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DESIGN AND WEAVING OF EXPERIMENTAL CARBON FABRICS

CELANESE CORPORATION CELANESE RESEARCH COMPANY SUMMIT, NEW JERSEY 07901

APRIL 1980

TECHNICAL REPORT AFWAL-TR-80-4054 Final Report for period July 1978 — January 1980

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

STANLEY SCHOLMAN, Project Engineer

FOR THE COMMANDER FRANK D. CHERRY, Chief Nonmetallic Materials Division

WILLIAM C. KESSLER, Chief Coatings & Thermal Protection Materials Branch Nonmetallic Materials Division

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6=102F UNCLASSIFIED SECURITY CLASSIFICATION OF THIS PAGE (When Date Entered) **READ INSTRUCTIONS** *QREPORT DOCUMENTATION PAGE* BEFORE COMPLETING FORM 2. GOVT ACCESSION NO. 3. RECIPIENT'S CATALOG NUMBER TR-80-4054 HORO AFWAL LE Good Sub A. DOD COV RED Technical Report. Design and Weaving of Experimental July 78-January 4080 Carbon Fabrics 8. CONTRACT OR GRANT NUMBER(a) Rober 10 15 🛋 🗛 A./ Bonsall F33615-78-C-5043 9. PERFORMING ORGANIZATION NAM 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Celanese Corporation / Project 2417 Celanese Research Company Task 241701 Summit, NJ 07901 1. CONTROLLING OFFICE NAME AND ADDRESS Air Force Wright Aeronautical Laborater Apr **19**80 Materials Laboratory NUMBER OF PAGES Wright-Patterson AFB, Ohio 45433 35 14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) SECURITY CLASS. (of th Materials Laboratory Unclassified Nonmetallic Materials Division Composite and Fibrous Materials Branch DECLASSIFICATION/DO 16. DISTRIBUTION STATEMENT (of this Report) Approved for Public release; distribution unlimited. 17. DISTRIBUTION STATEMENT (of the ebstract entered in Block 20. if different from Report) Same 18. SUPPLEMENTARY NOTES 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Carbon fibers Low Thermal Conductivity (LTC) Carbon fabrics Polyacrylonitrile (PAN) 6. ABSTRACT (Continue on reverse side if necessary and identify by block number) Polyacrylonitrile (PAN preoxidized fibers were processed and subdeg. C sequently woven into various carbon fabrics of low thermal conductivity. The axial thermal conductivity of the yarn variants was determined using a Colora CMBH thermoconductometer. The values ranged from 0.0072 cal/cm-sec- to 0.0128 cal/cm-sec-C and three of the variants met the thermal conductivity target of 0.010 cal/cm-sec-(°C) or less. Fiber densities and carbon contents exceeded the targets because of the pyrolysis temperature used. DD 1 JAN 73 1473 EDITION OF I NOV 65 IS OBSOLETE UNCLASSIFIED SECURITY CLASSIFICATION OF THIS PAGE (When Date Entered) 401863

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At the specified pyrolysis temperature, 1075%C, the more critical thermal conductivity requirement was met, but at the expense of density and carbon content. The density of the fibers examined ranged from 1.742 g/cc to 1.789 g/cc. The carbon composition of the fabrics ranged from 79.86% to 86.17%.

Several purification treatments were examined to reduce the alkali metal content of the fabrics in an attempt to meet the purity requirements. Two fabric samples were treated by a commercial purification process, but alk=`i levels after treatment remained above the targets of < 25ppm s. m and < 50ppm total alkali content. The effects of purificatic. processing on fabric cost and strength were estimated.

Cost estimates for reproducing each of the fabrics studied on a commercial scale were prepared. The estimates ranged from \$35.54/ yd. to \$85.74/yd. The effects of increasing the yarn size and also fabric weaving prior to carbonization were examined from both a cost and physical properties standpoint.

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FOREWORD

This report was prepared by <u>Robert A.</u> Bonsall, Research Engineer, Celanese Research Company, 86 Morris Avenue, Summit, New Jersey. The work was performed under Contract No. F33615-78-C-5043, sponsored by the Composite and Fibrous Materials Branch (AFML/MBC), Nonmetallic Materials Division of the Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio. The time period covered by the effort was July 1978 to January 1980. Mr. Stanley Schulman was the AFML Project Engineer.

Besides R.A. Bonsall as the principal investigator, the efforts of William F. Speer, Narmco Materials Division and Nelson Lazear (formerly, Celanese Research Company) are noted. Dr. J.R. Leal, Senior Staff Associate, served as Contract Administrator.

This is the Final Technical Report issued under Contract No. F33615-78-C-5043. It was submitted by the author on February 29, 1980.

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TABLE OF CONTENTS

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44.

والمتحدث والمعاجد

SECTION	I - INTRODUCTION	1
1.	PROGRAM BACKGROUND AND OBJECTIVES	1
2.	ORIGINAL PROGRAM TASKS	1
3.	REVISED PROGRAM TASKS	3
SECTION	II - ALKALI METAL REMOVAL STUDIES	6
1.	BACKGROUND	6
2.	PURIFICATION ROUTES EXAMINED	6
SECTION	III - FABRIC VARIANT CHARACTERIZATION AND PROPERTIES	14
1.	VARIANT SAMPLE FABRICATION ROUTES	14
2.	THERMAL CONDUCTIVITY	15
3.	DENSITY	17
4.	COALESCENCE	17
5.	CHEMICAL PROPERTIES	21
6.	PHYSICAL PROPERTIES	23
SECTION	IV - ECONOMIC EVALUATION	27
1.	COMMERCIAL SCALE PRODUCTION METHODOLOGY	27
2.	SAMPLE ROUTE VS. COMMERCIAL ROUTE	27
3.	ENVIRONMENTAL CONSIDERATIONS AND SAFETY	31
4.	COMMERCIAL COST OBSERVATIONS	33
REF	ERENCES	35

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PAGE

LIST OF TABLES

A State of the second se

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a water and the second

والمعدر 4

TABLE	NO.	PAGE
1.	ORIGINAL PROGRAM TASKS	2
2.	REVISED PROGRAM TASKS	5
3.	CHEMICAL ANALYSIS RESULTS PURIFICATION ROUTE "A"	8
4.	CHEMICAL ANALYSIS RESULTS PURIFICATION ROUTE "B"	9
5.	CHEMICAL ANALYSIS RESULTS PURIFICATION ROUTES "C", "D", "E", AND "F"	11
6.	ALTERNATE APPROACHES TO PURIFICATION TREATMENT	13
7.	FABRIC VARIANT THERMAL CONDUCTIVITY	16
8.	VARIANT FIBER DENSITIES	17
9.	FABRIC VARIANT CARBON COMPOSITION	21
10.	SODIUM AND TOTAL ALKALINITY - TASK I	22
11.	VARIANT FABRIC DIMENSIONAL PROPERTIES	24
12.	RAVELED STRIP BREAKING LOADS	26
13.	COMMERCIAL ROUTE AND COST ESTIMATE - TASK I	29
14.	COMMERCIAL ROUTE AND COST ESTIMATE - TASK II	30
15.	COMMERCIAL ROUTE AND COST ESTIMATE - TASK III	32
16.	FABRIC COST SUMMARY	33

vii

1.5.2

LIST OF ILLUSTRATIONS

FIGURE	NO.	PAGE
1	VARIANT 5, WARP FIBERS, PREOX STATE, COLLOIDAL GRAPHITE TREATED.	19
2	VARIANT 4, WARP FIBERS, PYROLYZED, NO COLLOIDAL GRAPHITE.	20

ix

SECTION I INTRODUCTION

1. PROGRAM BACKGROUND AND OBJECTIVES

The development of rayon-based carbon fabrics for use in carbon/phenolic ablative composites has demonstrated substantial improvement in the design of critical thermal protection systems for missile and spacecraft re-entry operations. ⁽¹⁾ However, the future availability of rayon yarn has become questionable as a result of declining industrial demand and production over the last decade. ⁽²⁾ The development and demonstration of an acceptable alternate precursor yarn may become critical to maintaining the commercial production of reliable composites for heatshield applications.

The principal objective of this program was the development and characterization of PAN-based carbon fabrics which possess properties desirable for use in carbon/phenolic heatshield composites. Among the properties of interest for the end use application were low thermal conductivity, low fiber density, high carbon content and high alkali metal purity. In addition, suitable fabric strength and integrity were necessary. The program also focuses on the economics of the various fabric routes investigated and the effects of weaving prior to pyrolysis as opposed to the more conventional fabrication route of weaving carbonized yarns. Finally, the environmental impact of the processing routes is examined as it would pertain to fabric production on a commercial scale.

2. ORIGINAL PROGRAM TASKS

The program structure initially consisted of three tasks designed to accommodate several comparisons between the fabric routes to be investigated under each task. Table 1 schematically shows the processing routes for each of the eight original fabric variants and also lists the potential comparisons between variants.

TABLE 1

ORIGINAL PROGRAM TASKS

TASK I			TASK II		TASK III	
3K preox 1K preox			lK preox	lK preox	lK preox	384 preox
Carbonize – Summit			-	spun yarn preox	Carbonize -	- Summit
			v Weave-Text: الالالالة	j ile Products Ivenum verm	Purify -	Summit
v Purify-Summit	Hercules	u.c.c.	VIIVI		Weave	- Textile Products
Weaving done at 1	↓ Vextile Prod	l lots	Carbonize-1	Polycarbon		
			v Purify -	∳ Summit		
3Kx3K 1Kx1K	~	~			lKxlK	384x384
Variant #1 Variant #2	Variant #3	Variant #4	Variant #5	ب Variant #6	Variant #7	Variant #8
Evaluate Fabric at	↓ Summit	>	↓ Evaluate fi	, abric at Summit	Evaluate fab	oric at Summit

POSSIBLE COMPARISONS:

. 2 vs. 7 - effect of purification step on fabric properties

. 2 vs. 7 - effect of purification step on weavability

. 5 vs. 7 - compare weaving cost (preoxidized yarn vs. carbon yarn)

. 5 vs. 6 - effect of spun yarn shrinkage on fabric integrity

1 - base for comparison with fabrics made in earlier military contracts ۍ. .

1 vs. 7 vs. 8 - compare three Celanese yarn variants processed similarly ،

All Variants - comparison of Celanese, Hercules, and UCC. L.T.C. yarn variants 7.

Task I fabric routes included three variants composed of yarns from three commercial sources; all routes involved carbonization prior to weaving (variants 2, 3 and 4). Variant 1, a 3K x 3K construction, was scheduled for yarn purification prior to weaving by a feasible route which was to be determined by the investigation of alkali metal removal treatments (Section II). The overall task scheme would then provide a comparison base (Variant 1) for fibers studied under previous military contracts⁽³⁾ and a comparison of the properties and weavability of Low Thermal Conductivity (LTC) fibers from three independent sources (variants 2, 3 and 4).

Variant routes of Task II would implement the processing sequence of weaving 1000 fil continuous yarns and a 10 worsted count/ 2 ply spun yarn, followed by fabric carbonization and finally purification. These two fabric routes would provide an economic and physical/chemical properties assessment for weaving prior to pyrolysis and also examine the feasibility of using a 2-ply spun yarn as a fabric fiber for ablative composites.

The fabrication route employed for the two variants of Task III revised the processing sequence of Task II such that variant yarns would be first carbonized and then subjected to the purification treatment before the fabric weaving step. This sequencing provided a direct comparison with Task II for evaluating the cost and property effects of weaving prior to carbonization and purification (Task II) as opposed to weaving already carbonized and purified yarns. As shown in Table 1, variants 7 and 2 would allow an examination of the effect of purification treatment on weavability and fabric characterization.

3. REVISED PROGRAM TASKS

Two major complications occurred which prevented the exact preparation of all eight variants as outlined above by Section I-2 and Table 1: (1) adequate and timely procurement of LTC carbon fiber from sources other than Celanese; and (2) failure to define a purification treatment that would reduce the alkali metal content below

the level desired. Because some of the original variants and comparisons were no longer applicable, the program tasks were reconstructed as shown in Table 2.

The variants comprised of fibers from sources other than Celanese were dropped from Task 1 and the purification step of original variants 1 and 2 was subcontracted to Hitco Materials Division. (Variant 1 became variant 3 under the revised task.) A new variant #1 was added which called for 2 plies of 384 fil fiber in both warp and fil directions but this fabric was never achieved because it was not possible to develop an acceptable plying operation compatible with the strength and fil count of this yarn. Variant 1 was attempted without plying using a 54 x 54 twill weave construction but excessive warp breakage occurred during weaving. Time and funding did not permit any further development of this variant.

The purification route was dropped from Task II variants but the processing otherwise remained unchanged. Still of primary interest in this task is the effect of weaving prior to pyrolysis and the feasibility of pyrolyzing a fabric form.

Purification was also removed from Task III variant routes. A 6K x 6K variant was added (No. 7), and variant 6 was redesigned as a 1K x 3/384 fabric which required the plying of three 384 fil ends. Lack of an adequate plying operation prevented the development of variant 6.

The revised task routes were selected to (1) maintain an investigation of weaving prior to pyrolysis, (2) examine the feasibility of alkali metal purification treatment of carbon fabrics and (3) examine a variety of yarn fil counts under similar process conditions.

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REVISED PROGRAM TASKS

TASK I			TASK II		TASK III	
384 Preox 1K Pi	reox	3K Preox 	lK Preox	lK Preox & spun yarn preox	lK Preox & 384 Preov	6K Preox
• Carbonize at Ply (2)	Summit	» —	ν Weave at Te: 	ktile Products	Carbonize at Summit Ply ⁽³⁾	> -
ب Weave at Textile ! ا	Products Purify at	↓ HITCO	↓ Carboníze ∣	ہ at Polycarbon	لا Weave at Textile Pr ا	oducts
2/384 x 2/384 1K ¹ Variant #1 Variar	x lK ht # 2	3K x 3K Variant #3	↓ IK × IK Variant #4	lk x Spun Yarn Variant #5	lK x 3/384 Variant #6	¢ 6K x 6K Variant #7
↓ Evaulate Fabı	ric at Sum	mit 🤚	L Evaluate 1	abric at Summit	ل Evaluate Fabric a	↓ t Summit

POSSIBLE COMPARISONS:

5

. weaving carbon yarn).	d properties.	itary contracts.			arly.
its (carbonizing preox cloth vs	ırinkage on fabric integrity an	th fabrics made in earlier mil.	384 (3-ply) as filling materia	arns.	e yarn variants processed simil.
Compare production cos	Effect of spun yarn sh	Base for comparison wi	· Comparison of IK with	Effect of plying fil y	Compare three Celanese
	1	I	I	I	- 14
#4	#2		9#	# 6	, #3,
vs.	vs.		vs.	vs.	, #2,
#2	*	#3	#2	#1	# 1,

1

SECTION II ALKALI METAL REMOVAL STUDIES

1. BACKGROUND

One of the general requirements desirable for carbon fabrics which are designated for fabrication of carbon/phenolic heatshield composites is high alkali metal purity; specifically, a sodium content of less than 25 parts per million and a total alkali metal* content of less than 50 ppm. Commercially available PAN-based carbon fibers contain sodium at levels of 150 ppm or greater and total alkali metal concentrations which usually exceed 250 ppm; therefore, an investigation was conducted of various treatments for reducing the alkali metal content of preoxidized and carbonized PAN-based fibers. The investigation initially focused around the Hitco purification process as described in the patent literature⁽⁴⁾ but attempts to duplicate the claims of this patent failed. The investigation was expanded to include a variety of other treatments for alkali metal extraction as well as an extension of the treatment described by the aforementioned patent. Details of all the treatments examined are described below; none of the methods examined were found to reduce significantly the sodium or total alkali metal levels of the preoxidized or carbonized PAN-based fibers under study.

To evaluate further the feasibility of reducing the alkali metal content to the desired levels mentioned above, two of the fabric variants were subcontracted to Hitco Materials Division for purification; this work is described in Section III-5.b., "Sodium and Alkali Metal Composition."

2. PURIFICATION ROUTES EXAMINED

A. HITCO PATENT (U.S. No. 3,413,094)

*Typically taken as Na, K, Ca, Mg and Li.

The first method of treatment examined was that described by the Hitco patent and consisted of separate trials in both 1% HBr and 1% HI at room temperature with a five minute exposure period in each case. After drying, all samples were then heated in a muffle furnace for five minutes at 985°C (1805°F) in a helium environment. Carbon fibers selected for this study were DG-112 (3000 fil @ 1075°C), DG-123 (GY-70 preox, 384 fil @ 1075°C) and DG-126 (1000 fil @ 1075°C); these three fibers were also in the group of fibers being studied for fabrication of the variant samples to fulfill the tasks of the contract. Chemical analysis of the treated samples was done by emission spectrography of the ashed samples; sodium and lithium levels were obtained by atomic absorption. A review of the chemical analysis results (Table 3) shows that neither the HBr nor the HI treatment significantly affected the sodium or total alkalinity levels of the carbon fibers studied and that effective penetration of HX was not achieved for any of the samples treated.

B. EXTENSION OF HITCO PATENT TREATMENT

The method of treatment described under part A above was extended in an effort to enhance the HX absorption. Both 1% HBr and 1% HI treatments were again used but the exposure period was increased from 5 to 30 minutes and the treatment temperature was raised from room temperature to 50° C. After drying, all samples were heated to 1050° C for 10 minutes in nitrogen. The carbon fiber selected for study was preox fiber (Celion CP7-7711) and chemical analysis was again done by emission spectrography of the ashed samples. The chemical analysis results for this purification method are shown in Table 4. While some reduction in total alkalinity is apparent from the table for both HBr and HI treated samples, desired sodium and total alkalinity levels were not achieved so that effective HX penetration cannot be claimed for either approach.

C. 55% HI TREATMENT

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This method of purification treatment utilized a 72 hour exposure to 55% HI at 100°C; the fiber selected for study was DG-112 (3000 fil @ 1075°C). Following drying, the sample was heated in nitrogen to 1000°C

CHEMICAL ANALYSIS RESULTS - PURIFICATION ROUTE A

		DG 112		DG I	23	DG 126		DG 112		DG 12	e	DG 126		DG 112		DG 12:	m	DG 126	
ſ			-1° H	Br @ R	oom Te	- du	1		14 %T-	@ Roo	n Tem		1		Ŭ 	ontrol.			
	Ash	0.178		0.03	68	0.23%		0.19%		0.06%		0.31%		0.18%		0.08%		0.20%	
		Semi-Qua	intita	tive 1	Emissi	on Spect	rogra	phic And	alysis	of Asi	hes a	o mdd pu	f Sam	ple.					
			(mgg)		(mdd)	Ŭ	(mdd		(mgg)	a)	(ud	Ú.	(mgg	Ū	(udd)		(mdo		(udd)
	Si	10.8	170	7.8	25	10.8	230	9. 8	171	10.8	60	7.8	217	9.8	162	а. в.	24	10.8	200
	6 4	12.	204	0.5	2	10.	230	12.	228	н.	و	5.	155	12.	216	2.	16	12.	240
	£	<0.1	\$	<0.1	<u>,</u>	<0.1	\$	<0.1	?	0.3	~ ~	0.1	Ŷ	<0.1	\$ \$:0.1	4	0.1	6
	pMa	4.	68	ı.	4	5.	115	4.	76	2.	12	4.	124	4.	72	1 .	8	5.	100
	qa	<0.1	ç	<0.1	4	0.2	S	0.2	4	<0.1	<u>~</u>	0.1	ů	<0.1	\$	0.4	m	<0.1	ç
	Sn	0.2	e	0.3	1	0.3	2	0.2	4	0.2	~ ~	0.1	ŝ	<0.1	\$	0.3	7	<0.1	\$
	Fe	1.	17	г.	4	0.8	18	ι.	19	2.	12	0.8	25	2.	36	г.	80	2.	40
8	с,	0.2	m	0.2		0.2	S	0.1	2	0.2	-	0.1	m	0.3	S	0.3	N	0.4	80
	Nİ	1.	17	0.8	e	0.8	18	0.8	15	0.8	ъ	0.8	25	1.	18	ı.	8	ч.	20
	Al	0.5	6	°.	11	0.8	18	0.5	10	ъ.	e S	2.	62	0.5	6	0.8	9	0.5	10
	#Ca	ъ.	85	0.5	5	12.	276	5.	95	m.	18	5.	155	10.	180	0.4	m	12.	240
	อื	ι.	17	12.	43	8.	184	5.	95	10.	60 <u>1</u>	.	310	ı.	18	<u>ی</u> ٥.	160	ъ.	100
	**BN¥	10.	170	10.	36	7.	161	6.	114	10.	60	6.	186	7.	126	5 .	40	6.	120
	Zn	ъ.	85	2.	7	÷.	69	5.	95	г.	و	ı.	31	8.	144	ı.	80	з.	60
	Ti	0.1	2	0.5	7	0.2	S	0.1	7	5.	12	0.2	9	0.1	2	ı.	80	0.1	2
	≠Li **	24 ppm	1 2	*	*	64 ppm	4	49 ppm	4	*	*	5 ppm	ů	13 ppm	4	*	*	45 ppm	4

*Not enough ash for analysis.

**Na and Li values by atomic absorption.

All samples checked by X-ray fluorescence for Br and I. All nine samples estimated <0.02% N.D. for both Br and I. All samples treated in HBr and HI at 1%, 5 min., room temp. and heated in a muffle furnace for 5 min. @ 985 C in Heilum. FTotal alkalinity components; potassium was not reported.

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IICAL ANALYSIS
EMICAL ANALYSIS
CHEMICAL ANALYSIS

			Preox Control	2.05%
ates	18 HI	@ 50°C	Preox III	1.13%
Duplic	1% HI	0 50°C	Preox	0.23%
cates	1% HBr	e 50°C	Preox II	0.86%
Duplic	1% HBr	e 50°C	Preox	0.23%
				t Ash

Semi-Quan. Emission Spectrographic Analysis of Ash and ppm of Sample

				ខ្ល		Edd		udd	, ,	unda		uidd
	Ø	0.2%		ß	0.2%	17	0.1%	2	0.2%	23	0.3%	62
	Si	8.	ī	84	10.	860	8.	184	.8	904	8.	1640
	4	12.	2	76	з.	258	з.	69	2.	226	э .	615
	WU	.		23	1.	86	0.5	12	0.8	06	1.0	21
c	•м в	12.	5	76	15.	1290	15.	345	15.	1695 *	15.	3075
\$	đ	0.1		0	0.2	17	0.2	ß	0.1	11	0.2	41
	Sn	0.3		۲	0.1	6	0.1	7	0.1	11	0.2	41
	Fe	ч.	-	69	6.	516	4.	92	7.	161	6.	1230
	5	0.3		2	0.4	34	0.3		0.5	57	ц.	205
	Nİ	.		23	0.4	34	0.6	14	1.	113	ι.	205
	Al	2.	-	46	з.	258	1.	23	З.	339	5,	1025
-	*Ca	9.	й	07	12.	1032	7.	161	9.	1017	11.	2255
	Mo	0.3		7	0.1	6	1.	23	0.1	11	0.3	62
	5 C	0.7		16	0.7	60	0.5	12	0.7	79	0.7	144
AA	*Na	2.	*	46	з.	258	4.	92	2.	226	2.	410
	An	7.	ň	61	5.	430	2.	46	з.	339	э .	615
	Ti	0.3		7	0.6	52	0.1	0	6.0	102	6.0	185
	Sr	0.1		7	0.1	6	0.1	2	1.0	11	1.0	21
FE	*K	0.5	• =	12	1.	86	0.5	12	2.	226		205
FE	Li	28 ppi	•	<u>1</u>	61 ppm	ţ.	26 ppm	1	44 ppm	Ī	39 ppm	2
	On neat	spl. F	by XRF	All fiv	re samples -	detected	no Cl <0.2%					
	On neat	spl. I	N XRF	All fiv	re samples -	detected	no S <0.02%					
	On neat	spl. I	3Y XRF	All fiv	re samples -	detected	no Br <0.02%					
	On neat	spl. 1	3y XRF	Sample	18 HI 30 mir	1. Preox I	II detected I	N.D. in c	thers.			
	Samples	tested	in HBr	and HI	in ultra-son	nic bath a	t 50°C and su	bsequently	heated to 105	0°C in N.		
	*Total a	lkalinit	y compo	onents.						N		

for 24 hours. Chemical analysis of the samples was done by emission spectrography of 650°C ash; Na, K and Li levels were determined by atomic absorption. The results (Table 5) again show no reduction in alkali metal content or effective penetration of HX species.

D. 47% HBr TREATMENT

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Carbon fiber DG-112 (3000 fil @ 1075°C) was exposed to 47% HBr at 100°C for 72 hours in this approach. The sample was then dried and heated to 1000°C in nitrogen for 24 hours using a pyrolysis furnace. Chemical analysis was again performed by emission spectrography of the 650°C ash samples; Na, K and Li levels were determined by flame emission. Review of the results for this treatment presented in Table 5 shows no reduction in sodium or total alkalinity.

E. 10% $(NH_A)_2$ SO_A TREATMENT

This purification route involved exposure of DG-112 carbon fiber to 10% aqueous ammonium sulfate for a period of 72 hours at 100°C. After drying, the sample was heated in nitrogen for 24 hours at 1000°C. The results in Table 5 again show no reduction in alkalinity.

F. LIQUID NH, TREATMENT

Carbon fiber DG-112 was exposed to liquid ammonia at -33°C for 72 hours under this approach. Sample drying was again followed by heating at 1000°C in nitrogen for 24 hours. Chemical analysis by emission spectrography of the sample ash (605°C) was performed and flame emission was used to determine Na, K and Li levels. Table 5 shows that no alkalinity reduction was achieved by this method of treatment.

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CHEMICAL ANALYSIS RESULTS - PURIFICATION ROUTES C, D, E AND F

	SAMPLE TREATMENT	CONTROL		C. 55% HI @ 1	00 0 C	D. 47%HBR @	100°C	108 AQ (NH	E. So <u>e 100°C</u>	LIQ.NH3	e -33°C
	Ash	0.17%		0.52	æ.	0.72	46	0.3	38	0.	39 8
	Semi-quant.	itative Emi	ission	Spectrog	raphic Analy	rsis of Ash a	nd (ppm) of	Sample			
		ia)	om) Sample	5	opm) Sample	-1	(ppm) Sample	э	opm) Sample		ppm) Sample
	Si	5. #	85	5. &	260	2.	144	З.	66	5.	195
	4	.8	136	12.	624	г.	72	т.	33	з.	117
	Mn	0.1	2	10.	520	з.	216	1.	33	5.	195
11	€W ¥	10.	170	з.	156	2.	144	8.	264	10.	390
	Fe	0.5	6	5.	260	15.	1080	10.	330	5.	195
	ង	0.2	m	ι.	52	з.	216	2.	66	0.5	20
	NÍ	<0.1	<2	0.5	26	2.	144	0.3	10	0.5	20
	Al	0.5	6	ı	1	2.	144	4.	132	.01	390
	≠ Ca	5.	85	8 .	416	2.	101	2.	66	10.	06E
	Cu	0.3	Ś	2.	104	0.3	22	0.3	10	۱.	39
	≠ Na*	6.	102	2.	104	7.	504	6.	198	9.	351
	Zn	15.	255	15.	780	2.	144	2.	66	15.	585
	Ti	0.5	6	0.5	26	2.	144	0.5	17	0.5	20
	Sr	0.1	7	0.05	٣	0.1	7	0.1	£	0.1	4
	≠ K*	1 .	17	0.5	26	0.6	43	0.5	17	0.7	27
	≠ Li*	44 ppm	4	18 ppm	<1	19 ppm	٢	321 ppm	I	555 ppm	7

All Samples DG-112 (3000 Fil @ 1075°C). Total Alkalinity Components. Na, K and Li determined by flame emission except for sample by Treatment C where atomic absorption was used.

G. OTHER POSSIBLE APPROACHES

Throughout the course of investigating the purification treatments outlined above in Sections A through F, all of which showed no level of confidence for reducing the sodium and total alkalinity levels to the desired levels, several alternate approaches were postulated and these alternate methods are listed in Table 6. Time and funding constraints did not permit investigation of the alternate methods postulated. While these alternate approaches might merit further research in the area of alkali metal reduction in LTC carbon fibers, they remain speculative and untested.

ALTERNATE APPROACHES TO PURIFICATION TREATMENT

- Treat the carbon fiber with an oxidizing agent to increase the porosity of the fiber surface skin thereby enhancing the penetration of the alkali metal extracting agent.
- Conduct the pyrolysis of the preox fiber in an ammonia atmosphere to alleviate the problem of skin penetration after pyrolysis.
- 3. Treat the fiber in the precursor form to achieve maximum penetration of the alkali metal extracting agent.

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4. Replace the redox initiator system, which is the most probable source of the alkali metal contamination, with hydrogen peroxide or some other alkali metal-free initiator system suitable for acrylonitrile polymerization.

SECTION III

FABRIC VARIANT CHARACTERIZATION AND PROPERTIES

1. VARIANT SAMPLE FABRICATION ROUTES

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Before attempting to relate and compare the properties of the fabric samples developed, the treatment and processing steps for each variant are first examined below.

Task I - Variants 2 and 3. Stabilized carbon fibers of 1000 fil and 3000 fil counts were purchased and carbonized at 1075° C using a pyrolysis furnace. Fabric weaving was subcontracted and an epoxy sizing application was specified to minimize yarn abrasion during weaving. Both samples utilized an 8 harness satin (HNS) construction with end counts of 43x43 for Variant 2 (1Kx1K) and 15x15 for Variant 3 (3Kx3K). Fabric samples of each variant were next submitted for purification treatment to a subcontractor. Finally, fabric evaluation was initiated.

Task II - Variants 4 and 5. Spun stabilized yarn (10 worsted count, Z twist, 7 TPI/2 ply S twist, 4 TPI) and 1000 fil stabilized yarn were purchased and subcontracted for weaving. Fabric constructions specified were 39EPIx39PPI for Variant 4 (1Kx1K) and 39EPIx28PPI for Variant 5 (1Kxspun yarn); an 8 HNS weave was selected for both fabrics. Unsized fibers were purchased intentionally to minimize the alkali metal levels in the fabrics.

Initial weaving attempts were plagued by fuzz generation and loom fly from the abrasion of the unsized fibers, therefore, all LK warp material was sized with an epoxy resin (6% wt.) to facilitate smoother weaving. Since sizing the warp yarns alone did not sufficiently reduce the degree of fuzz generation, the twist level was increased from the 0.38 TPI of producer's S twist to 1.5 TPI using a ring twister. Subsequently, sample weaving proceeded with a satisfactory reduction in fuzz ball occurrence.

In order to prevent coalescence of the fabric samples during carbonization, a colloidal graphite application was recommended. To impregnate the fabrics properly with graphite particles, the epoxy sizing was removed using a methylene chloride bath. Two 7.5 gallon baths were used in series and the fabrics were manually drawn through each bath in two yard lengths, each length being quenched separately for 15 minutes followed by room temperature drying.

Both fabric samples were next dipped in a 1.1% colloidal graphite dispersion (1-2 micron average diameter particles in isopropanol) and allowed to dry ambiently. A few feet of the tail of Variant 4 was not dipped for coalescence evaluation. Carbonization was subcontracted with a specified peak temperature of 1075°C. Fabric evaluation followed.

Task III - Variant 7. Six thousand fil stabilized carbon fiber was purchased and carbonized at the target temperature of 1075°C. Epoxy sizing (6% wt.) was applied prior to weaving and a 4 HNS weave, 8EPIx8PPI construction, was specified. This fabric was then submitted for evaluation.

2. THERMAL CONDUCTIVITY

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The thermal conductivity (TC) of each different fiber variant was determined from the thermal conductivity of their epoxy composites measured by a Colora GMBH thermoconductometer and known methods of calculation⁽⁵⁾.

Test bars were fabricated by using 45 - 6.5in.x0.480in. plys of the epoxy/fabric laminate with a curing cycle of 30 min. at 175°F followed by 15 min. at 310°F. Test specimens cut from the bars were surface polished for good contact of the conducting surfaces during testing.

Because the thermal conductivity of the fiber in the axial direction is usually at least 20 times greater than the thermal conductivity of the epoxy resin and also much larger than the radial thermal conductivity of the fiber $^{(5)}$, the fibers horizontal to the direction of measurement will be treated as resin for the TC calculation. This assumes the TC of the fiber in the radial direction is equal to the resin TC. The void-free TC reported in Table 7 was based on an assumed fractional void content of 4%

FABRIC VARIANT THERMAL CONDUCTIVITY

FABRIC SAMPLE & DESCRIPTION	TEST DIRECTION (YARN)	VOL. FRAC. OF AXIAL YARN IN <u>SPECIMEN</u> (3)	VOID-FREE COMPOSITE T.C. CAL/SEC. °C-cm.	FIBER T.C. CAL/SEC. °C-cm.
NEAT Resin	-	_	.00079 ⁽⁵⁾	-
2 1Kx1K PURIFIED	WARP (1K)	.3565	.0045	.0112
2A 1Kx1K UNPURIFIED	WARP (1K)	•3355	.0043	.0113
3 ⁽¹⁾				
3Kx3K UNPURIFIED	WARP (3K)	.3009	.0044	.0128
4 ⁽²⁾				
IKx1K COLLOIDAL GRAPHITE	WARP (1K)	• 3094	.0033	.0089
5 1KxSY	WARP			
COLLOIDAL GRAPHITE	(1K)	.2832	.0026	.0072
5A	BII			
TKX21	(SY)	.2677	.0028	.0083
7				
6Kx6K	WARP (6K)	.3256	.0041	.0109

(1) Test specimen could not be made for the purified sample of this fabric due to damage during processing.

(2) Test specimen could not be made for the untreated sample of this fabric because of lack of material.

(3) Based on yarn denier, fiber density, and the cross-sectional area of the heat conducting surface.

(4) Test specimens assumed to be 4% void except as noted. Based on equation given in Section III-2.

(5) Neat resin test specimen assumed to be void-free.

(6) Based on void-free composite T.C., volume fraction of the yarn in the test direction and T.C. of the epoxy resin. See reference 5.

and the composite TC by the relationship (5):

$K=K_{a}(1-2.3V)$

where V is the void content, K_0 the void-free TC and K the measured composite TC. The fiber TC was calculated from the void-free TC, the fiber volume fraction and the resin TC.

3. DENSITY

The densities of the different fiber variants were determined using gradient columns and are listed below in Table 8.

TABLE 8

VARIANT FIBER DENSITIES

FABRIC SAMPLE	2	3	4	4A	5	i	7
CONSTRUCTION	lKxlK	3 Kx 3K	lKxlK	lKxlK	1KxSPUN	YARN	6 K x6K
TREATMENT	PURIFIED	PURIFIED	(1)	(2)	(1)	-
FIBER	lK	3К	lĸ	lk	lĸ	SPUN	6K
DENSITY, g/cc ⁽³⁾	1.789	1.776	1.769	1.753	1.742	1.749	1.783
 Treated with No colloidal 	colloidal graphite.	graphite.					

(3) n=3

All fiber densities exceed the desired density of less than 1.6 g/cc. However, this was to be expected from the target pyrolysis temperature of 1075°C. Past experience with the relationship between PAN-based carbon fiber density and pyrolysis temperature indicates that the desired density could be attained with a maximum pyrolysis temperature of approximately 650°C or less. The target temperature of 1075°C was selected to meet the more critical thermal conductivity requirement.

4. COALESCENCE

Previous work in the area of carbonizing preox fabrics indicated that coalescence could possibly develop from the high stress areas which result from shrinkage during pyrolysis. A more important factor

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may be the composition and displacement rate of the carbonization environment. Regardless of the direct cause of coalescence, preventing its occurrence in the variant samples was essential as it is usually indicative of fabrics with poor integrity and inferior properties. Applying colloidal graphite particles has been effective in separating fibers and reducing surface abrasion from fiber-fiber linear movement. This application (see Section III-1 for application technique) was recommended for Variants 4 and 5 to insure the delivery of coalescencefree samples and to evaluate colloidal graphite as an agent for reducing coalescence.

Figure 1 micrograph at 5000X shows two warp fibers from Variant 5. This sample was taken from the colloidal-graphite treated preox fabric. Heavy depositions of colloidal graphite and a particulate bridging of the adjacent fibers is shown.

The micrograph of Figure 2 shows two warp fibers from Variant 4 at a magnification of 5000X. This sample was taken after carbonization from the fabric tail which was not treated with colloidal graphite. The small but distinct gap between the two fibers indicates that coalescing did not occur during pyrolysis. Minor surface contamination is apparent from the figure.

To quantify any coalescence which might be present, an internal method for measuring the degree of coalescence was applied to the treated and untreated carbonized samples of Variant 4. The technique involves the separation of 20 fils from a fiber bundle 9 cm. in length. The number of fils which readily separate plus any fil breakage is noted and then correlated to an absolute scale of 0-5 with a 5 rating indicative of maximum coalescence. The result was a 0 rating for both samples, i.e., no coalescence was observed in either the treated or untreated fabric.

The trial indicates that it is possible to carbonize preox fabrics which are free from coalescence without the use of an agent such as



FIGURE 1 - VARIANT 5, WARP FIBERS, PREOX STATE, COLLOIDAL GRAPHITE TREATED



FIGURE 2 - VARIANT 4, WARP FIBERS, PYROLYZED, NO COLLOIDAL GRAPHITE

colloidal graphite, given the proper carbonizing conditions and environment. While colloidal graphite may minimize the severity and effects of coalescence when it occurs, and may also impart some added breaking strength due to its tendency to bridge between fibers (see Section III-6.B), it is not recommended for use as a coalescence deterent for commercial scale applications.

5. CHEMICAL PROPERTIES

A. CARBON CONTENT

The carbon content of the variants given below in Table 9 was determined by standard microanalytical combustion methods.

TABLE 9 FABRIC VARIANT CARBON COMPOSITION

VAL	RIANT NO	. (DESCRIPTION)	* CARBON [#]
2	(lKxlK,	PURIFIED)	86.17
2 A	(lKxlK,	UNPURIFIED)	85.19
3	(3Kx3K,	UNPURIFIED)	85.21
4	(lKxlK,	COLLOIDAL GRAPHITE)	82.69
4A	(lKxlK,	NO COLLOIDAL GRAPHITE)	80.07
5	(lKxSY,	COLLOIDAL GRAPHITE)	79.86
7	(6Kx6K)		85.15

 \neq Average of 2 determinations.

All of the samples tested possess a carbon content less than the desired 88% minimum. Again, this was to be anticipated from the target pyrolysis temperature of 1075°C, which was selected to meet the more important thermal conductivity requirement.

The weight loss indicated by the small difference in the carbon content of the purified and unpurified lKxlK variant (2 and 2A) is most likely due to the sizing removed during the purification treatment. Variant Samples 4, 4A and 5 show a somewhat lower carbon content; these samples were subcontracted for carbonization in the fabric form. Further development work with the subcontractor would be required to optimize the pyrolysis residence time for the desired combination of fabric properties.

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B. SODIUM AND ALKALI METAL COMPOSITION

A low sodium and total alkalinity concentration is desirable for fabrics to be used in composite heatshield applications. Trace amounts of alkali will enhance radar detectability of the heatshield device during ablation⁽²⁾. The attempts to develop a purification treatment, as discussed already in Section II, did not produce a method that would reduce the alkalinity to the desired levels. Variants 2 and 3 were therefore subcontracted to evaluate the feasibility of purification treatment.

The data listed in Table 10, which was supplied by the subcontractor, shows before and after levels of sodium and total alkalinity in parts per million.

TABLE 10

SODIUM AND TOTAL ALKALINITY - TASK I

FABRIC SAMPLE	SODIUM, PPM		TOTAL ALKALINITY*, PPM		
	BEFORE	AFTER	BEFORE	AFTER	
2,1Kx1K	120	40	190	90	
3,3Kx3K	250	70	460	150	
* Na,K,Ca,Mg and Li.					

The purification treatment rendered a sodium reduction of approximately 70% and a reduction in total alkalinity of 50-70%. The subcontractor believes that the desired alkalinity levels could possibly be reached by treating fabrics in the preox state; but, further development would be required to verify an increased efficiency by this sequence of processing.

Variant 3, the 3Kx3K constructed fabric, was badly damaged during purification processing. This physical damage resulted in part from a defective furnace and also from the high weight of this fabric which caused sagging during the operation. It is believed that this problem can be anticipated and the appropriate process changes made to prevent its reoccurrence in the future.

The fabric breaking strengths, reported in Table 12 of Section III-6.B., show a 4-fold strength reduction and a 50% decrease in elongation for the purified sample of Variant 2 when compared with its unpurified counterpart. This indicates that purification processing may physically and/or chemically weaken the fabric. The relative importance of fabric strength versus purity for the end-use application must be weighted in justifying a purification treatment.

6. PHYSICAL PROPERTIES

A. FABRIC THICKNESS, WEIGHT AND CONSTRUCTION The fabric construction, thickness, width and areal weight are given in Table 11 for the samples and corresponding treatments listed. As noted, thickness determination was done by ASTM Method D-1777 and areal weights were calculated from the dry weight of a 2in.x2in. sample. Fabric counts were done in accordance with ASTM-1910.

The thickness of Samples 4, 5 and 7 exceeded the desired thickness of less than 17 mils. The high thickness of Variant 7 is due to the high fil count (6000 fil) of the warp and fill yarns used. The addition of colloidal graphite and the increased twist given to the warp yarns of Variants 4 and 5 make their thickness slightly higher than would normally be expected.

The end counts and fabric width of Variants 4 and 5 show a 15-20% shrinkage from carbonization of the graphite-treated preox fabrics when compared to the constructions before carbonization (39x39 and 39x28 for Variants 4 and 5, respectively, before carbonization).

The counts and widths shown for Samples 4 and 4A indicate that the presence of colloidal graphite had a negligible effect on shrinkage during carbonization.

B. FABRIC BREAKING STRENGTH

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Fabric breaking strengths were determined in accordance with ASTM Method D - 1682 using the raveled strip test method. The breaking loads and

VARIANT FABRIC DIMENSIONAL PROPERTIES

abric ample	Construction, End Count	Fabric Thickness(1)	Fabric Width,	Fabric Areal Weight(2)
(No.)	(Treatment)	(in.)	(in.)	(oz/yd ²)
2	lKxlK, 8HNS 43x43 (Purified)	0.0142	24.75	7.38
2A	1Kx1K, 8HNS 43x43 (Unpurified)	0.0115	25	7.36
3	3Kx3K, 8HNS 15x15 (Unpurified)	0.0124	25	8.27
4	lKxlK, 8HNS 47x45 (Colloidal Graphite)	0.0183	22	8.33
4A (1Kx1K, 8HNS 47x44 No Colloidal Graphin	0.0146 te)	21.5	9.73
5	1KxSPUN YARN, 8HN 47x33 (Colloidal Graphite)	NS 0.0224	22	9.08
7	6Kx6K, 4HNS 8x8 (None)	0.0291	24.75	8.67

(2) Based on Dry Weight of 2 in. x 2 in. sample

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elongations for the fabric samples are listed in Table 12. This test could not be conducted for a purified sample of Variant 3 (3Kx3K) because of the damage that occurred during the purification treatment (See Section III-5.b.).

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The purified samples of Variant 2 showed a 50% drop in elongation and a 75% reduction in breaking strength when compared to the unpurified Sample, 2A. This indicates that a physical or chemical weakening of the fabric may be imparted by the purification treatment.

The colloidal graphite treated sample of Variant 4 showed 25% lower elongation and a 75% higher breaking strength per end when compared to Sample 4A which was not treated with colloidal graphite. The increased strength may result from the tendency for the colloidal graphite particles to bridge between adjacent fibers (See Section III-4.). Further work would be required to verify this theory.

The breaking strength per end of Variant 5 in the spun yarn filling direction is 35-40% less than the strength in the 1000 filament warp direction. Nonetheless, spun yarn may still be an acceptable filling material depending on the breaking strength required for the end use application.

The breaking strength per end increases sharply with the increase in filament count as shown by the results for Samples 2A, 3 and 7. Again, the breaking strength required should be strongly considered when determining the filament count to be used.

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RAVELED STRIP BREAKING LOADS (1)

-1	SAMPLE	DESCRIPTION	TEST DIRECTION	ELONG.	BST (lbs.)	NO. ENDS	BST (1bs/end)
	2	lKxlK, Purified, 43x43	Warp	0.87	80	42	1.90
	2 A	lKxlK, Unpurified, 43x43	Warp	1.71	327	42	7.78
	3	3Kx3K, Unpurified, 15x15	Warp	2.24	637	30	21.23
26	4	lKxlK, Colloidal Graphite Treated, 47x45	Warp	1.50	168	4 6	3.65
	44	IKxIK, No Colloidal Graphite, 47x44	Warp	2.00	88	42	2.09
	5	lKxSY, Colloidal Graphite Treated, 47x33	Warp Fill	1.79 1.78	204 97	43 33	4.74 2.94
	7	6K×6K, 8×8	Warp	2.00	810	20	40.50

(1) n=3

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SECTION IV

ECONOMIC EVALUATION

1. COMMERCIAL SCALE PRODUCTION METHODOLOGY

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Several assumptions must be made with regard to costing and process staging when estimating the production cost of each fabric variant on an escalated commercial scale. All of the processing cost components are dependent on quantity; others are dependent on both quantity and timing so that a common production rate must be assumed for estimating purposes. Major assumptions applicable to the commercial scale routes are as follows:

- All commercial scale routes are based on processing a minimum of 10,000 pounds of material.
- (2) Raw material fiber costs are based on year-end 1979 selling prices for carbonized yarns and are subject to inflation.
- (3) Variant routes 2, 3 and 7 assume that the carbon fibers are special ordered to be pyrolyzed to the target temperature of 1075°C. This special ordering may require a lead time up to 6 months.
- (4) Weaving costs are based on minimum fabric widths of 50 inches for 3000 fil and 6000 fil variants and 36 inches for 1000 fil variants.
- (5) The cost of carbonizing fabric forms (variant routes 4 and 5) is dependent on both quantity and timing (i.e., monthly production rate). The cost estimate assumes that the minimum material requirement of 10,000 pounds is a minimum annual production rate. The estimate is based on a 48 inch fabric width and a 98% yield.
- (6) A purification yield of 98% is assumed.
- (7) Estimates for weaving and carbonization are valid through 1980 and are subject to inflationary increase thereafter.
- (8) A weight-based yield of 95% is assumed for the weaving operation.

2. SAMPLE ROUTE VS. COMMERCIAL SCALE ROUTE

<u>Variants 2 and 3, Task I.</u> As shown by the fabrication routes listed above in Table 2, these samples were developed by purchasing preox yarns followed by carbonization of multiple ends of these yarns. The fabrication

route and cost given in Table 13 assume that the yarns are purchased in the carbonized form; purchasing commercial scale qualities should allow this. This is believed to be cost effective by eliminating sub-contracting of the carabonization step.

Variants 4 and 5, Task II. The intention of the sample routes of Variants 4 and 5 (Table 2) was to weave preox fibers without size and then carbonize the fabric forms. Sizing was not planned prior to weaving to minimize the chances of alkali metal contamination, however, fuzz and loom fly generation from the unsized fibers gave an unacceptable fabric. To reduce the fuzz level, the warp fibers were sized with epoxy resin (6% by wt.), but upon resuming sample weaving, fuzz generation was still evident. The 1000 fil preox warp was next twisted with a ring twister to increase the S-twist from 0.38 TPI to 1.50 TPI. The increased twist of the warp fiber adequately reduced the fuzz generation to permit weaving the preox yarns.

Both variant samples were subcontracted for carbonization of the preox fabrics to 1075°C. Past experience with other preox fabrics indicated that coalescence might result from shrinkage-induced tension and stress concentrations which occur during carbonization. To minimize the risk of coalescing the variant samples, both fabrics were treated in a 1.1% colloidal graphite dispersion[#] after the epoxy finish had been stripped using a methylene chloride bath.

The commercial route shown by Table 14 for Variants 4 and 5 does not include the warp fiber twisting operation nor does it include the finish removal and colloidal graphite impregnation steps. It is believed that further development in the area of weaving preox yarns and carbonizing preox fabric forms would eliminate these steps from commercial scale processing.

The problem of fuzz generation experienced during sample weaving should be resolvable with the proper combination of producer twist and sizing level and composition. This should not require an individual processing step and would have little, if any, effect on the cost of the preox yarns.

Isopropanol carrier with 1-2µ diameter particles.

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COMMERCIAL ROUTE AND COST ESTIMATE - TASK I

Variant 2, 1Kx1K -- Purchase 1000 fil carbon fiber, 1075°C, sized, Variant 3, 3Kx3K -- Purchase 3000 fil carbon fiber, 1075°C, sized, ship Delivery

<u>Cost Component</u>	Cost, \$/11	o. Fabric
	Variant 2	Variant 3
	1Kx1K	3Kx3K
Purchase 1075°C carbon fiber		
sized(1)	\$112.78	\$32.22
Weave as specified ⁽²⁾	45.00	8.00
Purify fabric ⁽³⁾	28,95	19.76
Total Manuf. Cost	\$186.73	\$59.98
Shipping Costs ⁽⁴⁾	1.30	1.30
Total Delivered Cost	\$188.03	\$61.28
Total Delivered Cost, \$/yd ⁽⁵⁾	\$ 85.74	\$40.94

- (1) 1K Fiber cost = \$105/1b base, a 95% weaving yield and 98% purification yield.
 3K Fiber cost = \$30/1b base, a 95% weaving yield and 98% purification yield.
- (2) Variant 2 = 1Kx1K, 43EPIx43PPI, 8HNS, 36 inch width.
 Variant 3 = 3Kx3K, 15EPIx15PPI, 8HNS, 50 inch width.
- (3) Based on \$13.20/linear yard, minimum 10,000 yards.

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- (4) Estimated at current rates for the three transfers shown above in commercial route.
- (5) Based on 0.456 and 0.668 lbs/yd for variants 2 and 3, respectively.
 (Based on specified fabric width.)

COMMERCIAL ROUTE AND COST ESTIMATE - TASK II

Variant 4, 1Kx1K -- Purchase 1000 fil preox fiber, sized w/twist

Variant 5, 1KxSY -- Purchase 1000 fil and spun yarn preox fibers, sized, w/twist

Cost Component	Cost, \$/1	b. of Fabric
	Variant 4	Variant 5
	1Kx1K	1KxSpun Yarn
Purchase preox fibers, sized, twisted(1)	\$ 60.05	\$ 40.06
Weave as specified ⁽²⁾	35.00	32.00
Carbonize fabric ⁽³⁾	9.00	9.00
Purify fabric ⁽⁴⁾	27.67	25.38
Total Manuf. Cost	\$131.72	\$106.44
Shipping Costs ⁽⁵⁾	1.70	1.70
Total Delivered Cost	\$133.42	\$108.14
Total Delivered Cost, \$/yd. ⁽⁶⁾	\$ 63.64	\$ 56.23

 1Kx1K Fiber cost = \$38.90/1b. base plus 95% weaving yield, 29% carbonization wt. loss and 98% yield, and 98% purification yield. 1KxSY Fiber cost = \$25.95/1b. base for equal amounts of 1K and spun yarn for 36" wide fabric. Same yields apply.
 Variant 4 = 1Kx1K, 39EPIx39PPI, 8HNS, 36 inch width. Variant 5 = 1KxSY, 39EPIx28PPI, 8HNS, 36 inch width.

- (3) Based on carbonized wt. at \$10.00/1b. less \$.20/1b.-100 lb.month to a minimum of \$8.00/1b.
- (4) Based on \$13.20/linear yard, minimum of 10,000 yards.
- (5) Estimated at current rates for transfers shown above.
- (6) Based on 0.477 and 0.520 lbs./yd. for Variants 4 and 5 respectively (based on specified fabric width).

The colloidal graphite application is undesirable for commercial scale operation because it would require two additional steps - stripping of any sizing used for weaving followed by the colloidal graphite dip. Short drying cycles would be needed after each step prior to fabric winding. Additional planning and equipment needed for protecting personnel from exposure to graphite dust and solvent and carrier vapors also diminishes the feasibility of carrying out this application commercially.

The coalescing of preox fabrics during carbonization can be avoided without colloidal graphite application. This phenomena is believed to be related to fabric construction and end counts and results from high strain areas developed by shrinkage during carbonization. Oxidative attach and an imbalance or stagnation in the carbonizing environment are also believed to foster coalescence. Therefore, selection of the proper fabric construction and close monitoring for shrinkage control combined with proper control of the carbonizing environment and its exhaust should produce coalescence-free fabrics. Neither the colloidal graphite treated nor the untreated section of Variant 4 showed any degree of coalescence after carbonization (see Section III-4).

Although Variant 4 and 5 samples were not treated for alkali metal removal, the cost for purification was included in the estimate for comparison.

<u>Variant 7, Task III.</u> The commercial fabrication route (Table 15) assumes purchasing of the 6000 fil yarn in the carbonized form which eliminates the individual carbonization step shown previously for the sample route in Table 2. Purification is again included in the cost estimate for comparison.

3. ENVIRONMENTAL CONSIDERATIONS AND SAFETY

A major environmental concern to be addressed for any of the commercial fabrication routes as outlined, is the control, containment and subsequent disposal of carbon dust or airborne fibrous carbon and fiber/fabric scrap which will be generated during the weaving, carbonizing and purification steps. Adequate exhaust capacity applied at critical handling points in the process steps is recommended with collection by a bag filter or centifugal separation system. Waste should be propertly contained and packaged and disposed of by land filling or other acceptable method for handling non-combustible

COMMERCIAL ROUTE AND COST ESTIMATE - TASK III

Variant 7, 6Kx6K -- Purchase 6K carbon fiber, 1075°C, sized-T S h

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Cost Component	Variant 7 Cost, \$/1b. Fabri	c
Purchase 1075°C, 6K carbon fiber, sized(1)	\$24.70	
Weave as specified ⁽²⁾	6.00	
Purify fabric(3)	16.54	
Total Manuf. Cost	\$47.24	
Shipping Costs ⁽⁴⁾	1.05	
Total Delivered Cost	\$48.29	
Total Delivered Cost, \$/yd. ⁽⁵⁾	\$38.54	

- (1) 6K Fiber cost = \$23/1b. base, a 95% weaving yield and 98% purification yield.
- (2) 6Kx6K, 8EPIx8PPI, 4HNS, 50 inch width.

- (3) Based on \$13.20/linear yard, minimum 10,000 yards.
- (4) Estimated at current rates for the three transfers shown above in the commercial route.
- (5) Based on 0.798 lbs./yd. using specified fabric width.

solid waste. Incineration is not recommended as a means of disposal.

The weaving, carbonizing, and purification of preox and carbon fibers and fabrics has been commercially demonstrated and the problems and practice of controlling and disposing of carbon dust and scrap is well known. No environmental or pollution related problems are foreseen which would impact the cost estimates as developed above.

During carbonization of the preox fabrics, approximately a 30% weight loss occurs from the evolution of waste gases which includes HCN, CO, CO_2 , N_2 , NH_3 and higher nitrile forms. The handling and subsequent method and rate of emission for these components must be in compliance with federal and state environmental protection regulations where they apply.

The potential for electrical hazards exists when carbon dust and airborne fibers are generated because of their electrically conductive nature. Precautions to isolate electrical equipment (particularly high voltage panels) in proximity with processing operations, are recommended.

Skin irritations and respiratory problems could occur from exposure and inhalation in areas where carbon dust and fibers are generated. Protective equipment including respirators and arm gauntlets and gloves should be provided for work areas where dust levels may become severe.

4. COMMERCIAL COST OBSERVATIONS

Table 16 shows the developed fabric variants and the corresponding commercial scale manufacturing cost estimate for each.

TABLE 16

FABRIC COST SUMMARY

NO.	FABRIC	CONSTRUCTION	MANUFACTURING COST ESTIMATE, \$/LB FABRIC
2	lKxlK	8HNS, 43EPIx43PPI	\$188.03
3	3Kx3K	8HNS, 15EPIx15PPI	61.28
4	1Kx1K	8HNS, 47EPIx45PPI≠	133.42
5	1KxSpun Yarn	8HNS, 47EPIx33PPI≠	108.14
7	6Kx6K	4HNS, 8EPI x8PPI	48.29

Construction after fabric shrinkage during carbonization.

From reviewing the data of Tables 13 through 16, the following cost observations can be made:

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- The raw material fiber cost, measured as \$/lb. fabric is substantially reduced by a factor of 3 to 5 by using the larger fil count yarns (3000 fil and 6000 fil).
- (2) The increased throughput of weaving the smaller end-count fabrics made from the larger fil count yarns reduces weaving cost (\$/lb. fabric) by a factor of 5 to 7.
- (3) Processing the widest fabric practical is a cost effective measure, particularly for the purification step, which is not based on weight but rather on linear yards of processed fabric.
- (4) Utilizing spun yarn as a fil material in place of continuous fiber can reduce the raw material fiber cost of the preox fabric by 30%.
- (5) Carbonization of the preox fabric form after weaving reduces the total raw material fiber and weaving cost by as much as 30%.
- (6) Depending on fabric construction, the cost of purification comprises 15-35% of the total manufacturing cost of the fabric.

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- (3) Celanese Research Company, Technical Report AFML-TR-73-191. Pt. I, August, 1973; Pt. II, September, 1974.
- (4) Hitco Materials Division, US 3,413,094, November 26, 1968.
- (5) Kalnin, I. L. in <u>Composite Reliability</u>, ASTM STP 580, ASTM (1975), p. 560.