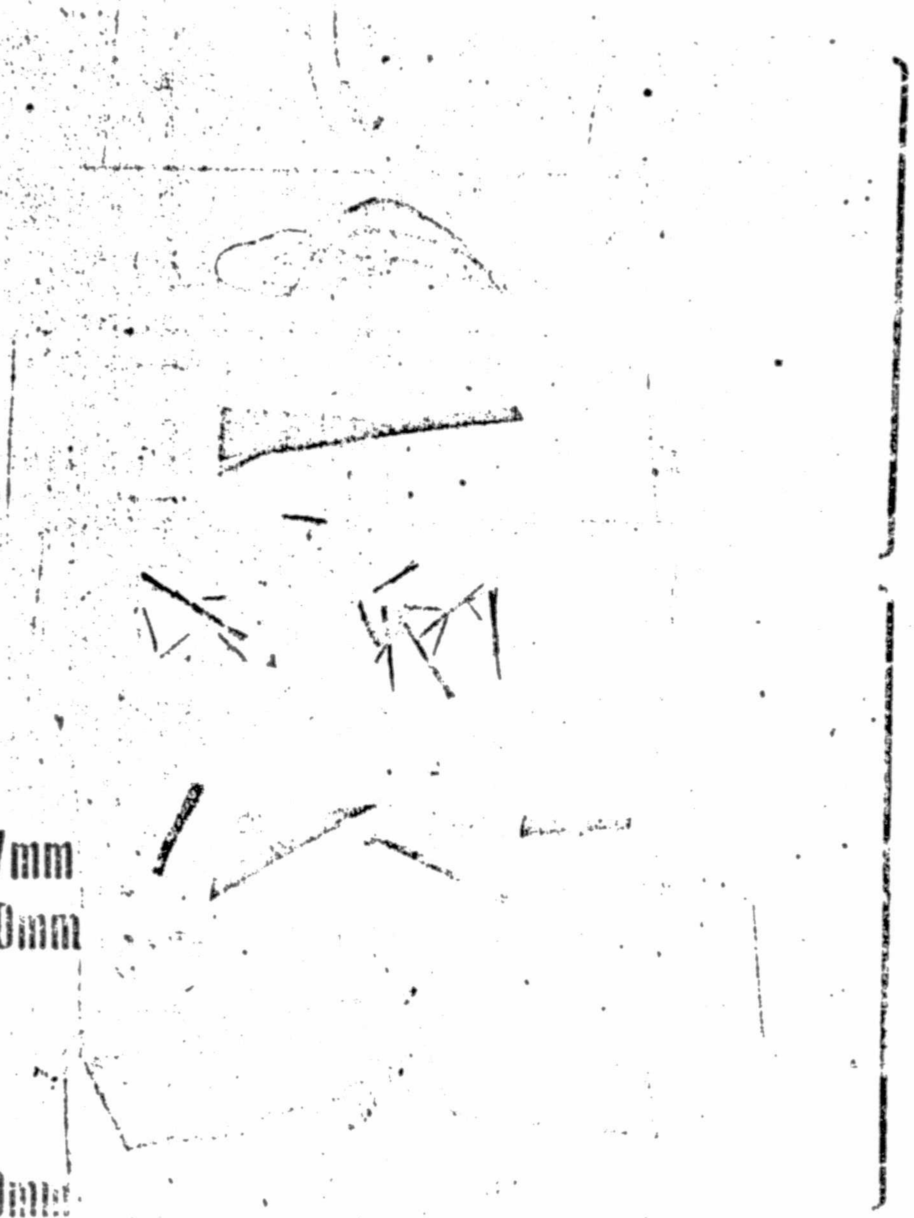


NAVY/DAHLGREN CHAMBER TESTS

TEST FIXTURE:	SAMPLE HOLDER
	FUEL PAN OR GAS BURNER
	EXPLOSIVE DELIVERY ARM
TEST PROCEDURES:	STATIC UNBURNED/EXPLODED
	STATIC BURNED/EXPLODED
	DYNAMIC BURNED/EXPLODED
	STATIC BURNED
RESIDUE COLLECTION:	GRID OF 8.9 cm PETRI DISHES (24)
	0.91 m GRID - 15.2 X 20.3 cm SHEETS (107) ADHESIVE-BACKED CELLULOSE ACETATE
	HAND PICKUP OF LARGE FRAGMENTS
	BROOM SWEEP OF FIBROUS MATERIALS
	POWER VACUUM SWEEP

COMPOSITE MATERIAL GROUPINGS

1. SINGLE FIBERS
2. LINT
3. BRUSH/CLUMP
4. BLAST FRAGMENTS
   WIDTH < 2mm
5. BLAST FRAGMENTS
   WIDTH = 2–7mm
   LENGTH < 25.0mm
6. LAMINAR
   WIDTH > 7mm
   LENGTH > 17.0mm



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COMPOSITE MATERIAL GROUPINGS

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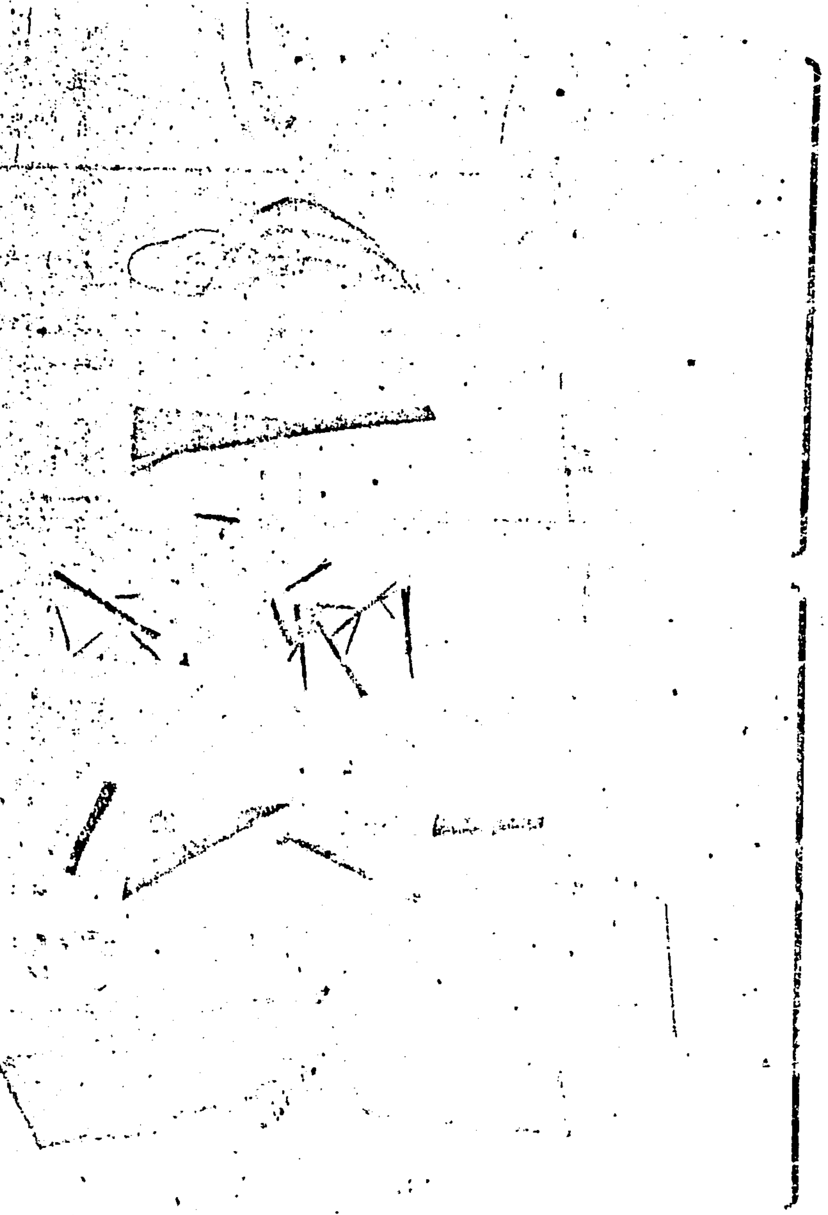

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GRAPHITE FIBER MODIFICATIONS

DR. R. J. DIEFENDORF, CHAIRMAN

NAME	ORGANIZATION
Roger T. Pepper	FMI Maine
Dennis Riggs	AMMRC
John Hurt	Army Research Office
J. R. Leal	Celanese Research Co.
L. H. Peebles	ONR/Boston
F. L. Vogel	Univ. of PA
H. P. Edelstein	DWT Naval Ship R&D Center
Judd Diefendorf	Renssalaer Polytechnic Institute
Brian Ence	George Washington University
J. T. Paul	Hercules Research Center
S. M. Rozowski	Ball State University
D. B. Fischbach	Univ. of Washington
D.M. Estering	George Washington University
W. D. Lee	US Army, MERADCOM
W. C. Schwemer	Vought Advanced Technology Center
C. A. Gaulin	Aerospace Corp.
R. Prescott	Great Lakes Research
Bill Chard	Battelle Columbus Lab
Guilio Varsi	Jet Propulsion Lab
Fred Hansen	NASA Ames

NASA Reporters: W.D. Brewer and R. K. Clark, LaRC

3/23/78

ISSUES FOR
GRAPHITE FIBER MODIFICATION
WORKING GROUP

1. Upon what principles might the electrical conductivity of graphite fibers be reduced?

2. What treatments should be investigated as appications of these principles?

3. For each treatment:

   (a) What are the likely effects on fiber mechanical properties?

   (b) What are the prospects for reducing the conductivity by a factor 10, 100, or 1000?

   (c) What are the prospects for retention of effectiveness after exposure to the high temperature encountered in a burning composite?

   (d) What is the likely impact on production costs?

   (e) What will be the effect on fiber matrix bonding?

4. Considering the aspects raised in issue 3 above, which treatments do you recommend for detailed investigation?

5. Can larger diameter fibers be produced without significant reductions in mechanical properties and handleability?

6. Can the cross-sectional shape of the fibers be altered so that their aerodynamic characteristics would be changed?

7. Could selected surface imperfections be introduced so that fibers would be less resistant to fire?

8. Can additives be used in the precursor that would make the fibers less resistant to fire?

9. What is your assessment of the current NASA research program in this area, and what changes do you recommend?

10. Rank the different generic (fiber modifications, fiber coatings, alternative fibers, epoxy resin modifications, epoxy resin replacements, hybrid composites) solutions as to their probability of success.

NASA REPORTERS' SUMMARY FOR GRAPHITE FIBER MODIFICATION WORKING GROUP

Two presentations were given prior to the working group general discussions. Roger Prescott of Great Lakes Carbon gave a summary of his company's experience with graphite fibers. Donald Esterling of George Washington University discussed his plans for hydrogenation of graphite fibers for increased electrical resistivity.

The focus of the fiber modification working group was on ways to alter the electrical, oxidative, and disseminative properties of graphite fibers. In particular, emphasis was placed on ways to increase the electrical resistivity of the fibers to eliminate the electrical hazards even though the fibers may be released to the environment, and on decreasing the stability of the fibers so that they would likely burn up in a fire and not be released. Changing the size and shape of the fibers to minimize the area over which they are disseminated was discussed briefly.

At the outset, the group recognized the importance of understanding the fundamentals of electrical conductivity and oxidative properties of graphite fibers. It was also noted that better definitions are required of what levels of resistivity are acceptable and of what the exposure conditions are in an actual fire.

INCREASED RESISTIVITY

Four potential solutions to the graphite fiber problem by way of fiber modification to increase electrical resistivity were identified:

1. Low temperature heat treamtent

2. Hydrogenation

3. Conversion to graphitic oxide

4. Doping

Low Temperature Heat Treatment.- It was suggested that by heat treating at low temperatures, the defect substructure of carbon fibers could be retained while maintaining the preferred orientation necessary for good mechanical properties. Increasing the defect concentration should significantly increase the electrical resistivity. The group consensus was that this technique could readily produce changes in resistivity by a factor of 10 or 20 and possibly 100. However, changes of three orders-of-magnitude or more were considered very unlikely. In addition, it was thought that the resulting fibers could be of significantly lower-strength than those treated at higher temperatures. It was also suggested that the low temperature heat treatment results in a less stable fiber which should be consumed more readily in a fire. It was noted that the environment in a large pool fire is reducing (oxygen depleted) and it is doubtful that even an oxidation-susceptible fiber would be consumed. An oxidation-susceptible fiber may be consumed upon inceneration of composite scrap. The question was raised as to whether or not changes in the wavelength and amplitude of the "undulating ribbons" in the fibers could affect the resistivity (crystallite scattering). For a number of reasons, the group thought that it was unlikely that ribbon changes would have any significant effect. The primary reason is that the mean free path of a carrier electron is probably shorter than the shortest wavelength one could produce in a ribbon and electron interactions with other defects predominate.

The low temperature heat treatment technique was considered to be the most advantageous as far as manufacturing is concerned. In fact, the carbon producers indicated that such a process would be welcomed and would have little impact on the cost of the fibers.

Hydrogenation of Fibers.- Electrical conduction is thought to be associated, in part, with the migration of electron holes created by surface defects such as unsatisfied chemical bonds, improperly coordinated atoms, etc. Those defects tend to trap electrons, creating holes by which electricity can be conducted. It was suggested that if these traps can be eliminated, the resistivity can be significantly increased. The procedure would be to introduce hydrogen into the fibers, to lock onto those dangling bonds, thus removing acceptor sites and eliminating the holes. The details of the hydrogenation procedure were not defined; however, it is likely that the fibers would be exposed to a hydrogen atmosphere at about 1000°C and 1 or 2 atmospheres pressure for about 1/2 hour. It could not be said whether or not there would be any effect, but the effect, if present could potentially be large.

The working group was not aware of any successful attempt to hydrogenate graphite. The question was also raised as to whether the hydrogenation process would be reversed in a fire. No one had anything firm to say about this question, but it was thought that if the hydrogen could be put in, it would probably stay.

The carbon manufacturers noted that whatever process was used, it would not be cost effective because of the hazards of working with hydrogen at high temperatures. They felt that, at present, hydrogenation would not be a viable approach from the manufacturing standpoint. The feeling of the group was that this approach had a small probability of success, but encouraged continuation of the work.

Conversion of Fibers to Graphitic Oxide.- The general procedure is to expose fibers to strong oxidizing solutions for a few minutes. The oxygen apparently enters between the graphite layers, locks onto loose double bonds, and eliminates current carriers. There are two positive features about this approach. First, available literature indicates that increases in resistivity of several orders of magnitude are possible.

Second, the graphitic oxide may be inherently less stable and burn up in a fire. Even if the exposure conditions were reducing, the fiber itself may be a sufficient source of oxygen to cause it to burn. The question was raised as to whether this instability would allow the fiber to survive fabrication. No one could say with any confidence what would happen in fabrication or in a fire. The major concerns about this approach were the instability and possible degradation of mechanical properties. At present, these are unknown factors.

The graphitic oxide approach would be expensive, again because of working with potentially explosive mixtures. However, the problems could probably be overcome in a production process.

In general, the group considered the graphitic oxide approach to have some promise. There were some suggestions to investigate perhaps fluorine, nitrogen or sulfur in addition to oxygen.

Doping.- This approach attempts to remove positive or negative carriers by introducing electron donor or acceptor atoms into the graphite structure. Doping was suggested, but was discussed very little by the group. It was suggested that there were some dopants such as nitrogen or boron and nitrogen together which could be beneficial.

DECREASED STABILITY AND CHANGES IN SHAPE AND SIZE

The group felt that introducing additives into precursors or introducing surface imperfections in fibers are probably not viable approaches for making fibers less resistant to fires. Surface imperfections would no doubt degrade fiber strength significantly and precursor additives may not be effective in a reducing (oxygen depleted) atmosphere.

The working group briefly considered changing the shape and size of fibers to alter the aerodynamic characteristics. It was decided that a circular cross-section fiber would have the greatest fall rate, and there is no incentive to produce fibers with different shapes. Fiber diameter could be increased by a factor of 2 while maintaining reasonable mechanical properties, probably without greatly affecting cost. However, producing fibers with changes in diameter greater than a factor of two would be prohibitively time consuming and costly.

In general, the potential solutions proposed by the Fiber Modification Working Group were not considered to be short term fixes. The expected time frame and cost for conducting feasibility studies, process development, and materials qualification program for just one approach was considered to be 2-5 years and $2M.

CONCLUSIONS

1. Fiber modification does not hold much promise for complete solutions to the graphite fiber problems.

2. Of the potential solutions discussed, the graphitic oxide appears to have the best chance of success in meeting electrical requirements.

3. Changes in fiber resistivity by a factor of 10 are achievable. Changes of more than two orders of magnitude are unlikely.

4. Introducing additives to reduce fiber stability is probably not a viable approach.

5. Changing size and shape of fibers is not likely to significantly improve the fall rate characteristics.

6. The proposed potential solutions are not short term fixes even if they work. The expected time frame and cost for just one approach to be fully developed is considered to be 2-5 years and $2M.

RECOMMENDATIONS

1. Continue concentrated research efforts in all the areas discussed.

2. Research should be conducted by university, government or other research labs (as opposed to fiber manufacturers).

3. Fiber manufacturers should be consulted and become actively involved when the feasibility of an approach has been demonstrated.

4. Rapid and effective information transfer between persons and organizations working on graphite fiber modification should be maintained through:

    (a) informal bimonthly newsletters

    (b) group meetings of actual researchers

REPORT OF

GRAPHITE FIBER MODIFICATION
WORKING GROUP

R. J. DIEFENDORF, CHAIRMAN

GRAPHITE FIBER MODIFICATIONS

- LOW TEMPERATURE HEAT TREATMENT
- DOPING
- HYDROGENATION
- GRAPHITIC OXIDE

DISCUSSION TOPICS

(TECHNICAL)

- CONDUCTIVITY
- OXIDATION
- DISSEMINATION

CONDUCTIVITY

- CHARGE CARRIER (WHERE FROM?)
- GRAPHITE
  - FEW CARRIERS
  - HIGH MOBILITY
- CARBON
  - MANY CARRIERS
  - LOW MOBILITY

POSSIBLE SOLUTIONS

- DOUBLE BONDS
  - GRAPHITIC OXIDE
- DANGLING BONDS
  - HYDROGENATE
- NITROGEN COMPENSATION
- LOW TEMPERATURE HEAT TREATMENT
- CRYSTALLITE SCATTERING

PROBABILITY OF CONDUCTIVITY CHANGE

10 X - EXCELLENT

100 X - FAIR

1000 X - POOR

FIRE SURVIVABILITY

(REDUCING CONDITIONS)

- HIGHER OXIDIZABILITY
- LOWER HEAT TREATMENT TEMPERATURE
- ADDITIVES

FIBER DISSEMINATION

- SHAPE - ROUND BEST
- MASS - LARGER DIAMETER

COSTS PER MODIFICATION

$$\left.\begin{array}{l}\text{FEASIBILITY}\\[1em] \text{PROCESS DEVELOPMENT}\\[1em] \text{QUALIFICATION}\end{array}\right\} \quad \$2 \text{ X } 10^6$$

INFORMATION TRANSFER

- BIMONTHLY INFORMAL REPORTS
- GROUP MEETINGS

RANKING OF GENERIC SOLUTIONS

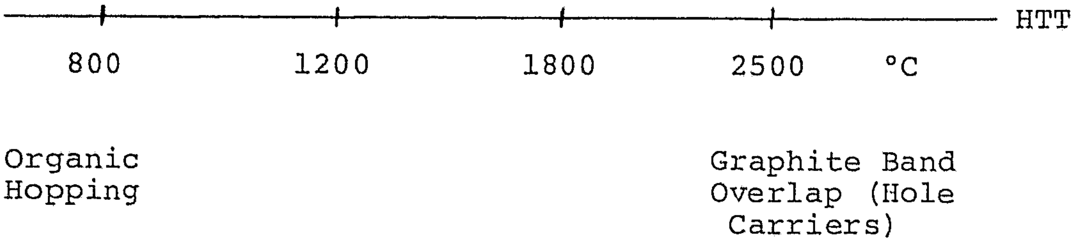
(1 - 3 BASIS)

	RANK
FIBER MODIFICATION	1.94
FIBER COATING	1.82
ALTERNATE FIBERS	1.35
EPOXY MODIFICATION	2.53
EPOXY REPLACEMENT	2.53
HYBRIDS	1.71

HYDROGENATION OF CARBON FIBERS

by

D. M. Esterling
The George Washington University



What are charge carriers?

What is conduction mechanism?

How are the carriers introduced?

(Band overlap vs. defects vs. impurities (N))

Different answers for different HTT.

Sensible way to decrease σ for HTT 2,500 °C (e.g. introduce impurities) may be exactly wrong at HTT of 1400 °C.

High HTT - High mobility, few carriers (Little hope, only small changes in σ at best).

Low HTT ($\leq$ 1800 °C) - lower mobility, many carriers.

Electron states

- Gap?
- Continuous
  - Localized (Mott/Anderson)
  - Delocalized

Conduction - Holes in disordered system

Origin of holes - acceptor sites of unknown origin (electron traps)

- Surface?
- Dangling Bonds?
  Improperly coordinated atoms?

Remove electron traps by eliminating defects.

Hydrogen Bonds - Saturate dangling bonds (fill electron trap with electron that is not coming from carbon chain)

- Why not dope with donor atoms (alkalais)
- Really looking for chemical effect (Local change in structure). Dopants give global change in electron density.

How?? 900° - 1000 °C @ 1 ATM H_2 (No Catalyst)

400° - 500 °C @ 1 ATM H_2 (Catalyst)

GRAPHITE FIBER COATING & ALTERNATIVE FIBERS

Dr. James Economy, Chairman

NAME	ORGANIZATION
Sam C. Aker	Bell Helicopter
Robert Curley	McDonnell Douglas Corp.
James Economy	IBM Research Lab.
Frank Galasso	United Technologies
James V. Gauchel	DeSoto Inc.
John H. Gaul, Jr.	Dow Corning Corp.
Max F. Grandey	General Electric Co.
Robert S. Hamilton	Carborundum Corp.
Lee McKague	General Dynamics
Paul E. McMahon	Celanese Research Co.
Roger T. Pepper	Fiber Materials, Inc.
Kumar Ramokalli	Jet Propulsion Lab.
S. R. Riccitiello	NASA Ames
V. N. Saffire	General Electric Co.
John T. Schell	NASA Marshall
Richard J. Shuford	Army Mat. & Mech. Research Center
Robert A. Simon	Naval Surface Weapons Center
R. V. Subramanian	Washington State University
Raymond J. Suplinskas	AVCO Specialty Materials
R. J. Tomerlin	Bell-Helicopter Textron
Herbert F. Volk, Sr.	Union Carbide Corp.
Charles B. Whitset	McDonnell Douglas Corp.

NASA Reporters: S. S. Tompkins and C. M. Pittman, LaRC

ISSUES FOR

GRAPHITE FIBER COATING ALTERNATIVE FIBERS

WORKING GROUP

1. What high electrical resistance coatings can be applied to graphite fibers? How thick would they need to be? What coating method would be employed?

2. Which of these coatings is likely to remain intact after fire and explosion?

3. Which of these coatings can be readily applied during the fiber manufacturing process?

4. What precursor coatings can be applied that would convert to a high electrical resistance coating in-situ during fire and explosion?

5. What coatings can be applied that might result in fiber "clumping" as a result of exposure to fire and explosion?

6. For all types of coatings considered, what is the likely effect on fiber-matrix bonding?

7. What other fibers (e.g., BN, Kevlar, SiC) should be considered as alternatives to graphite? What are their advantages and disadvantages?

8. Rank the potential replacement fibers as to the probability that they could be incorporated into the ACEE program.

9. Would hollow glass or graphite fibers be worth developing as a potential solution?

10. What is your assessment of the current NASA research program in this area, and what changes do you recommend?

11. Rank the different generic solutions (fiber modifications, fiber coatings, alternative fibers, epoxy resin modifications, epoxy resin replacements, hybrid composites) as to their probability of success.

NASA REPORTERS' SUMMARY FOR FIBER COATINGS AND ALTERNATIVE FIBERS WORKING GROUP

Four presentations preceded the working group open discussions. Kumar Ramokalli discussed work at JPL on coating graphite fibers to increase electrical resistivity as well as to promote clumping of fibers to reduce their dissemination. R. V. Subramanian of Washington State University discussed an electrolytic technique for coating fibers with a polymer. Robert Hamilton of Carborundum discussed his company's development of a BN fiber. Ashok Dhingra gave a report on DuPont's development of Kevlar and FP (Al_2O_3) fibers as possible replacement for graphite.

COATINGS

The working group discussions of coatings were directed toward four areas:

1. Inorganic coatings - SiC, B, B_4C, BN, Si_3N_4, SiO_2

2. Organic and metallorganic coatings to provide a high density char layer on the fiber surface.

3. Metallic coatings - Al, Cr, Ni

4. Catalytic coatings to increase the fiber oxidation rate.

Items 1 and 2 received the most attention. The rationale for using metallic coatings, item 3, was the possiblity of forming a metal oxide on the fiber surface during a fire. However, considerable doubt was expressed as to whether sufficient oxygen would be available to form the oxide. Catalytic coatings, item 4, were thought to be more in the province of the fiber modification working group and were only briefly discussed.

Inorganic Coatings.- The consensus of the working group was that the inorganic coating work, underway or being initiated, includes the most promising coating materials. These coating materials include:

1. SiC
2. B
3. B_4C
4. BN
5. Si_3N_4
6. SiO_2
7. Metallic silicates

The working group felt that the coating efforts should critically examine:

1. The effect of the coating on composite mechanical properties.

2. The effect of the coating on fiber release, fall rate, and electrical properties.

3. The effect of the coating on cost.

4. The chemical stability of nitride coatings.

Organic Coatings Which Char.- The objective of this work is to find an organic coating which, when charred, would facilitate fiber clumping and/or act as an insulative coating. The coating must have a high char yield and also provide an effective fiber-matrix bond. The group encouraged continued work on silicones, high temperature polymers such as polybenzimidazole (PBI) and polyphenylquinoxoline (PPQ) and evaluation of new techniques of electrolytic polymer coating deposition.

Alternate Fibers

The alternate fibers which were discussed included:

1. BN fibers

2. High modulus organic fibers

3. αAl_2O_3 (FP fibers from DuPont)

4. SiC - both large and small diameter fibers

5. B fibers with a carbon core

6. Glass fibers

7. B_4C fibers

8. 33 μm carbon fibers

9. AlB_2 flakes

These alternate fibers are listed more or less in the order in which the working group felt that the fibers showed the most promise. Boron and glass fibers were not discussed extensively. The general consensus was that these fibers are available and should be considered for some applications. The large diameter carbon fibers, item

8, were mentioned because of their potential for increasing the fiber fall rate, however, their mechanical properties would require substantial improvement. The AlB_2 flakes were mentioned in connection with a hybrid composite of AlB_2 flakes and carbon fibers. This approach could reduce the amount of carbon fibers and, therefore, reduce the risk.

BN Fibers.- Carborundum has prepared small experimental samples of BN fibers with the following properties.

E = 30-50 Msi
σ = 300 ksi
ρ = 1.8 g/cc

The primary advantage of BN fibers is that they are very similar to carbon fibers and therefore, would probably perturb the present composite technology less than any other alternate fiber. The main disadvantage of BN fibers is that at least 4-5 years of work would be required to develop a commercial fiber at the present research pace.

High Modulus Organic Fibers.- DuPont has five new experimental fibers with the following properties:

E = 20-30 Msi
σ = 300-600 ksi
ρ = 1.22-1.48 g/cc

One or more of these fibers could replace carbon in some applications. However, these fibers have poor compression properties, and composite fabrication technology would require development. The working group recommended that these fibers be evaluated in hybrid configurations because of the low fiber modulus.

α Al_2O_3 (FP) Fibers. -DuPont has developed Al_2O_3 yarn which is cost competitive with carbon fiber and has the following properties:

E = 55 Msi
σ = 200 ksi (300 ksi expected with smaller diameter)
ρ = 3.9 g/cc
diameter = 20 μm

This fiber could be commercially available in the very near future. The disadvantages of FP fibers are their high density and brittleness. The recommendation of the working group was to evaluate FP fibers in hybrids in an attempt to improve composite fracture strain.

SiC Fibers.- AVCO has developed a 130 μm SiC (carbon core) fiber with the following properties:

$E = 50\text{-}60$ Msi
$\sigma = 500$ ksi
$\rho = 3.2$ g/cc

The advantages of this fiber are its excellent mechanical properties. The disadvantages are the large fiber diameter and high density. The working group recommended that these fibers be evaluated in hybrid composites and that a small diameter SiC fiber be developed. (Japan has reportedly developed a small diameter SiC fiber.)

B_4C Fibers .- A continuous filament B_4C yarn, with the following properties has been reported:

$E = 40\text{-}55$ Msi
$\sigma = 300\text{-}400$ ksi
$\rho = 2.28$ g/cc
yarn - 720 ends, 9 μm diameter

The advantages of this yarn are that the properties are similar to carbon fibers. The disadvantages are that only a laboratory process has been defined and 2-3 years are required for scale-up. Also the fibers will be more expensive than carbon. The working group recommended that a cost analysis, including production scale-up, be made to determine B_4C fiber feasibility.

CONCLUSIONS

1. No particular coating is presently favored over any other.

2. No coating should be eliminated without more information and tests.

3. BN fibers should be considered a long term substitute for carbon. Other alternate fibers should only be considered for hybrid composites.

4. Any change in fiber or coating is necessarily a long term solution (3-5 years).

5. A critical lack of quantitative information on the properties required to alleviate the electrical hazard is apparent. For example:

a. How much must the overall fiber resistance be increased?

b. How much fiber clumping is required and how many fibers make a clump?

c. How much must the settling rate be increased?

Answers to these and similar questions should be obtained as soon as possible so that the research effort can proceed toward known objectives.

RECOMMENDATIONS

The working group made the following recommendations.

Continue work on:

1. Inorganic coatings
2. Organic coatings
3. Organometallic coatings
4. BN fibers

Initiate programs on:

1. Hybrid composites of high modulus organic fibers with B (carbon core) fibers, SiC (carbon core) fibers and Al_2O_3 (FP) fibers.

2. Producing small diameter SiC fibers.

3. B_4C yarn cost analysis and production scale-up.

REPORT OF

GRAPHITE FIBER COATING & ALTERNATIVE FIBERS WORKING GROUP

Dr. JAMES ECONOMY, CHAIRMAN

GRAPHITE FIBER COATING AND ALTERNATIVE FIBERS

OVERVIEW

COATINGS

- INORGANIC: SiC, B, B_4C, BN, Si_3N_4, SiO_2
- ORGANIC/METALLORGANIC: HIGH CHAR
- METALLIC: Al, Cr, Ni
- CATALYTIC: OXIDATION OF CARBON
- SEVERAL POINTS OF CONCERN

ALTERNATIVE FIBERS

- HIGH MODULUS ORGANICS
- BN
- α Al_2O_3(FP)
- SiC LARGE, SMALL DIAMETER
- B(CARBON CORE)
- GLASS
- B_4C
- 33 μm CARBON
- AlB_2 FLAKES

ORIGINAL PAGE IS
OF POOR QUALITY

INORGANIC COATINGS

- PROGRAMS INITIATED AT JPL, AVCO, UTC AND UCC ON

  SiC
  B
  B_4C
  BN
  Si_3N_4
  $M_2Si_2O_3$

- CRITICAL ISSUES
  - COATING THICKNESS VS. VOLTAGE
  - EFFECT ON STRENGTH
  - CHEMICAL STABILITY OF NITRIDES
  - POTENTIAL FOR CLUMPING
  - COATING PROCESS/COST

ORGANIC COATINGS WHICH CHAR

PURPOSE:
- WOULD BE REQUIRED FOR CHAR FORMING MATRIX
- MAY FACILITATE CLUMPING
- CHAR MAY ACT AS INSULATOR

REQUIREMENTS:
- HIGH CHAR YIELD
- EFFECTIVE FIBER-MATRIX BOND

RECOMMENDATIONS:

- CONTINUE STUDIES ON SILICONE

- EVALUATE HIGH TEMPERATURE POLYMERS AS COUPLERS, PBI, PPQ

- EVALUATE NEW TECHNIQUES TO IMPROVE INTERLAMINAR SHEAR PROPERTIES, ELECTROLYTIC POLYMERIZATION

HIGH MODULUS ORGANIC FIBERS

DUPONT HAS FIVE NEW EXPERIMENTAL FIBERS

E 20 - 30 msi

σ 300 - 600 ksi

ρ 1.22 - 1.48 g/cc

ADVANTAGES: COULD REPLACE CARBON IN CERTAIN AREAS

DISADVANTAGES: POOR COMPRESSION PROPERTIES, BONDING

RECOMMENDATION: EXPLORE IN HYBRIDS.

BN FIBERS

CARBORUNDUM HAS PREPARED SMALL EXPERIMENTAL SAMPLES OF HIGH MODULUS BN FIBERS

E	30 - 50 Msi
σ	300 ksi
ρ	1.8 g/cc

ADVANTAGES: BN FIBER IS VERY SIMILAR TO GRAPHITE

DISADVANTAGES: 4 - 5 YEARS OF DEVELOPMENT REQUIRED AT PRESENT PACE

PLAN: NASA/ONR PLANNING JOINT SUPPORT

α Al_2O_3 (FP)

DuPONT HAS DEVELOPED Al_2O_3 YARN COST COMPETIVE WITH GRAPHITE FIBER

E 55 Msi

σ 200 ksi (300 ksi SEEN)

ρ 3.9 g/cc

DIAMETER 20 μm

ADVANTAGES: AVAILABLE IN VERY NEAR FUTURE

DISADVANTAGES: HIGH DENSITY, BRITTLENESS

RECOMMENDATIONS: EVALUATE IN HYBRID
IMPROVE FRACTURE STRAIN

SiC

AVCO HAS DEVELOPED A 130 μm SiC (C-CORE) FILAMENT

E 50 - 60 Msi

σ 500 ksi

ρ 3.2. g/cc

ADVANTAGES: EXCELLENT MECHANICAL PROPERTY

DISADVANTAGES: DIAMETER AND DENSITY

RECOMMENDATIONS: EVALUATE IN HYBRID
DEVELOP SMALL DIAMETER TOW

B_4C YARN

A CONTINUOUS FILAMENT YARN HAS BEEN REPORTED

E 40 - 55 Msi

σ 300 - 400 ksi

ρ 2.28 g/cc

YARN 720 ENDS, 9 μm DIAMETER

ADVANTAGES: SIMILAR IN PROPERTIES TO GRAPHITE

DISADVANTAGES: LAB PROCESS DEFINED BUT WILL REQUIRE
2 - 3 YR. SCALE-UP.
COST GRAPHITE

RECOMMENDATION: CARRY OUT COST ANALYSIS

RECOMMENDATIONS

CONTINUE PLANS WITH

- INORGANIC COATINGS
- ORGANOMETALLIC COATINGS
- BN FIBERS

INITIATE PROGRAMS ON

- HIGH CHAR YIELD ORGANIC COATINGS
- HYBRID OF HIGH MODULUS ORGANICS
  WITH B (CARBON CONE), SIC (CARBON CORE)
  Al_2O_3 (FP)
- B_4C YARN SCALE-UP
- LOW COST SiC TOW

ORGANIC FIBERS AND HYBRID COMPOSITES

ASHOK DHRINGRA
E.I. DuPONT

MARCH 23, 1978

EXPERIMENTAL HIGH MODULUS ORGANIC FIBERS

Properties of certain experimental organic fibers exhibiting very high strengths and high moduli will be discussed. These have tensile strengths ranging from 400 Kpsi to 600 Kpsi and tensile moduli ranging from 25 to 30 x 10^6 psi. Fiber densities are low and range from 1.22 to 1.46 g/cc. These fibers should be of interest in composites provided an effective transfer of their properties into laminates can be achieved.

FP/KEVLAR® AND GRAPHITE/KEVLAR® HYBRID COMPOSITES

An experimental inorganic aluminum oxide fiber designated Fiber FP is currently under development in the Du Pont Company. This fiber is characterized by high modulus, outstanding compressive strength, hydrolytic and chemical stability and nonconductivity. Combining Fiber FP or graphite with Kevlar® aramid fiber produces hybrid composite structures having significantly improved combination of properties not attainable with single fibers. The properties of FP/epoxy, FP/polyimide, FP/Kevlar®/epoxy hybrid and Graphite/Kevlar®/epoxy hybrid will be discussed.

POSSIBLE SOLUTIONS

NEW FIBERS

1. HIGHER MODULUS ORGANIC FIBERS (BEYOND KEVLAR®)
2. HIGHER TENSILE STRENGTH FP FIBER
3. LOWER DENSITY INORGANIC FIBER (MODIFIED FP)

● MODULUS	40MM PSI
● STRENGTH	300 KPSI
● ELONGATION	0.8%

APPROACH

HYBRID COMPOSITES

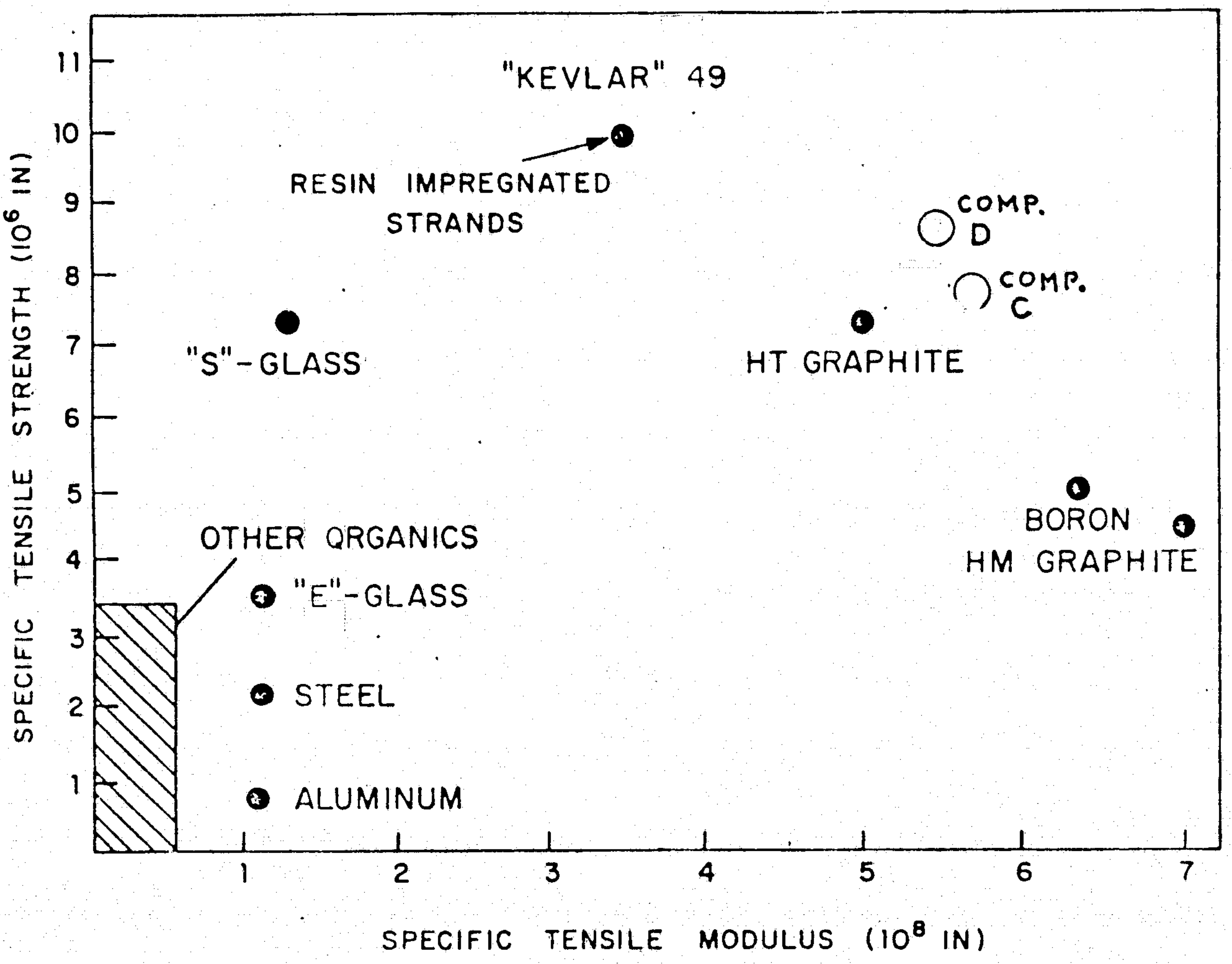
C-3

EXPERIMENTAL HIGH MODULUS ORGANIC FIBERS

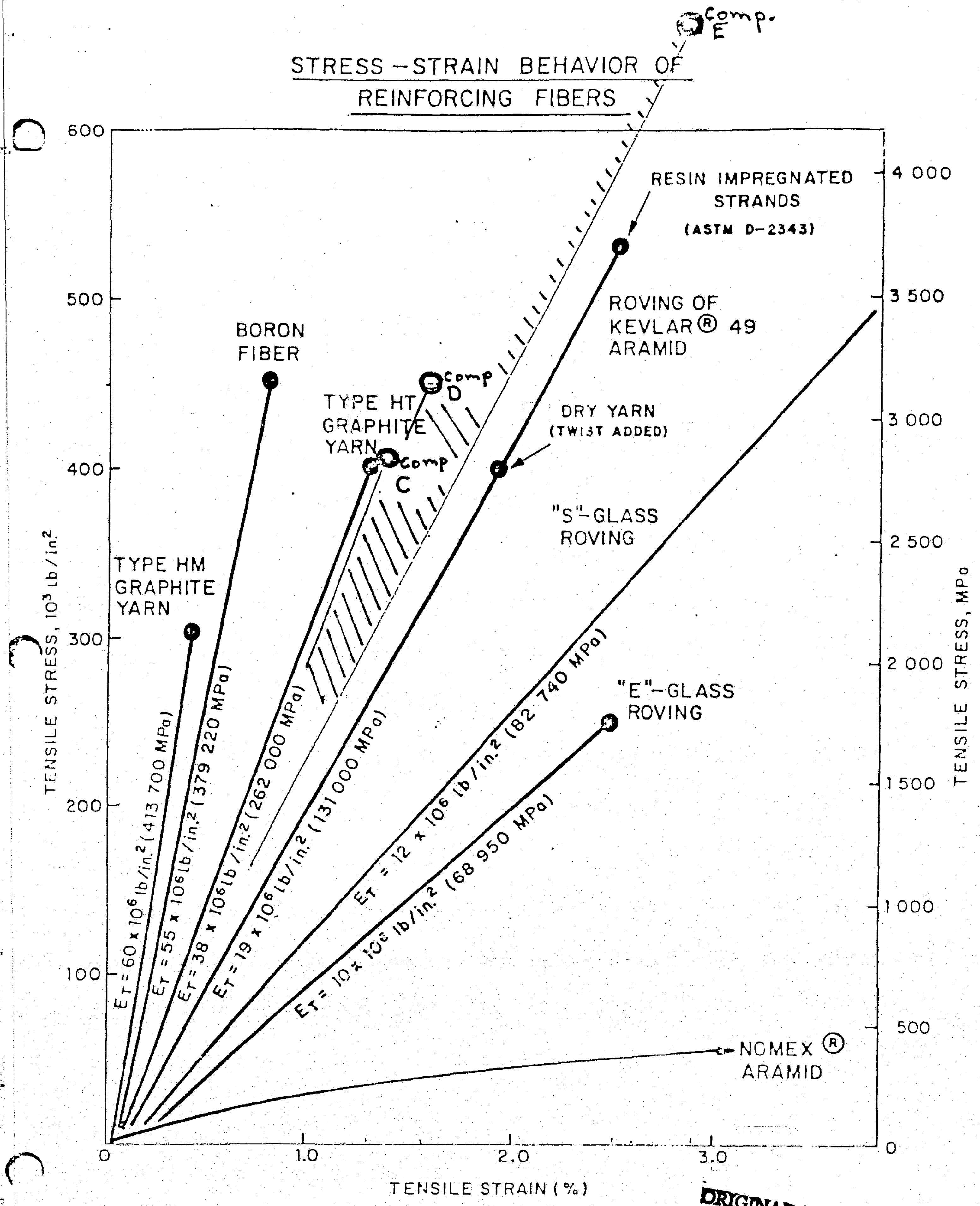
	Density (lb/in^3)	Tensile Strength (Kpsi)	Tensile Modulus (10^6 psi)	Specific Strength (10^6 in)	Specific Modulus (10^8 in)	How Tested
Composition A	.052	341	25.8	6.6	5.0	10 in. yarn
Composition B	.052	336	27.4	6.5	5.3	10 in. yarn
Composition C	.052	408	29.6	7.8	5.7	10 in. yarn
Composition D	.052	450	28.8	8.7	5.5	10 in. yarn
Composition E	.044	664	20.5	15.1	4.7	10 in. yarn in resin

COMP.
E

SPECIFIC TENSILE STRENGTH AND SPECIFIC TENSILE MODULUS OF REINFORCING FIBERS



STRESS – STRAIN BEHAVIOR OF REINFORCING FIBERS



ASTM D2343-67 RESIN IMPREGNATED STRAND TEST

MECHANICAL PROPERTY COMPARISON
FP/KEVLAR® 49/EPOXY -VS- KEVLAR® 49/EPOXY

PROPERTY	KEVLAR®/EPOXY (60/40)	FP/KEVLAR®/EPOXY (30/30/40)	CHANGE
COMPRESSIVE MODULUS, MPSI	11.5	21	1.8X
COMPRESSIVE STRENGTH, KPSI	40	150	3.75X
TENSILE MODULUS, MPSI	14	20	1.4X
TENSILE STRENGTH, KPSI	193	148	-23%

- COMBINING FP WITH KEVLAR® GREATLY IMPROVES STIFFNESS AND COMPRESSIVE STRENGTH

TABLE II

PROPERTIES OF UNIDIRECTIONAL "THORNEL" 300, "KEVLAR" 49 AND HYBRID COMPOSITES - NOMINAL FIBER VOLUME FRACTION = 0.60

		Tension		Compression		Flexure		Short Beam Shear Stress (ksi)	Prepreg Cost $/lb
Percentages of "Thornel" 300/ "Kevlar" 49 Fibers	Specific* Gravity	Modulus (10^6psi)	Ultimate Stress (ksi)	Stress at 0.02% Offset (ksi)	Ultimate Stress (ksi)	Stress at 0.02% Offset (ksi)	Ultimate Stress (ksi)		
100/0	1.60	21.1	227	98.4	146	233	233	13.2	60
75/25	1.56	17.4	186	68.8	136	181	197	11.0	48
50/50	1.51	15.7	176	59.9	99.8	120	160	8.1	35
0/100	1.35	11.2	183	26.4	41.5	49.2	91.9	7.1	10

---

*Data supplied by Fiberite

TABLE III

MECHANICAL PROPERTIES OF "KEVLAR" 49-"THORNEL" 300 HYBRID BALANCED FABRIC COMPOSITES

Tension and Compression Data
Normalized to 65% Fiber Volume Fraction

Ratio of "Kevlar" 49-to-"Thornel" 300	Resin	Specific Gravity	Modulus (10^6 psi)	Tensile Strength (10^3 psi)	Compressive Stress		Short Beam Shear Strength (10^3 psi)
					At 0.02% Offset (10^3 psi)	Ultimate (10^3 psi)	
100/0	Fiberite 934	1.40	5.2	79	11.0	22	3.8
50/50	"	1.49	7.0	58	23	33	4.2
25/75	"	1.57	8.3	63	32	46	4.7
0/100	"	1.60	8.7	63	47	81	5.8
50/50	BP-907	1.44	6.7	60	24	42	7.0

TABLE VI

MECHANICAL PROPERTIES OF "KEVLAR" 49-"THORNEL" 300 HYBRID UNIDIRECTIONAL FABRIC COMPOSITES

Tension and Compression Data
Normalized to 65% Fiber Volume Fraction

Ratio of "Kevlar" 49-to-"Thornel" 300	Resin	Specific Gravity	Modulus (10^6 psi)	Tensile Strength (10^3 psi)	Compressive Stress		Short Beam Shear Strength (10^3 psi)
					At 0.02% Offset (10^3 psi)	Ultimate (10^3 psi)	
50/50	Fiberite 934	1.44	12.6	103	32	52	7.9
50/50	BP-907	1.40	11.3	104	44	56	8.1

TABLE V

NOTCH SENSITIVITY OF [0/90] AS GRAPHITE-"KEVLAR" 49 HYBRID COMPOSITES

Reinforcement	Modulus (10^6psi)	Thick. (in.)	Nominal Crack Length (in.)	Stress at Failure		Fracture Toughness K_c (ksi-in$^{1/2}$)	Stress Concentration Factor K
				Gross σ_g (ksi)	Net σ_n (ksi)		
AS Graphite (Tape) 8-Ply	7.67	0.048	0	75.8	75.8	--	--
	--	0.048	0.25	14.88	19.88	9.37	3.82
12-Ply	7.87	0.072	0	78.5	78.5	--	--
	--	0.072	0.25	15.31	20.5	9.66	3.82
"Kevlar" 49 (Style 120 Fabric)	4.17	0.030	0	72.9	72.9	--	--
	--	0.030	0.25	25.2	34.3	16.16	2.13
Hybrid (8 Plies of Graphite Tape + 4 Plies of "Kevlar" 49 Fabric)	6.32	0.078	0	66.5	66.5	--	--
	--	0.078	0.25	20.2	27.0	12.75	2.46

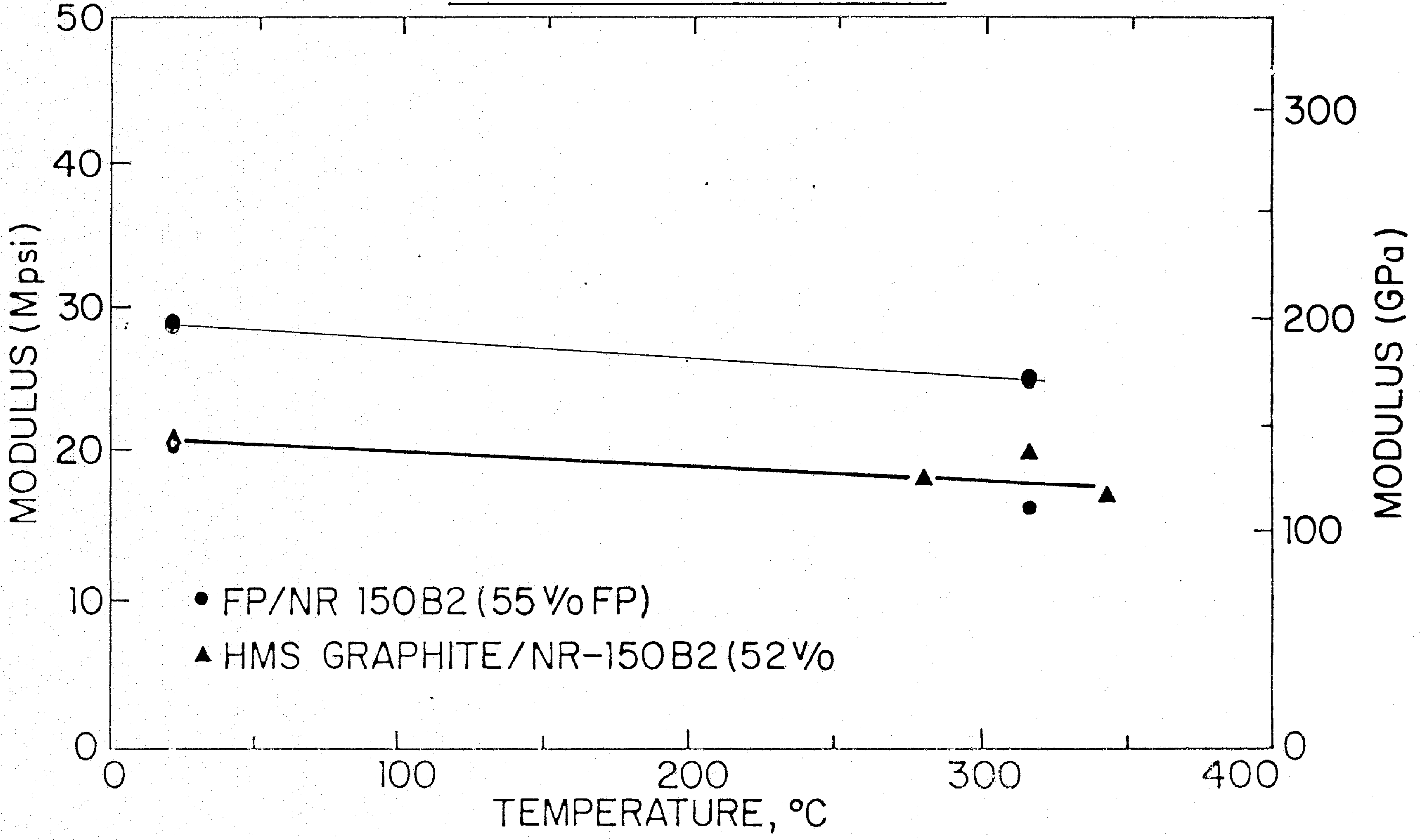
MECHANICAL PROPERTY COMPARISON OF HYBRID COMPOSITES

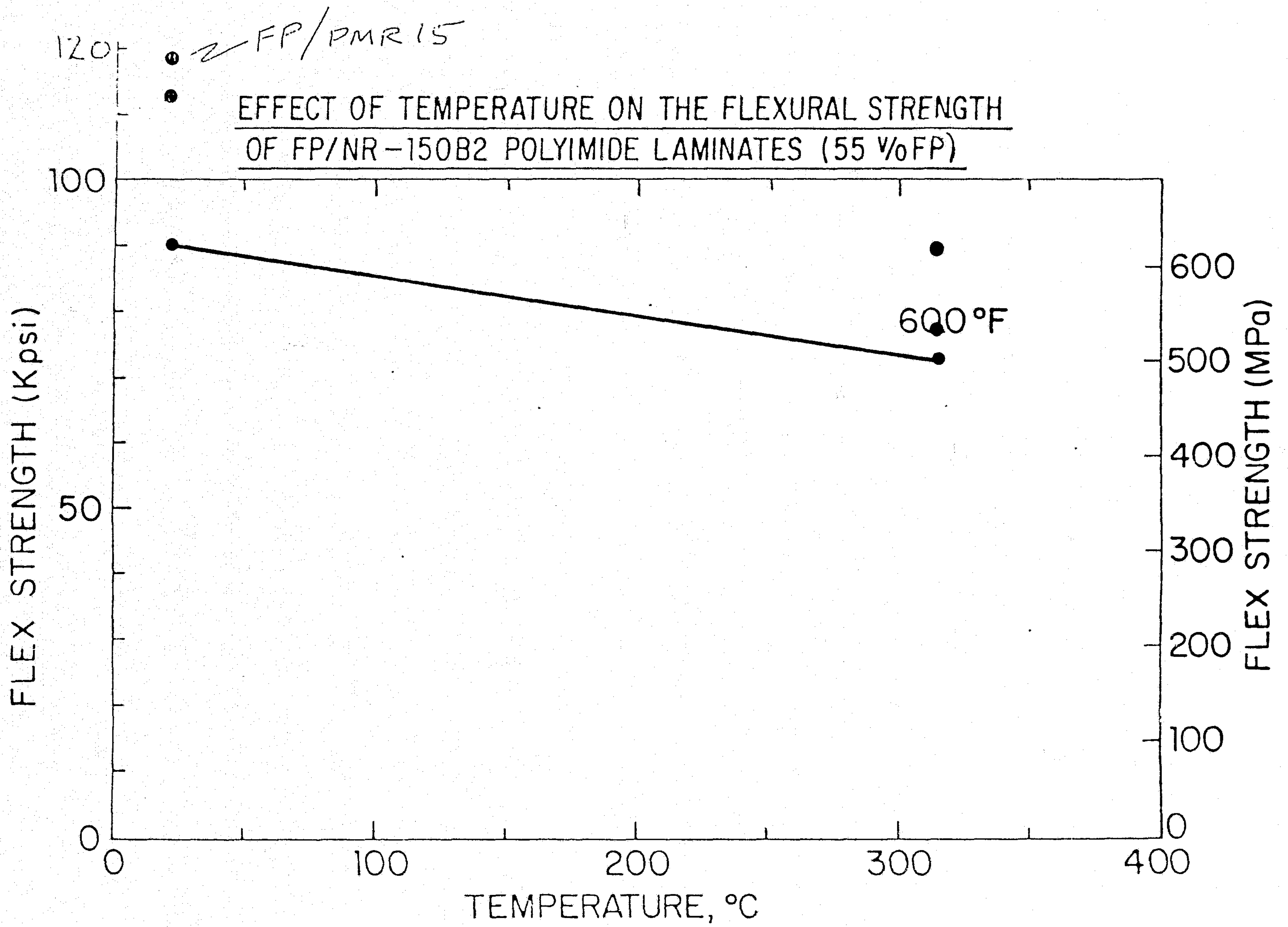
PROPERTY	KEVLAR®/TH 300/EPOXY (30/30/40)	FP/KEVLAR®/EPOXY (30/30/40)	KEVLAR®/EPOXY (60/40)	TH 300/EPOXY (60/40)
TENSILE MODULUS, MPSI	16	20	11	21
TENSILE STRENGTH, KPSI	176	148	183	227
COMPRESSIVE MODULUS, MPSI	16	21	11	21
COMPRESSIVE STRENGTH, KPSI	100	150	40	146
FLEXURE STRENGTH, KPSI	160	180	92	233
SHORT BEAM SHEAR, KPSI	8.1	9.1	7.1	13.2
DENSITY, G/CM^3 (LB/IN^3)	1.51 .055	1.95 .070	1.35 .049	1.60 .058

SPECIFIC PROPERTY COMPARISON OF HYBRID COMPOSITES

SPECIFIC PROPERTY	KEVLAR®/TH 300/EPOXY (30/30/40)	FP/KEVLAR®/EPOXY (30/30/40)	KEVLAR®/EPOXY (60/40)	TH 300/EPOXY (60/40)
SPECIFIC TENSILE MODULUS, 10^8 IN	2.91	2.86	2.24	3.62
SPECIFIC TENSILE STRENGTH, 10^6 IN	3.2	2.11	3.73	3.91
SPECIFIC COMPRESSIVE MODULUS, 10^8 IN	2.91	3.0	2.24	3.62
SPECIFIC COMPRESSIVE STRENGTH, 10^6 IN	1.82	2.14	0.82	2.52

FLEXURAL MODULUS vs TEMPERATURE
NR-150 POLYIMIDE COMPOSITES

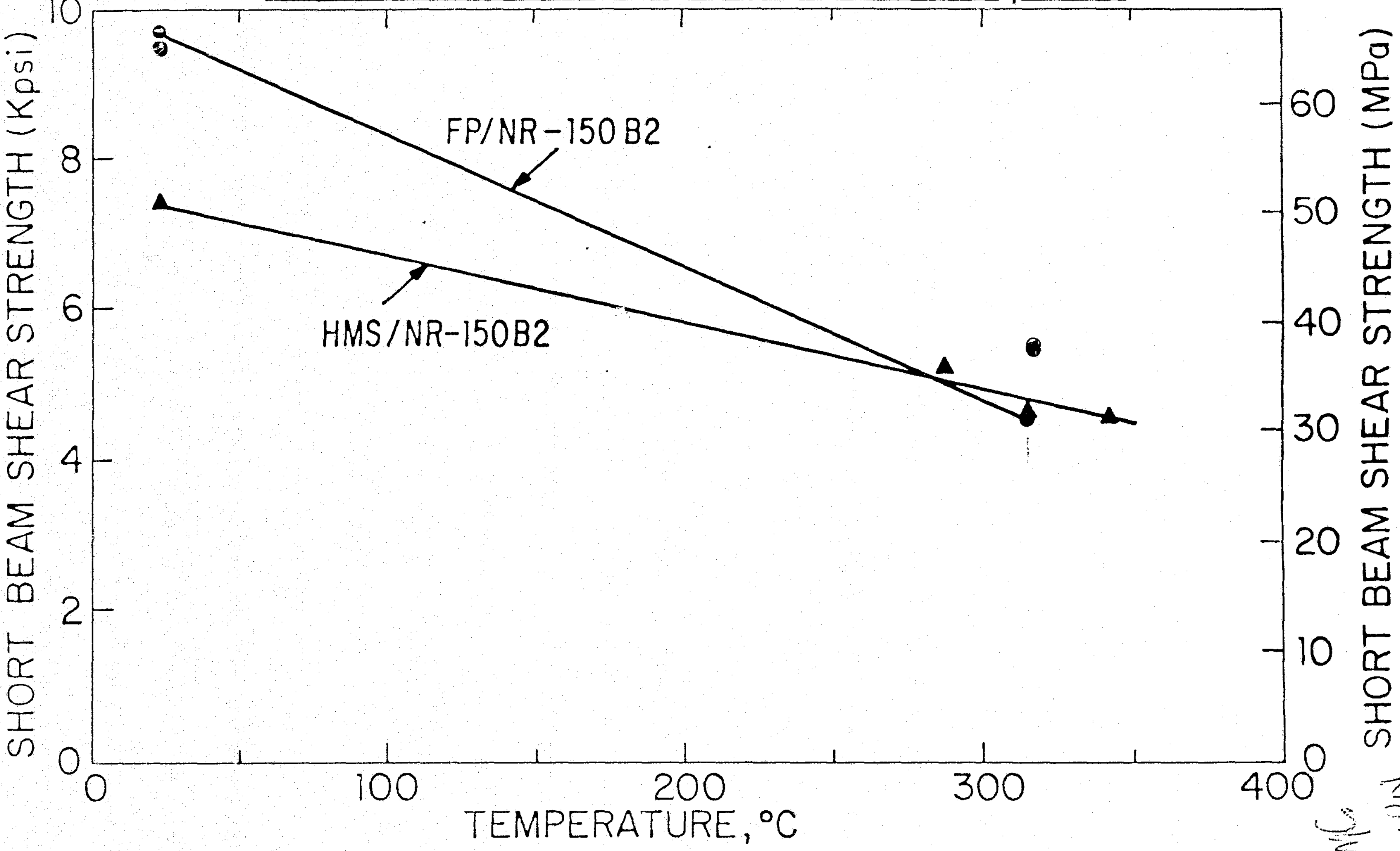




EFFECT OF TEMPERATURE ON THE FLEXURAL STRENGTH OF FP/NR-150B2 POLYIMIDE LAMINATES (55 V/o FP)

EFFECT OF TEMPERATURE ON THE SHORT BEAM SHEAR STRENGTH OF

● F.P. ALUMINA / NR–150B2 POLYIMIDE LAMINATES (V_f = 0.55)



BORON NITRIDE FIBERS

ROBERT S. HAMILTON
THE CARBORUNDUM COMPANY

MARCH 23, 1978

Dielectric Properties - The dielectric properties of boron nitride composites using boron nitride fiber are displayed in Table 3.

CHEMICAL PROPERTIES

Acid-Base Stability - Boron nitride is very stable to acidic and basic medium. Table 4 compares the weight loss upon refluxing for boron nitride fiber, carbon fiber and Pyrex fibers. Also, included in Table 4 is the action of room temperature hydrofluoric acid on these fibers. Boron nitride fibers shows 0.1% weight loss after 75 hours exposure to 100°C water. A loss of 0.8% after 1 hour of 700°C steam. Boron nitride fibers are also stable in melts of silicon, copper, cryolite, sodium chloride, lithium chloride, potassium chloride mixtures and molten cast iron and aluminum.

PREPARATION OF BORON NITRIDE FIBER

Boron nitride fiber is currently prepared by the method of Economy and Anderson as patented in 1972 (U.S. #3,668,059).

The three step process:

1. Fiberization of a boric oxide melt.
2. Nitriding of the boric oxide fiber.
3. Orientation/stabilization of the nitrided boric oxide fiber

where Step 1 uses commercially similar fiber glass drawing techniques. Step 2 is a unique gas phase - solid phase chemical conversion step and Step 3 is similar to processing used to produce high performance graphite fiber.

Process Chemistry - The chemistry of Step 2 and 3 can be expressed as:

$$nB_2O_3\text{(fiber)} \xrightarrow[200^{\circ}C]{NH_3} (B_2O_3)_n \cdot NH_3 \qquad \text{Eq. 1}$$

$$(B_2O_3)_n \cdot NH_3 \xrightarrow[350^{\circ}C]{NH_3} (BN)_x(B_2O_3)_y \cdot (NH_3)_z + H_2O \qquad \text{Eq. 2}$$

$$(BN)_x(B_2O_3)_y \cdot (NH_3)_z \xrightarrow{2200^{\circ}C} BN\text{ (fiber)} + B_2O_3 + H_2O + NH_3 \qquad \text{Eq. 3}$$

with Equation 1 and 2 describing the gas phase - solid phase chemical nitriding of boric oxide fiber of Step 2 and Equation 3 describing the Purification/Stabilization process of Step 3. The reactions of Equation 1, diffusion of ammonia into the solid boric oxide fiber and the diffusion of H_2O

BN

Test Speed .02 in/min.
Gage Length 1.00 in.

Diameter (Microns)	Stress (psi)	Modulus (psi)
4.03	106736	31158036
4.48	145736	30398249
4.10	170063	22093583
3.75	162268	46708458
5.37	65131	26168747
3.30	337774	50896127
3.36	76766	24459884
3.94	103412	32176816
3.54	135765	26929805
3.98	109705	27147841
4.87	62571	26453153
3.56	175463	43466871
3.63	99009	26484057
3.30	116473	32446280
3.46	176578	41304888
3.96	106305	33588282
3.30	91515	53704189
3.52	99444	30968947
4.25	64992	23753659
3.72	75579	25623728
4.22	34529	11852551
3.92	86949	28640527
Mean	118307	31655667
Std. Dev.	62810	9981718

Table 5. Boron Nitride Fiber Tensile Test
(Fiber Stretched 30%)

ELECTRODIC COATINGS

R. V. SUBRAMANIAN

WASHINGTON STATE UNIVERSITY

MARCH 23, 1978

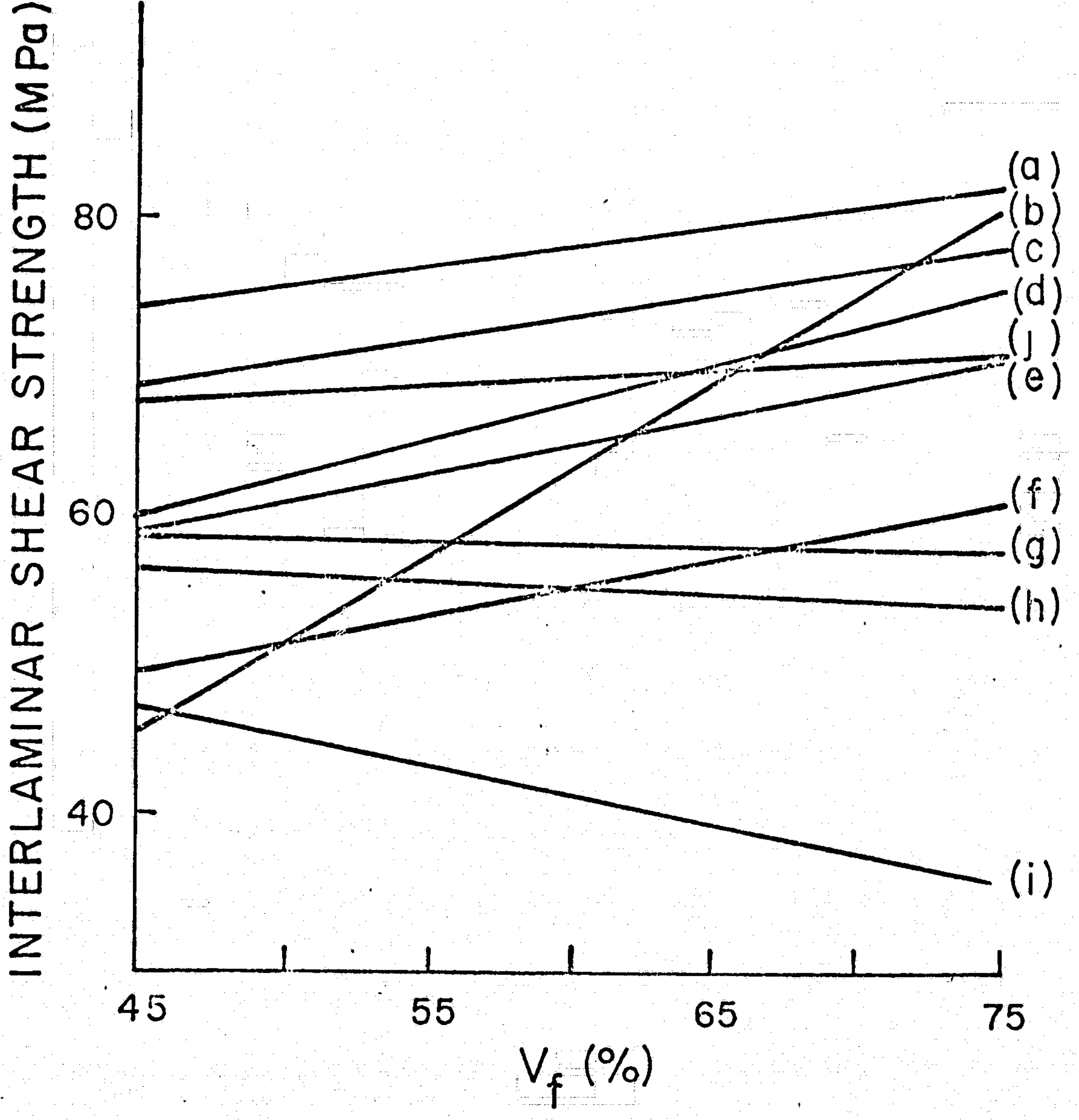


FIGURE 2

Interlaminar Shear of Composites Prepared from Fibers Coated with (a) Acrylic Acid (b) PFAZ 300 (c) DAA 2.5 seconds (d) Styrene (e) MMA (f) Styrene/Acrylonitrile (g) ε-Caprolactam (h) EPON 828/Phthalic Anhydride (i) VTBN (j) and Untreated Hercules AU Carbon Fiber

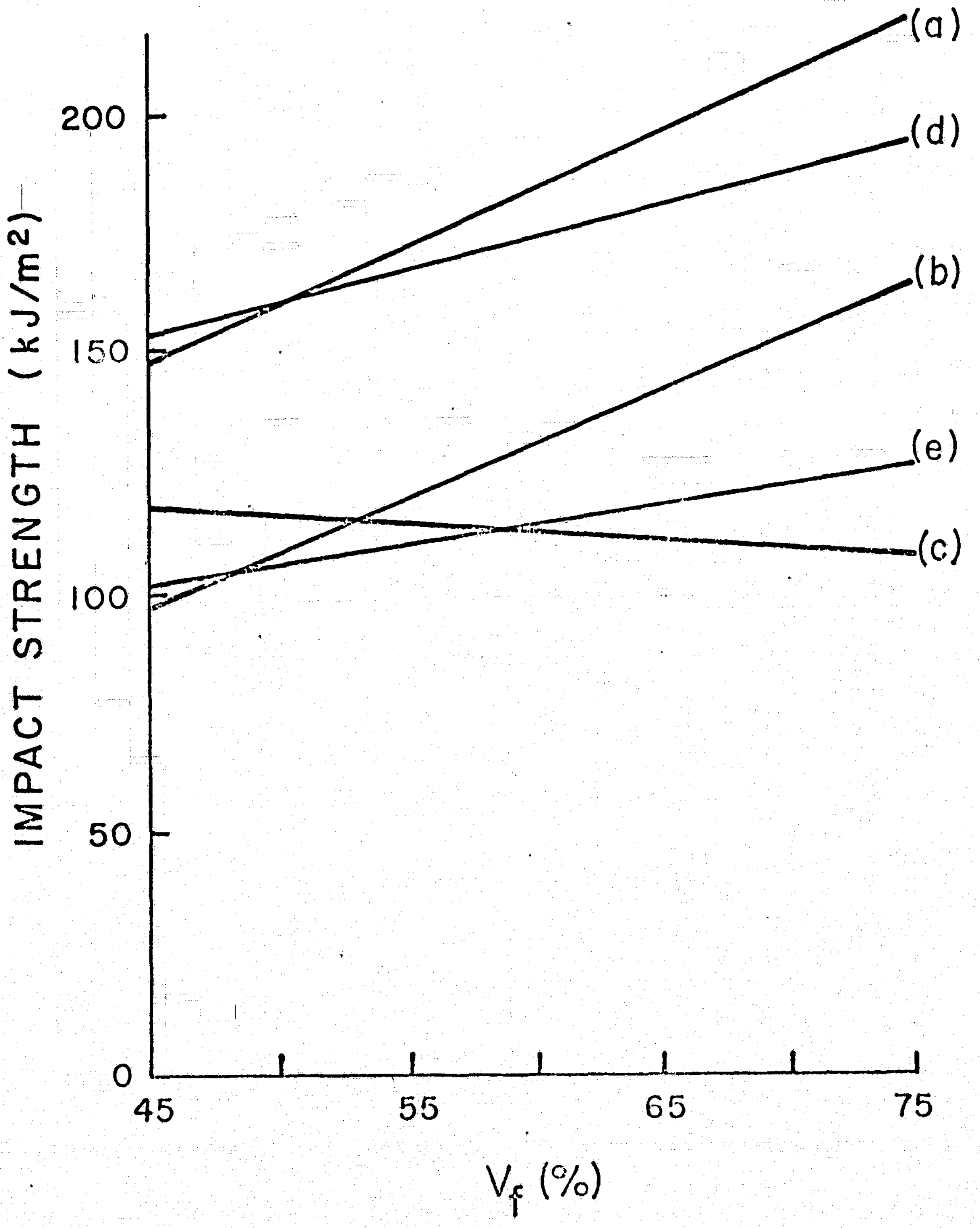
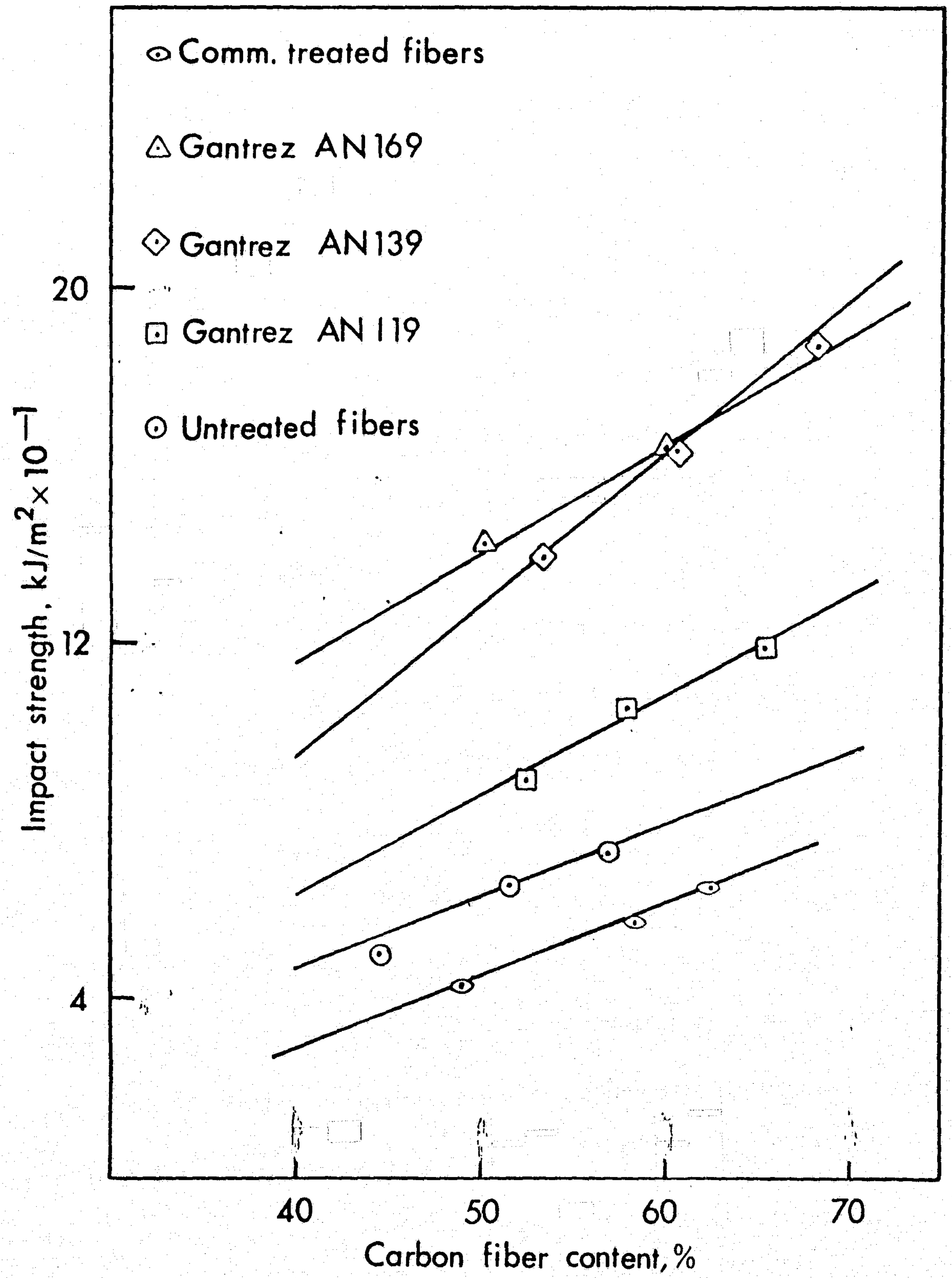
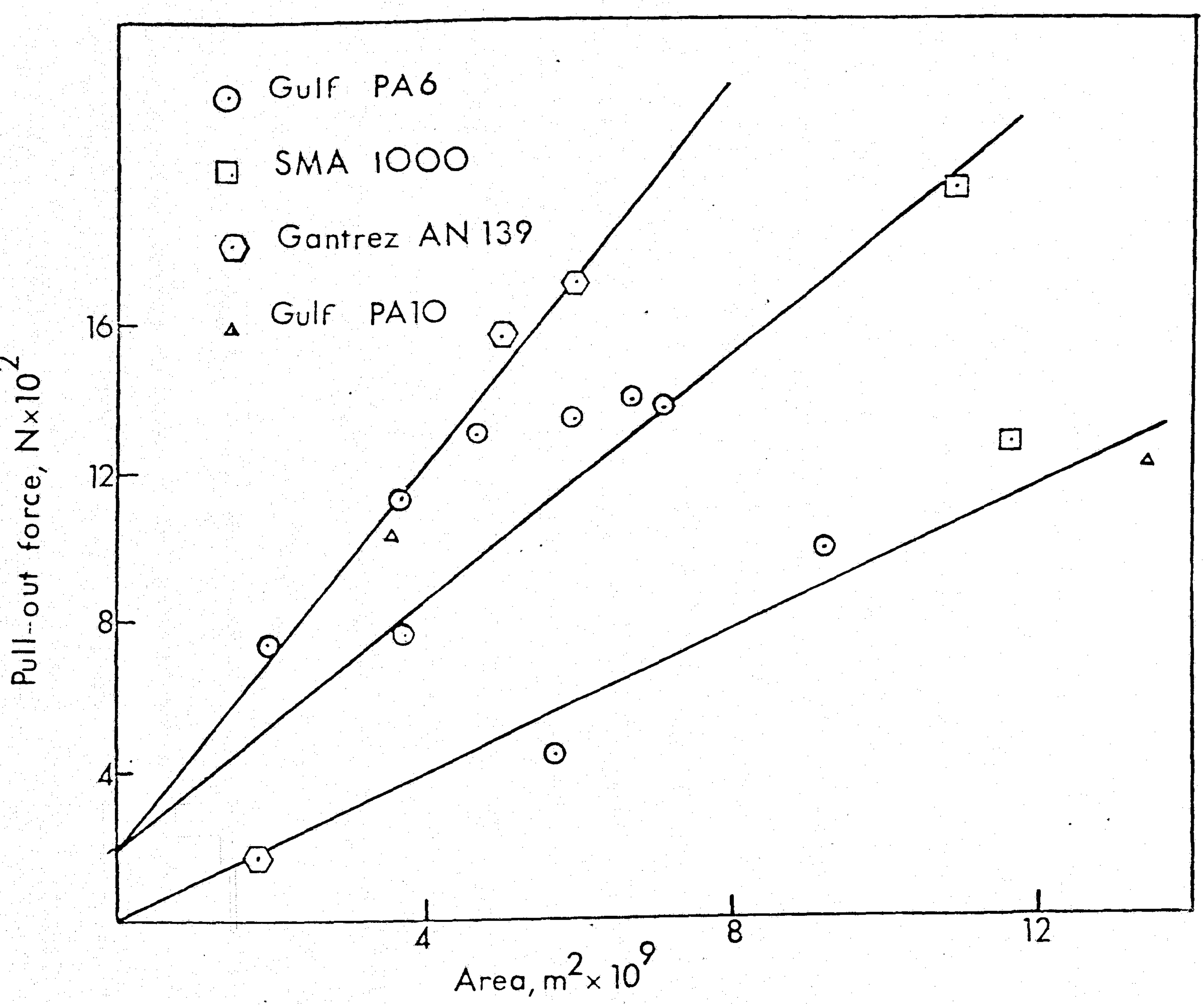
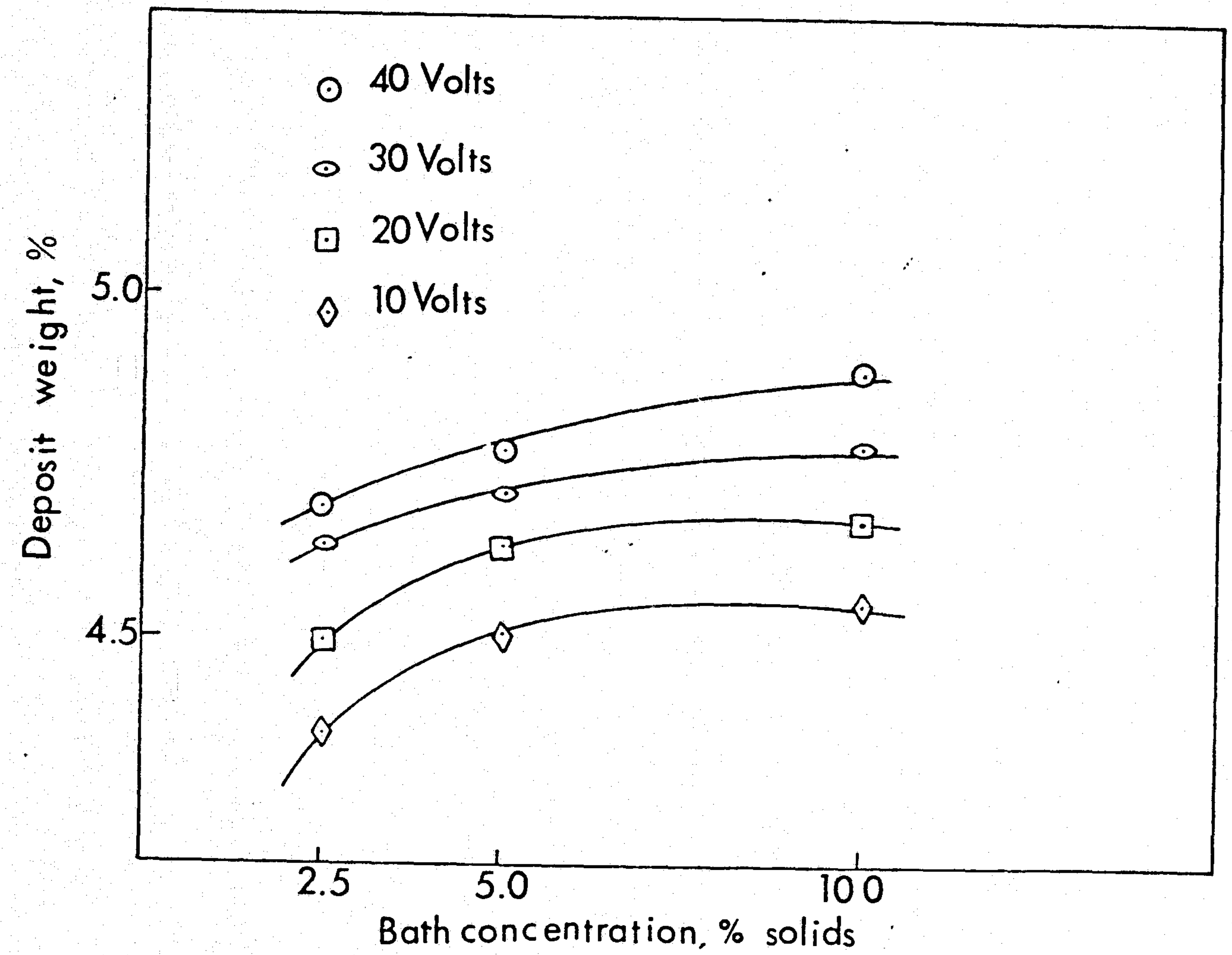


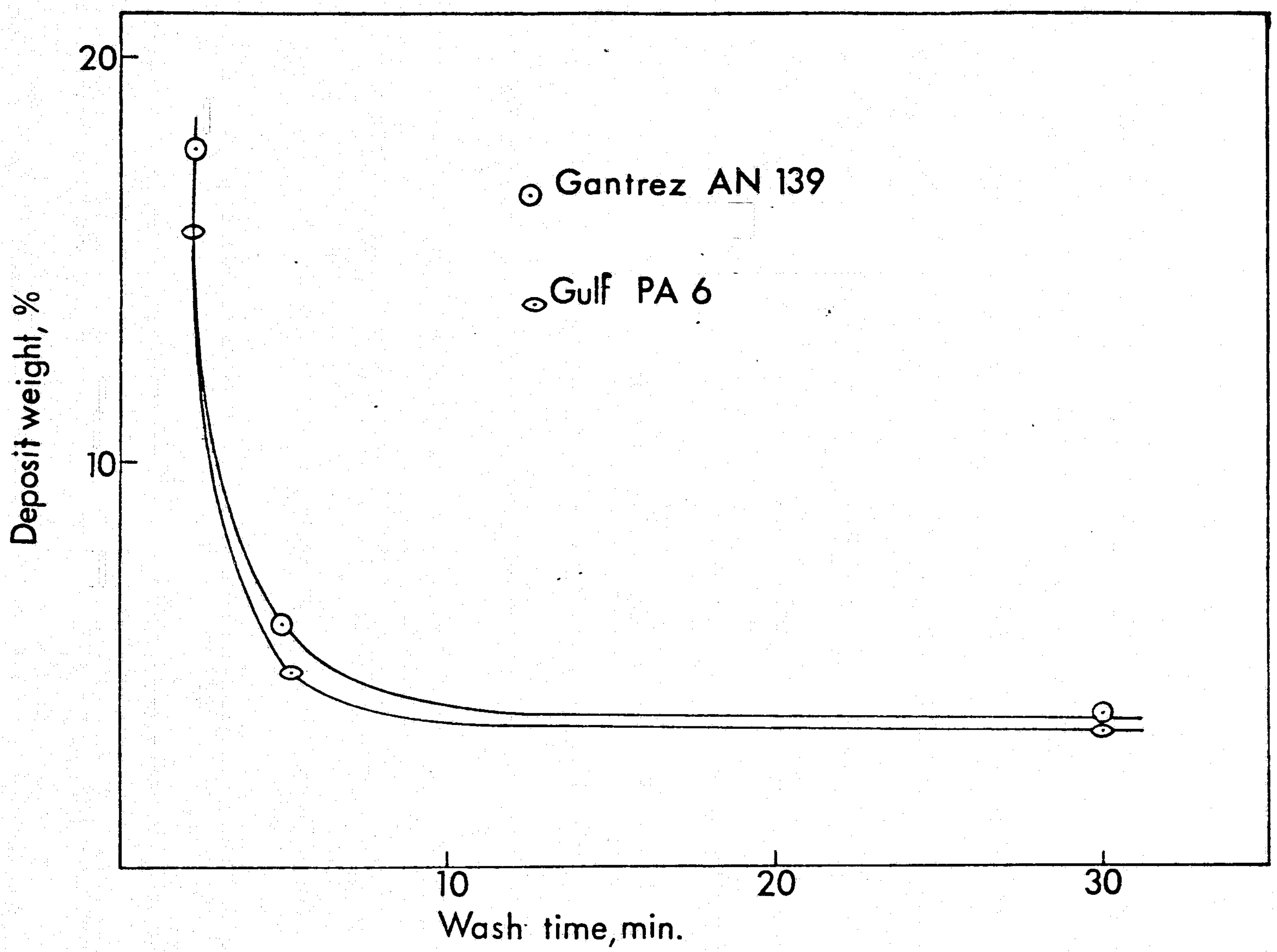
FIGURE 3

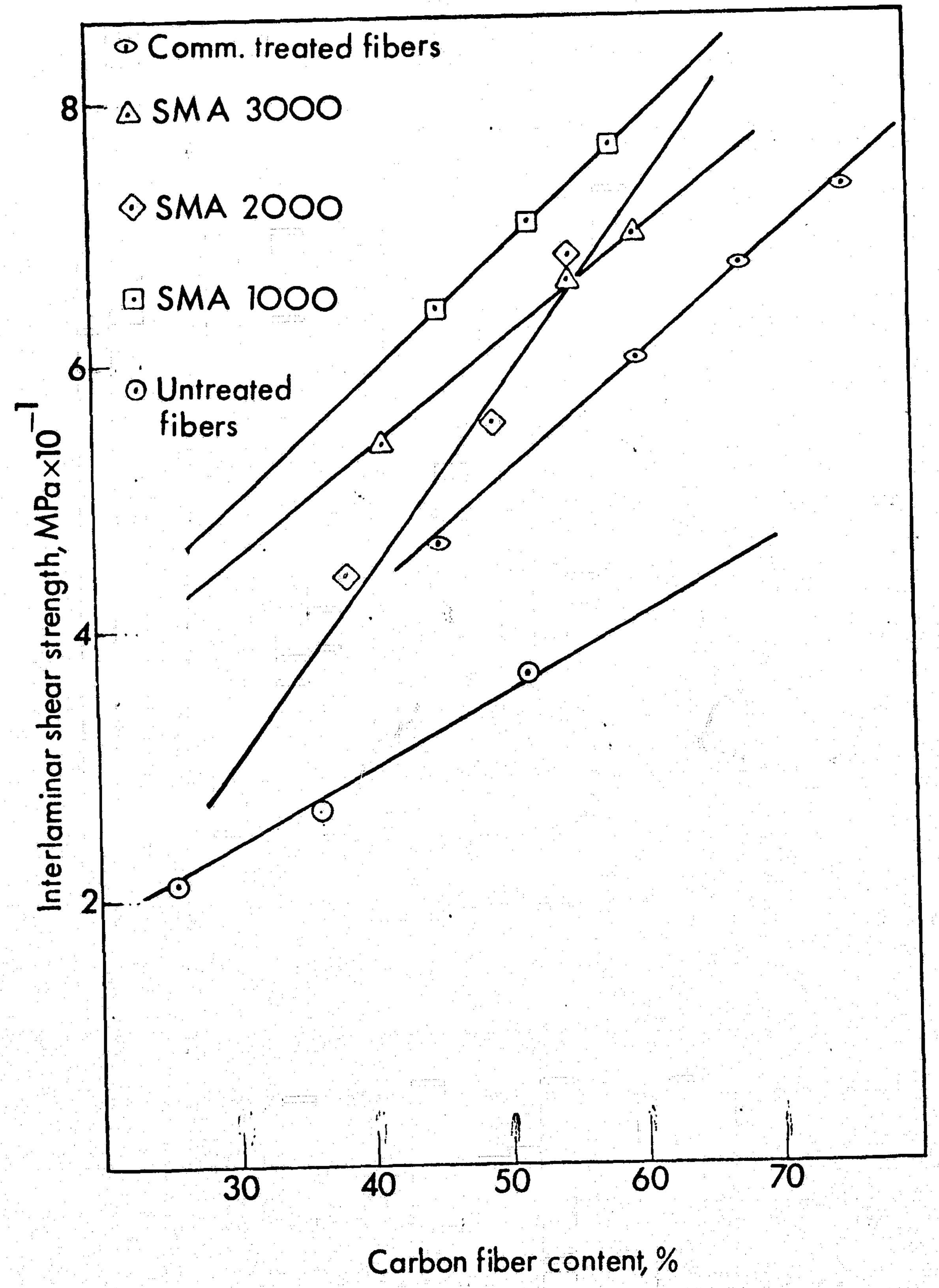
Impact Strength of Composites Prepared from Fibers Coated with (a) PFAZ 300 (b) DAA 10 Seconds (c) DAA 2.5 Seconds (d) Hercules Au and (e) Hercules AS Carbon Fiber

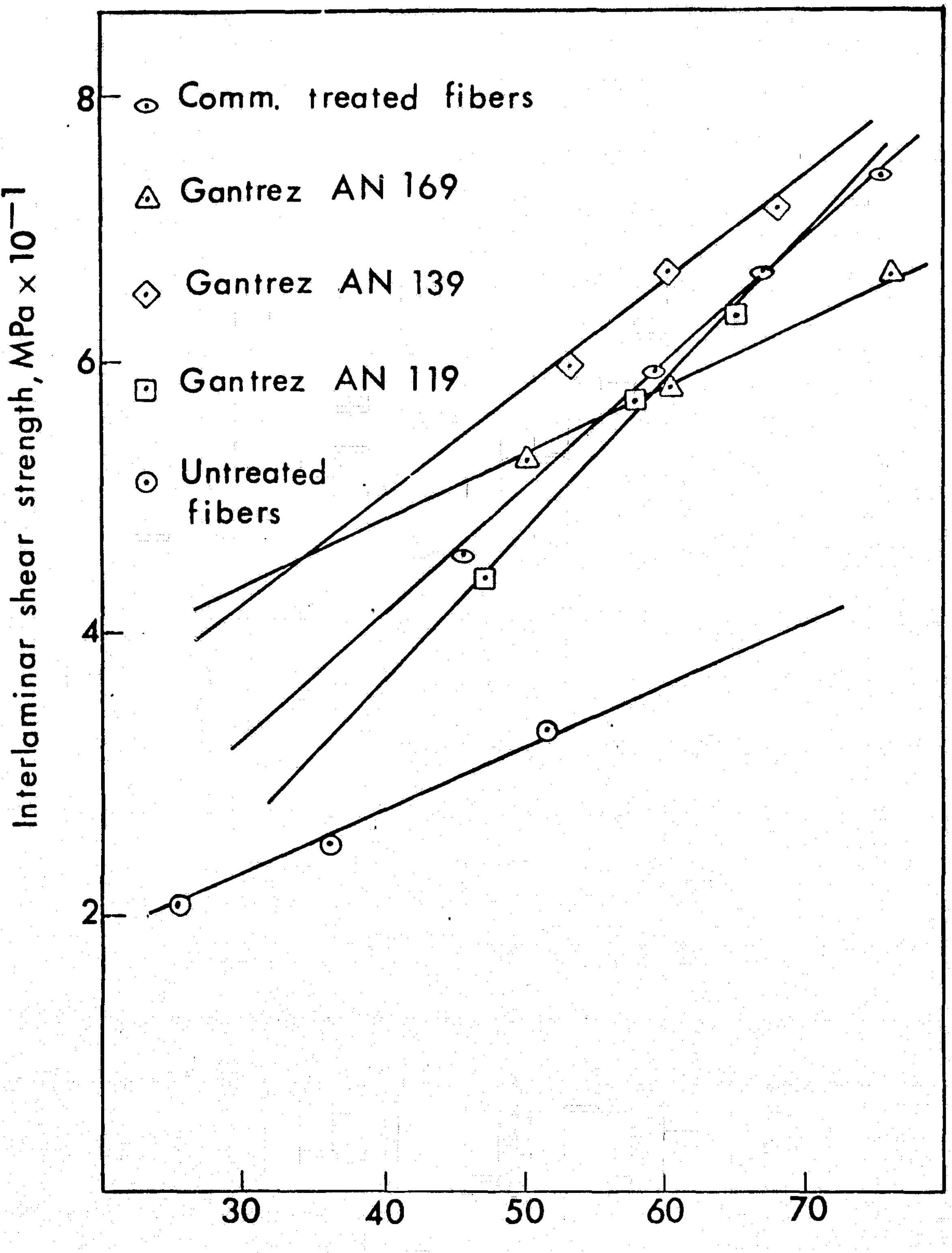

Comm. treated fibers
Gantrez AN 169
Gantrez AN 139
Gantrez AN 119
Untreated fibers
20
12
4
Impact strength, kJ/m^2 × 10^{-1}
40
50
60
70
Carbon fiber content, %


⊙ Gulf PA6
□ SMA 1000
⬡ Gantrez AN 139
▵ Gulf PA10
16
12
8
4
Pull-out force, N×10^2
4
8
12
Area, m^2× 10^9


40 Volts
30 Volts
20 Volts
10 Volts
Deposit weight, %
5.0
4.5
2.5
5.0
10 0
Bath concentration, % solids


Gantrez AN 139
Gulf PA 6
Deposit weight, %
20
10
10
20
30
Wash time, min.


Comm. treated fibers
SMA 3000
SMA 2000
SMA 1000
Untreated fibers
Interlaminar shear strength, $MPa \times 10^{-1}$
8
6
4
2
30
40
50
60
70
Carbon fiber content, %


Comm. treated fibers
Gantrez AN 169
Gantrez AN 139
Gantrez AN 119
Untreated fibers
Interlaminar shear strength, MPa × 10⁻¹
8
6
4
2
30
40
50
60
70
Carbon fiber content, %

SOME IDEAS AND PRELIMINARY RESULTS TO ALLEVIATE ELECTRICAL PROBLEMS OF CARBON FIBER COMPOSITES

Kumar Ramohalli

WARREN DOWLER, ROBERT GAULDIN, JOHN QUINN, FRED TERVET
DONALD UDLOCK, GIULIO VARSI, LIEN YANG

SOLID PROPULSION AND ENVIRONMENTAL SYSTEMS SECTION
JET PROPULSION LABORATORY
PASADENA, CALIFORNIA

WORKSHOP ON CARBON FIBERS, N.A.S.A. LANGLEY RESEARCH CENTER
HAMPTON, VIRGINIA
23, 24 MARCH 1978

INTRODUCTION

- CARBON FIBER COMPOSITES HAVE RELEASED FIBERS WHEN BURNED WITH AGITATION
- FIBERS HAVE CAUSED ELECTRICAL PROBLEMS

NASA TM 78652
DOC NEWS
ITA-78-13
TIME 13 MARCH

- ULTIMATE AIM: PREVENT RELEASE OF CONDUCTING FIBERS

  IMMEDIATE AIM: GENERATE IDEAS AND RESULTS SHOWING PROMISE
- THIS PRESENTATION
  - BASIC IDEAS
  - TEST METHODS
  - EXPERIMENTAL RESULTS
  - SUMMARY AND FUTURE WORK

BASIC APPROACH

- PREVENT RELEASE OF CONDUCTING FIBERS
  - BEFORE USE IN RESIN
    - COAT FIBERS WITH DIELECTRIC
    - COAT FIBERS WITH CATALYST FOR GASIFICATION (C, CO, CO_2)
    - COAT FIBERS WITH CHEMICALS TO HOLD THEM IN MATRIX (CROSSLINK, CHAR)
- TEST METHODS
  - AROUND A BURNING COMPOSITE, FOR SPECIFIED TIME
    - COUNT NUMBER OF FIBERS
    - COUNT NUMBER OF SHORTS IN TYPICAL CIRCUIT
- EXPERIMENTS
    - BURN TESTS, TGA STUDIES, SEM, EDAX DATA
    - TEST CIRCUITS

CATALYSIS

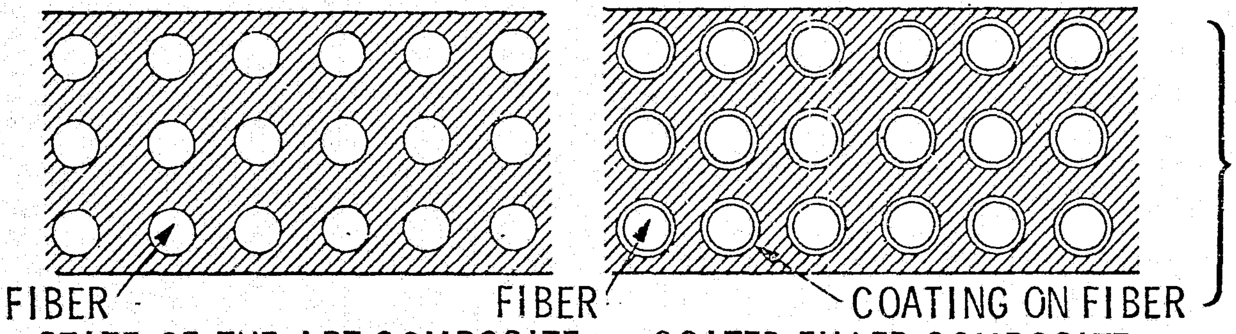
- SODIUM IS SHOWN TO CATALYSE GASIFICATION (REF WENDT et. al.)
- PREFER
  - SMALL AMOUNTS ON FIBER
  - SHOULD NOT AFFECT SERVICE LIFE
- CANDIDATES SO FAR:
  - $NaNO_3$, $LiNO_3$, $KMnO_4$, PPQ, FeAA, COBALT NAPHTHENATE
- TGA STUDIES:
  - IN AIR AND NITROGEN (ALSO ARGON AS A CHECK IN FEW CASES)
  - THORNEL-300 (PLAIN, AND COATED BY DIP IN SOLUTION)
  - 20°C/MIN TO 1000°C
  - REPRODUCIBILITY CHECKED (5% MAXIMUM ERROR)
- PPQ APPEARS PROMISING ON THORNEL-300 (IN AIR)

• TEMPERATURE °C	WEIGHT LOSS PERCENT	
	PLAIN	COATED WITH PPQ
500	40	7
550	43	23
600	49	56
650	81	100 AT 665°C
700	100	

PREVENTION OF RELEASE FROM MATRIX

- BASIC IDEA

  COAT FIBER WITH CHEMICALS THAT DEGRADE AT SURFACE TEMPERATURE OF BURNING COMPOSITE



STATE-OF-THE-ART COMPOSITE   COATED FILLER COMPOSITE

- SIMILAR IDEA WORKED WELL IN ANOTHER COMPOSITE SYSTEM (REF. WSS/CI 77-16)

- CANDIDATE CHEMICALS:
  1. (95% ETHYL CELLULOSE + 5% TRICRESYL PHOSPHATE)
  2. COBALT NAPHTENATE
  3. SODIUM SILICATE

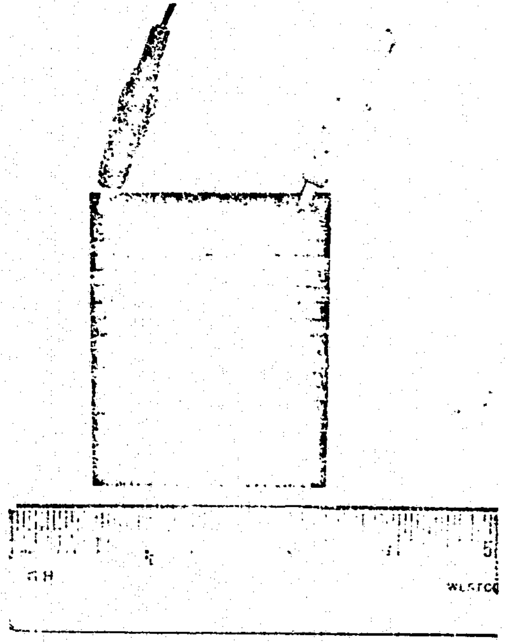
- COMPOSITES PREPARED IN
  - EPOXY (80% RF-3000 + 20% RF-61)
  - POLYIMIDE (NR-150)

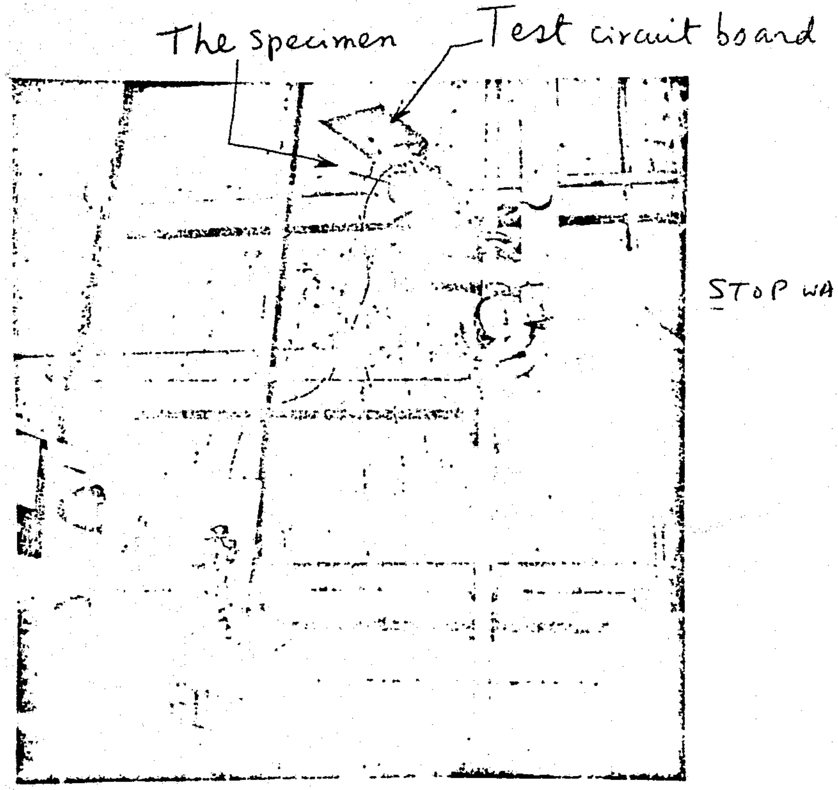
  MOST OF THE TESTS AIMED AT 30% RESIN AND 70% FIBERS

- TESTS NEEDED FOR PROOF OF CONCEPT

TEST TECHNIQUE

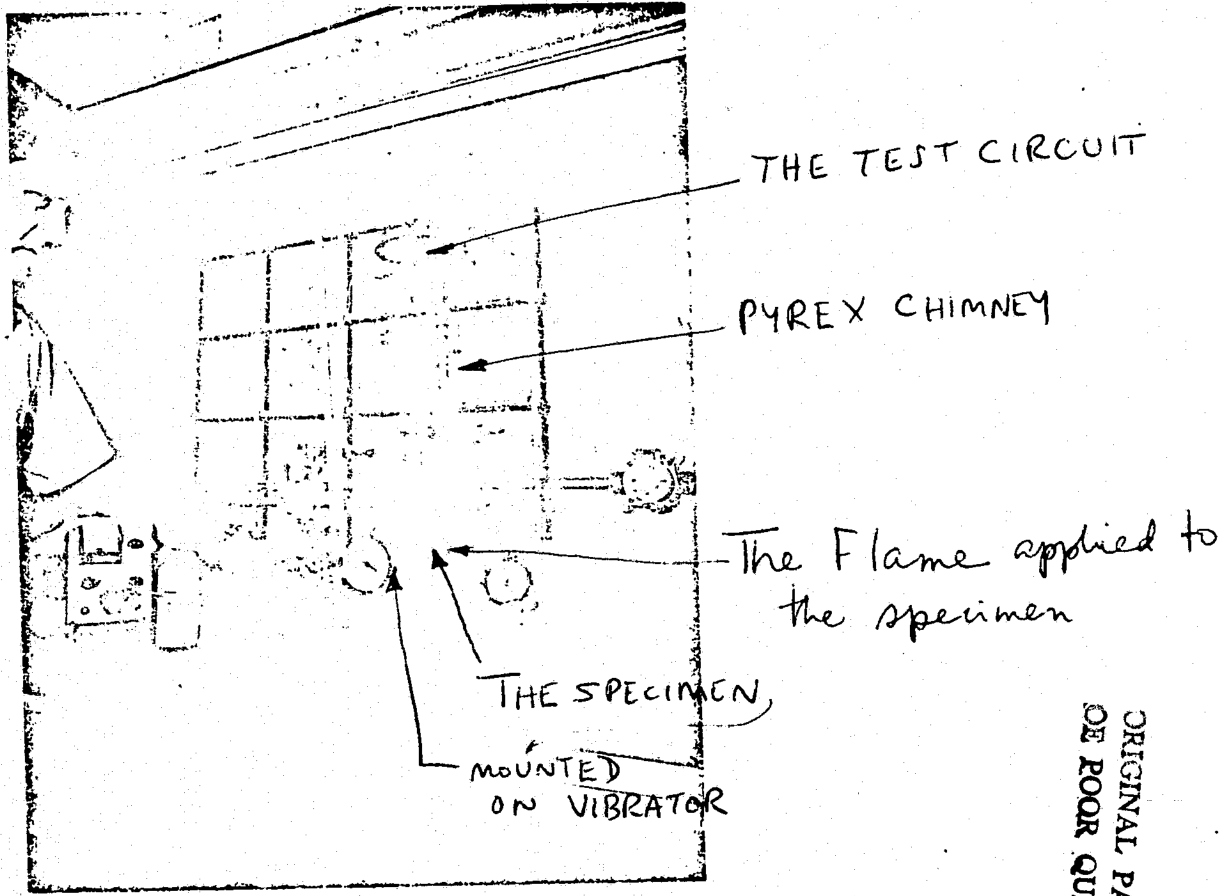
- TIME FOR SHORT CIRCUIT AROUND BURNING COMPOSITE
- INITIAL ARRANGEMENT
  COPPER STRIPS ON MASONITE





- PROBLEMS WITH BOARD
  GAVE SHORTS WITH RESIN ALONE
- IMPROVED DESIGN

PRESENT ARRANGEMENT



RESULTS

- INITIAL BOARD DESIGN (TIME FOR SHORT)

PLAIN	COATED WITH ECtTCP
55	22
15	21
5	22
12	12
15	22
10	18
10	19
20	21
14	21

- PRESENT SET UP

PLAIN	COATED WITH ECtTCP
12 SEC	18 SEC

- PRELIMINARY TESTS WITH SODIUM SILICATE AS THE COAT:
  - NO SHORTS IN WELL OVER A MINUTE
  - THE COAT CONTENT WAS ABOUT 20%
  - TESTS UNDERWAY TO HAVE SMALL COAT CONTENT

THE LATEST RESULTS

- SODIUM SILICATE APPEARS VERY PROMISING
  - WEIGHT PERCENT COATING IS CAREFULLY CONTROLLED
  - 2%, 5%, 6.93%, 12%, 19.06%
  - ALL OF THEM ARE CAST IN EPOXY (40%/60%-FIBERS/EPOXY)
  - BURNED IN STANDARD SETUP
  - THE 2% COATED SAMPLES GAVE NO SHORTS AT ALL (>90 SECS)
  - RESIN BURNED OFF IN 7 SECONDS
  - FIBERS FELL DOWN IN BUNDLES
- WILL BE PURSUED IN DETAIL

SUMMARY AND FUTURE PLANS

- PROBLEM RECOGNIZED
- THREE TASKS
  - CATALYZE GASIFICATION
    PPQ SHOWS PROMISE
  - PREVENT RELEASE FROM RESIN CHAR
    EC+TCP SHOWS PROMISE
    SODIUM SILICATE LOOKS VERY GOOD
  - DEVELOP TEST METHODS
    CIRCUIT BOARD APPEARS ADEQUATE FOR RANKING
- FUTURE
  - CONTROL COAT CONTENT AND RESIN CONTENT
  - MORE TESTS (IN NBS SMOKE DENSITY CHAMBER ALSO)
  - MECHANICAL PROPERTIES
  - AGING STUDIES (SERVICE LIFE)
  - THERMOCHEMICAL MODEL

EPOXY RESIN MODIFICATIONS

Dr. James Noland, Chairman

NAME	ORGANIZATION
Norman B. Sunshine	Narmco Materials Inc.
David Crabtree	Northrop Aircraft Co.
C. V. Wittenwyler	Shell Development Co.
Sidney W. Street	U.S. Polymeric (Div. of HITCO)
Richard J. Moulton	HEXCEL
M. J. Katsumoto	Boeing Commercial Airplane, Co.
Robert A. Frigstad	3-M Co.
C. E. Browning	AFML/MBC
James D. Allen	Fiberite Corp.
James Noland	American Cyanamid Co.
Clayton May	Lockheed M&S
Mal Katsumoto	Boeing C/AC
R. J. Tomerlin	Bell Helicopter
William A. Mueller	JPL
R. C. Curley	McDonnell Douglas
R. E. Hoffman	Hercules Inc.
Marvin Rhodes	NASA LaRC
John Parker	NASA Ames
Walter S. Cremens	Lockheed-Georgia

NASA Reporters: Paul Hergenrother, Norman Johnston, LaRC

ISSUES FOR
EPOXY RESIN MODIFICATIONS
WORKING GROUP

1. What is the most important new resin property that must be designed into any modified epoxy?

2. Can char formers be mixed into an epoxy matrix and still be effective?

3. For each epoxy modification considered:

    (a) What is the minimum modification that will retard fiber release?

    (b) Are current synthetic and fabrication processes applicable to the modified epoxy?

    (c) Will this modification be cost effective?

    (d) How soon can the modification be made and produced in large quantity for the aerospace industry?

    (e) Will this modification possess the environmental durability of current epoxy?

    (f) Will the data base already in hand with current graphite-epoxy composites have to be regenerated using this modified material? If so, how much would have to be regenerated?

    (g) What is the main principle that the modification uses to retard graphite fiber release?

4. What is your assessment of the current NASA research program in this area, and what changes do you recommend?

5. Rank the different generic solutions (fiber modifications, fiber coatings, alternative fibers, epoxy resin modifications, epoxy resin replacements, hybrid composites) as to their probability of success.

NASA REPORTERS' SUMMARY FOR EPOXY RESIN MODIFICATIONS WORKING GROUP

Proposed solutions involving epoxy resin modification were divided into two categories: short-term approaches and long-term approaches. The prepreggers and fabricators adamantly opposed any change to the resin or reinforcement since such modifications would require complete resin and composite requalification. The group also felt that any fix must impose a minimum weight penalty on the composite structure. Since the primary driving force for the use of graphite composite in place of the more conventional material (Al) is a 20 percent weight savings, they felt that this advantage should not be compromised.

Short-term Solutions.- Proposed short-term solutions were restricted to changes that did not involve alteration of the chemical structure or chemical content of the matrix. The group proposed the use of an outer coat of an intumescent point and/or a ply (plies) of flame retardant intumescent resin. However, the group felt that an outer intumescent surface would be unlikely to restrict the release of fibers since the char foam formed by intumescent materials is weak and friable.

Long-term Solutions.- Proposed long-term solutions included the use of flame retardant additives such as red phosphorus, phosphate compounds, aluminum hydroxide, subliming salts and trimethoxy boroxine. Unfortunately, each additive introduces its own peculiar problem such as the difficulty of obtaining and handling red phosphorus of small particle size (e.g., 1 μm), the weight penalty associated with the use of aluminum hydroxide, and the moisture problem anticipated with the use of trimethoxy boroxine. Brominated epoxy resins were also proposed, but their poor char-forming characteristics and increased weight make them unattractive. Also, blends of epoxy resins with high char-forming non-epoxy resins such as bis-maleiimides and phenolics were proposed. No changes in epoxy resin chemistry were suggested.

CONCLUSIONS

1. The present momentum in the development of graphite reinforced composites must be maintained. Any delay would severely impact the development and near-future use of these materials.

2. There is no "quick-fix" or short-term solution to the problem through modification of the epoxy matrix. The prepreggers, especially, indicated that the chemistry of epoxy resins does not permit a modification that would resolve the problem while maintaining all of the required features of a graphite-epoxy prepreg (e.g., low cost, tack and drape, shelf-life, autoclave cure at 350°F, etc.). In addition, the group complained that a lack of information existed to indicate what epoxy alterations, if any, (e.g., increased char formation) would alleviate the problem.

RECOMMENDATIONS

1. Insufficient manpower was proposed to conduct the resin modification work as proposed. Therefore, the group recommended that NASA increase its manpower loadings in this activity.

2. Inorganic coatings on graphite fiber were considered to be long-term high risk solutions. Insurmountable problems due to coefficient of thermal expansion mismatch resulting in a weak interface area and problems due to poor adhesion to epoxy resins, brittleness of the coating, and moisture sensitivity were anticipated from the use of inorganic coatings.

3. The most promising short-term solutions need more emphasis.

4. The risk analysis work should be completed as soon as possible and faster than the current proposed schedule (1.5 years).

5. A published schedule of NASA decision points such as dates for completion of the risk analysis and development of standardized tests is urgently needed.

REPORT OF

EPOXY RESIN MODIFICATIONS WORKING GROUP

DR. JAMES NOLAND, CHAIRMAN

EPOXY RESIN MODIFICATION

OVERVIEW

- MAINTENANCE OF PRESENT MOMENTUM
- NO MODIFICATION OF EPOXY AS SHORT-TERM SOLUTION
- RISK ANALYSIS NEEDS FASTER PACE
- PUBLISHED SCHEDULE FOR DECISION - POINTS NEEDED

SHORT-TERM SOLUTIONS

- CHANGE IN EPOXY RESIN REQUIRES TOTAL REQUALIFICATION
- ALL SHORT-TERM SOLUTIONS INVOLVE NON-STRUCTURAL MODIFICATIONS
  - INTUMESCENT PAINT
  - OUTER PLIES OF FLAME-RETARDANT INTUMESCENT RESIN
  - NO-WEIGHT OR MINIMUM-WEIGHT PENALTY

LONG-TERM SOLUTIONS

-EPOXY RESIN MODIFICATION-

- IMPROVED FIRE RESISTANT ADDITIVES
  - RED PHOSPHOROUS AND PHOSPHORUS COMPOUNDS
  - ALUMINUM HYDROXIDE
  - SUBLIMING SALTS
  - ENCAPSULATED TRIMETHOXY BOROXINE
  - BROMINATED EPOXY RESINS (UNLIKELY SOLUTION)

-CHANGES IN RESIN CHEMISTRY-

- PHENOLIC CURES
- BIS-MALEIMIDE BLENDS
- OTHERS!

RANKING OF LONG-TERM SOLUTIONS

PRIORITY	
1	EPOXY REPLACEMENTS
2	FIBER COATINGS (ORGANIC)
3	HYBRIDS
4	EPOXY MODIFICATIONS

RECOMMENDATIONS

- SCOPE OF RESIN MODIFICATIONS TOO BROAD FOR MANPOWER LOADINGS: RECOMMEND INCREASED MANPOWER
- INORGANIC FIBER COATINGS ARE LONG-TERM, HIGH RISK SOLUTIONS
- SHORT-TERM SOLUTIONS NEED MORE EMPHASIS
- NASA ROADMAP URGENTLY NEEDED

EPOXY RESIN REPLACEMENTS

Dr. B. F. Landrum, Chairman

NAME	ORGANIZATION
Ira Petker	Composites Horizons
Lynn Jarvis	Naval Research Lab
Chad Delano	Acurex/Aerotherm
Dan Scola	United Technologies Res. Ctr.
W. F. Baumgartner	Lockheed-California
Norm Bilow	Hughes Aircraft Co.
Henry M. Toellner	McDonnell Douglas
Walter S. Cremens	Lockheed-Georgia
Rick Moulton	Hexcel
Don Houston	Rockwell - Space
Jim Gauchel	DeSoto Inc.
William J. Bailey	U. of Maryland
John Parker	NASA Ames
Ronald Stocks	CIA OSI/LSD
Rex Gosnell	Riggs Engineering
Ed Harrison	General Dynamics/Convair
Vance Chase	General Dynamics/Conair
William Verzino	Aerospace Corp.
Mike O'Rell	TRW Systems
John T. Hoggatt	Boeing Aerospace
Hugh H. Gibbs	DuPont
Bill Landrum	Ciba-Geigy Corporation
George Sykes	NASA LaRC

NASA Reporter - Dr. Terry St. Clair, LaRC

ISSUES FOR
EPOXY RESIN REPLACEMENTS
WORKING GROUP

1. What principles would be employed by replacement resins to retard fiber release?

2. What combination of properties must a resin possess in order to replace epoxy and at the same time retard fiber release?

3. Are aromatic polyimides a good candidate resin system to replace epoxy for the purpose of retarding fiber release?

4. For each epoxy replacement resin proposed:

   (a) Are current synthetic and fabrication processes applicable to the new resin? Could improved processes be developed?

   (b) Will this new resin be cost effective?

   (c) Will this new resin possess the environmental durability of current epoxy?

   (d) What is the main principle that this new resin would employ to retard fiber release?

   (e) How soon can this new resin be produced in large quantity for the aerospace industry?

4\. What is your assessment of the current NASA research program in your area, and what changes do you recommend?

5\. Rank the generic solutions (fiber modifications, fiber coatings, alternative fibers, epoxy resin modifications, epoxy resin replacements, hybrid composites) as to their probability of success.

NASA REPORTERS' SUMMARY FOR
EPOXY RESIN REPLACEMENTS WORKING GROUP

The meeting was prefaced with four presentations which are summarized below.

1. Lynn Jarvis (NRL) - This was a summary of NRL work on polyphthalocyanine (PPCy). The polymer is a high char former, is made from a single monomer, has a high degree of toughness, and may be available for as little as $10/lb within 2 years. NRL is still modifying the chemistry of the system. The current versions have a 410-490°F cure and afford a dry, boardy prepreg. Very little data base exists for the PPCy. The group consensus was that this material needs further development before commercial applications could be realized.

2. Bill Bailey (U. of Maryland) - This was a presentation on the need for epoxy replacements to have low shrinkage. He feels that low shrinkage will minimize microcracking which promotes resin burnout. He also feels that lower shrinkage will cause better resin-to-fiber adhesion which would help hold the fibers together in a fire/explosion scenario. He presented the chemistry of a material he has developed which has applications as a dental adhesive because of its low shrinkage. The resin did not have the high temperature capability of 350°F cure epoxies.

3. Mel Katsumoto (Boeing) - This was a summary of the problems a commercial airplane builder faces in qualifying a resin for use on aircraft. He charged the group to look for a "quick fix," such as a composite protective coating, to solve the current fiber release problem, then formulate a long-term program to develop an epoxy replacement resin.

4. Raymond Kray (Ciba-Geigy) - This was a summary of some of the NCNS resin work performed on contract to NASA-Langley. Data were shown on NCNS's excellent resistance to burning, and the slight intumescent behavior of NCNS/graphite laminates was described. NCNS is not commercially available, at present, but may be in approximately one year. The resin is projected to cost about $5-$8/lb.

In response to the strawman issues posed by NASA to the group, a list was compiled of the properties that an effective epoxy replacement resin should possess.

1. It should have a high char yield and produce a tough char.

2. It should be intumescent.

3. It should have mechanical properties equal to those of the current epoxies.

4. It should have a high limiting oxygen index (LOI).

5. Its properties should match ignition and burn properties of the fiber.

6. It should be UV resistant.

7. It should meet processing requirements of current epoxies.

8. It should present no unacceptable toxic on environmental hazard.

9. It should be moisture stable.

10. It should sell for $10/lb or less.

11. It should have a maximum cure temperature of 350°F and preferably lower.

In response to the chairman's request for potential epoxy replacement resins from currently available materials, the following list of possible candidates was compiled:

1. <u>Polyimides and Cyanates</u>

    LaRC 160
    PMR-15 (First and Second Generation)
    NR-150 A2
    Thermid 600
    Hexcel F-178
    N-Cyanosulfonamide (NCNS)
    Triazine A

2. <u>Phenolics and Miscellaneous</u>

    Xylok
    Weyerhauser benzyl resin
    Phenolic prepregs from Ciba-Geigy, Fiberite,
        Hitco, and Narmco
    Polyphthalocyanines (PPCy)
    Polyphenylene sulfides
    Aryl sulfones
    Thermally cross-linked thermoplastics

CONCLUSIONS

1. For a short term solution, only existing resin systems should be considered as replacements for epoxy.

2. Toughness is an important property to be considered in evaluating potential replacement resins.

3. Hybrid composites and/or fiber coating concepts offer the best hope for a "quick fix" to the graphite fiber hazard. Fiber modification is the least promising approach.

RECOMMENDATIONS

1. NASA should conduct a screening test program on existing replacement resins to characterize their burn properties and identify promising candidates. Selection of systems for further research should be based on fabrication parameters such as prepreggability, handleability, and processability into laminates and on mechanical properties of composites.

2. NASA should appoint an Epoxy Replacement Panel that should meet every six months to review and discuss progress.

REPORT OF

EPOXY RESIN REPLACEMENTS
WORKING GROUP

DR. B. F. LANDRUM, CHAIRMAN

EPOXY RESIN REPLACEMENTS

OVERVIEW

PRINCIPLES TO BE EMPLOYED

CRITICAL PROPERTIES

PROMISING KNOWN SYSTEMS

PROBABILITY OF SUCCESS

ASSESSMENT OF CURRENT NASA PROGRAM

DESIRED RESIN CHARACTERISTICS

A NEW RESIN TO BE AN EFFECTIVE EPOXY REPLACEMENT MUST EMPLOY AS MANY OF THE FOLLOWING PRINCIPLES AS POSSIBLE -

- HIGH CHAR FORMATION
- INTUMESCENT
- HIGH LIMITING OXYGEN INDEX
- MATCH IGNITION & BURN CHARACTERISTICS OF FIBER
- PRODUCE TOUGH CHAR WITH GOOD FIBER ADHESION
- EXHIBIT ACCEPTABLE PROCESSING CHARACTERISTICS
- DEMONSTRATE EPOXY MECHANICAL PROPERTIES
- SELL FOR $10.00/LB OR LESS
- PRESENT NO UNACCEPTABLE TOXIC OR ENVIRONMENTAL HAZARD IN PROCESSING

CONSENSUS CONCLUSION

CURRENTLY AVAILABLE, WELL KNOWN RESIN SYSTEMS CANNOT BE RANKED IN ORDER OF PROMISE DUE TO LACK OF A SYSTEMATIC SCREENING STUDY BY A CENTRAL CLEARING HOUSE OR AUTHORITY.

RECOMMENDATION:

NASA ESTABLISH A SET OF STANDARD EVALUATION PROCEDURES AGAINST WHICH CANDIDATE RESIN PROPERTIES WILL BE DETERMINED.

POLYIMIDES & CYANATES

LaRC 160

PMR - 15 (1st & 2nd GENERATION)

NR - 150 A2

THERMID 600

F - 178

NCNS

TRIAZINE A

PHENOLICS & MISCELLANEOUS

XYLOK

WEYERHAUSER BENZYL RESINS

PHENOLIC PREPREG -
- NARMCO
- FIBERITE
- CIBA-GEIGY
- HITCO

POLYPHTHALOCYANINES

THERMOPLASTICS
- POLYPHENYLENE SULFIDES
- ARYL SULFONES
- THERMALLY CROSS LINKED THERMOPLASTICS

CURRENT NASA PROGRAM ASSESSMENT

- GOOD START
- NEED OPEN SCREENING OF AVAILABLE RESINS
- NEED BETTER DEFINITION OF REALISTIC SCREENING CRITERIA.
- EFFORTS SHOULD BE CONCENTRATED ON DEVELOPING 3 OR 4 MOST PROMISING SYSTEMS.
- NEED EARLY FEEDBACK FROM PREPREGGERS AND FABRICATORS

SUMMARY OF RECOMMENDATIONS

- SCREEN KNOWN RESIN SYSTEMS AGAINST A SET OF STANDARD CRITERIA
- SELECT MOST PROMISING CANDIDATES ABOVE FOR FURTHER EVALUATION
- COMPARE COST/PERFORMANCE AND SELECT MOST PROMISING FOR FULL SCALE DEVELOPMENT
- NASA SHOULD REQUEST DATA FROM RESIN PRODUCERS CONCERNING PERTINENT RESIN PROPERTIES
- UNDERTAKE SELECTIVE SYNTHETIC MODIFICATIONS TO EXISTING RESIN SYSTEMS
- ESTABLISH INDUSTRY/GOVERNMENT/UNIVERSITY REVIEW BOARD TO ASSESS PROGRESS

NRL WORK ON POLYPHTHALCYANINE

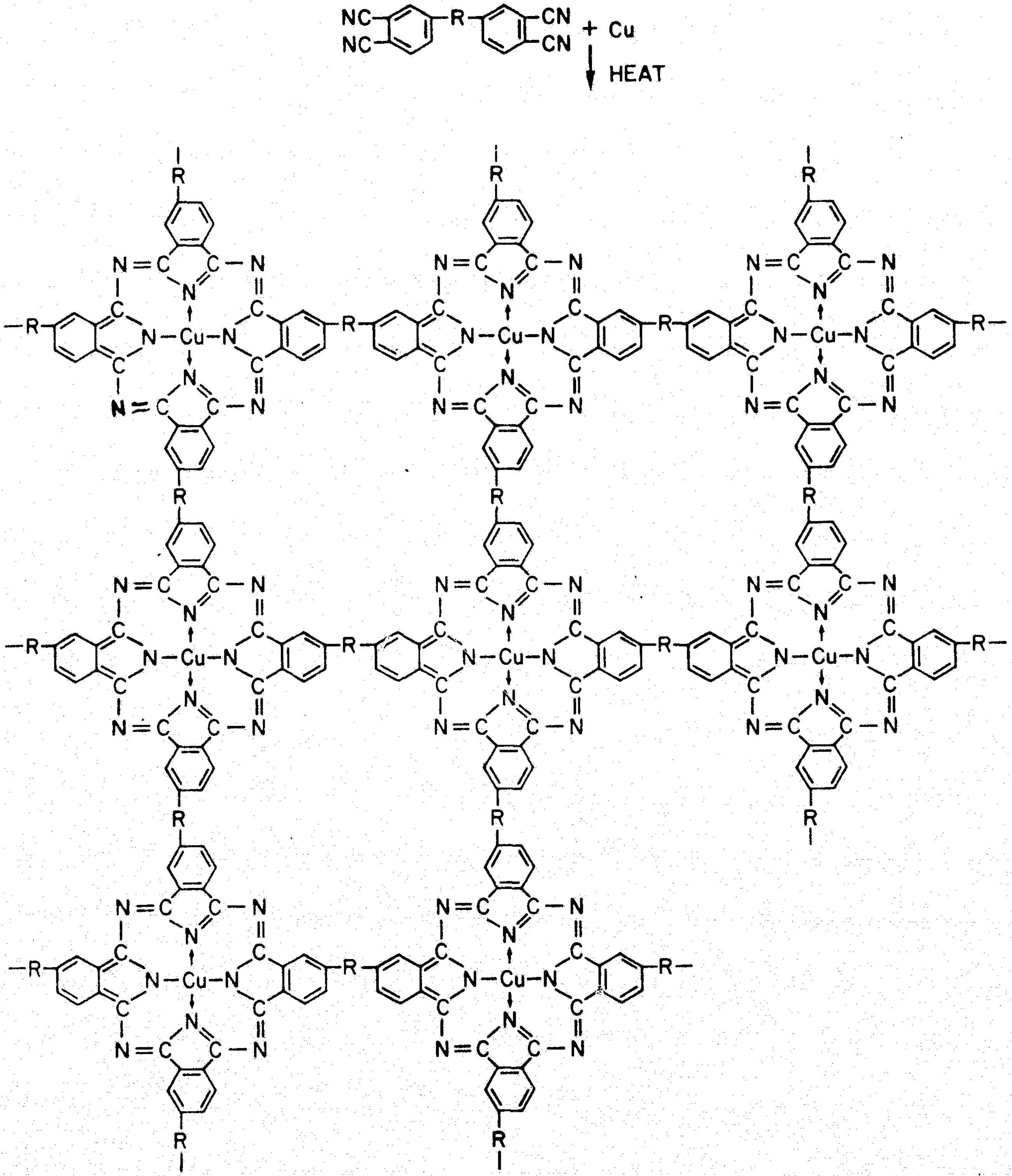
LYNN JARVIN
NRL

MARCH 23, 1978

Lynn Jarvis

Navy

POLYMERIZATION REACTION



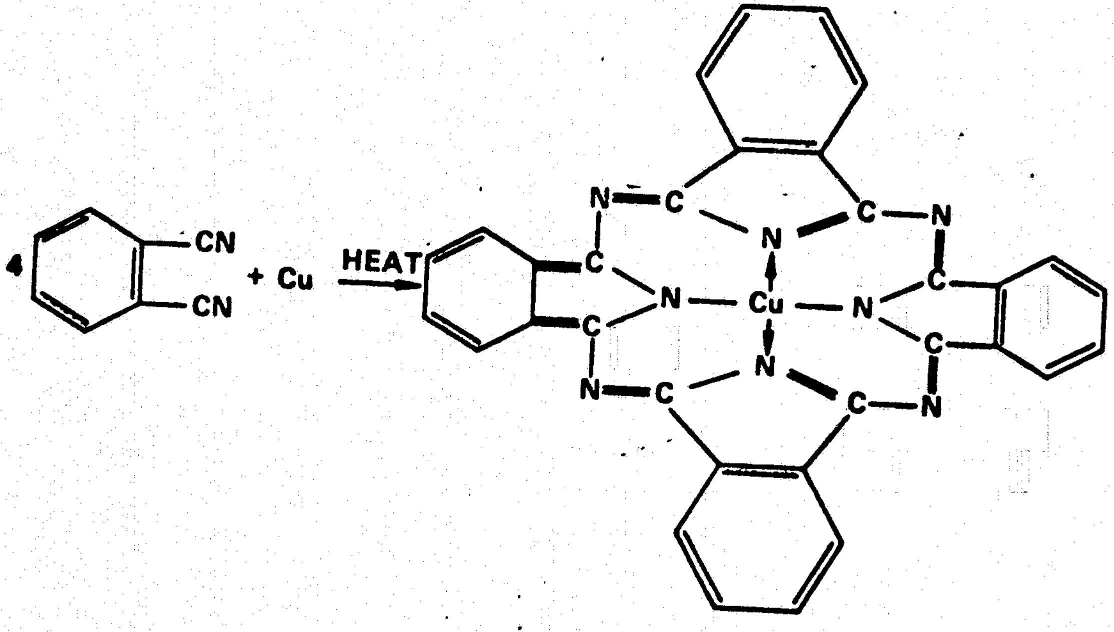
POSSIBLE RESEARCH DIRECTIONS

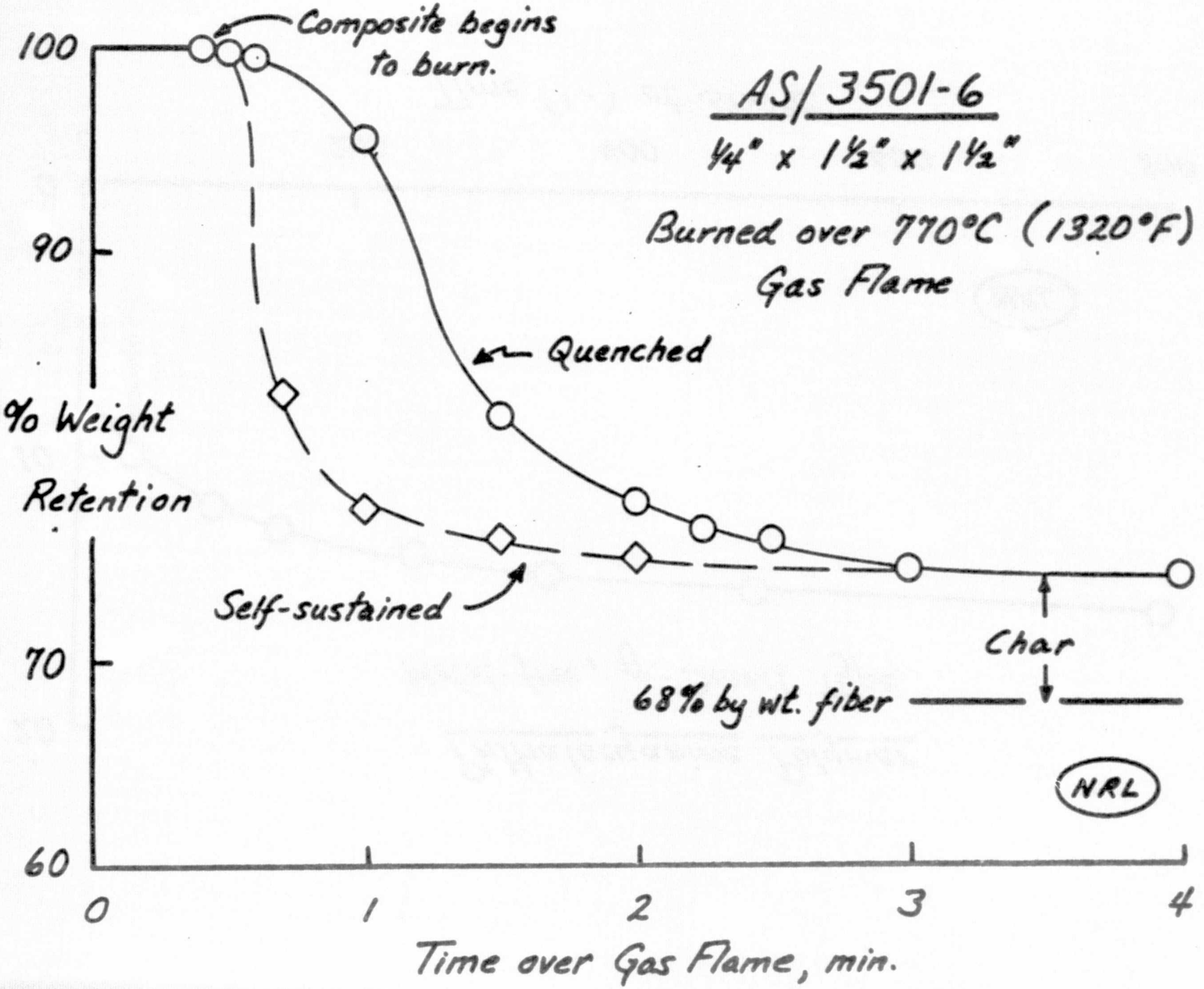
- MAY INCREASE CHAR YIELD BY:
  - ADDITION OF AROMATIC GROUPS TO R
  - ADDITION OF SUITABLE METAL ATOMS (SN$_1$--)
- MODIFY SYNTHESIS TO REDUCE COST
- MAINTAIN PROPERTIES AS MATRIX MATERIAL

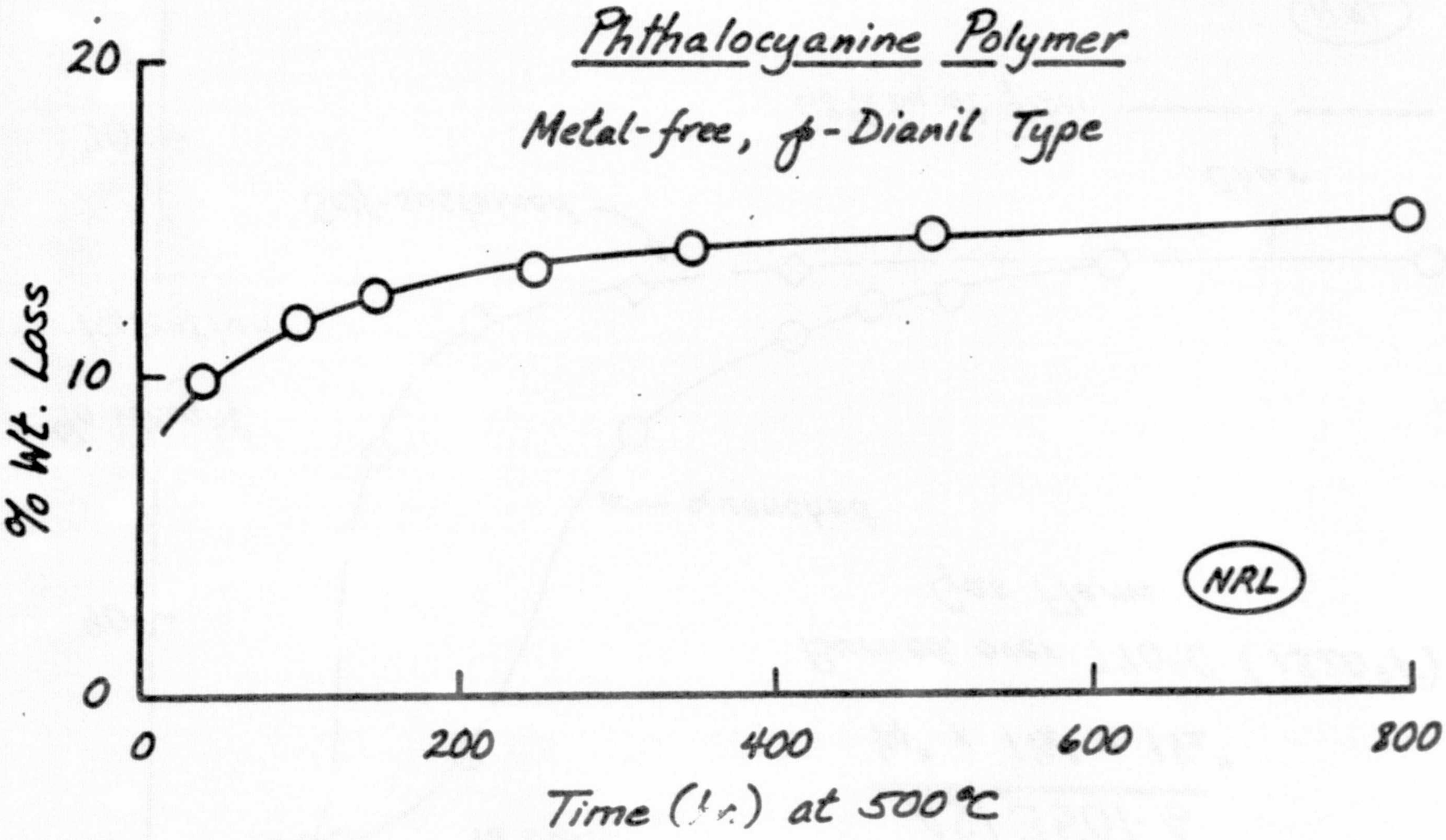
ADVANTAGES OF POLYPHTHALOCYANINES

- One phase system
- Infinite shelf life
- Potential low cost (~ $10/lb)
- Easily processed
- No volatiles on curing (no voids)
- High char yield possible

PHTHALOCYANINE REACTION



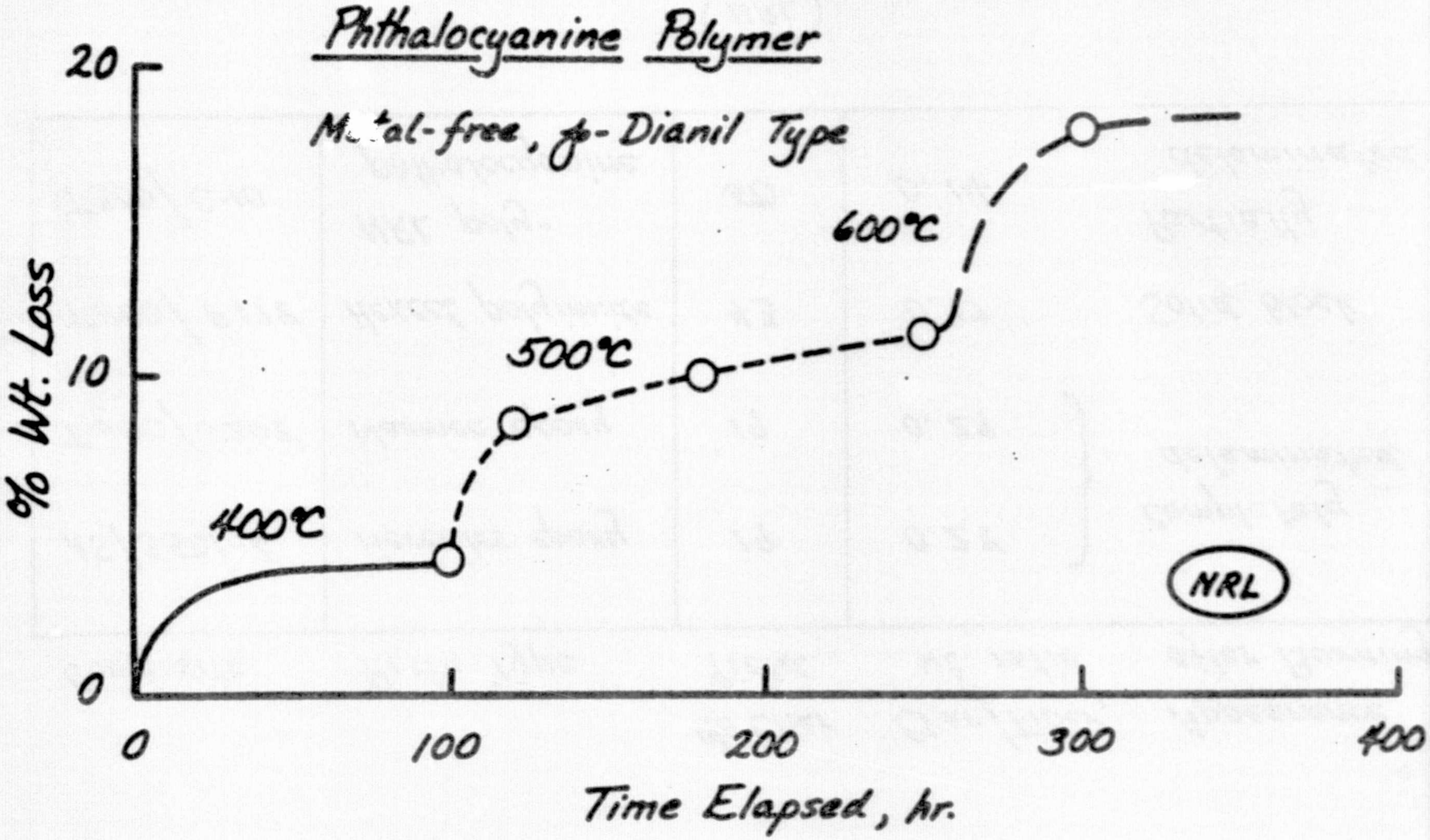

Composite begins to burn.
AS/3501-6
1/4" x 1 1/2" x 1 1/2"
Burned over 770°C (1320°F) Gas Flame
Quenched
% Weight Retention
Self-sustained
Char
68% by wt. fiber
NRL
100
90
70
60
0
1
2
3
4
Time over Gas Flame, min.


Phthalocyanine Polymer
Metal-free, p-Dianil Type
20
10
0
% Wt. Loss
0
200
400
600
800
Time (hr) at 500°C
NRL

Composites from 770°C Gas Fire

Composite	Resin Type	% Char Yield	Char/Fiber, wt. ratio	Appearance after Burning
AS/3501-6	Hercules epoxy	19	0.28	Completely delaminated
T300/5208	Narmco epoxy	19	0.29	
T300/F178	Hexcel polyimide	43	0.17	Solid block
T300/C-10	NRL poly-phthalocyanine	50	0.14	Partially delaminated

NRL


Phthalocyanine Polymer
Metal-free, p-Dianil Type
% Wt. Loss
20
10
0
400°C
500°C
600°C
0
100
200
300
400
Time Elapsed, hr.
NRL

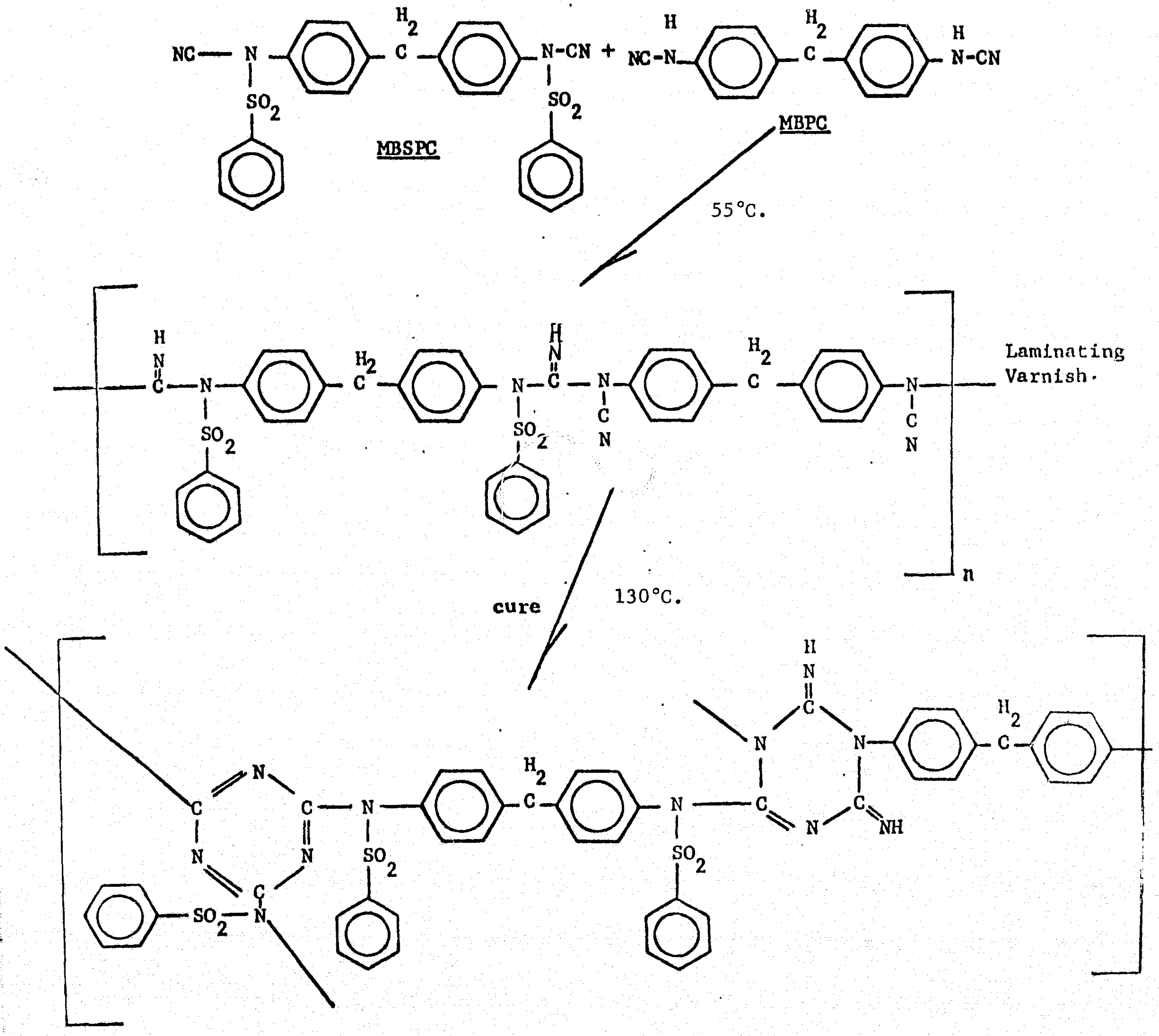
NCNS RESINS

RAY KRAY

CIBA-GEIGY

MARCH 23, 1978

COMPOSITION AND CURING MECHANISM OF N-CYANOSULFONAMIDE LAMINATING RESIN



NCNS-13P RESIN PILOT PLANT BATCH NO. 7/7/1002

LAMINATING VARNISH I-25R-99	30% NCNS-13P IN 60/40 METHANOL/ETHYL ACETATE
REINFORCEMENT	UNIDIRECTIONAL AS GRAPHITE FIBER
B-STAGING CONDITIONS FOR PREPREG	70°C/75 MIN. - 85°C/15 MIN.
NO. OF PLIES	15
PRESS LAMINATION CONDITIONS	350°F/300 PSI/1 HR.
POST CURE CONDITIONS	425°F/7 HRS. - 460°F/8 HRS.
RESIN SOLIDS CONTENT	30.3%
FIBER VOLUME	64.8%
VOID CONTENT	NONE
400°F SHORT BEAM SHEAR STRENGTH, PSI	11,400
400°F FLEXURAL STRENGTH, PSI	237,000
400°F FLEXURAL MODULUS, KSI	17,200

TMA Z-AXIS THERMAL EXPANSION

OF 110 MIL THICK NCNS-13P LAMINATE

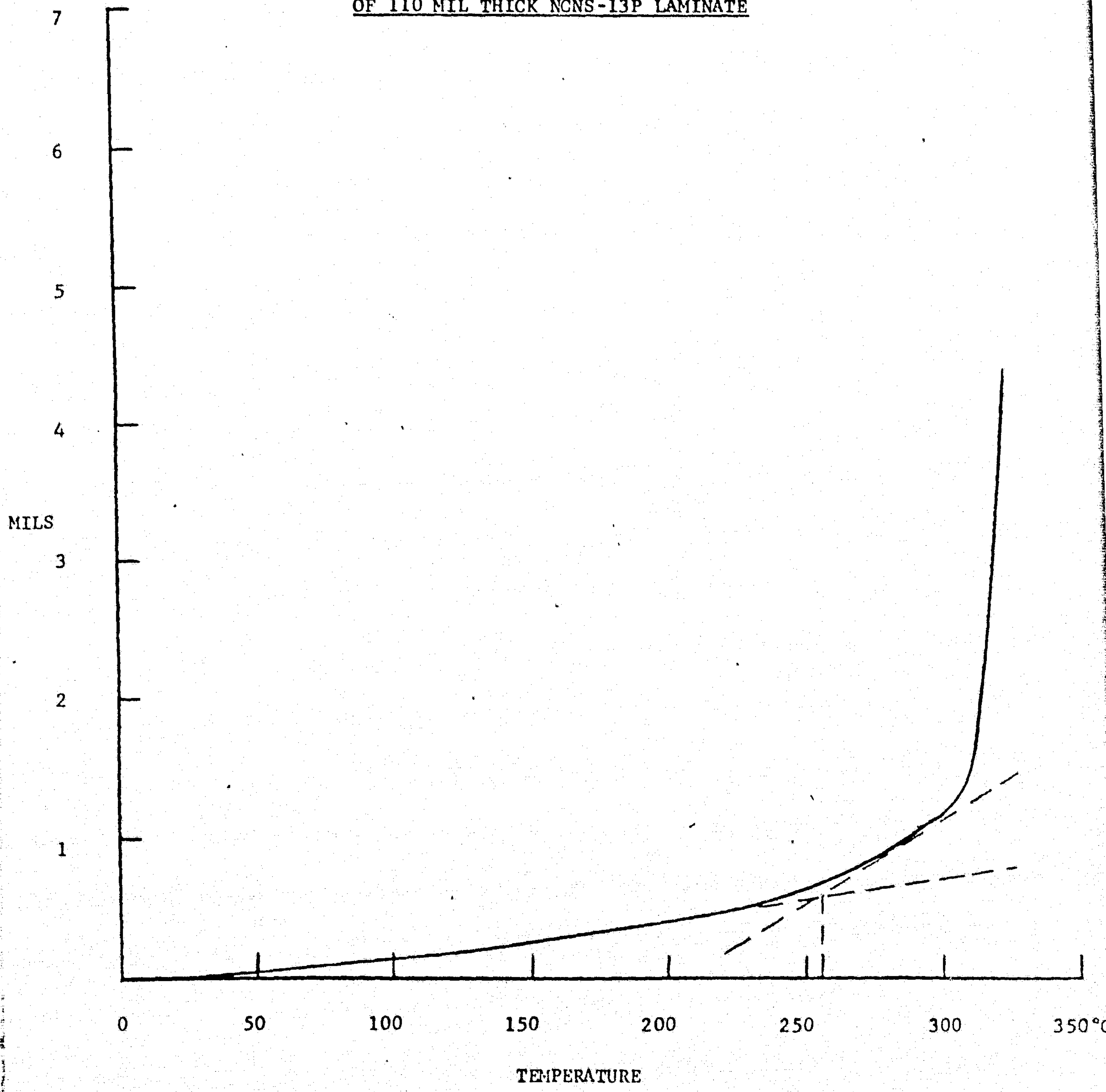


FIGURE 14

FLAMMABILITY AND SMOKE GENERATION

	1:2 NCNS RESIN	P13N RESIN	XYLOK 210
OXYGEN INDEX OF NEAT RESIN	29	31	--
RESIN CONTENT OF 181E GLASS LAMINATE	30	27	30
OXYGEN INDEX OF LAMINATE	86.2	--	69
MAXIMUM SPECIFIC OPTICAL DENSITY (DM)			
FLAMING	20	20	123
NON-FLAMING	6	0.3	44
TIME IN MINUTES TO DEVELOP SPECIFIC OPTICAL DENSITY = 16 (DS)			
FLAMING	6.6	7.5	1.8
NON-FLAMING	NOT REACHED	NOT REACHED	11.5

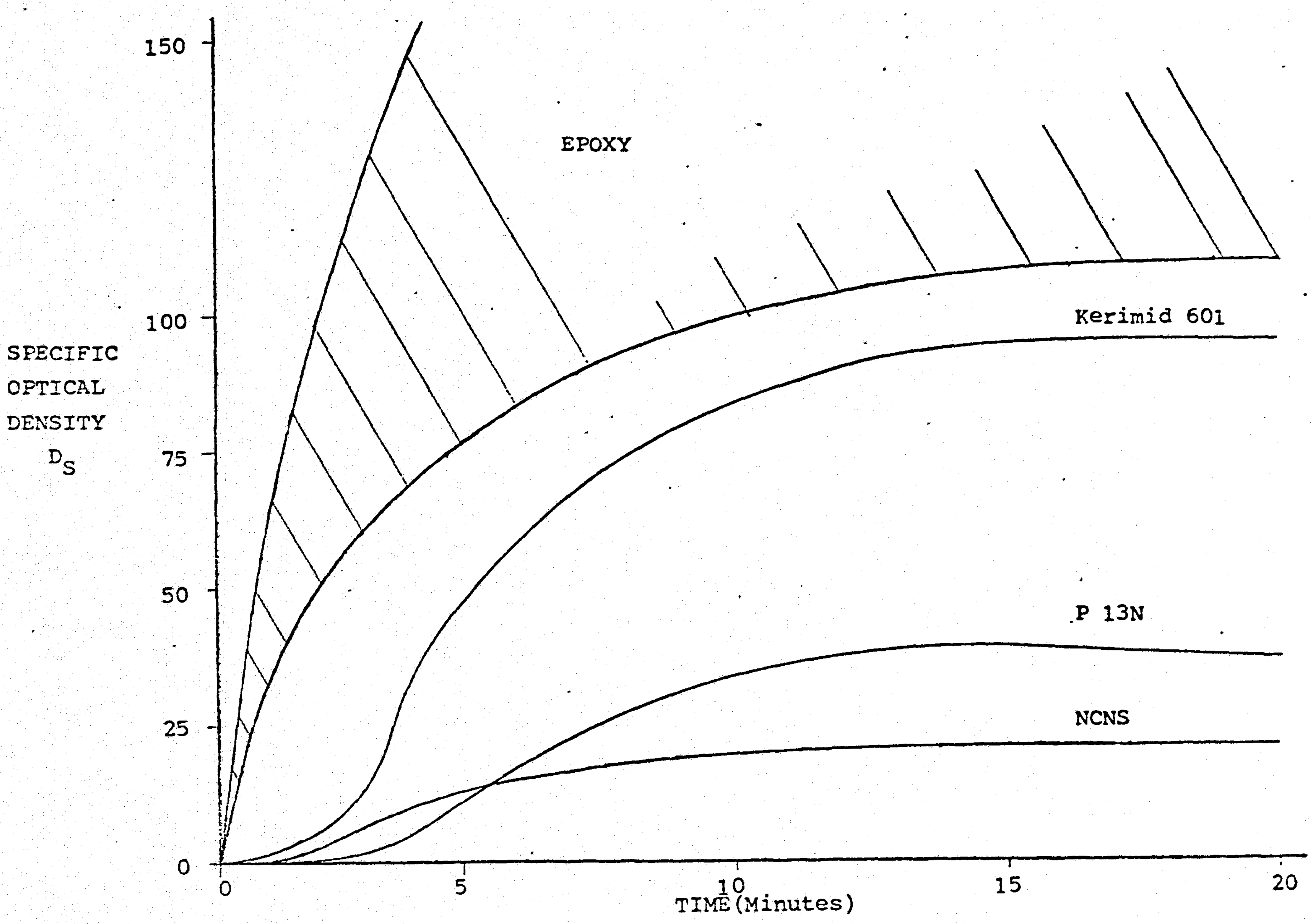
NON-BURNING CHARACTERISTICS OF NCNS/181E GLASS CLOTH LAMINATES

NO.	95
RESIN	NCNS-12M
RESIN CONTENT	22.8%
FAA VERTICAL BURN TEST 25.853A*	
FLAME TIME IN SECONDS	6.2
BURN LENGTH IN INCHES	1.1
LIMITING OXYGEN INDEX (LOI)	NON-BURNING IN 100% O_2

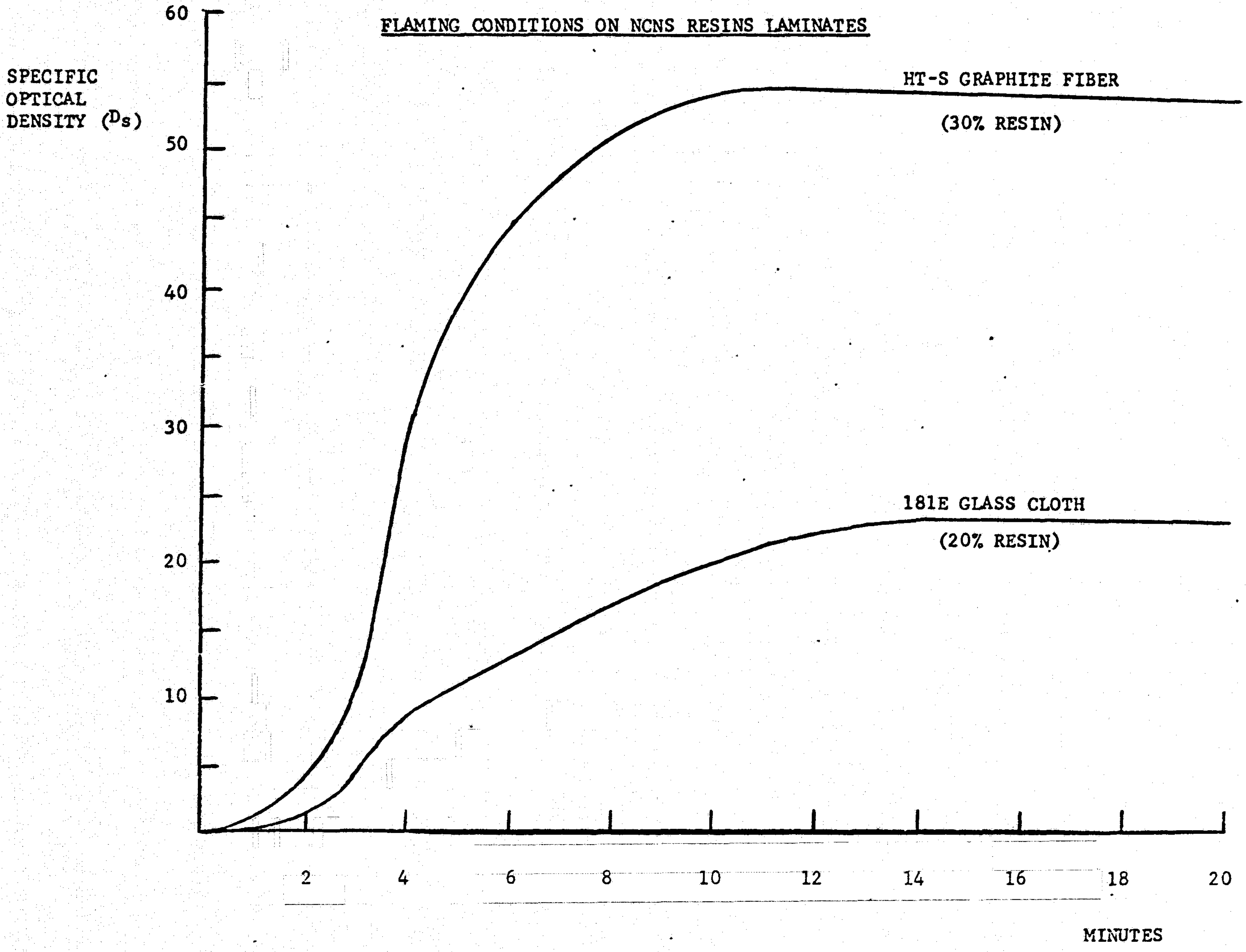
---

*ALL SAMPLES WERE SELF EXTINGUISHING AND DID NOT DRIP.

NBS SMOKE DENSITY ON GLASS LAMINATES



NBS SMOKE DENSITY MEASUREMENTS UNDER FLAMING CONDITIONS ON NCNS RESINS LAMINATES



TOXIC GASES FROM NCNS-13P/181E GLASS FABRIC LAMINATE I-24A-119A IN NBS SMOKE DENSITY CHAMBER

D_M		12		
TIME IN MINUTES	5	10	15	20
CO, PPM	10	30	70	110
HCN, PPM	1*	2	3.5	5
SO_2, PPM	2.5	5	5	5
NO_X, PPM	0.5	1	2	2

---

*COMPARATIVE VALUE FOR POLYIMIDE 3002 (DUPONT) WAS 15 PPM FOR HCN (D. ARNOLD & G. JOHNSON, BOEING, SAMPE SYMPOSIUM APRIL 1977).

LOW SHRINKAGE RESINS

BILL BAILEY
UNIVERSITY OF MARYLAND

MARCH 23, 1978

Bailey

MONOMER	SPECIFIC GRAVITY		SHRINKAGE
	MONOMER	POLYMER	%
VINYL CHLORIDE	0.919	1.406	34
ACRYLONITRILE	0.797	1.17	31
METHYL METHACRYLATE	0.940	1.19	21
VINYL ACETATE	0.932	1.19	21
STYRENE	0.907	1.06	15
DIALLYL PHTHALATE	1.12	1.27	12

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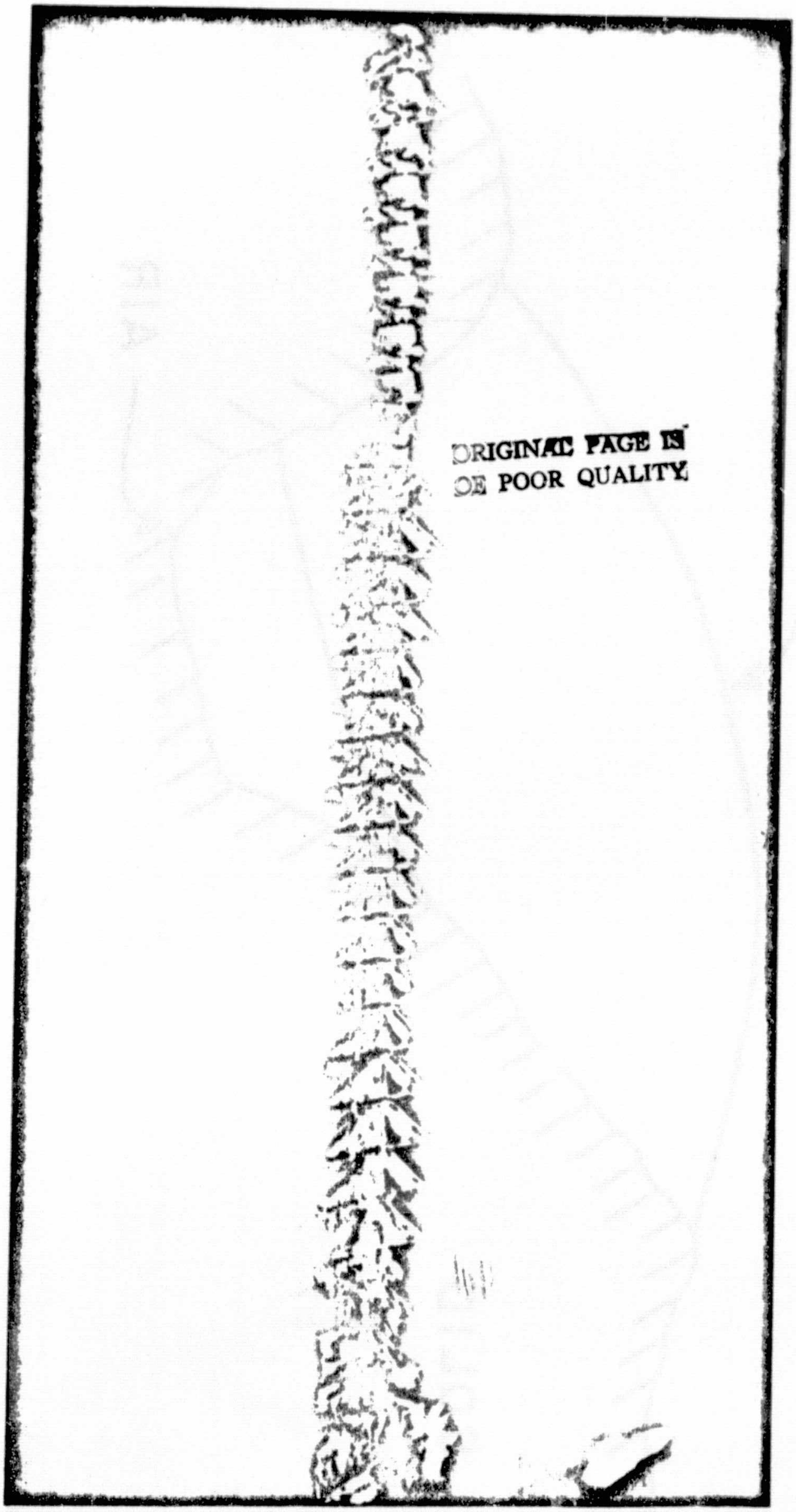
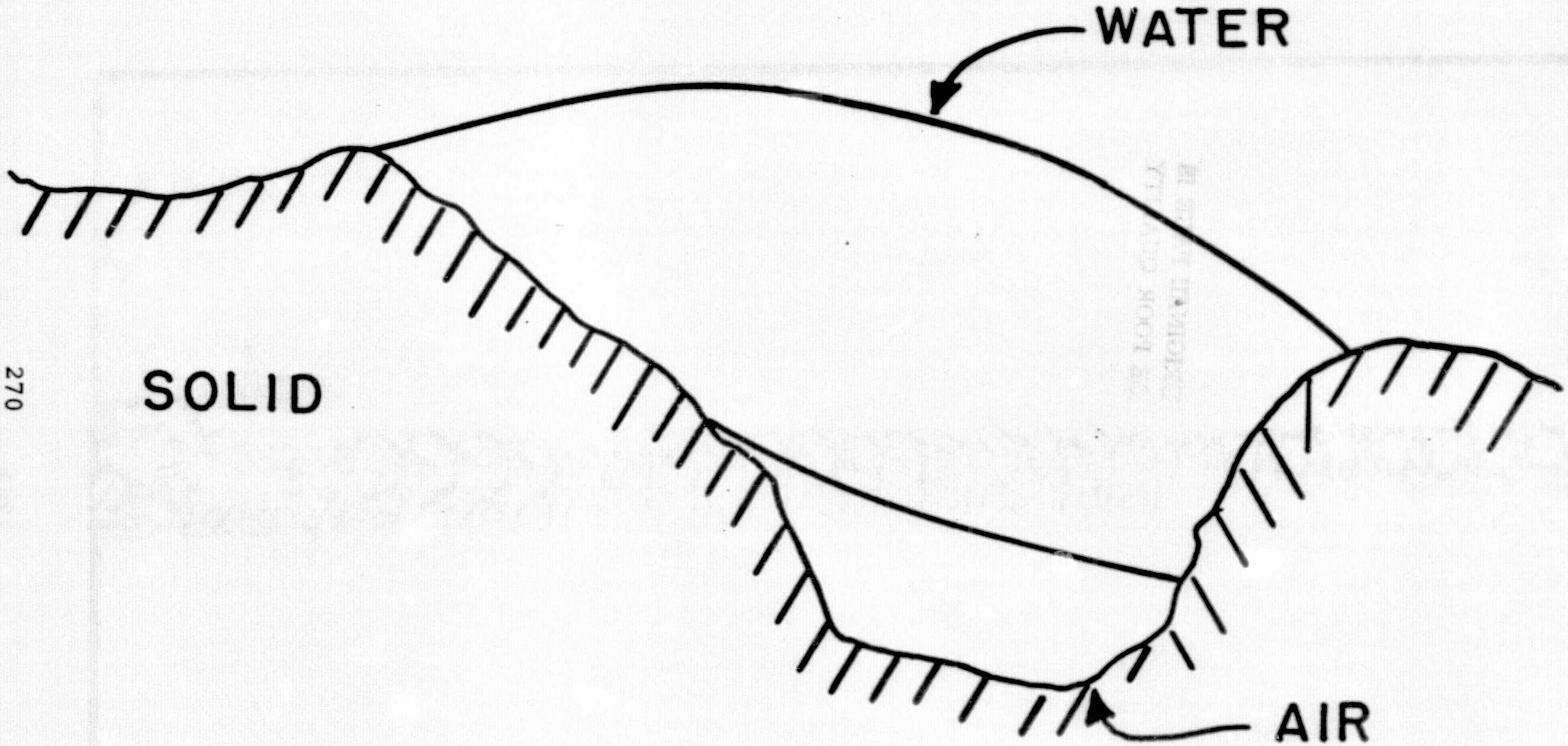
SHRINKAGE DURING RING-OPENING POLYMERIZATION

MONOMER	d_4^{20}	POLYMER d_4^{20}	SHRINKAGE, %
ETHYLENE OXIDE	0.869	1.13	23
PROPYLENE OXIDE	0.830	1.002	17
CYCLOPENTENE	0.772	0.91	15
STYRENE OXIDE	1.05	1.15	9
CYCLOOCTENE	0.849	0.89	5
CYCLODODECATRIENE	0.885	0.91	3

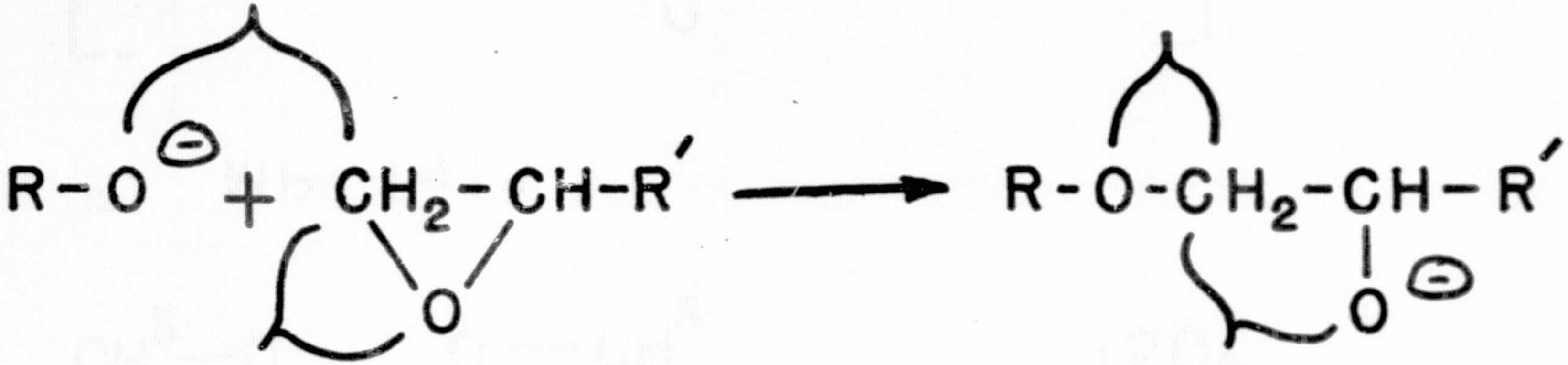


ORIGINAL PAGE IS
OF POOR QUALITY



MECHANICAL ATTACHMENT OF ICE TO A ROUGH SURFACE

SHRINKAGE DURING RING-OPENING POLYMERIZATION



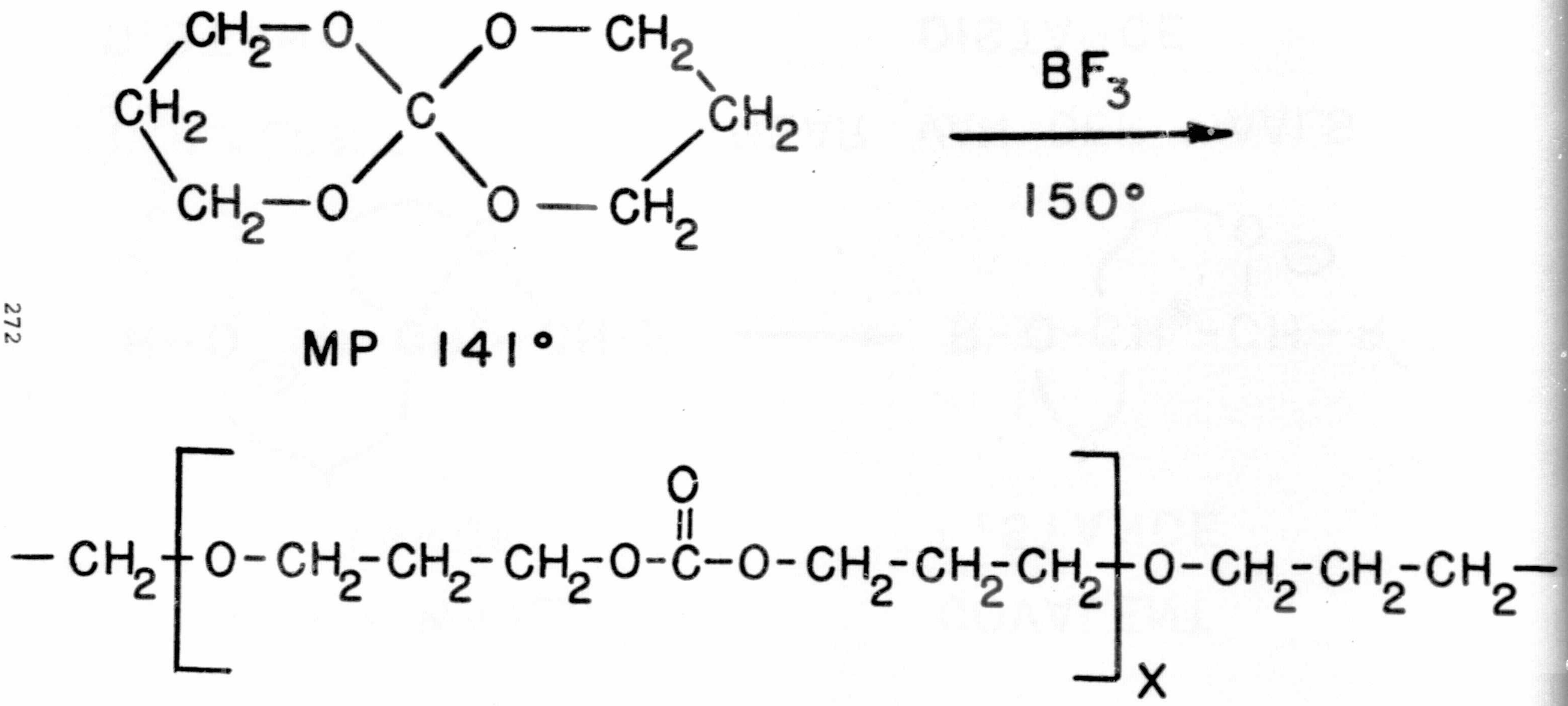
VAN DER WAALS DISTANCE

COVALENT DISTANCE

COVALENT DISTANCE

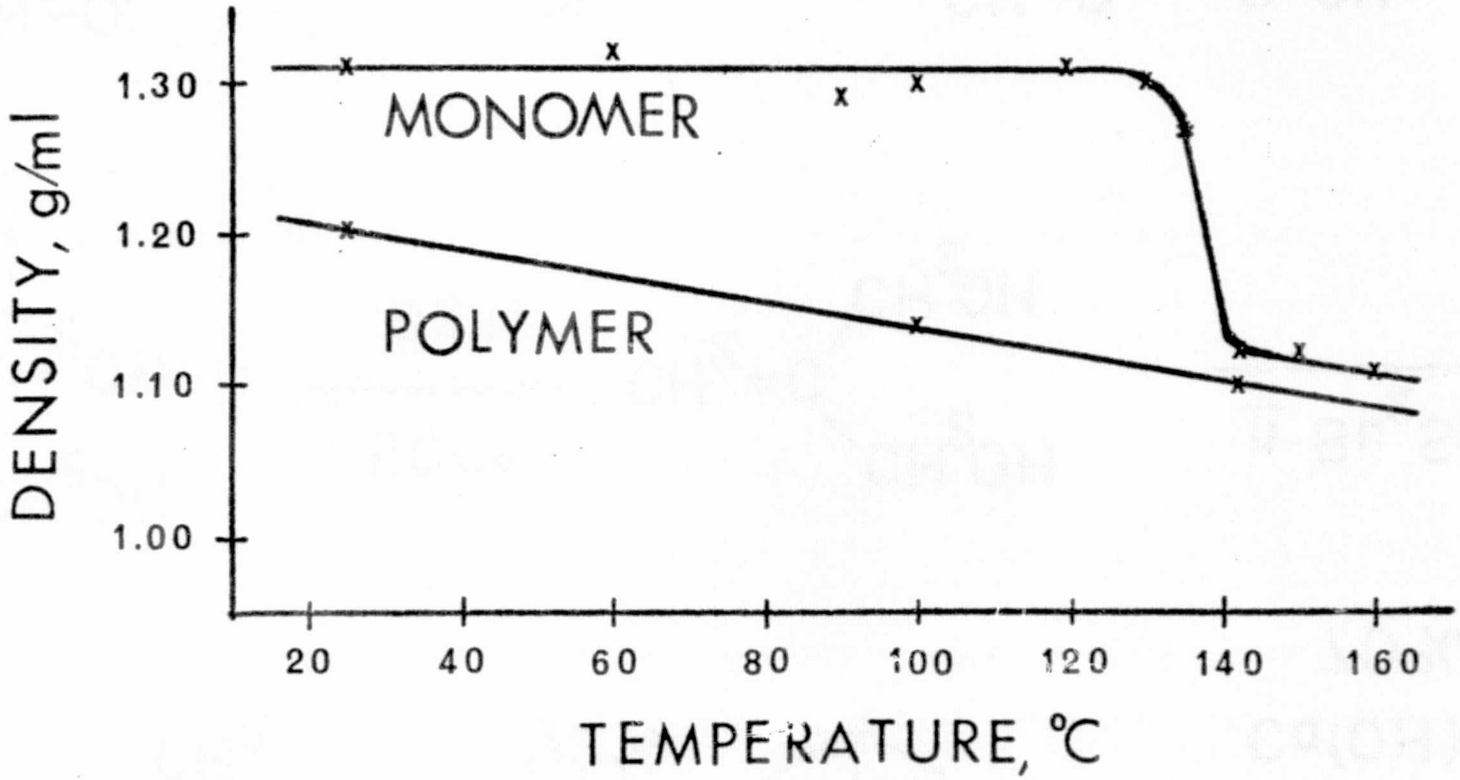
NEAR VAN DER WAALS DISTANCE

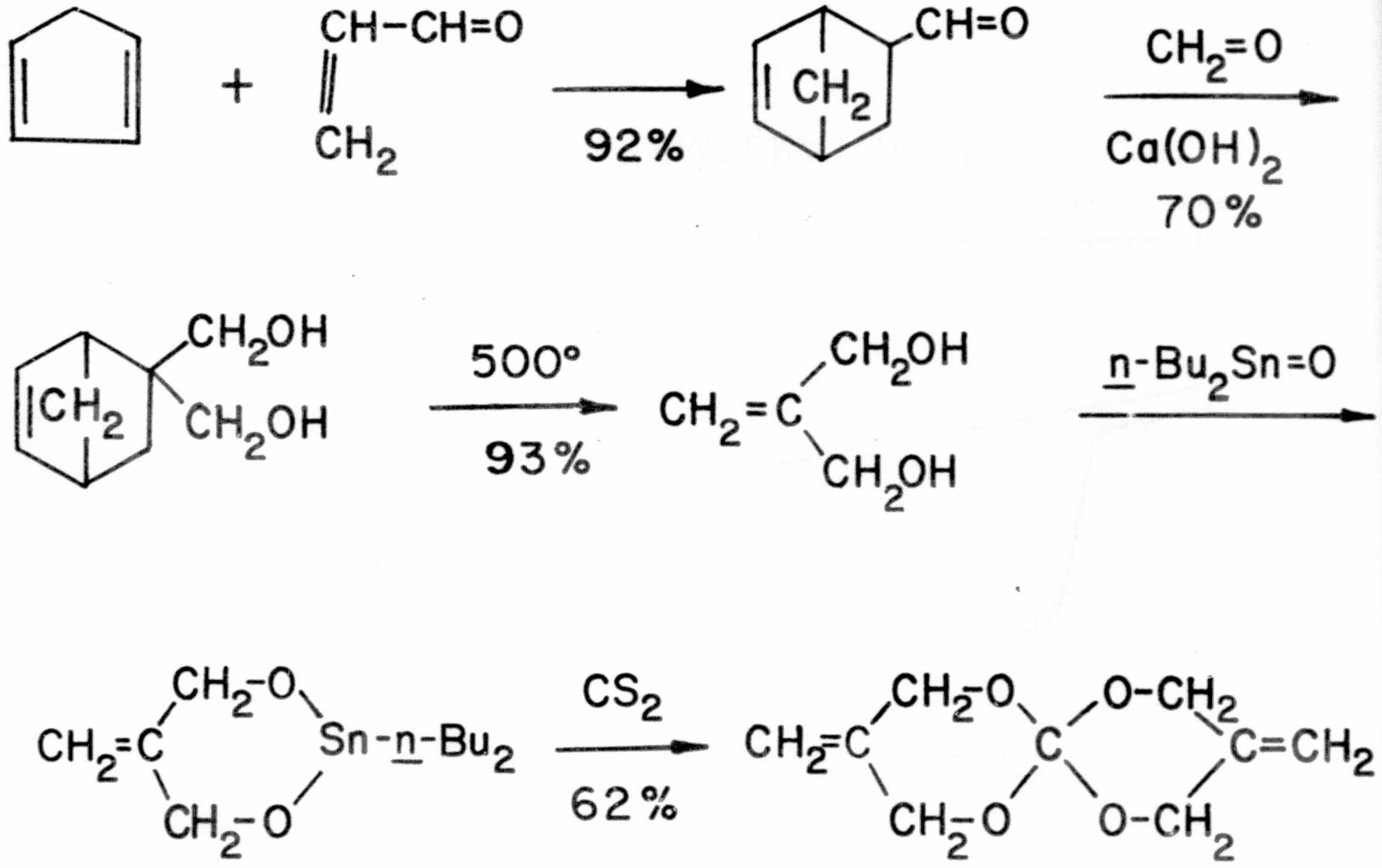
3-5 % SHRINKAGE

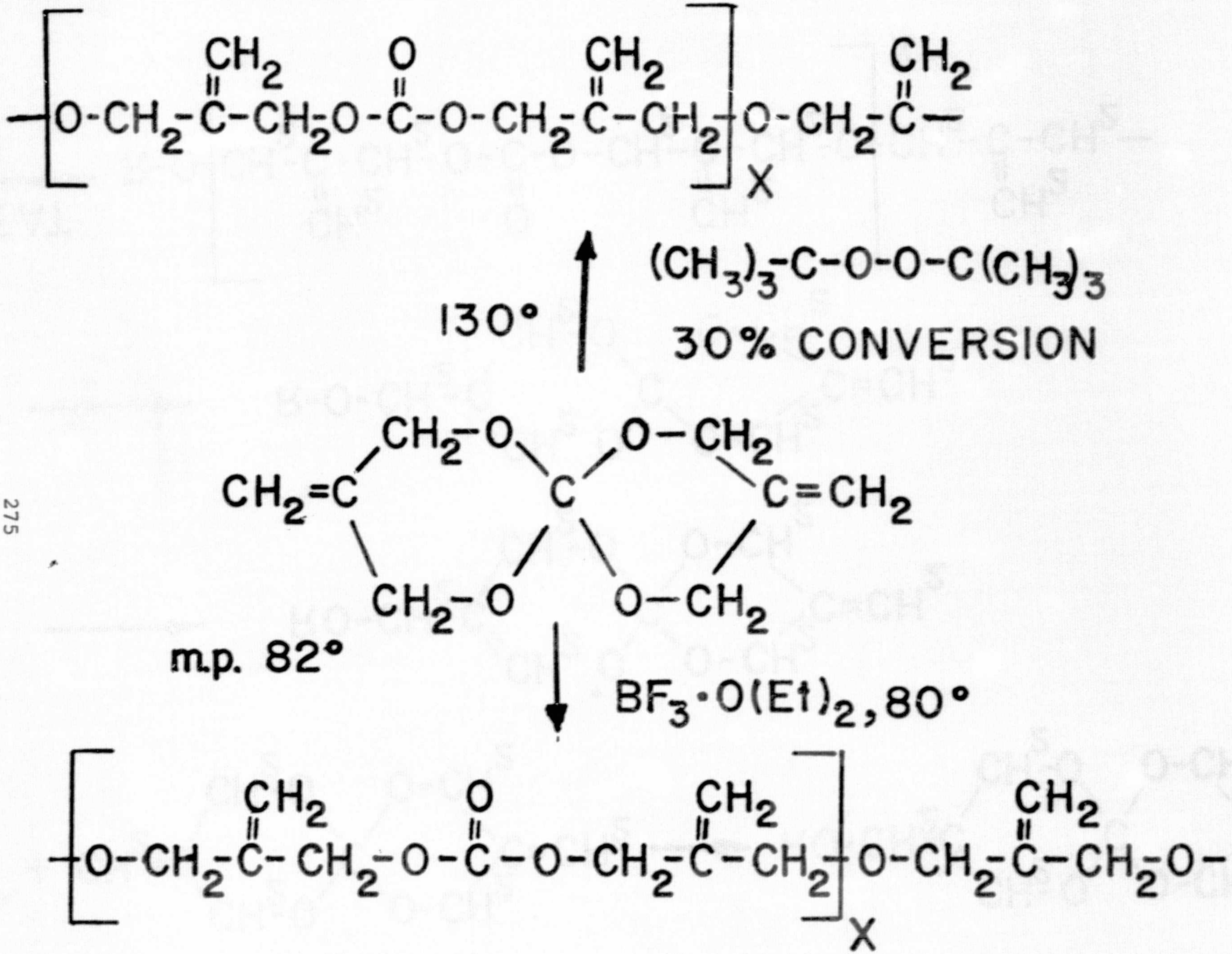


$$-CH_2\left[O-CH_2-CH_2-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_2-CH_2\right]_X O-CH_2-CH_2-CH_2-$$

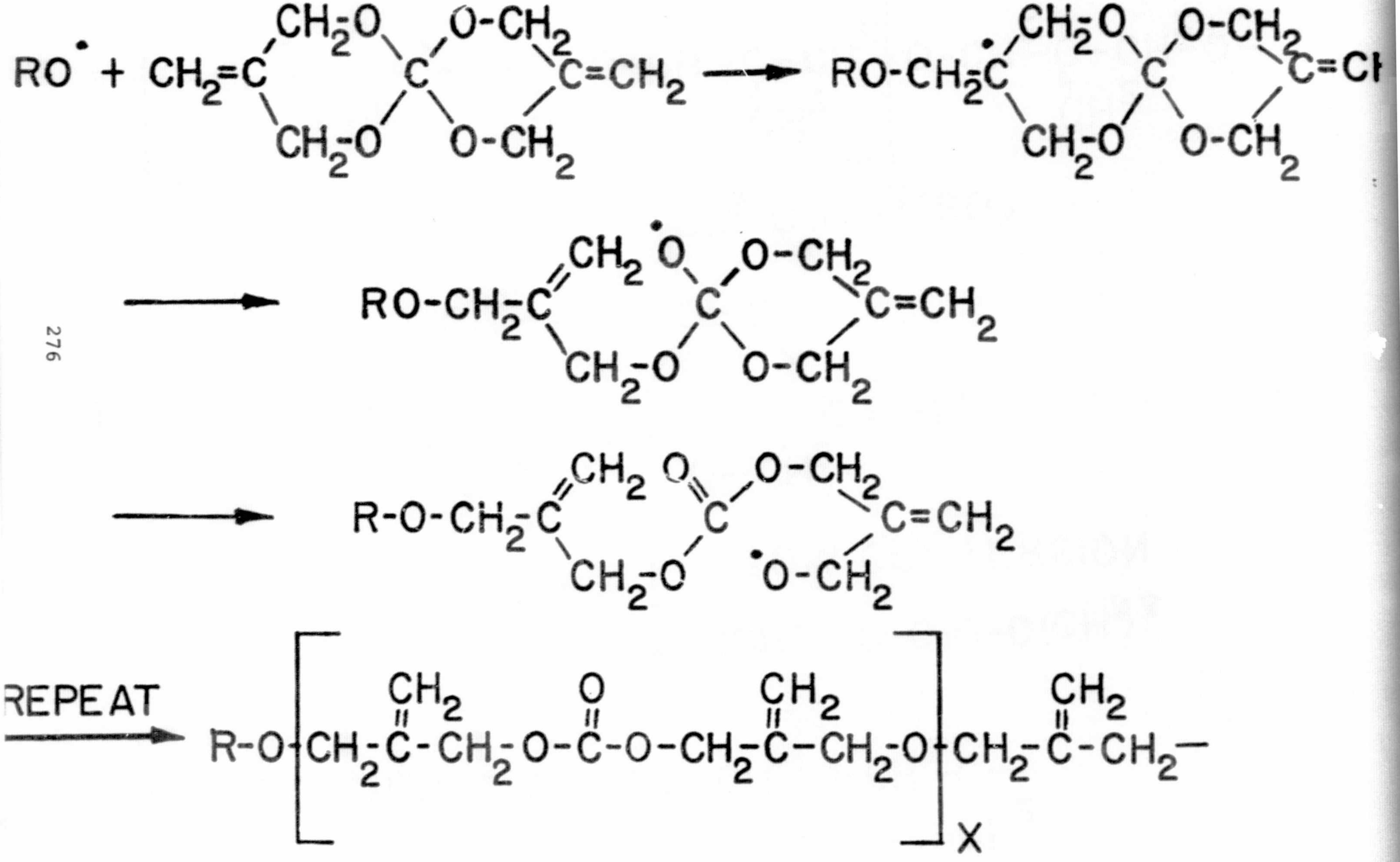
Densities of the Monomeric Spiro Ortho Carbonate and Related Polyoxycarbonate versus Temperature

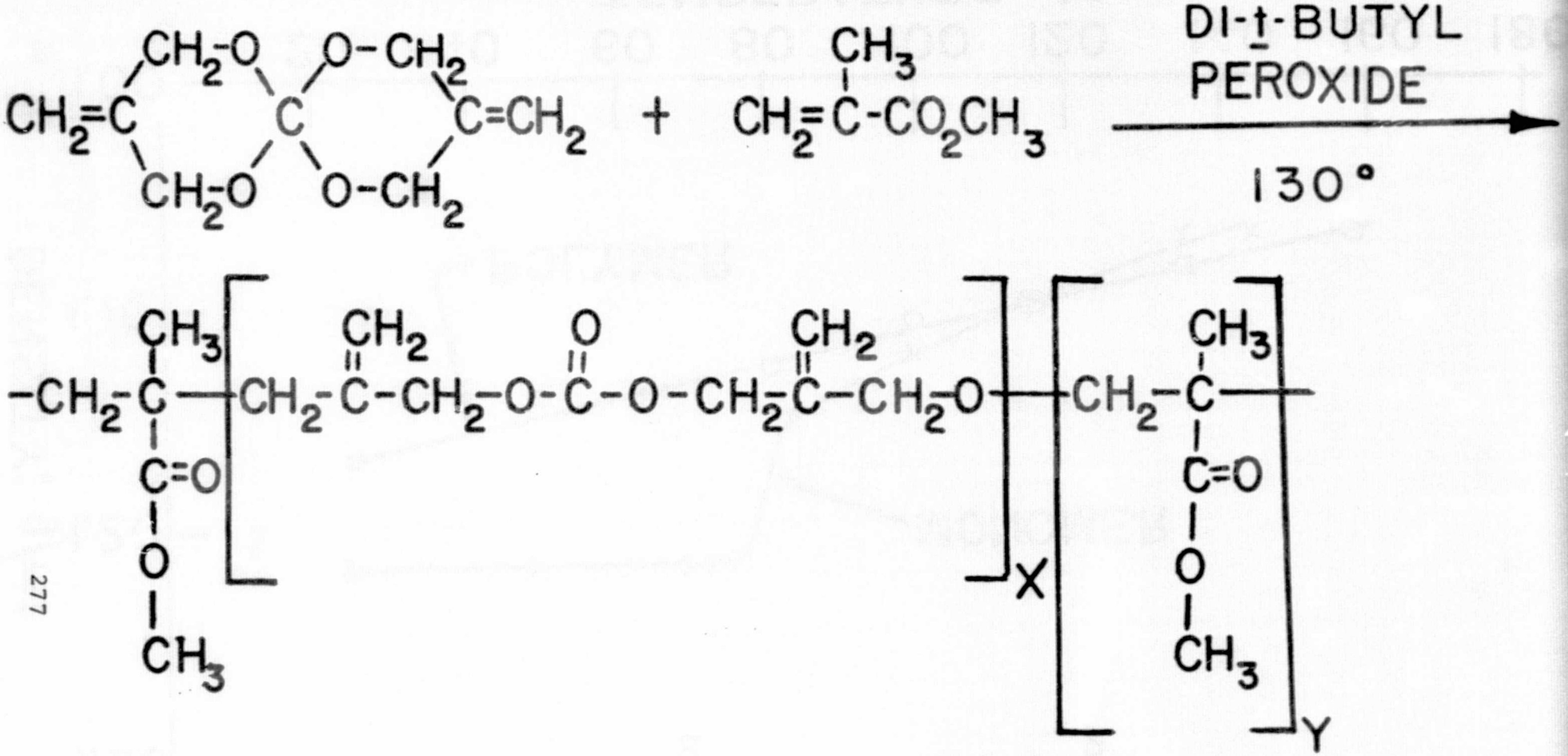



+
CH−CH=O
CH2
92%
CH=O
CH2
CH2=O
Ca(OH)2
70%
CH2OH
CH2
CH2OH
500°
93%
CH2=C
CH2OH
CH2OH
n-Bu2Sn=O
CH2-O
CH2=C
Sn-n-Bu2
CH2-O
CS2
62%
CH2-O
O-CH2
CH2=C
C
C=CH2
CH2-O
O-CH2



80% SOLUBLE; $[\eta] = 0.24$ ($CHCl_3$, 25°)

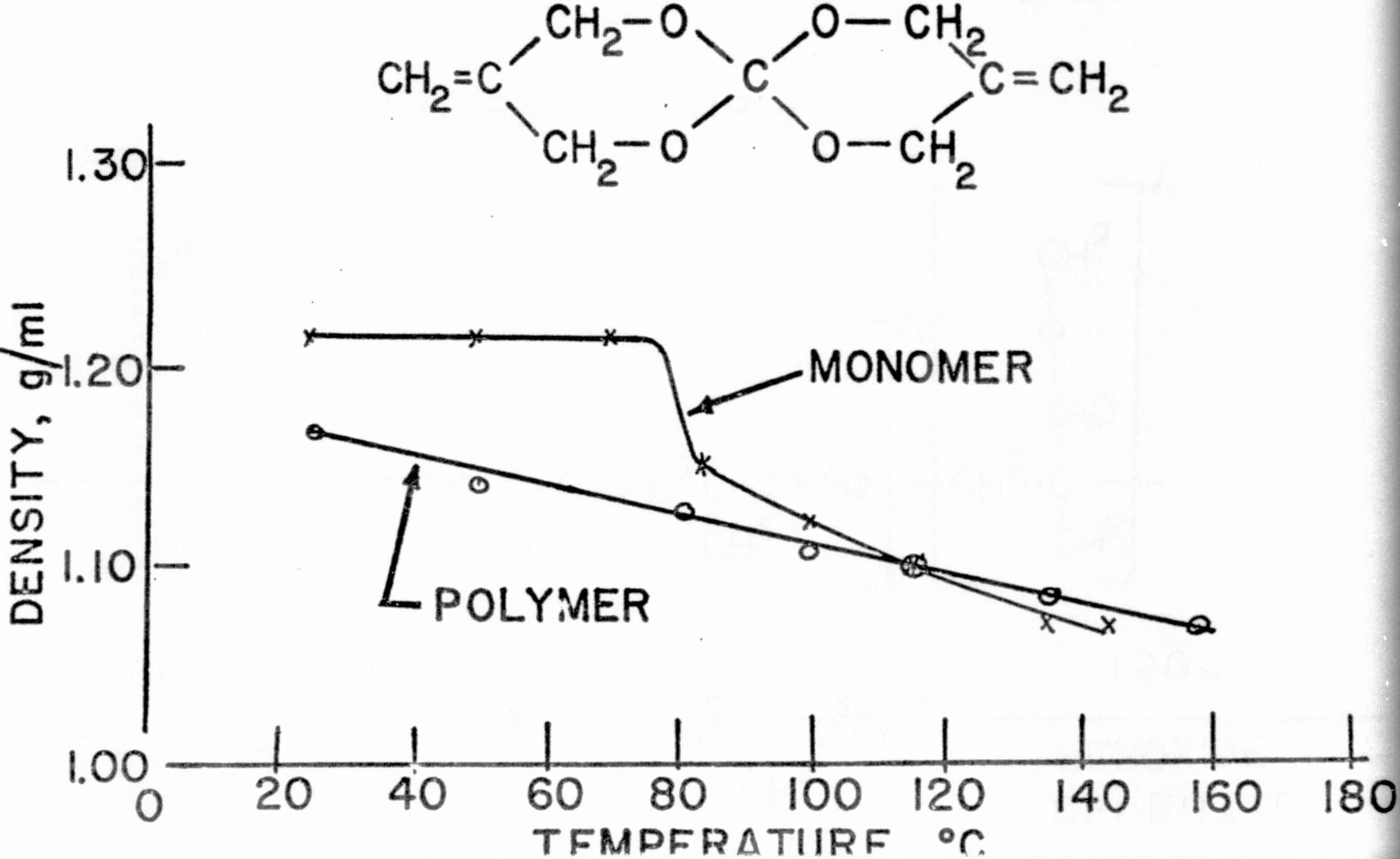

RO•
REPEAT
X



$r_1 = 0.87$ $r_2 = 16.4$

AT 69% CONVERSION, 10% SPIRO MONOMER IN FEED
GIVES 1% CARBONATE IN COPOLYMER

DENSITIES OF THE MONOMERIC SPIRO ORTHO CARBONATE AND RELATED POLYOXYCARBONATE VERSUS TEMPERATURE



MATERIALS DEVELOPMENT REQUIREMENTS
AIRBORNE CARBON/GRAPHITE FIBERS

M. T. KATSUMOTO

BOEING COMMERCIAL AIRPLANE CO.

MARCH 23, 1978

Mel Katsumoto
Boeing Commercial Airplane Co.

MATERIAL DEVELOPMENT REQUIREMENTS
AIRBORNE CARBON/GRAPHITE FIBERS

o PHASE I NEAR TERM REQUIREMENTS

CONTINUE WITH EXISTING EPOXY AND FIBER SYSTEM

- ESTABLISH VIABILITY OF HYBRIDIZATION, VARYING WEAVE AND TAPE FORMS, APPLICATION OF SUPPLEMENTAL COATING, ETC.

o PHASE II LONG TERM REQUIREMENTS

- MODIFICATION OF CURRENT EPOXY AND FIBER SYSTEMS

- DEVELOP NEW MATRIX AND FIBER SYSTEMS

RATIONALE - PHASE I

CONTINUE WITH EXISTING EPOXY AND FIBER SYSTEMS:

- DISPERSAL AND FRAGMENTATION PHENOMENA NOT COMPLETELY UNDERSTOOD
  - DIFFERENT WEAVE AND TAPE COMBINATION FORMS
  - HYBRID TAPE AND FABRIC
  - SUPPLEMENTAL COATING SYSTEM
- HARDWARE COMMITMENT ON CURRENT AND PROPOSED AIRPLANES
  - COMPOSITE TECHNOLOGY JEOPARDIZED IF CONTINUITY IN COMMITMENT NOT MAINTAINED
- LONG LEAD TIME REQUIRED-MATERIAL DEVELOPMENT TO CERTIFICATION
  - EVALUATION
  - SPECIFICATION
  - DESIGN — MINIMUM OF 5-7 YEARS
  - DURABILITY
  - ALLOWABLES
  - CERTIFICATION
- EXTENSIVE DATA BASE REQUIRED FOR AIRPLANE CERTIFICATION

TECHNICAL REQUIREMENTS

- IF REQUIRED IMPROVE AFTER BURN PROPERTIES TO CONTROL FRAGMENTATION AND DISPERSAL OF FIBERS
- INHERENT RESISTANCE TO AIRCRAFT FLUIDS

  HYDRAULIC FLUIDS
  FUEL
  ANTI-ICING
  ETC.

- COMPATIBLE WITH AIRCRAFT ENVIRONMENTS

  U.V.
  MOISTURE
  TEMP. (-65° to 180°F)
  ETC.

- COMPATIBILITY WITH AIRCRAFT MATERIALS
  PAINT
  SEALANT
  ADHESIVES
  ALUMINUM
  TITANIUM
  COMPOSITE
- EXHIBIT COST EFFECTIVE MANUFACTURING PROCESS

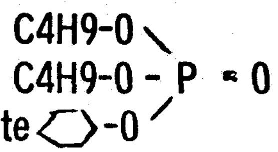
MATERIALS COMPATIBILITY

PHOSPHATE ESTER HYDRAULIC FLUIDS

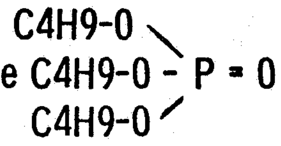
PROPERTIES

- LOW VOLATILITY
- LOW SURFACE TENSION
- EXCELLENT SOLVENT
- MISCIBLE WITH OTHER SYNTHETIC COMPOUNDS
- PLASTICIZER (PARTICULARLY FOR POLYVINYL TYPE RESINS)
- FIRE RESISTANT

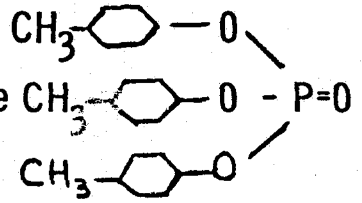
diButyl Phenyl Phosphate



tri Butyl Phosphate



tri Cresyl Phosphate



FLUID COMPATIBILITY

	PERCENT SWELL - 72 HOURS AT 160°F	
	PHOSPHATE ESTER HYDRAULIC FLUIDS (SKYDROL 500 TYPE)	TYPE III FUEL
NEOPRENE	150%	81%
HYPALON	250%	100%
BUTYL	7%	403%
VITON	225%	3%
POLYIMIDE	- 0.04%	
ETHYLENE PROPYLENE	4.5%	315%
EPOXY 350°F	.55%	
LARC 160	1.1%	
*POLYSULFONE	- 2.07%	
**TITANIUM	0%	

* Unsatisfactory under stress conditions

** Embrittlement problems at high temperatures

RATIONAL PHASE II

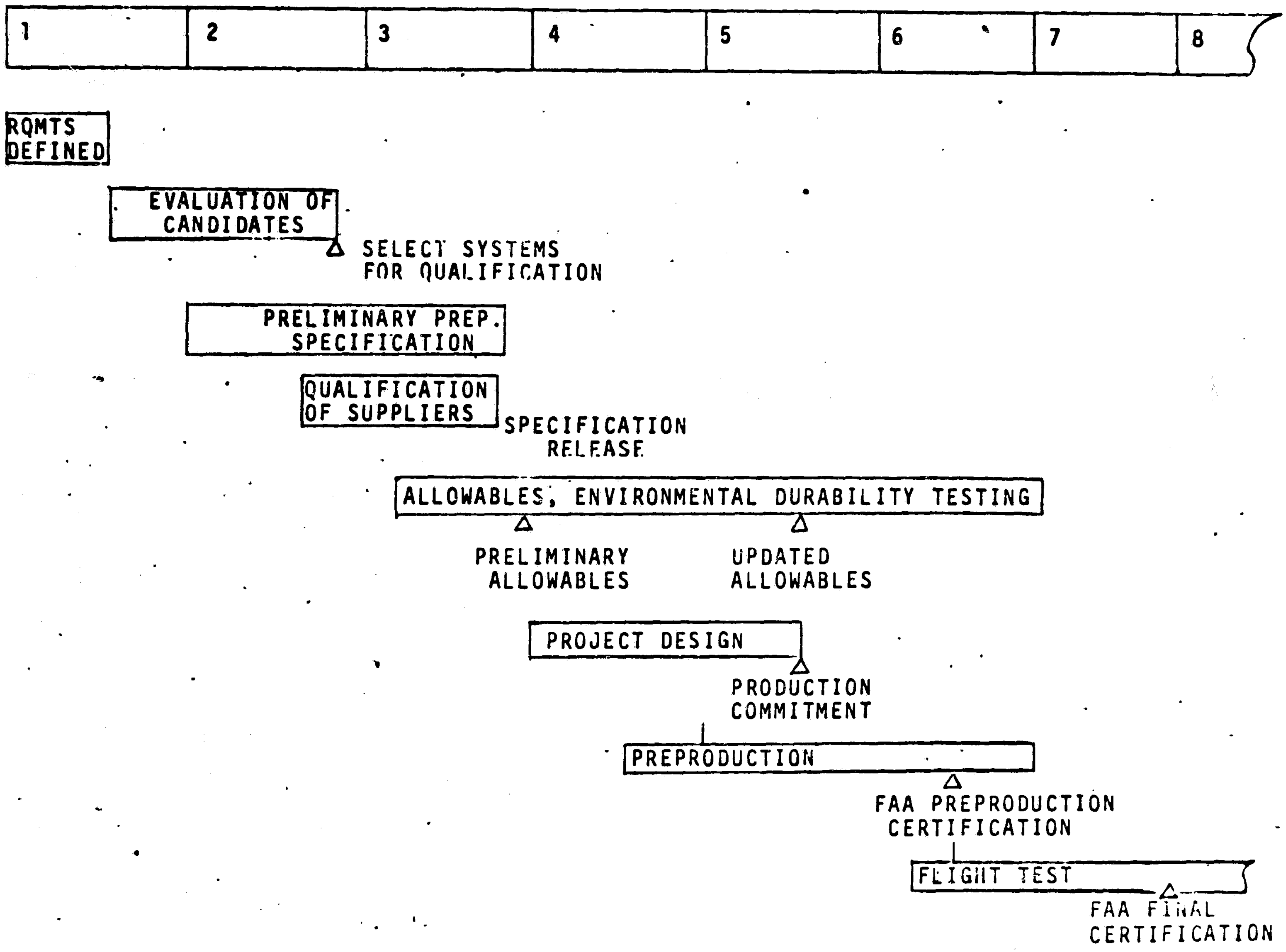
- IMPROVE ENVIRONMENTAL DURABILITY, FRACTURE TOUGHNESS & MECHANICAL PROPERTIES TO EXPAND USAGE TO PRIMARY STRUCTURE
- IMPROVE FLAMMABILITY RESISTANCE FOR INTERIOR AND FLAME CRITICAL AREAS (FUEL TANK, POWER PLANT, APU, ETC.)
- IMPROVE LIGHTNING STRIKE AND ELECTRICAL EFFECTS
- IF REQUIRED IMPROVE AFTER BURN PROPERTIES TO CONTROL FRAGMENTATION & DISPERSAL OF FIBERS

PRELIMINARY TECHNICAL REQUIREMENTS - PHASE II

COMPOSITE PROPERTIES	CURRENT EPOXY SYSTEM				PHASE II PROPOSED COMPOSITE SYSTEM			
	TAPE		FABRIC		TAPE		FABRIC	
TENSILE ULT 0° RT	185		70		200		90	
TENSILE MODULUS 0° RT	18 - 21		8.5 - 11		18 - 21		9-11	
TENSILE STRAIN 0° RT	9500		7000		10000		8000	
TENSILE 90° R.T.	4.5 KSI		70		5		90	
SHORT/BEAM/SHEAR	13		7		14		8	
COMPRESSION 0°	155		70		170		80	
COMPRESSION (MODULUS)	16.5-19		7.5-10		19 - 22		16.5-19	
COMPRESSION STRAIN	8500		6800		10,000		8000	
MOISTURE RESISTANCE	+45 Tens.	SBS	COMP.	SBS	+45 Tens.	SBS	COMP	SBS
% RETENTION OF STRENGTH @ RT	85	75	80	80	95	95	95	95
% RETENTION @ 270F	65	55	55	50	85	85	85	85
LIGHTNING STRIKE-ELECTRICAL EFFECTS	No		No		Yes		Yes	
FLUID RESISTANCE								
FUEL	Yes		Yes		Yes		Yes	
SKYDROL	Yes		Yes		Yes		Yes	
FIBER FRAGMENTATION & DISPERSAL	NO?		NO?		Yes		Yes	
FLAMMABILITY FAR 25	NO?		NO?		Yes		Yes	

C-1

MATERIAL DEVELOPMENT SCHEDULE



HYBRID COMPOSITES

Dr. KARL PREWO, CHAIRMAN

NAME	ORGANIZATION
Karl Prewo	United Technologies Research Ctr.
William E. Winters	TRW Equipment
John Wooley	Lockheed Calif. Co.
Harold Sanders	Grumman Aerospace
Karl Hergenrother	Transportation Systems Center - DOT
John Freche	NASA Lewis Research Ctr.
Jim McGann	Rockwell International (LAD)
Charlie King	NASA LaRC
Jim Henshaw	AVCO Specialty Materials Div.
Ashok Dhingra	DuPont
Ira Petker	Composites Horizons

NASA Reporters: A. J. Chapman and W. B. Lisagor, LaRC

ISSUES FOR
HYBRID COMPOSITES
WORKING GROUP

1. What principles would be employed by hybrid composites to retard fiber release?

2. Would metallic coatings applied to the surface of fabricated parts be effective in retarding fiber release?

3. Would intumescent coatings applied to the surface of fabricated parts be effective in retarding fiber release?

4. For each potential solution via hybridization:

   (a) What principle would this approach employ to retard fiber release?

   (b) What is the likely effect on the weight of fabricated parts?

   (c) Would this approach be cost effective?

   (d) How difficult would it be to fabricate this hybrid?

   (e) What effect would this approach have on mechanical properties?

   (f) What is the likely environmental durability of this hybrid as compared to graphite-epoxy?

   (g) Are any large scale production problems likley with this hybrid?

6. What is your assessment of the current NASA research program in this area, and what changes do you recommend?

7. Rank the generic solutions (fiber modifications, fiber coatings, alternative fibers, epoxy resin modifications, epoxy resin replacements, hybrid composites) as to their probability of success.

NASA REPORTERS' SUMMARY FOR HYBRID COMPOSITES WORKING GROUP

Prior to the general working group discussions, Ashok Dhingra presented a prepared review of DuPont's Kevlar and FP (Al_2O_3) fiber development (see Coatings Section for copy of visual aids). These fibers are being advanced as possible replacements for graphite or for use in hybrid laminates.

The working group focused mainly on ways to contain the graphite fibers and prevent their dispersion to the environment following damage, fire or explosion. The particular hybrid systems discussed included metallic surface layers, third material additives, intumescent coatings, outer composite envelope, multiple fiber hybrids, and resin hybridization.

Metallic Surface Layers.- Metal foils or wire mesh may be applied to composite surfaces to prevent graphite fiber dispersion by maintaining surface integrity. Such surfaces are presently incorporated in some composites for lightning damage protection, and they do not involve critical modifications to the basic composite. Disadvantages include the possiblity that the metal surfaces would not be effective in case of extreme damage, and may cause distortion during laminate fabrication.

Third Material Additive.- Structurally passive particulate or fiberous additives may prevent dispersion of graphite fibers in case of fire by melting and fusing over the fibers. Such additives include a glass fiber screen or weave, glass microballoons or solid particles, and a fiber "serving" or coating. This approach would require minimum changes in the matrix and in processing, and may require only minimum requalification of the composite. However, laminate density would be increased and specific properties would be decreased. The additives may contribute to fiber damage in normal service.

Intumescent Coatings.- An organic coating (~ .03") may be applied to the composite surface to minimize dispersion of graphite fibers in the event of damage and fire. Such coatings may be an immediate quick-fix for existing composite components and, although not a complete solution, these coatings may enable the continuation of existing composite flight programs. Apparent disadvantages of intumescent coatings include additional weight and short service life. It was also agreed that it would be difficult to keep the coating on.

Outer Composite Envelope.- Structurally active outer composite plies may be used to contain inner graphite fiber plies in the event of fire and damage. The outer plies would consist of fire resistant fibers in a high char forming resin matrix. This approach has the advantage of adding a structurally active part to the composite rather than passive weight. Possible disadvantages may include compatibility with graphite plies, weight, and cost.

Multiple Fiber Hybrids.- Non-conducting fibers may be used in combination with graphite to reduce the amount of conducting fibers released by a fire to some acceptable level. This approach would have the advantage of retaining many of the superior properties of graphite fibers, while possibly gaining some unique properties from a new fiber. For example, high modulus - low strength fibers would be combined with low modulus - high strength fibers. Laminates could be designed for ply combinations using various fibers.

Resin Hybridization.- This approach would involve distributing layers of different resin systems throughout the laminate. Most of the discussion centered on high char yield resins. Discrete layers of high char forming resin would be distributed between conventional plies throughout the laminate. In the event of fire, the resulting char may adhere to graphite fibers retarding their disperion. After some consideration, this approach did not seem too attractive; inclusion of such layers would probably lower fiber content, degrade mechanical properties, and require a new data base. Using a high char forming resin matrix throughout the composite appeared to be a better approach but would not be classified as a hybrid composite.

CONCLUSIONS

1. Hybridization is the only reasonable approach for a near term solution to the graphite fiber problem.

2. Significant changes in the graphite/epoxy system would destroy the utility of the data base and would require new material qualification programs.

3. Replacement of graphite fibers would result in inferior mechanical properties and replacement of the epoxy would reduce the efficiency of the composite. The advantages of composites would be destroyed.

4. Metallic coatings for containing fibers are probably not satisfactory.

5. Glass cloth or fiber outer layers may offer the most promise for preventing release of graphite fibers.

RECOMMENDATIONS

1. Promising solutions should be implemented in the short term to maintain impetus of existing programs avoiding dissumptions which could jeopardize program support.

2. Standardized tests must be developed to define the graphite fiber hazard potential as well as to evaluate potential fixes.

3. The hazard potential must be evaluated with respect to various aircraft zones (structure, systems, engines, etc.).

4. Continue research on long term optimum solutions while implementing short term solutions.

5. Long term solutions should consider epoxy resin replacement, alternate or modified fibers, new hybrids.

REPORT OF

HYBRID COMPOSITES
WORKING GROUP

DR. KARL PREWO, CHAIRMAN

HYBRID COMPOSITES

ISSUES CONSIDERED

- FIND SOLUTION THAT CAUSES MINIMUM DISRUPTION OF EXISTING TECHNOLOGY BASE
- LONGER TERM SOLUTION

INTUMESCENT COATING

APPROACH

USE AN ORGANIC COATING THAT MINIMIZES THE LIKELIHOOD OF BURNING AND ALSO THE ESCAPE OF GRAPHITE FIBERS.

ADVANTAGES

- VERY QUICK FIX
- CAN BE APPLIED TO EXISTING COMPONENTS

DISADVANTAGES

- WEIGHT PENALTY
- SHORT SERVICE LIFE

METALLIC SURFACE LAYERS

APPROACH

PREVENT FIBER ESCAPE BY MAINTAINING SURFACE INTEGRITY

- METAL FOIL OR WIRE MESH
- METALLIZED GLASS FIBERS

ADVANTAGES

- MAY ALREADY BE DESIGNED IN
- MEETS LIGHTNING PROTECTION REQUIREMENTS
- NO COMPOSITE MODIFICATION
- IMPROVED IMPACT TOLERANCE

DISADVANTAGES

- EXTREME DAMAGE MAY OVERCOME
- MAY CAUSE DISTORTION

THIRD MATERIAL ADDITIVE

APPROACH

PREVENT ESCAPE OF GRAPHITE THROUGH USE OF PARTICULATE OR FIBROUS ADDITIVE WHICH IS PASSIVE EXCEPT IN THE CASE OF FIRE

- GLASS FIBERS - SCRIM - "UNIWEAVE"
- FIBER "SERVING"
- MICROBALLOONS OR SOLID PARTICULATE

ADVANTAGES

- MINIMUM REQUALIFICATION
- MINIMUM CHANGE IN MATRIX AND PROCESSING
- NO CHANGE IN FIBER

DISADVANTAGES

- INCREASED WEIGHT
- FIBER DAMAGE

OUTER COMPOSITE ENVELOPE

APPROACH

USE "ACTIVE" OUTER COMPOSITE LAYERS AS CONTAINMENT.

- HIGH CHAR FORMING RESIN MATRIX PLIES
- FIRE RESISTANT FIBERS IN OUTER PLIES (E.G. B, GLASS)

ADVANTAGES

- CONTRIBUTES STRUCTURALLY

DISADVANTAGES

- COST PENALTY
- WEIGHT PENALTY

MULTIPLE FIBER HYBRIDS

APPROACH

USE NON CONDUCTING FIBERS IN COMBINATION WITH OR WITHOUT GRAPHITE FIBERS

ADVANTAGES

- SOME FIBERS CURRENTLY AVAILABLE
- UNIQUE PAY OFFS (TOUGHNESS)

DISADVANTAGES

- REQUIRES REDESIGN
- INCOMPLETE KNOWLEDGE OF FAILURE MECHANISMS
- INFERIOR SPECIFIC PROPERTIES MAY NOT BE ACCEPTABLE

RANKING OF GENERIC SOLUTIONS

SOLUTION	% PARTICIPANTS FAVORING
HYBRIDS	40
EPOXY MODIFICATION	15
"EXISTING" REPLACEMENT RESINS	15
FIBER MODIFICATIONS	10
FIBER COATINGS	10
ALTERNATE FIBERS	10

RECOMMENDATIONS

- FIND PROMISING SOLUTIONS IN THE SHORT TERM TO MAINTAIN COMPOSITE IMPETUS
- HYBRIDS OFFER BEST OPPORTUNITY TO ACHIEVE THIS
- NEED REPRESENTATIVE TESTS THAT CAN BE STANDARDIZED
- ZONE HAZARD LEVELS OF AIRCRAFT AND ENGINES
- LOOK FOR LONG TERM SOLUTION - ALTHOUGH SHORT TERM MAY SUFFICE
- MAINTAIN VISIBILITY

FIBER RELEASE SIMULATION TESTING

E. Bruce Belason, Chairman

NAME	ORGANIZATION
Raymond Foye	U.S. Army R&T LABS
T. C. Grimm	McDonnell Aircraft Co.
Robert E. Sanders	Rockwell International - Tulsa
Frank Riel	Rohr Industries, Inc.
H. C. Schjelderup	Douglas Aircraft Co.
Richard Tracy	Lear Avia Corp.
William J. Snyder	Bucknell University
Joe Mansfield	NASA Ames
Vernon Bell	NASA LaRC
Bill Brooks	NASA LaRC
Tito Serafini	NASA Lewis
Bruce Belason	AVCO Specialty Materials Div.
Wolf Elber	NASA LaRC
Joseph Reardon	Naval Res. Lab
Ken Musselman	Naval Surface Weapons Ctr (Dahlgren)
Edward Lopez	Lockheed Calif.
John McFerrin	Union Carbide
John Parker	NASA Ames
James Peterson	Boeing Commercial Airplane Co.
Guilio Varsi	JPL
Dell Williams	NASA Headquarters
Bob Schaffer	HITCO Defense Products

NASA Reporters: Robert Jewell and Don Rummler, LaRC

ISSUES FOR
FIBER RELEASE SIMULATION TESTING
WORKING GROUP

1. Can fiber release testing be realistically simulated?

2. What procedure do you recommend for laboratory scale testing? Are there alternative procedures? What are the advantages and disadvantages of each?

   (a) How should we conduct laboratory tests to reproduce the effects of fire and explosion on coated or treated fibers?

   (b) How should we screen the fiber release characteristics of hybrids or new resins in the laboratory?

3. What quick, relatively inexpensive, large scale tests can be used to screen resin modifications and hybrids for effectiveness in reducing fiber release?

4. What procedure do you recommend for large or full scale qualification testing? Are there alternative procedures? What are advantages and disadvantages of each?

5. What test temperatures, oxidation rates, burning times, smoke generation rates, flame oxygen content, and fiber dissemination procedures should be used in a simulation facility?

6. What are reasonable and appropriate specimen sizes, shapes, resin contents for each scale of testing?

7. What inputs are needed from risk analysis to evaluate the effectiveness of materials modifications?

NASA REPORTERS' SUMMARY FOR FIBER RELEASE SIMULATION TESTING WORKING GROUP

The meeting was prefaced with 5 presentations given by Jim Peterson (Boeing), Bruce Belason (AVCO), Joe Reardon (NRL), Guilio Varsi (JPL) and Joe Mansfield (NASA-Ames). The working group's deliberations are summarized in three parts according to the particular test parameter: burn conditions, fiber release mechanisms, and measurements on released fibers.

Burn conditions.- A concensus was reached on (a) the urgent need to establish a set of laboratory test procedures, and (b) the urgent need for risk analysis studies. The risks associated with release of graphite fibers in an aircraft accident are ill-defined. Bounds establishing the nature of a reasonable threat are needed as initial guidelines for selecting testing parameters.

For the composite materials in present use, the effects of variations in test temperature, flame oxygen content, heat flux, and other parameters should be determined and documented. It was agreed that NASA should take the lead in developing simulated test methods. Detailed issues, such as appropriate specimen geometry, types of large-scale tests, and methods for testing specific materials, e.g., hybrid laminates or composites composed of coated or treated fiber, were not discussed.

Fiber release mechanisms.- In the combustion of the composite material, the matrix resin is burned, with no fiber release occurring. Fiber dispersal requires some form of agitation during or after combustion.

Fiber release by detonation of an explosive charge is a violent method, tending to distort test results. Dissemination of fibers by mechanical vibration, by air currents or air blasts, by falling or swinging weights, and by other projectiles are some alternative methods. The working group did not select a preference.

Laboratory test methods are needed to simulate the effects of a large scale fire phenomena. Then, test methods to adequately simulate fiber release could be developed. A description of the thermal/physical environment (scenarios) considered most relevant to the problem is critically needed in order to select test parameters.

Measurements on released fibers.- Laboratory simulation of the burn and fiber release is not the main problem.

Methods and/or instruments for collection of meaningful data on fiber release represent a true bottleneck. Those now testing yearn for a "fiber dosimeter." Measurements of fiber release phenomena at present are rudimentary and crudely qualitative. Meaningful testing must discern fiber geometries and their distribution, fiber quantities, and fiber electrical properties. Applicable test methods and instrumentation are needed.

CONCLUSIONS

1. A set of laboratory test procedures is urgently needed. However, selection of suitable test conditions requires inputs from risk analysis as well as parametric data for various burning and impact conditions.

2. Further definition of the risk resulting from the carbon fiber hazard is necessary before companies will take strong independent roles in testing. In the meantime, NASA must play a major role in guiding and financing development in this area.

RECOMMENDATIONS

1. A working group of reasonable and effective size should be established to develop test methods and procedures. NASA should be charged with this duty.

2. The participants strongly suggested that the aircraft industry will not address problems associated with the accidental release of graphite fiber unless the problem area is more competently defined. The participants indicated that definition of the threat should be an NASA activity.

REPORT OF

FIBER RELEASE SIMULATION TESTING
WORKING GROUP

E. BRUCE BELASON, CHAIRMAN

FIBER RELEASE SIMULATION TESTING

GENERAL SCOPE OF ISSUES

1.) CAN FIBER RELEASE TESTING BE DONE SUCCESSFULLY?

i) SMALL SCALE/LAB/SCREENING TEST
ii) LARGER SCALE/FIELD/HARDWARE TEST   SUPPORT RISK ANALYSIS

2.) TEST SPECIMEN DESIGN: SIZE SHAPE ORIENTATION EDGE EFFECTS ETC.

3.) TEST CONDITIONS:

THERMAL:
- TEMP. (OF FIRE)
- HEAT FLUXES: RADIATIVE, CONVECTIVE
- TIME

CHEMICAL: OXIDATION EFFECTS

MECHANICAL PERTUBATIONS:
- BEFORE
- DURING BURNING?
- AFTER

4.) NECESSARY DEGREE OF ANALYSIS OF FIBER RELEASE?: CATCH ALL FIBERS ANALYZE
PRE/POST TEST SPECIMEN ANALYSIS

FIBER RELEASE SIMULATION TESTING
(Continued)

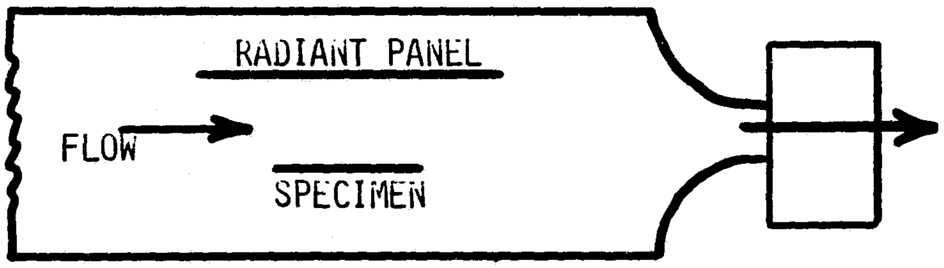
5.) TEST FACILITIES AND TECHNIQUES FOR THE ABOVE:

			IF DEV'T IS REQUIRED:	
STATUS	SMALL SCALE	LARGE SCALE	COST	TIME
EXISTING				
EXISTING, BUT REQUIRE MOD.	X	X ?		3 MOS.
MUST BE BUILT (OR DEVELOPED)				

6.) RISK ANALYSIS INTERFACE: INPUTS REQUIRED OUTPUTS REQUIRED

MATERIALS SCREENING TEST
(CONSENSUS)

FACILITY DESIGN



TEST CONCLUSIONS TO DATE:

IN CURRENT GRAPHITE/EPOXY, RESIN BURNS OUT QUICKLY (3 MINUTES), LEAVING FIBERS WHICH APPEAR TO BE READILY REMOVABLE IF MECHANICALLY PERTURBED.

EXPERIMENTAL NEEDS:

1.) IMPROVED DIAGNOSTICS FOR FIBER RELEASE MEASUREMENT.
2.) CORRELATION OF MEASURED FIBER RELEASE TO REAL LIFE ENV'TS.

UNRESOLVED:

WHETHER TO INCORPORATE MECHANICAL PERTURBATION AND IF SO, WHAT TYPE?

ACTION RECOMMENDED:

NASA TO FORM A WORKING GROUP

RISK ANALYSIS TEST

TEST FACILITY DESIGN

- LARGER SPECIMENS (VS SCREENING TEST)
- VARIOUS SHAPES
- VARIOUS MECHANICAL IMPACTS (SIMULTANEOUS TO FIRE EXPOSURE)
- INCORPORATE FIBER RELEASE DIAGNOSTICS
- RESULTS MUST BE EXTRAPOLATABLE TO RELIABLY ANALYZE POTENTIAL ACCIDENT SCENARIOS.

OTHER FACTORS/CONSIDERATIONS

- RISK ANALYSIS MUST CONSIDER WHAT PARTS OF AIRPLANES ARE TO USE COMPOSITES AND IN WHAT FORM, AND WHAT TYPE OF FIRE SCENARIO(S) THIS COMPONENT CAN LIKELY SEE.
- FIBER TRANSPORT (AFTER RELEASE) MUST BE DETERMINED
- CRITICAL FIBER SIZES MUST BE BETTER DEFINED
- CREDIBILITY GAP EXISTS

FIRE AND IMPACT TESTING

JOE MANSFIELD (ARC)

MARCH 23, 1978

TESTS CONSIDERED

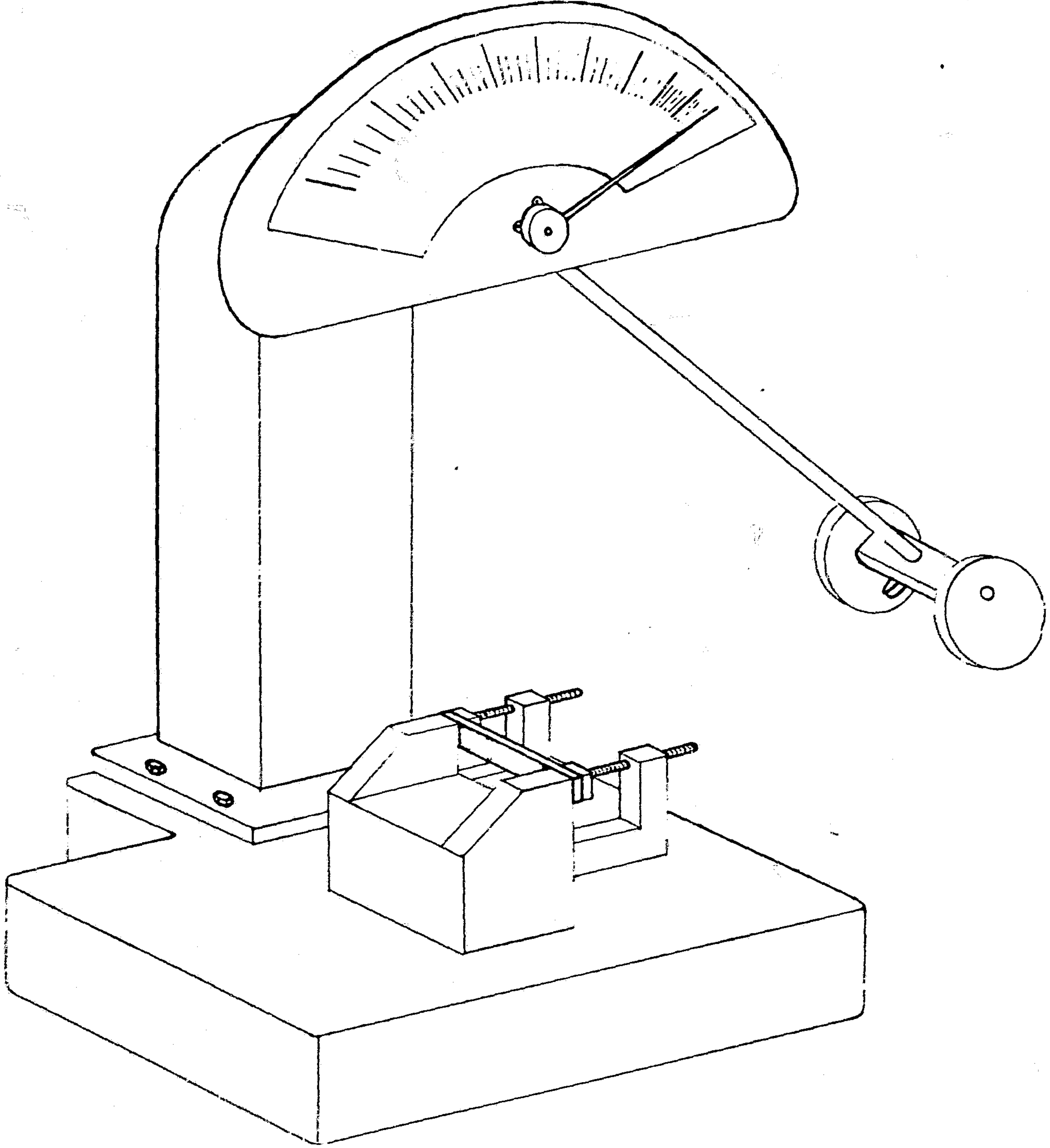
- SCREENING
- SIMULATION

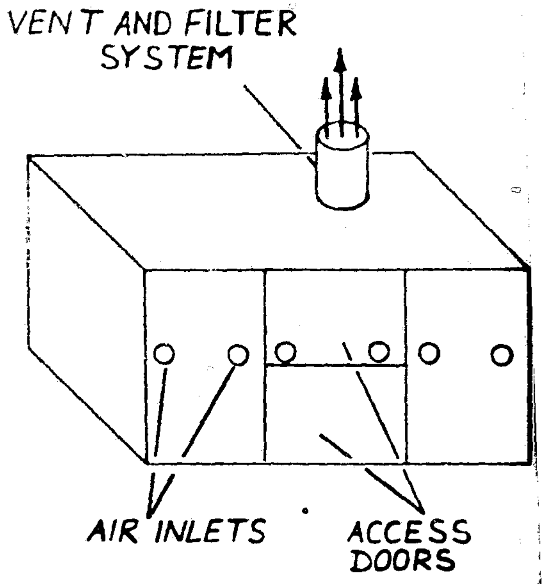
TEST PARAMETERS CONSIDERED

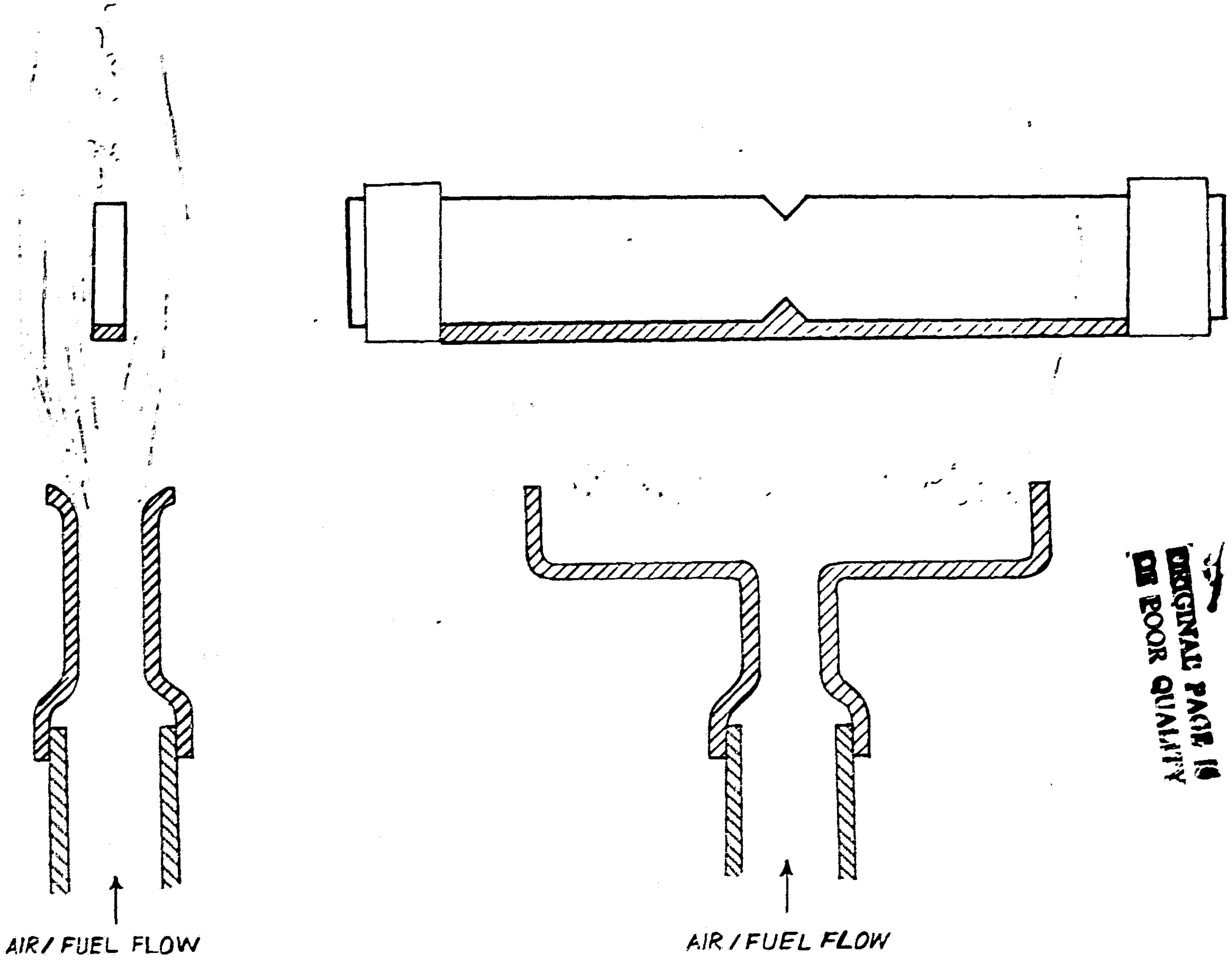
- REALISM OF FIRE EXPOSURE
- REALISM OF MECHANICAL EXPOSURE
- REALISM OF SAMPLE CONFIGURATION AND SUPPORT MECHANISMS
- TEST TIME REQUIREMENTS
- COSTS OF MANUFACTURE AND OPERATION

TEST PROGRAM LISTING

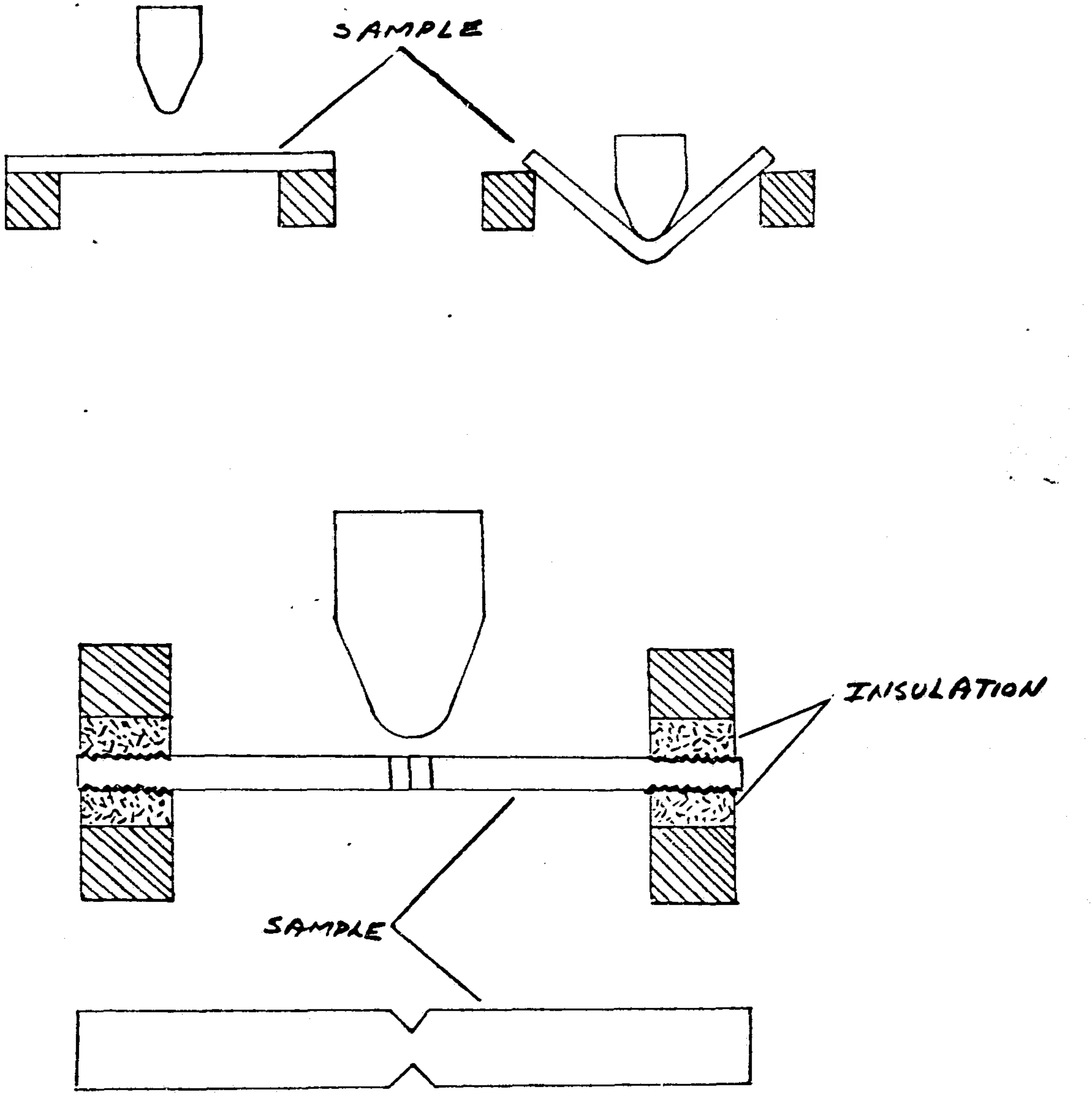
- SMALL-SCALE SCREENING TESTS
  - MODIFIED CHARPY IMPACT (BURNING SAMPLES)
  - STANDARD MECHANICAL TESTS (UNBURNED SAMPLES)
    - TENSILE
    - FLEXURE
    - CHARPY IMPACT (UNMODIFIED)
  - LABORATORY FLAMMABILITY TESTS
    - LIMITING OXYGEN INDEX
- SIMULATION TESTS
  - PROJECTILE IMPACT
    - ~ 30 FT/sec
    - 50 - 400 FT/sec
  - SHOCK WAVE EXPOSURE
  - HIGH VELOCITY FLOW EXPOSURE



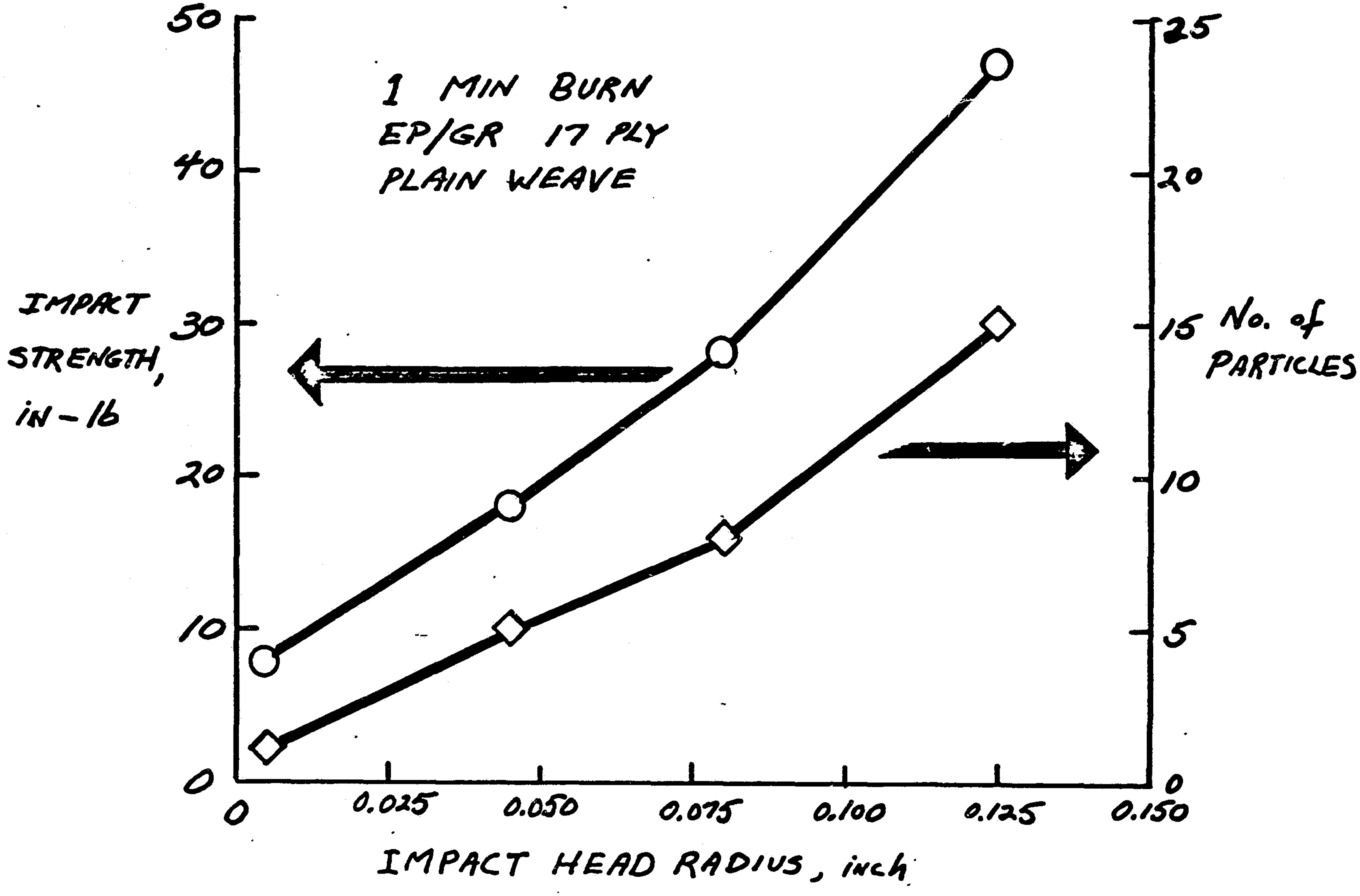

VENT AND FILTER SYSTEM
AIR INLETS
ACCESS DOORS



CHARPY TEST BURNER CONFIGURATION



CHARPY TEST SAMPLE AND SAMPLE SUPPORT MECHANISM


1 MIN BURN
EP/GR 17 PLY
PLAIN WEAVE
IMPACT STRENGTH, in - lb
50
40
30
20
10
0
No. of PARTICLES
25
20
15
10
5
0
0
0.025
0.050
0.075
0.100
0.125
0.150
IMPACT HEAD RADIUS, inch

RECOMMENDED SPECIFICATIONS FOR CHARPY IMPACT TEST

SAMPLE THICKNESS	~ .12"
SAMPLE WIDTH AT NOTCH	~ .20"
IMPACT HEAD RADIUS	.125"
IMPACT ARM WEIGHT	200 IN-lb
FUEL	PROPANE
FUEL FLOW RATE	
AIR FLOW RATE	
VENT RATE DURING BURNING	10 CFM
VENT RATE AFTER BURNING	50 CFM
BURN TIME	VARIABLE

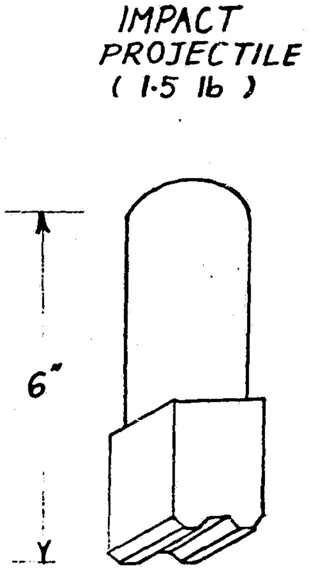
MODIFIED CHARPY SCREENING TEST

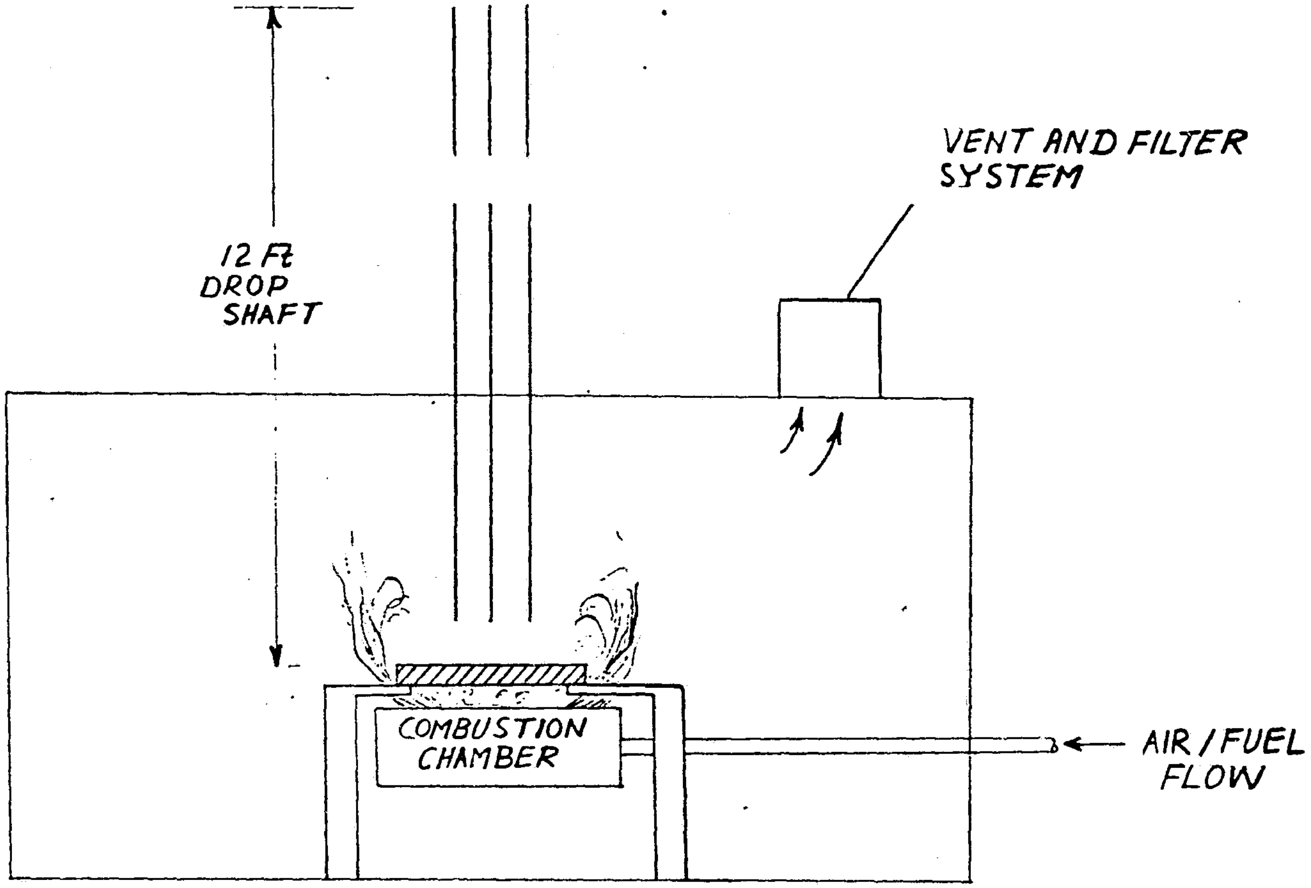
ADVANTAGES

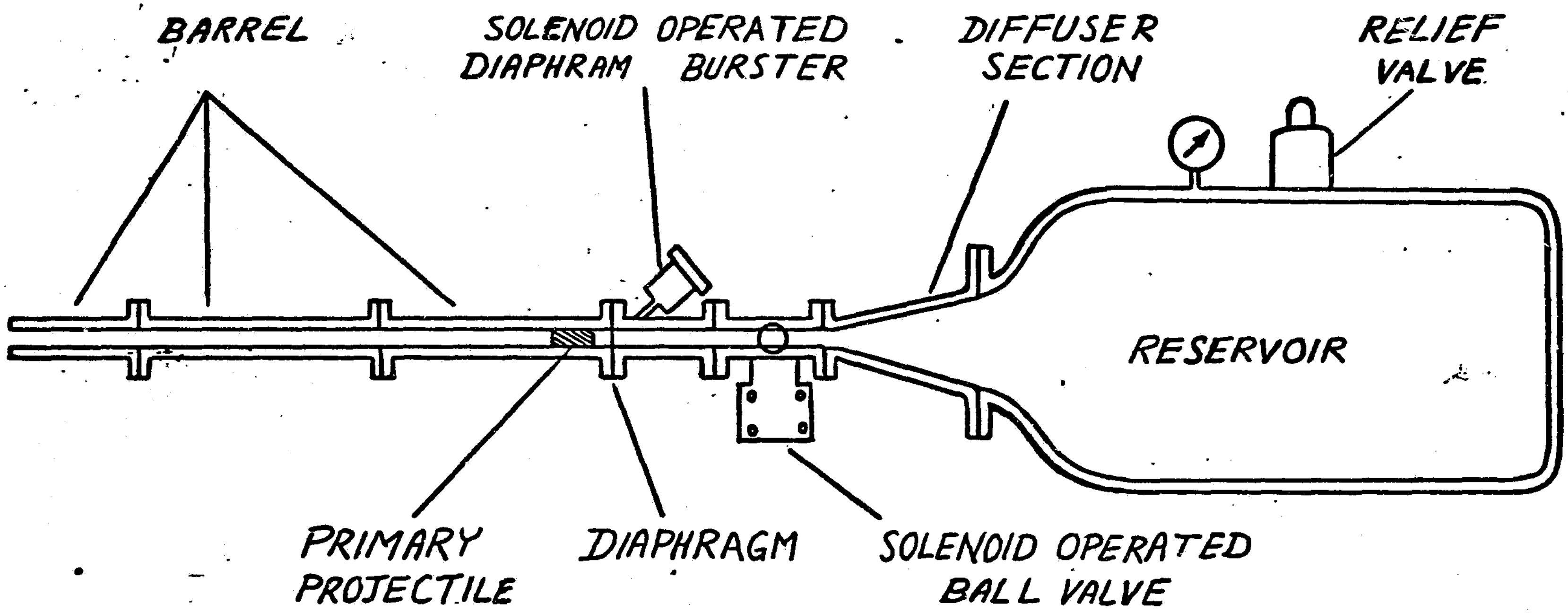
- TEST BOTH DURING AND AFTER BURNING
- USE COMMERCIAL INSTRUMENT WITH MINOR MODIFICATION
- USE SMALL AND EASILY FABRICATED SAMPLE
- REASONABLY SMALL TESTING TIME

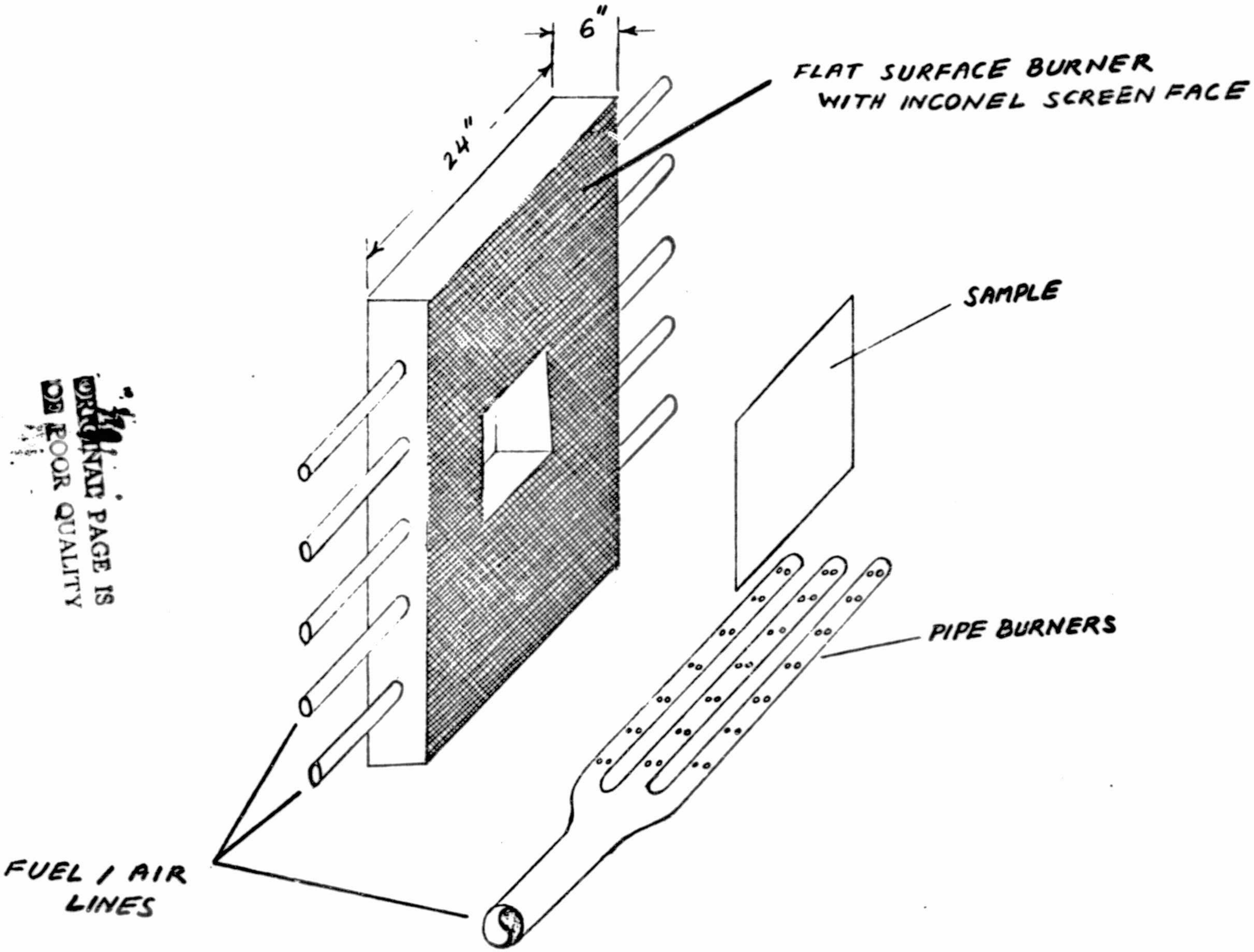
DISADVANTAGES

- DOES NOT COVER FULL RANGE OF MECHANICAL EXPOSURES
- DIFFICULT TO FULLY SIMULATE FIRE EXPOSURE
- REQUIRES FAIRLY EXTENSIVE REPLICATION


IMPACT
PROJECTILE
(1·5 lb)
6"


12 Ft
DROP
SHAFT
VENT AND FILTER
SYSTEM
COMBUSTION
CHAMBER
AIR / FUEL
FLOW


BARREL
SOLENOID OPERATED
DIAPHRAM BURSTER
DIFFUSER
SECTION
RELIEF
VALVE
RESERVOIR
PRIMARY
PROJECTILE
DIAPHRAGM
SOLENOID OPERATED
BALL VALVE



BURNER CONFIGURATION FOR SIMULATION TEST

FIBER RELEASE SIMULATION TESTING

JAMES M. PETERSEN

BOEING COMMERCIAL AIRPLANE CO.

MARCH 23, 1978

ABSTRACT

Fiber Release Simulation Testing

James M. Peterson, Boeing

The level of risk involving current technology graphite/epoxy hardware on commercial aircraft, due to the "floating fiber" phenomenon, has not been established. Resolving this question must be done by a systematic study that addresses the probability that the hardware is involved in a fire resulting in the release of fibers, that the fire is near a site housing vulnerable electrical components, and that loss or damage occurs due to any resulting electrical failure.

The type of thermal/physical environment that can result in substantial fiber release must be understood before a risk assessment can be made. Available files containing accident data should be utilized to determine the historical frequency of accidents in which composite hardware, had it been present, might have been involved. The pre-, during, and post-fire parameters that affect fiber release must be defined and evaluated. Appropriate laboratory test methodology is needed for research and development that can simulate the effects of large scale fire phenomena on fiber release, and on the subsequent transport of the fibers away from the fire site.

GRAPHITE/EPOXY HARDWARE ON COMMERCIAL AIRPLANES

LEVEL OF RISK HAS NOT BEEN ESTABLISHED

PARAMETERS (PROBABILITIES) AFFECTING RISK

- AIRCRAFT ACCIDENT OCCURENCE
  - FIRE INVOLVED
    - GRAPHITE COMPOSITE INVOLVED IN FIRE
      - FIRE/PHYSICAL ENVIRONMENT CAUSES FIBER RELEASE
        - RELEASED FIBERS TRANSPORTED FROM FIRE SITE
          - VULNERABLE ELECTRICAL COMPONENTS IN TRANSPORTED FIBER PATH
            - ELECTRICAL FAULTING OR FAILURE OCCURS
              - LOSS RESULTS FROM FAULT OR FAILURE

DEVELOPMENT OF OCCURRENCE DATA AND REPRESENTATIVE AIRCRAFT ACCIDENT/FIRE DAMAGE SCENARIOS

OBJECTIVE:

1. Establish the probability of aircraft accidents involving fires, composite structure and composite part damage based on accident data and composite materials useage forecasts.
2. Develop scenarios based on accident histories to provide representative fire, intensity and duration, structural involvement, structural damage, additional damage aspects such as explosion or fire fighting.

REQUIRED OUTPUT:

1. Probability of occurrence of representative conditions
2. Series of representative scenarios
3. Representative test conditions

DATA SOURCES:

1. Accident statistics files (NTSB & Others)
2. Accident reports
3. Accident investigator statements
4. Photo records of accidents

ESTABLISHMENT OF TEST METHODOLOGY REQUIRES

- DEVELOPMENT OF OCCURRENCE DATA AND REPRESENTATIVE AIRCRAFT ACCIDENT/FIRE DAMAGE SCENARIOS
- DETERMINATION OF CONDITIONS IN FIRE ENVIRONMENT IN SCENARIOS
- ESTABLISHMENT OF SMALL SCALE TESTS THAT REPRODUCE CONDITIONS IN LARGE SCALE FIRES

DETERMINATION OF CONDITIONS OF FIRE ENVIRONMENT IN SCENARIOS

OBJECTIVE: Establish the fire environment in scenarios based on fire intensity, duration, ventilation, etc. To determine parameters needed for design representative tests.

REQUIRED OUTPUT:

Representative test conditions

DATA SOURCES:

1. Accident statistics files (NTSB & Others)
2. Accident reports
3. Data from Large-Scale experimental fire test

ESTABLISHMENT OF SMALL SCALE TEST METHODOLOGY TO SIMULATE CONDITIONS IN LARGE SCALE FIRES

OBJECTIVE: Establish small scale test apparatus, conditions, and procedures that can be utilized to assess the effects of large scale fires on composite materials.

REQUIRED OUTPUT:

1. Test apparatus and methodology

DATA SOURCES:

1. Current fire R&D pertaining to aircraft
2. Standard reference works

REQUIRED MATERIALS PARAMETERS FROM TESTS FOR RISK ASSESSMENT

- AMOUNT OF FIBER RELEASED
- RELEASED FIBER PHYSICAL CHARACTERISTICS
  - SINGLE, MULTIPLE
  - LENGTH
- RELEASED FIBER ELECTRICAL CHARACTERISTICS

DEVELOP ENTRAINMENT, REENTRAINMENT, TRANSPORT DATA AND RELATE TO POTENTIAL PROBLEM SITES

OBJECTIVE:

1. Using the characteristic fiber release develop entrainment models and assumptions-generate entrainment data.
2. Using the characteristic fiber release develop reentrainment models and assumptions-generate reentrainment data.
3. Identify and select representative transport models with appropriate assumptions.
4. Identify representative potential problem sites.

REQUIRED OUTPUT:

1. Tabulation of entrainment, reentrainment data for characteristic fibers.
2. Selected transport model with assumptions.
3. Characteristic potential problem sites-accident aircraft, other aircraft, air control equipment, community locations.

DATA SOURCES:

1. Standard entrainment, reentrainment models
2. Standard transport models
3. Standard reference works

FIRE TESTING OF GRAPHITE-EPOXY COMPOSITES IN AVCO'S MODEL 25 FIRE TEST FACILITY

By

E. Bruce Belason

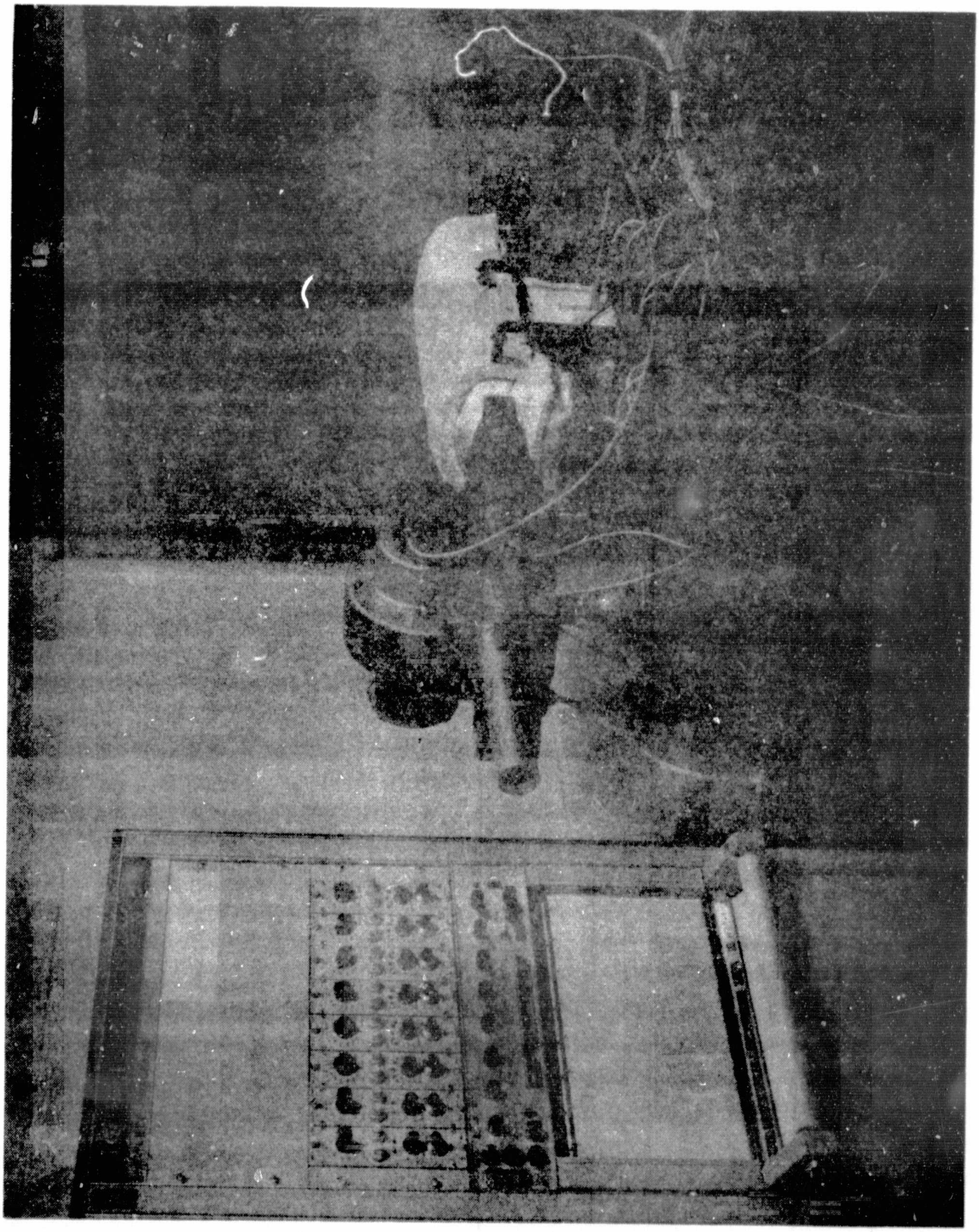
Avco Specialty Materials Div.

March 23, 1978

NASA Langley Composites Workshop

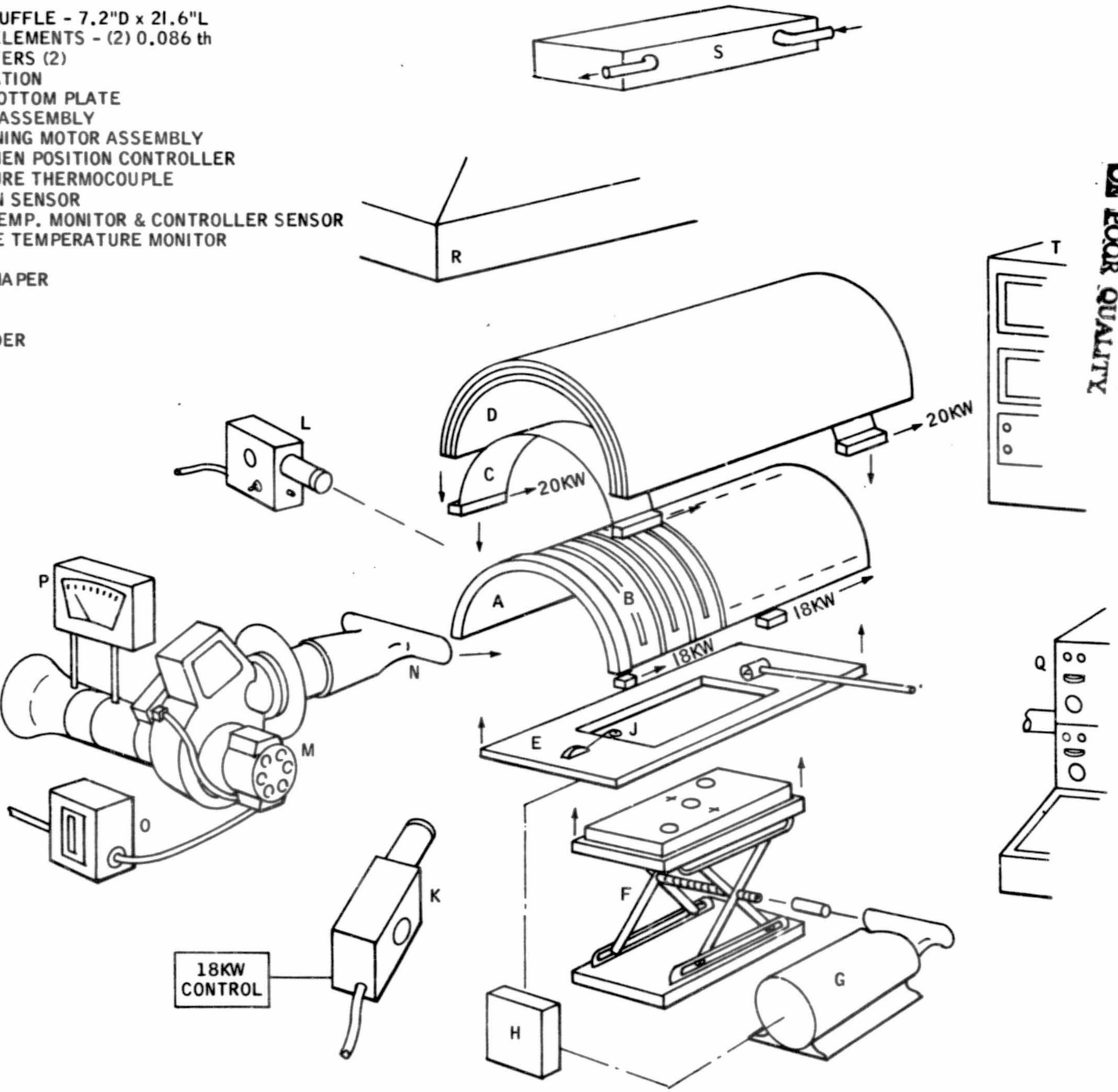
TYPICAL THERMAL CONDITIONS IN FREE-BURNING HYDROCARBON POOL FIRES

FIRE CONDITION	TEMPERATURE, °F	HEAT FLUXES, BTU/FT^2 SEC		
		$\dot{q}_R$, Radiative	$\dot{q}_c$, Convective	$\dot{q}_T$, Total
1.) SMALL FIRE, OR, CLOSE TO GROUND IN LARGE FIRE	~ 1800°F	~ 10	~ 1-2	11-12
2.) LARGE FIRE, ESPECIALLY AT HIGHER LEVELS	1800-2000°F	~ 10	8-10; PULSES TO ~ 25	18-20



FIRE SIMULATION FACILITY

A	CRYSTOLON (SIC) MUFFLE - 7.2"D x 21.6"L
B	KANTHOL HEATER ELEMENTS - (2) 0.086 th
C	KANTHOL END HEATERS (2)
D	MULTI-FOIL INSULATION
E	CRYSTOLON (SIC) BOTTOM PLATE
F	SPECIMEN HOLDER ASSEMBLY
G	SPECIMEN POSITIONING MOTOR ASSEMBLY
H	AUTOMATIC SPECIMEN POSITION CONTROLLER
I	FLAME TEMPERATURE THERMOCOUPLE
J	SPECIMEN POSITION SENSOR
K	RADIANT SOURCE TEMP. MONITOR & CONTROLLER SENSOR
L	SPECIMEN SURFACE TEMPERATURE MONITOR
M	OIL BURNER
N	CERAMIC FLAME SHAPER
O	OIL FLOW METER
P	AIR FLOW METER
Q	8 CHANNEL RECORDER
R	EXHAUST HOOD
S	HEAT EXCHANGER
T	CONTROL CONSOLE



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EXPLODED VIEW OF THE MODEL 25 FIRE SIMULATION FACILITY

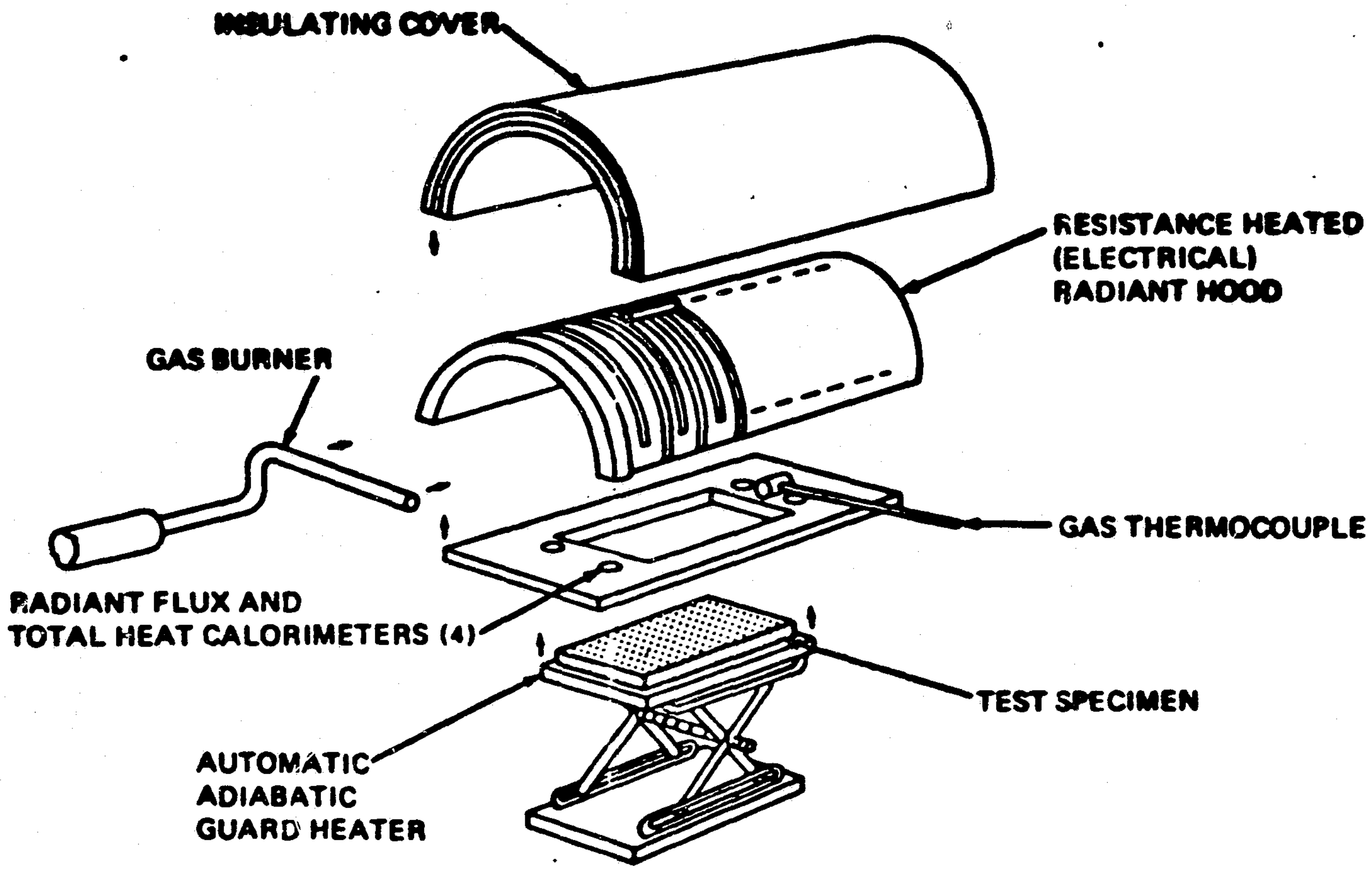
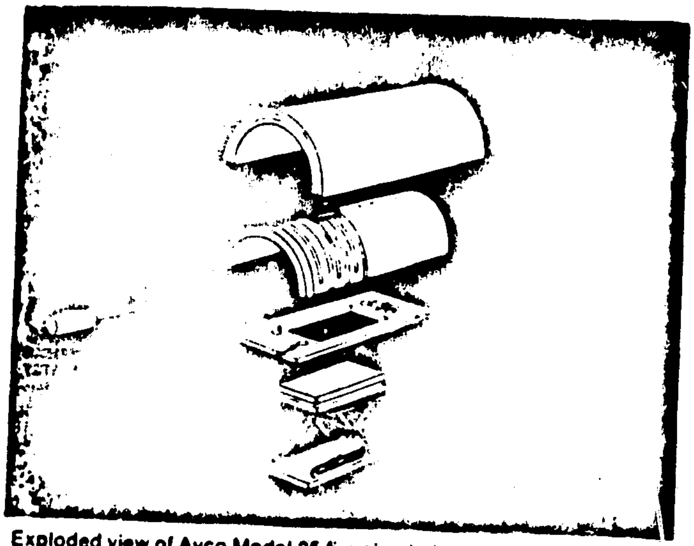


FIG. 3



Exploded view of Avco Model 25 fire simulation facility.

Fig 2.5-1

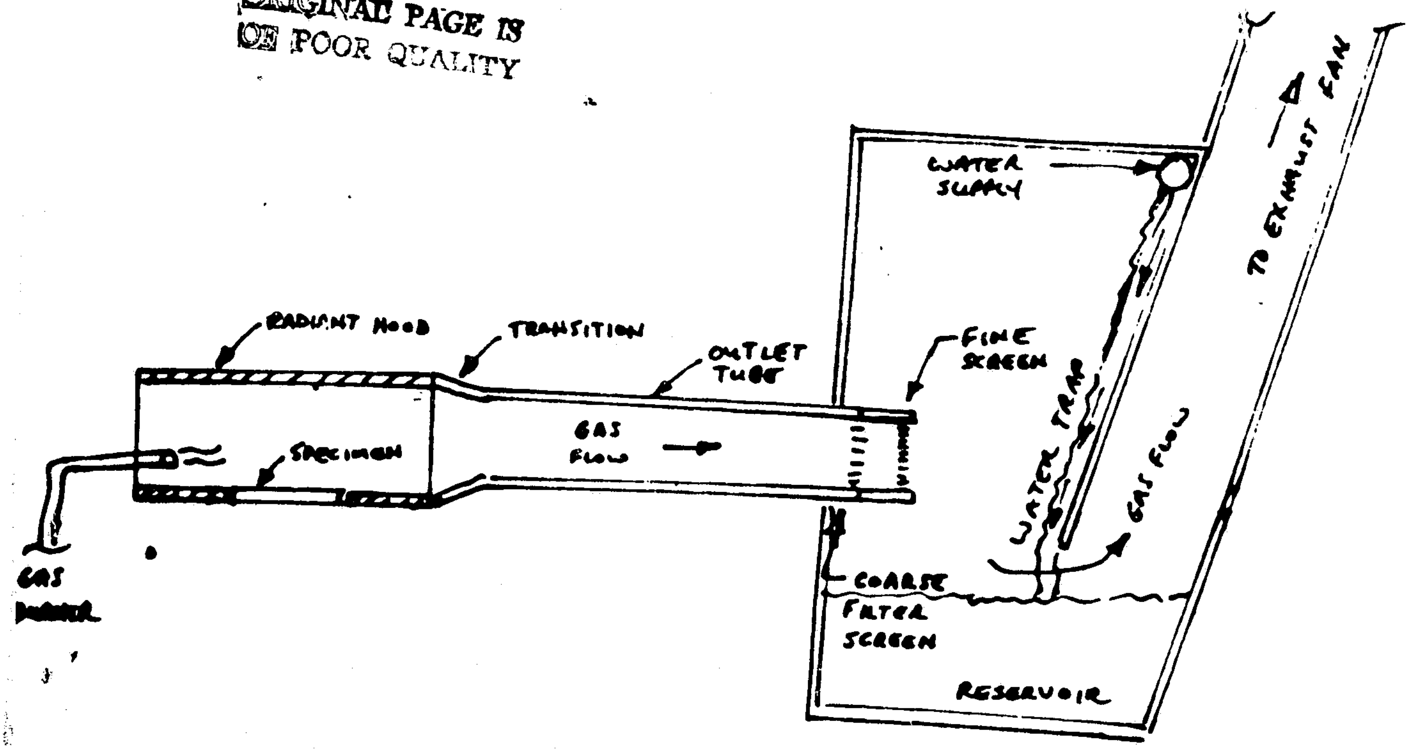


Figure 2.5-2

Model 25 Facility Modified for Fiber Containment

FIRE TEST RESULTS OF GRAPHITE-EPOXY COMPOSITES IN AVCO'S MODEL 25 FIRE TEST FACILITY

PARAMETER	SPECIMEN NUMBER	
	#153	#4
MATERIAL DESCRIPTION:		
FIBER	T-300 GRAPHITE	T-300 GRAPHITE
RESIN	AS 3501-6 EPOXY	AS 3501-6 EPOXY
MANUFACTURER	HERCULES	HERCULES
LAMINATION	(±45,0,90,∓45,0,90) X2	UNIDIRECTIONAL
SPECIMEN THICKNESS	~ 0.1 INCH	0.125 INCH
RESIN CONTENT	~ 30%	26%
THERMAL ENVIRONMENT:		
FIRE TEMP.	1850°F	1850°F
RADIATIVE HEAT FLUX (1)	9.5 BTU/FT^2 SEC	9.5 BTU/FT^2 SEC
CONVECTIVE HEAT FLUX (1)	1.5 BTU/FT^2 SEC	1.5 BTU/FT^2 SEC
REMARKS	CONVECTIVE HEAT FLUX OBTAINED FROM A FORCED AIR DRAFT--i.e., THERE WAS NO OIL OR GAS BURNER USED FOR THIS SET OF TESTS	
TEST TIME	10 MINUTES	10 MINUTES
TEST DATA:		
WEIGHT LOSS	63%	46%
MAXIMUM BACKFACE TEMP	~ 1650°F	1660°F

NOTES:

(1) AS MEASURED BY RADIOMETER AND CALORIMETER, RESPECTIVELY

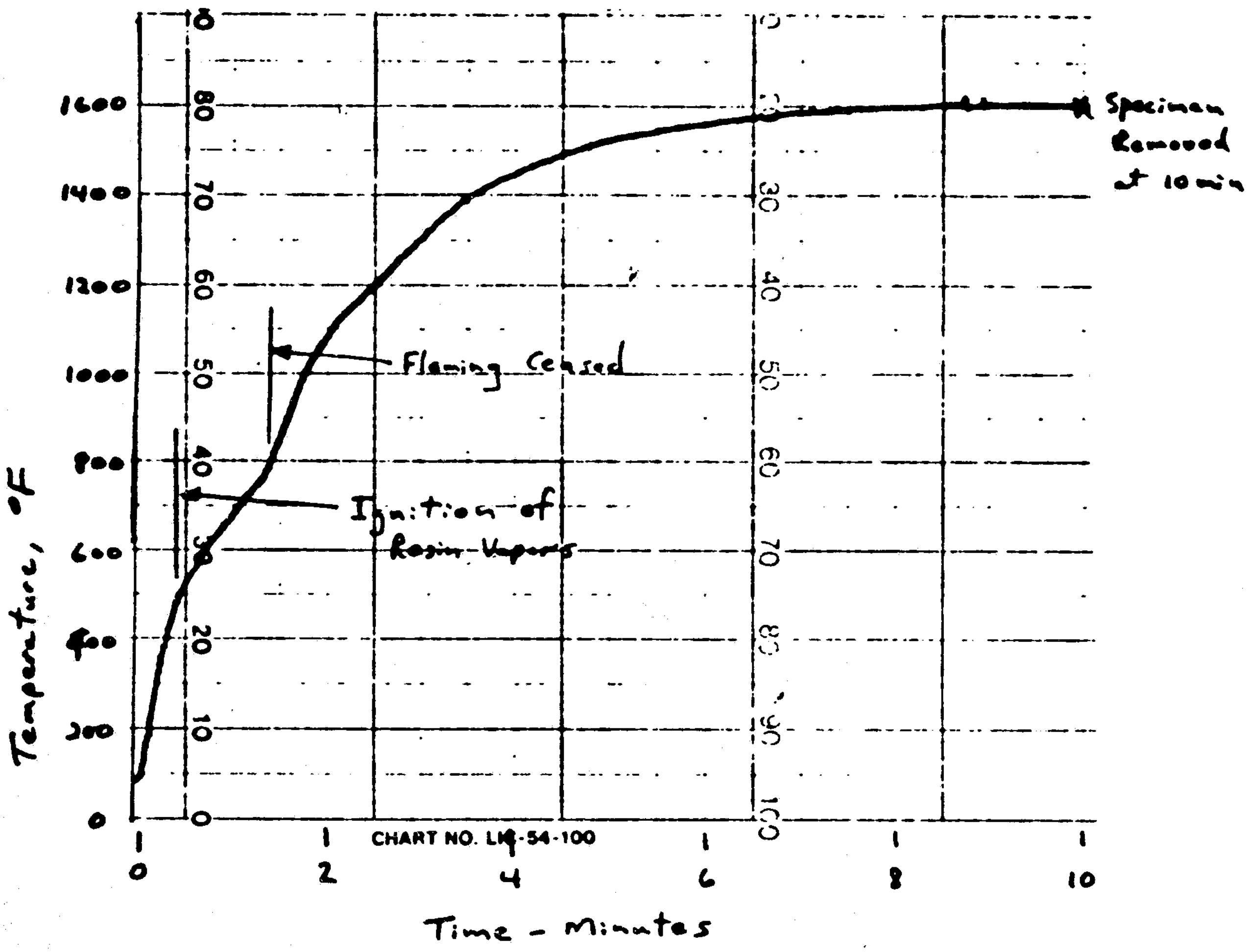
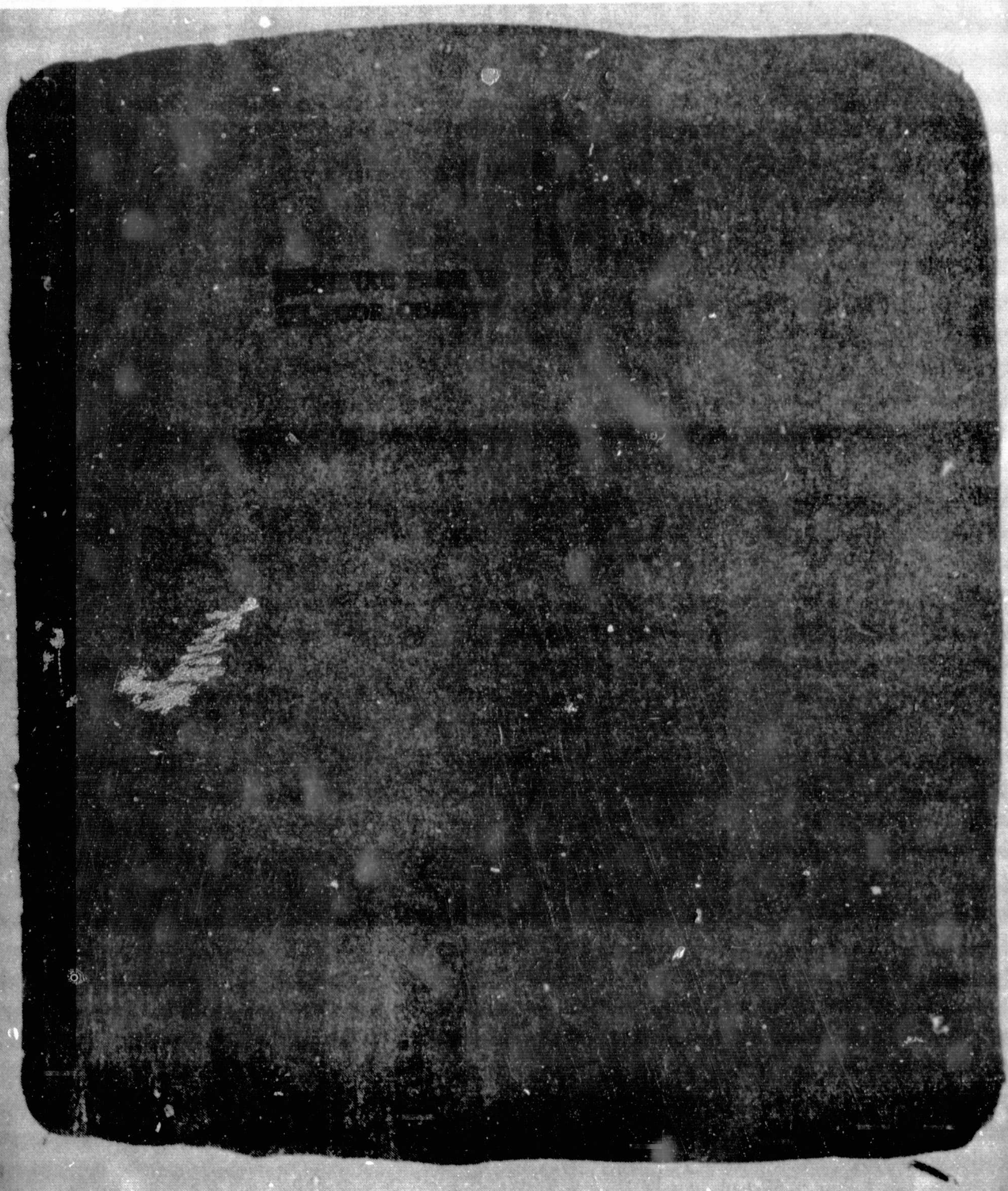


Figure 2.5-3 Backface Temperature Response, Specimen 187

#153 CROSS-PLY LAMINATE

RADIATIVE

ORIGINAL PAGE IS
OF POOR QUALITY



#4 Langley Unidirectional Radiative

CONCLUSIONS FROM FIRE TEST EVALUATION OF GRAPHITE EPOXY LAMINATES

1.) RESIN BURNED OFF IN LESS THAN 3 MINUTES.

2.) AFTER RESIN IS BURNED OFF, FIBERS ARE READILY REMOVED--ESPECIALLY IF MECHANICAL PERTURBATION OCCURS.

3.) FIBER RELEASE MORE PRONOUNCED ON CROSS-PLY LAMMATES VS. UNIDIRECTIONAL LAMINATES.

4.) UNIDIRECTIONAL LAMINATES WARPED DURING TEST

5.) ALL LIMINATES SWELLED TO AT LEAST 2X ORIGINAL THICKNESS WITHIN THE FIRST 1-3 MINUTES OF FIRE EXPOSURE.

FIRE TEST FACILITY DEVELOPMENT

1.) IMPROVE FIBER COLLECTION TECHNIQUE AND/OR QUANTITATIVE M'MENT OF FIBER RELEASE.

2.) ADD SELAS BURNER FOR HIGH $\dot{q}$ c

3.) ADD MECHANICAL LOAD CAPABILITY

4.) SEAL AIR INGRESS LEAKS

5.) INCREASE SPECIMEN OR HOOD SIZE?

6.) CUT HOLD FOR BETTER MOVIE ACCESS? VIDEO TAPE?

APPENDIX A

CONVERSION OF MISCELLANEOUS UNITS TO SI UNITS

The International System of Units (SI) was adopted by the Eleventh General Conference on Weights and Measures in Paris, October 1960[a]. Factors for the conversion of the miscellaneous units used in this document to SI units are given in the following table:

Physical Quantity	Miscellaneous Unit	Conversion Factor (b)	SI Unit
Density	g/cc=g/cm^3	10^3	kg/m^3
	g/ml	10^3	kg/m^3
	lb/in^3	2.768×10^4	kg/m^3
Energy	in-lb	0.113	J
Flow rate, volume	CFM=ft^3/min	4.719×10^{-4}	m^3/s
Heat flux	Btu/ft^{2}s	1.135×10^4	W/m^2
Length	Å	10^{-10}	m
	ft	0.3048	m
	" = in.	0.0254	m
	μ = micron	10^{-6}	m
	mil=10^{-3} in.	2.54×10^{-5}	m
Mass	lb	0.4536	kg
Pressure	mm Hg	133.3	Pa
Stress	psi=lbf/in^2	6895	Pa
	kpsi=ksi=10^3lbf/in^2	6.895×10^6	Pa
	Mpsi=Msi=10^6lbf/in^2	6.895×10^9	Pa
Stress intensity	ksi-in$^{1/2}$	1.099×10^6	N/m$^{3/2}$
Temperature	°C	°C+273.15	K
	°F	(°F+459.67)/1.8	K
Thermal efficiency	Btu/lb	2324	J/kg
Velocity	ft/s	0.3048	m/s
	knot	0.5144	m/s

[a] Anon.: Standard for Metric Practice. ASTM Designation: E 380-76. Amer. Soc. Testing Mater., c. 1977.

[b] Multiply value given in miscellaneous unit by conversion factor to obtain equivalent value in SI unit (with the exception of temperature).