NASA CR 71295

"INVESTIGATION OF THE EFFECT OF MATERIAL PROPERTIES ON COMPOSITE ABLATIVE MATERIAL BEHAVIOR"

THIRD QUARTERLY REPORT: December 11, 1965 to March 10, 1966

of

Contract NAS 3-6291

to

NASA

Lewis Research Center

Cleveland, Ohio

GPO PRICE $ ________

CFSTI PRICE(S) $ ________

Hard copy (HC) $2.00

Microfiche (MF) .50

ff 653 July 65

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3rd QUARTERLY PROGRESS REPORT

Overall Progress

During the last quarterly period the second phase of the contract, that of determining the influences and limitations of the four properties, found in the first phase to have the most significant effect upon the surface recession of silica cloth/phenolic resin, graphite cloth/phenolic resin and graphite cloth/epoxy resin materials, was completed. In addition, nearly all of the detailed numerical calculations for the evaluation of the material performance for Phase III have been completed. The completion of this calculation was delayed until after the March 10 meeting with the NASA Lewis Research center Project Manager since there were some questions concerning the method of calculating the surface recession of the silica cloth/phenolic resin material. The approach being used to predict the recession rate is one in which the surface temperature is allowed to reach a maximum value equal to the melting temperature of the silica material. After which melting will take place until the received heat flux at the surface drops below the thermal radiation value corresponding to the melt temperature. During the melting process the amount of thermal energy absorbed per pound of material melted is equal to the latent heat of fusion of silica. This approach of predicting the surface recession of silica cloth has been verified by a number of ground tests.

The primary objective of the Phase II study was to determine the variation in thermal properties resulting from processing and fabrication techniques --- namely, due to changes in lamination angle, resin contact, density, and lot-to-lot variation --- upon silica cloth/phenolic resin, graphite cloth/phenolic resin, and graphite cloth/epoxy resin materials. The effort was primarily accomplished by conducting an extensive literature search of existing data, generated by both government and industry sponsored efforts.

Certain prominent trends and peculiarities are discernible from the variations in thermal conductivity and specific heat coefficients due to changes in the above mentioned parameters shown in figures 1 through 4. Figure 3 illustrates that in general, an increase in the resin content of the graphite-phenolic laminates, keeping lamination angle constant, decreased the thermal conductivity. For example, an increase in resin from 30 percent to 50 percent (which corresponds to an decrease in density) decreased the "C" (across lamina) and "A" (with lamina) direction (see Figure 10) conductivities by 40 percent and 25 percent, respectively This observation was noted by C. D. Pears in reference 12. Table 3 identifies the data plotted in figure 3 with respect to lamination angle, resin content, density and source of information. This dependence of thermal conductivity upon changes in resin content (or density) may well explain the scatter obtained on specimens machined within a given panel since the resin content can vary significantly within the panel.

The above correlation between conductivity and resin content (or density) is not noticeable with silica phenolic (figure 1). In fact there is no trend whatsoever. It can therefore be concluded that other masked variables influence the conductivity of silica-phenolic. Although there is considerable knowledge in fabrication methods, test methods and standards vary with vendors, thereby necessitating a standard method of determining resin content more accurately.

Figures 2 and 4 show hardly any variation in specific heat for silica-phenolic or graphite phenolic, respectively.

The wide spread in density for silica-phenolic was much narrower for graphite-phenolic --- $\pm$ 15 LB/FT^3 vs. $\pm$ 5LB/FT^3. This is because the controls on fabricating, impregnating, and laminating the <u>graphite</u> web are much more critical than the equivalent controls in processing the <u>silica</u> web (reference 13).

Based on the data presented in figures 1 through 4, nominal values for the thermal conductivity and specific heat coefficients of the subject materials are shown with a tolerance band in figures 5 through 9.

The available thermal data on graphite-epoxy is quite limited. Therefore, the nominal values of thermal conductivity and specific heat are based on previous experiences with this material, which is the reason for assuming that the conductivity and specific heat of graphite-epoxy are the same as that of graphite-phenolic with one exception (reference 9). It can be seen from figures 7 and 9 that this exception is in the region of partial decomposition, i.e. where the virgin and charred portions of the curve are connected. Here the thermal conductivity of graphite-epoxy has a steeper slope than that of graphite-phenolic. This is because the epoxy resin decomposes at approximately 600°F, losing about 80% of its initial weight at 800°F. The region of decomposition of the phenolic resin on the other hand, extends over a wider temperature range and decomposes at approximately 700°F losing about 47% of its initial weight at 1200°F.

<u>Conclusions</u>:

As a result of this study, the following conclusions were observed:

(1) Tolerances of $\pm$ 50%, $\pm$ 80%, $\pm$ 80% are assigned to thermal conductivity data on silica phenolic, graphite phenolic, and graphite epoxy, respectively.

(2) Tolerances of $\pm$ 15%, $\pm$ 20%, $\pm$ 20% are assigned to specific heat data on silica phenolic, graphite phenolic, and graphite epoxy, respectively.

(3) Thermal conductivity of the materials in this study are more dependent upon lamination angle than on the resin or fiber content.

(4) Orientation angle does not affect specific heat coefficients.

(5) Resin content does not significantly alter specific heat coefficients.

(6) Lot-to-lot variation of thermal parameters masks out any property interrelationship.

(7) Silica phenolic has the lowest thermal conductivity and specific heat coefficients.

(8) Heat flows more easily along the warp direction than along the fill or thickness direction, thereby explaining the 22% difference in thermal conductivity of graphite phenolic specimens of identical composition in the warp and thickness direction.

Based on the conclusions of the Phase II investigation that the variations of the thermal parameters (densities, specific heat and thermal conductivities) are more dependent on lamination angles than on the resin or fiber content. The parameters found to have a major effect on the surface recession rate, such as melting temperature of the silica fibers and the surface reaction constants of the carbonaceous char, are independent of the char or virgin plastic densities, thermal conductivity, or activation energy. The activation energy is only a function of the resin material and not dependent on the other parameters of interest. Therefore, it appears that each of the properties under consideration within Phase III of this contract is independent of the others. The material performance during Phase III was calculated, allowing each of the properties given in Tables 5, 6 and 7 to vary over their entire range. The remaining properties required for the analytical evaluation of the ablation performance are tabulated in Table 8

Work to be Performed Next Month

The steady state surface recession rates of each of the materials under investigation will be plotted as a functionof the four parameters. The possibility of presenting the final information in the form of a nomograph will be investigated.

Current Problems

No problems have been encountered to data.

Table 1 - SILICA CLOTH/PHENOLIC RESIN ---- THERMAL CONDUCTIVITY

FIGURE NO.	CURVE NO.	DIRECTION OF MEASUREMENT	RESIN CONTENT (%)	DENSITY (LB/FT^3)	LITERATURE SOURCE REF. NO. (See Referances)
1	1	With Lamina	30	106	10
	2	With Lamina	20	88	10
	3	With Lamina	30	112	10
	4	With Lamina	30	108	10
	5	With Lamina	20	88	10
	6	Across Lamina	30	106	10
	7	Across Lamina	30	110	1
	8	Across Lamina	30	112	10
	9	Across Lamina	31	109	1
	10	Across Lamina	30	108	10
	11	Across Lamina	20	88	10
	12	Across Lamina	20	88	10
	13	---------	--	---	11

Table 2 --- SILICA CLOTH/PHENOLIC RESIN ---- SPECIFIC HEAT

FIGURE NO	CURVE NO.	DIRECTION OF MEASUREMENT	RESIN CONTENT (%)	DENSITY (lb/FT^3)	LITERATURE SOURCE REF. NO. (See References)
2	1	Does Not Affect	30	112	10
	2	Specific Heat	--	104	18
	3		30	106	10
	4		31	109	1
	5		30	110	1
	6		20	88	10
	7		--	---	5,11

TABLE 3 - GRAPHITE CLOTH/PHENOLIC RESIN ----- THERMAL CONDUCTIVITY

FIGURE NO.	CURVE NO.	DIRECTION OF MEASUREMENT	RESIN CONTENT (%)	DENSITY (LB/FT^3)	LITERATURE SOURCE REF. NO. (See References)
3	1	With Lamina	30	----	12
	2	With Lamina	29 ± 2.5	93.5	1
	3	With Lamina	30	----	12
	4	With Lamina	36	92	1
	5	With Lamina	36	92	1
	6	With Lamina	50	----	12
	7	Across Lamina	29 ± 2.5	93.5	1
	8	Across Lamina	29 ± 2.5	93.5	1
	9	Across Lamina	50	----	12
	10	Across Lamina	29 ± 2.5	93.5	1
	11	Across Lamina	30	90	10
	12	Across Lamina	36	92	1
	13	Across Lamina	30	90	10
	14	Across Lamina	40	89	10
	15	Across Lamina	40	85	10
	16	Across Lamina	50	----	12
	17	-------------	--	70	15
	18	-------------	--	76	2

TABLE 4 - GRAPHITE CLOTH/PHENOLIC RESIN - SPECIFIC HEAT

FIGURE NO.	CURVE NO.	DIRECTION OF MEASUREMENT	RESIN CONTENT (%)	DENSITY (LB/FT^3)	LITERATURE SOURCE REF. NO. (see References)
4	1	Does not Affect	50	87	10
	2	Specific Heat	50	86	10
	3		30	90	10
	4		36	92	1
	5		40	89	10
	6		--	--	17
	7		--	87	3
	8		--	76	2

Table 5 - PROPERTY VARIATION FOR SIGNIFICANT PROPERTIES FOR SILICA CLOTH/PHENOLIC RESIN

PROPERTY	RANGE Minimum	Nominal	Maximum
Melting Temperature of Reinforcing Fibers (^oR)	3000	3500	4000
Virgin Plastic Density (lb/ft^3)	88	103	118
Specific Heat (Solid) (Btu/lb^oF)		See Figure 6	
Activation Energy	21600	48600	75600

Table 6 - PROPERTY VARIATION FOR SIGNIFICANT PROPERTIES FOR GRAPHITE CLOTH/PHENOLIC RESIN

PROPERTY	RANGE Minimum	Nominal	Maximum
Surface Reaction Constants K_1 and K_2	K_1=1000 K_2=2	K_1-4240 K_2=5.77	K_1=12000 K_2=10
Char Density (lb/ft^3)	70	76	82
Thermal Conductivity (Btu/ft^oF sec)		See Figure 7	
Virgin Plastic Density (lb/ft^3)	85	90	95

Table 7 - PROPERTY VARIATION FOR SIGNIFICANT PROPERTIES FOR GRAPHITE CLOTH/EPOXY RESIN

PROPERTY	RANGE Minimum	Nominal	Maximum
Surface Reaction Constants K_1 and K_2	K_1=1000 K_2=2	K_1=4240 K_2=5.77	K_1=12000 K_2=10
Char Density (lb/ft^3)	64	70	76
Thermal Conductivity (Btu/ft sec^{o}F)		See Figure 8	
Virgin Plastic density (lb/ft^3)	85	90	95

Table 8 - NOMINAL PROPERTY VALUES FOR REKAP ANALYSIS

PROPERTY	SILICA CLOTH/ PHENOLIC RESIN	GRAPHITE CLOTH/ PHENOLIC RESIN	GRAPHITE CLOTH/ EPOXY RESIN
Heat of Gasification (BTU/lb)	550	550	550
Collision Frequency (1/sec)	3×10^4	3×10^4	3×10^4
Activation Energy (Btu/lb)	Table 5	48600	37500
Melting Temperature of Fibers (^oR)	Table 5	Table 6	Table 7
Heat of Vaporization of Reinforcing Fibers (Btu/lb)	71	Table 6	Table 7
Wall Emissivity	.65	.8	.8
Recovery Temperature (^oR)			
a) N_2O_4/Aerozine 50	4500	---	---
b) OF_2/B_2H_6	---	5000	5000
Film Coefficient (Btu/ft^{2}sec^{o}R)			
a) 1.2 in. dia. Throat	.294	.425	.425
b) 7.82 in.dia. Throat	.22	---	---
Specific Heat of = Ablation Gases (Btu/lb^{o}R)	.75	.75	.75
Molecular Weight of Ablation Gases	30	30	30
Virgin Plastic Density (lb/ft^3)	Table 5	Table 6	Table 7
Char Density (lb/ft^3)	92	Table 6	Table 7
Thermal Conductivity (Btu/ft sec^{o}F)	Figure 5	Table 6	Table 7
Specific Heat (Btu/lb)	Table 5	Figure 8	Figure 8
Order of Reaction	2	2	2

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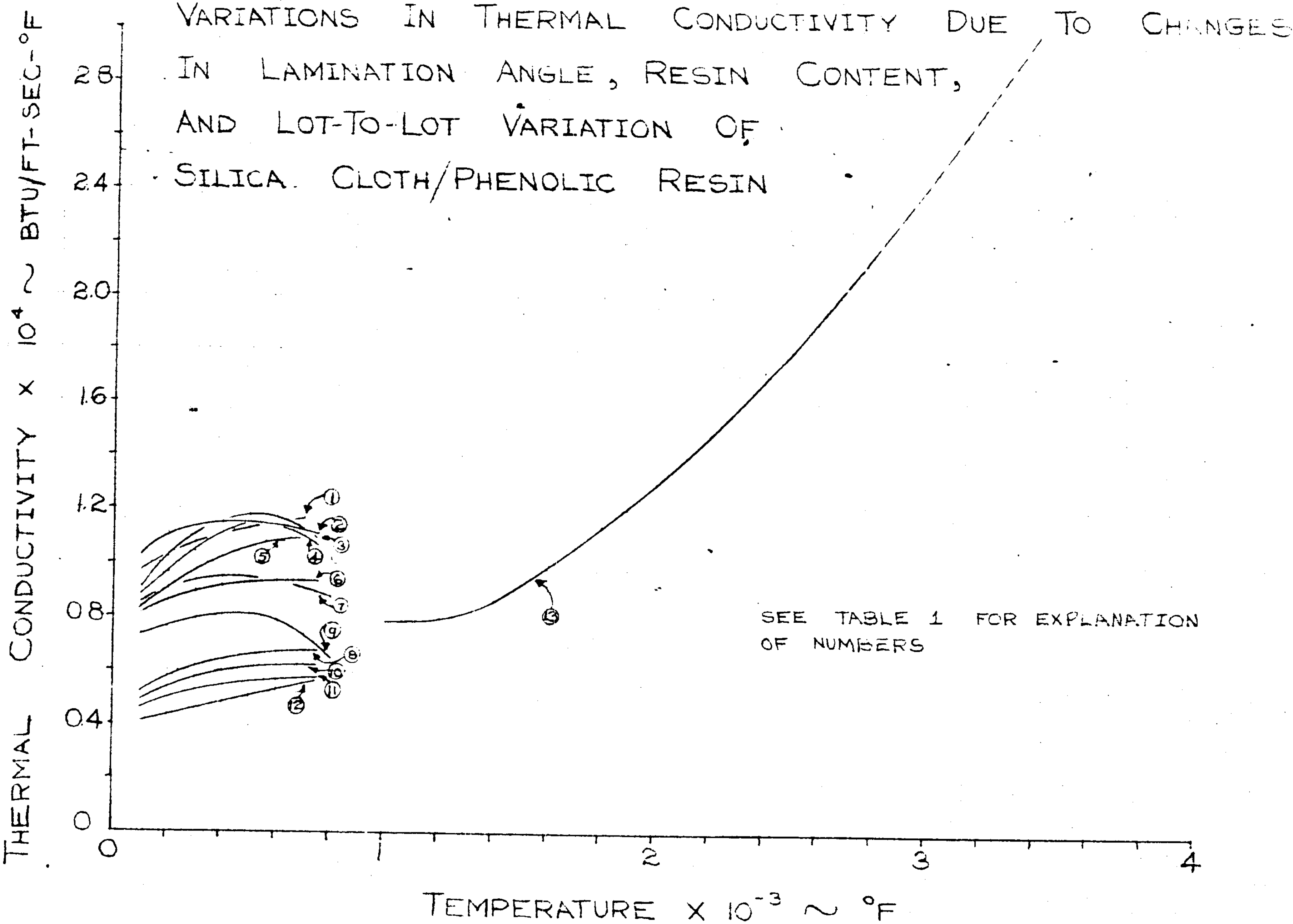


VARIATIONS IN THERMAL CONDUCTIVITY DUE TO CHANGES IN LAMINATION ANGLE, RESIN CONTENT, AND LOT-TO-LOT VARIATION OF SILICA CLOTH/PHENOLIC RESIN

FIGURE 1

VARIATIONS IN SPECIFIC HEAT DUE TO CHANGES IN LAMINATION ANGLE, RESIN CONTENT; AND LOT-TO-LOT VARIATION OF SILICA CLOTH/PHENOLIC RESIN

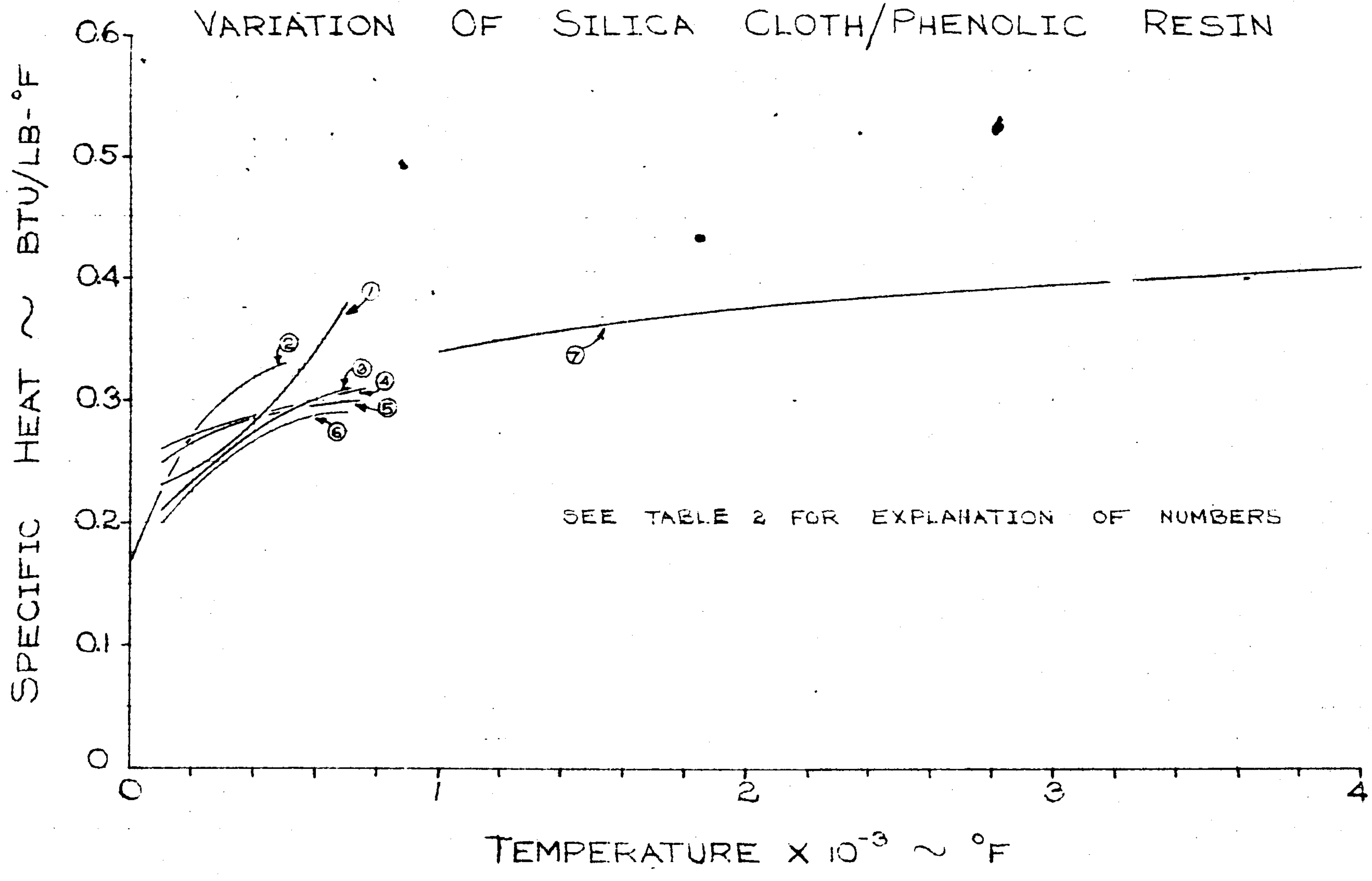


FIGURE 2

VARIATIONS IN THERMAL CONDUCTIVITY DUE TO CHANGES IN LAMINATION ANGLE, RESIN CONTENT, AND LOT-TO-LOT VARIATION OF GRAPHITE CLOTH/PHENOLIC RESIN

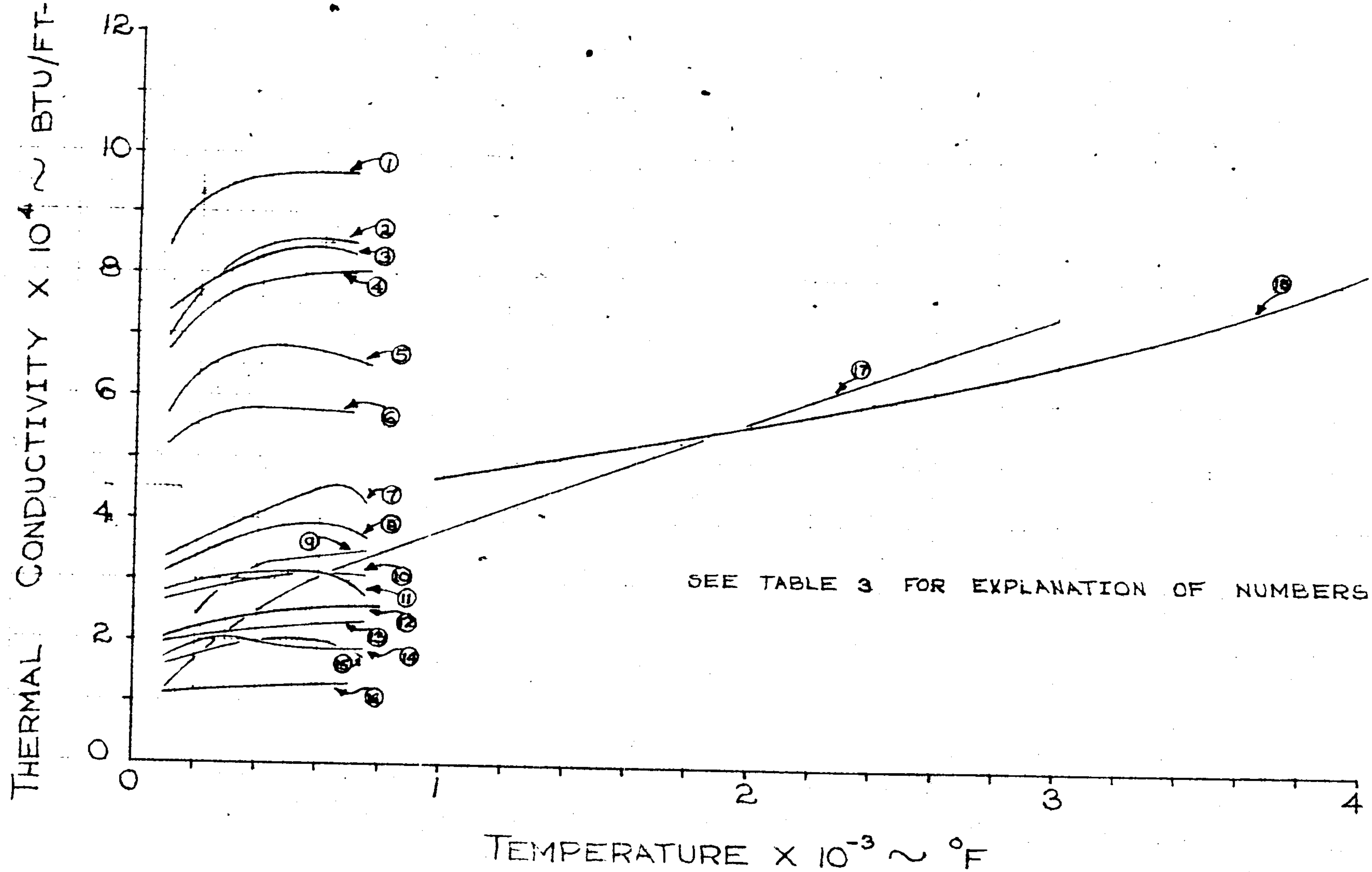


FIGURE 3

VARIATIONS IN SPECIFIC HEAT DUE TO CHANGES IN LAMINATION ANGLE, RESIN CONTENT, AND LOT-TO-LOT VARIATION OF GRAPHITE CLOTH/PHENOLIC RESIN

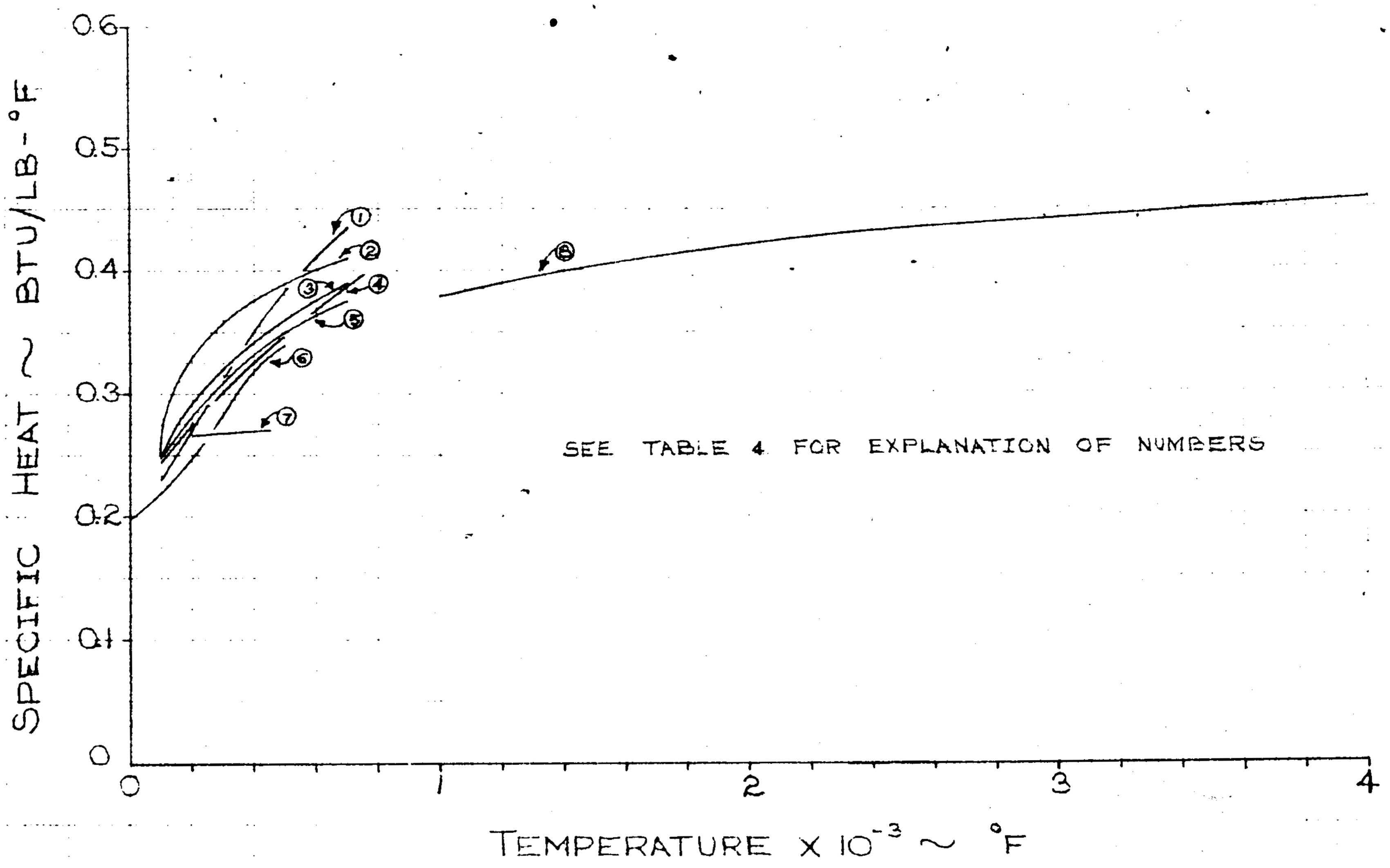


FIGURE 4

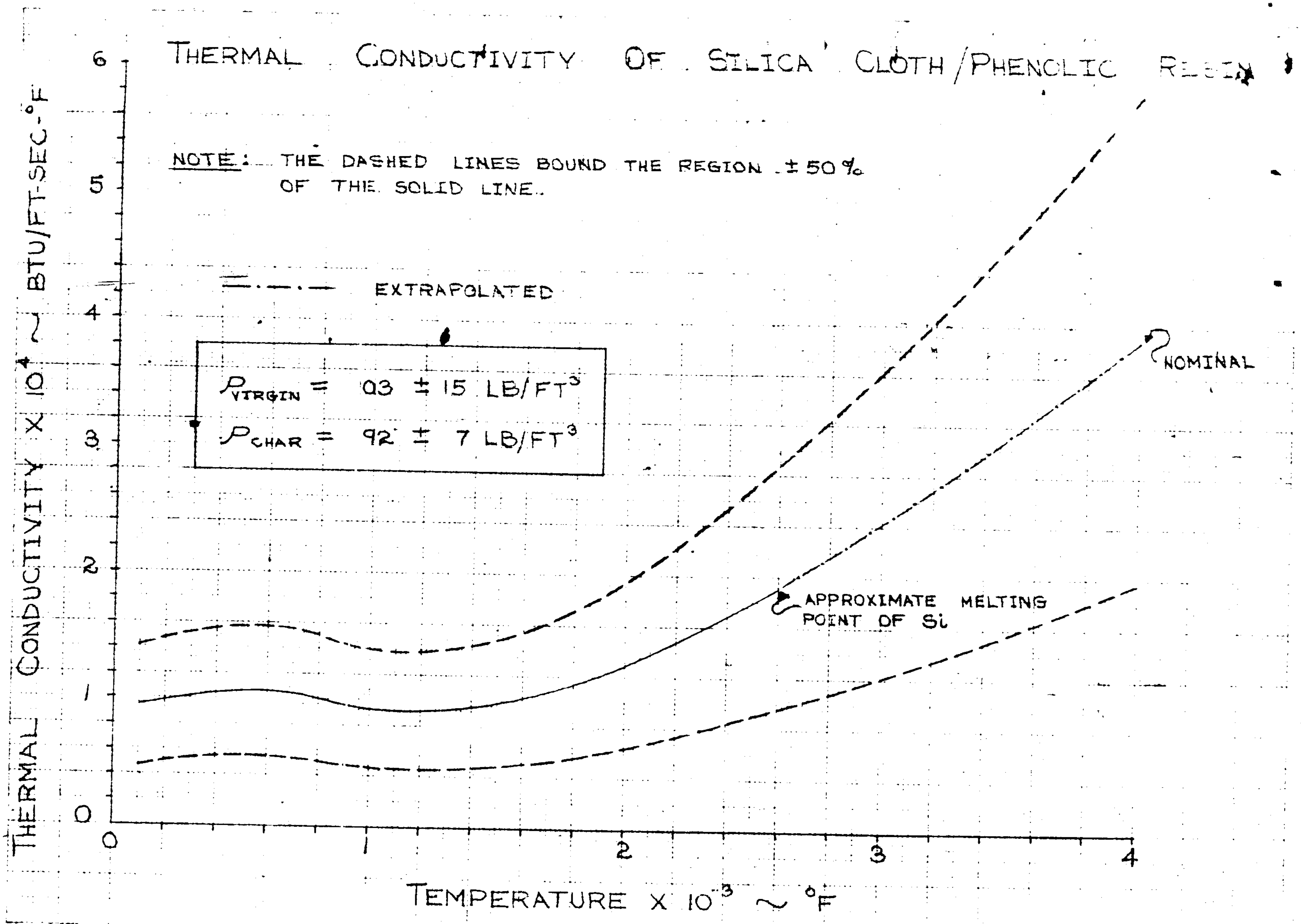

THERMAL CONDUCTIVITY OF SILICA CLOTH/PHENOLIC RESIN
NOTE: THE DASHED LINES BOUND THE REGION ±50% OF THE SOLID LINE.
EXTRAPOLATED
ρ_{VIRGIN} = 103 ± 15 LB/FT^3
ρ_{CHAR} = 92 ± 7 LB/FT^3
NOMINAL
APPROXIMATE MELTING POINT OF Si
THERMAL CONDUCTIVITY X 10^4 ~ BTU/FT-SEC-°F
TEMPERATURE X 10^{-3} ~ °F
0
1
2
3
4
5
6

FIGURE 5

SPECIFIC HEAT OF SILICA CLOTH / PHENOLIC RESIN

NOTE: THE DASHED LINES BOUND THE REGION ± 15 % OF THE SOLID LINE

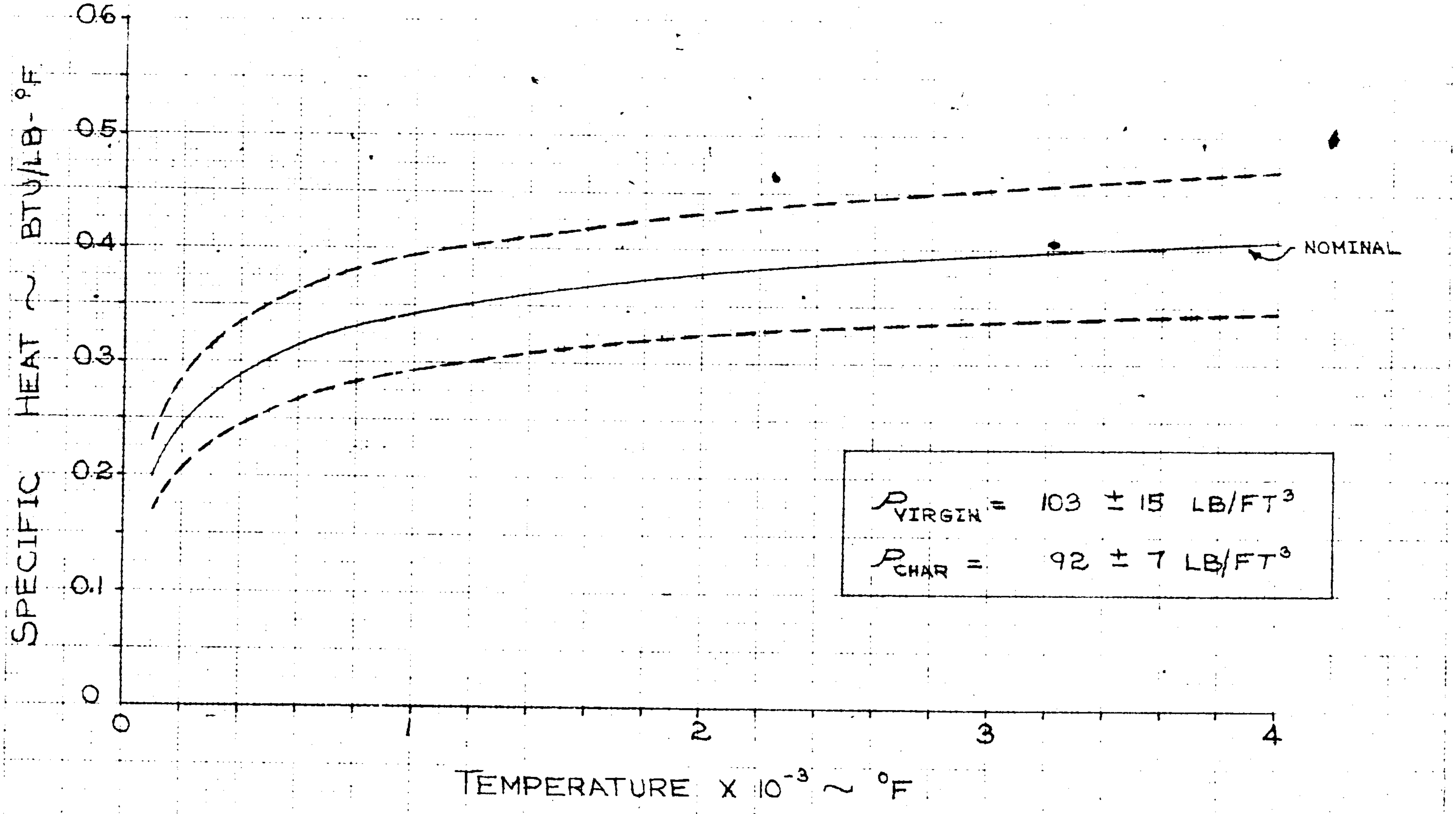


FIGURE 6

THERMAL CONDUCTIVITY OF GRAPHITE CLOTH/PHENOLIC RESIN

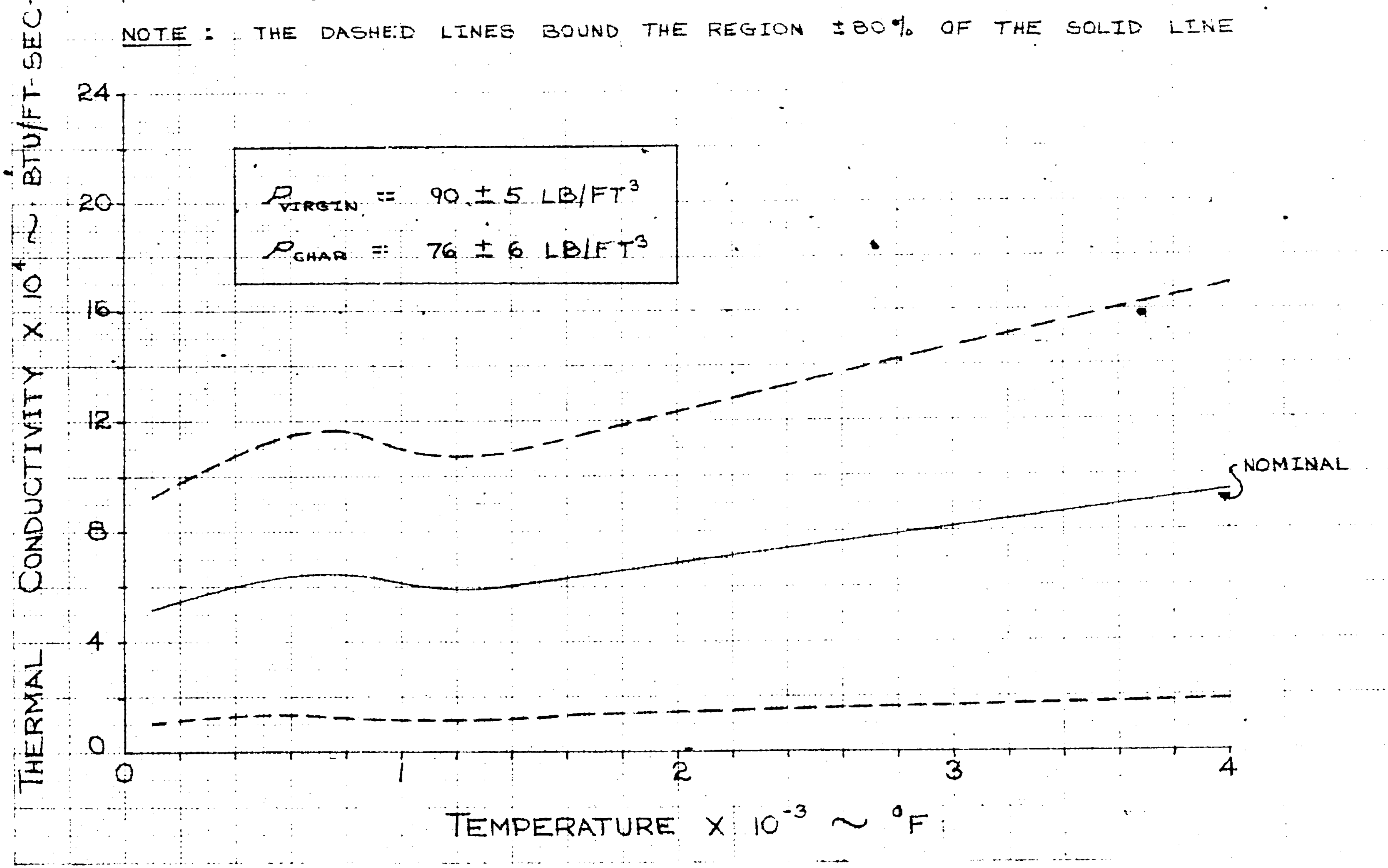


FIGURE 7

SPECIFIC HEAT OF GRAPHITE CLOTH/PHENOLIC RESIN AND GRAPHITE CLOTH/EPOXY RESIN

NOTE: THE DASHED LINES BOUND THE REGION ± 20 % OF THE SOLID LINE

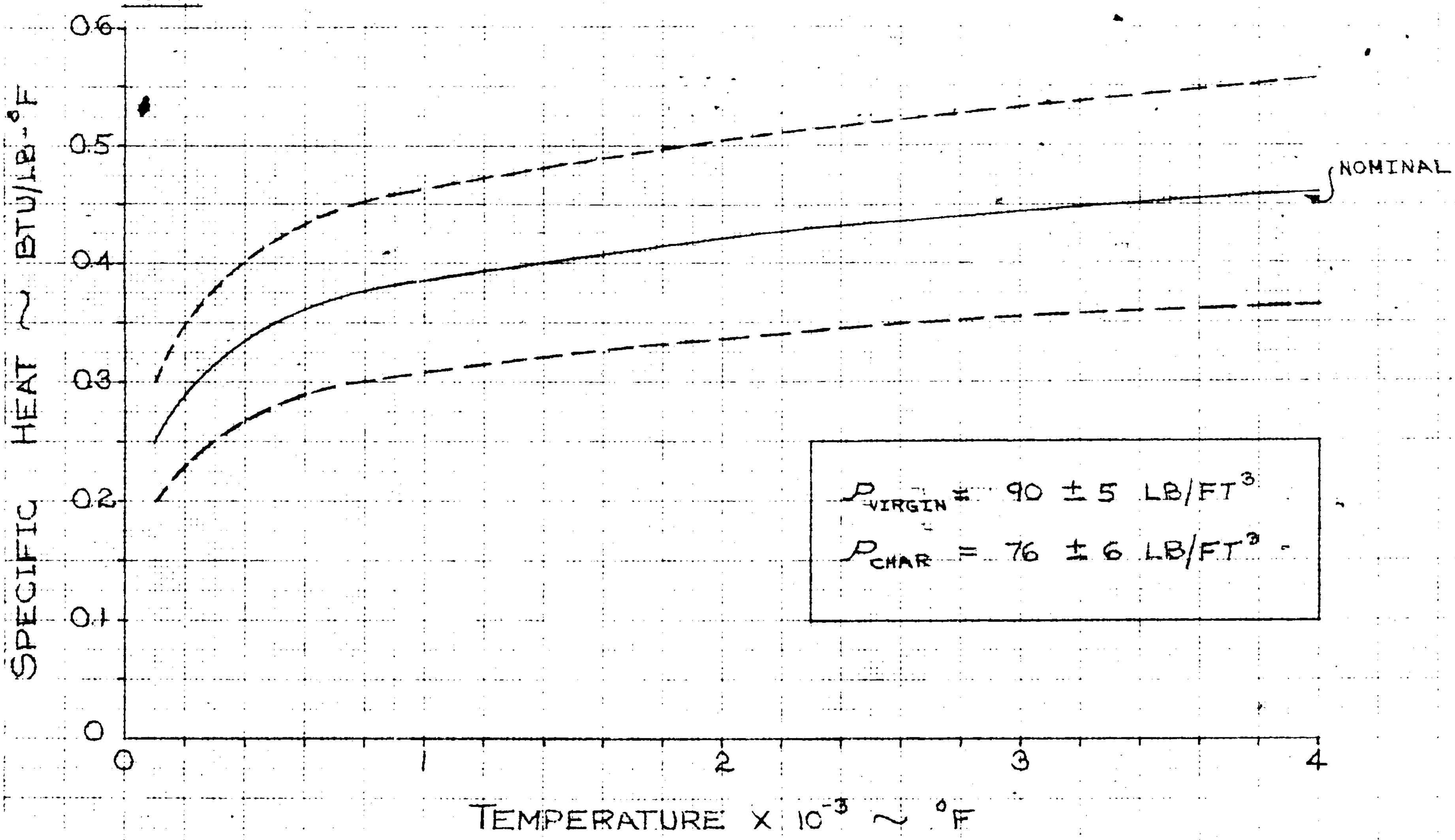


FIGURE 8

THERMAL CONDUCTIVITY OF GRAPHITE CLOTH/EPOXY RESIN

NOTE: THE DASHED LINES BOUND THE REGION ± 80 % OF THE SOLID LINE

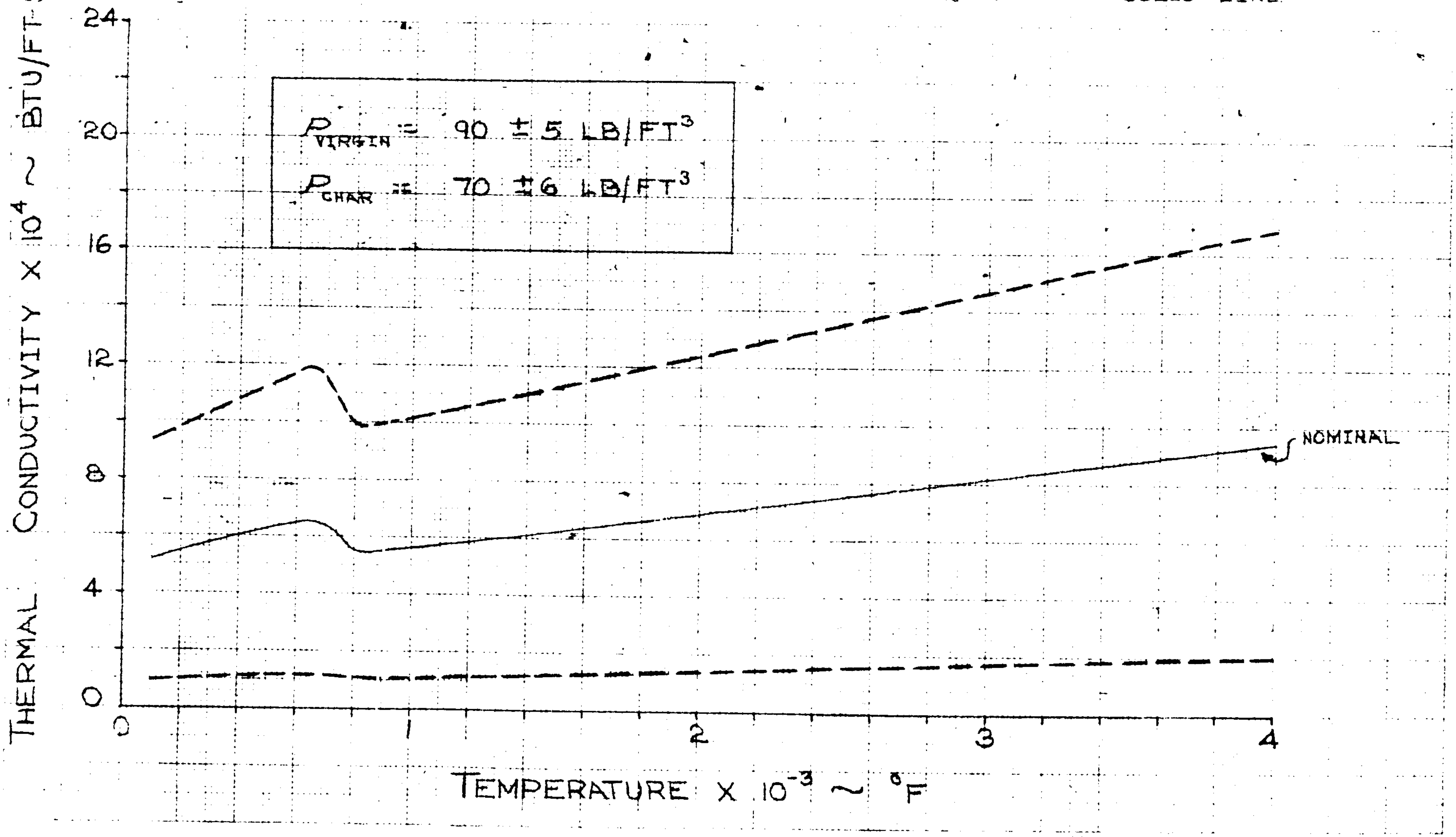
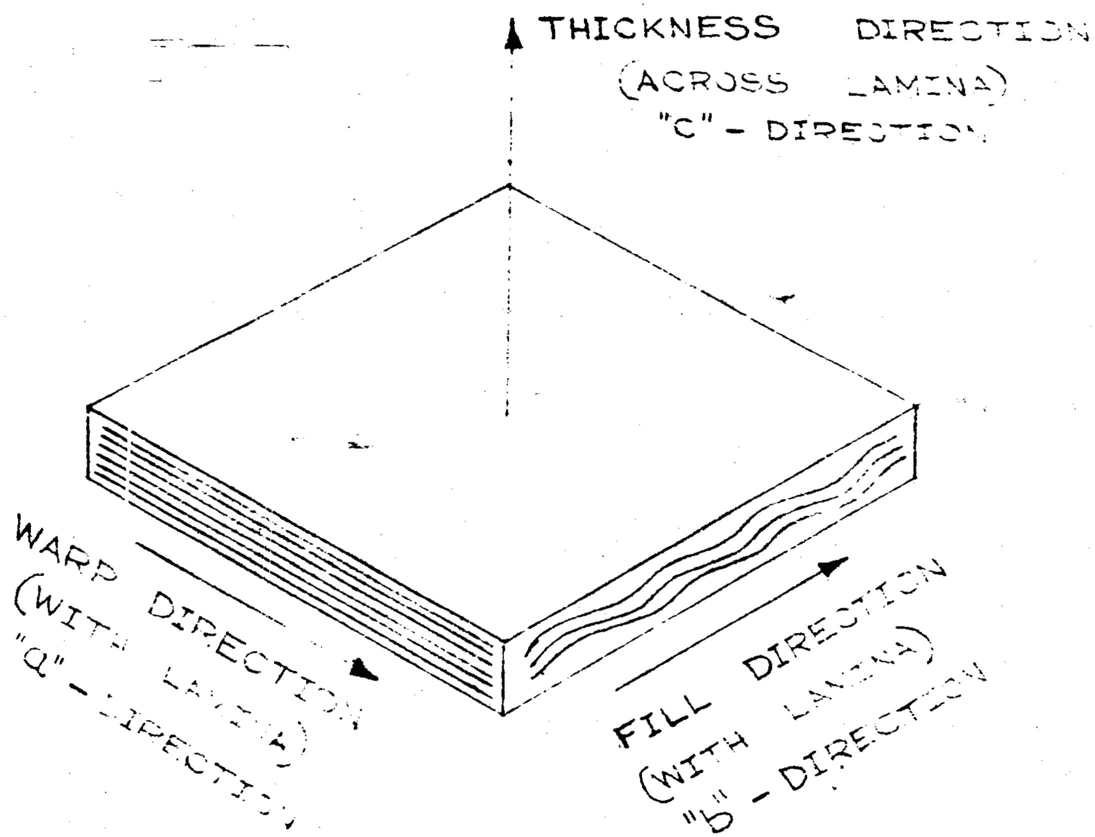


FIGURE 9

SKETCH OF DIRECTIONS OF HEAT FLOW



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