

AD-A046 294

NAVAL SURFACE WEAPONS CENTER WHITE OAK LAB SILVER SP--ETC F/6 11/4
THE EFFECT OF MOISTURE ON CARBON FIBER REINFORCED COMPOSITES. I--ETC(U)
JUN 77 J M AUGL, A E BERGER

UNCLASSIFIED

NSWC/WOL/TR-77-13

NL

| OF |
AD
A046294



END
DATE
FILMED
12-77
DDC

AD A 046294

NSWC/WOL TR 77-13

12

J

THE EFFECT OF MOISTURE ON CARBON
FIBER REINFORCED COMPOSITES. III
PREDICTION OF MOISTURE SORPTION
IN A REAL OUTDOOR ENVIRONMENT

BY J. M. AUGL
A. E. BERGER

RESEARCH AND TECHNOLOGY DEPARTMENT

14 JUNE 1977

AD No. _____
DDC FILE COPY

DDC
RECEIVED
NOV 14 1977
A



NAVAL SURFACE WEAPONS CENTER

Dahlgren, Virginia 22448 • Silver Spring, Maryland 20910

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NSWC/WOL/TR-77-13	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Effect of Moisture on Carbon Fiber Reinforced Composites. <u>III</u> . Prediction of Moisture Sorption in a Real Outdoor Environment.		5. TYPE OF REPORT & PERIOD COVERED
6. PERFORMING ORG. REPORT NUMBER		8. CONTRACT OR GRANT NUMBER(s)
7. AUTHOR(s) J ^{SRP} M./Augl A ^{SRP} E./Berger	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61153N; WR02204; WR0220401; WR31AA;	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Surface Weapons Center White Oak Laboratory White Oak, Silver Spring, Maryland 20910	12. REPORT DATE 14 June 1977	13. NUMBER OF PAGES 46
11. CONTROLLING OFFICE NAME AND ADDRESS Rept. for 1 May - 30 Sep 76,	15. SECURITY CLASS. (of this report) Unclassified	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 1254p.	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Carbon Fiber Composites Environmental Effect Outdoor Modelling Moisture Effects		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Two methods are described to model the moisture uptake and internal distribution in fiber reinforced organic composites in real outdoor environments. Required for the calculations are the diffusion coefficients of the composites as a fraction of temperature and the moisture equilibrium concentration as a function of relative humidity. The effect of moisture barriers is briefly discussed.		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

391 596

LB

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)



SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

NSWC/WOL/TR 77-13

14 June 1977

The Effect of Moisture on Carbon Fiber Reinforced Composites.
III Prediction of Moisture Sorption in a Real Outdoor Environment.

The high cost of modern weapons systems force increasingly stringent requirements on structural integrity and durability of new military hardware. Prediction of durability in storage and service environments requires therefore an increase in sophistication which necessitates a strong interaction between experiment and analysis.

This report is Part III of an investigation into the moisture effects in carbon fiber reinforced epoxy composites. Specifically, it deals with the prediction of moisture sorption and internal distribution in these composites in some real natural environments. Such knowledge is essential for the analysis and prediction of mechanical property changes.

This program was funded by the Naval Air Systems Command Task No. A3200000010123 during the period of May 1, to September 30, 1976.

J. R. Dixon, acting
J. R. DIXON
By direction

SEARCHED BY	
RTS	DATE SEARCHED <input checked="" type="checkbox"/>
ED	DATE SERIALIZED <input type="checkbox"/>
CLASSIFIED	<input type="checkbox"/>
INDEXED	<input type="checkbox"/>
BY <i>8</i>	
DEPARTMENT/AVAILABILITY CODE	
ORG	FILE NO. & PAGE
<i>A</i>	

CONTENTS

	Page
INTRODUCTION.....	5
EXPERIMENTAL.....	5
DISCUSSION.....	5
A. Prediction of Moisture Absorption and Internal Moisture Distribution in Organic Materials.....	6
B. Solution of the Diffusion Equation by a Temperature and Humidity Averaging Procedure.....	7
C. Solution of the Diffusion Equation by a Finite Difference Method.....	13
D. Eight Categories of Climatic Conditions.....	15
E. Limitation of the Averaging Procedure.....	16
F. Additional Corrections for Exposure to Direct Sun Radiation.....	19
G. Effect of Coatings as a Moisture Barrier.....	20
H. Engineering Examples.....	22
I. Expansion to other Organic Materials and to Military Hardware in Service Environment.....	24
CONCLUSIONS.....	25
ACKNOWLEDGEMENT.....	25
Symbols.....	26
Appendix A.....	A-1

TABLES

Table	Title	Page
1	Average and Kinetic Average Temperature and Humidity Conditions and Kinetic Average Diffusion Coefficients of Narmco 5208/T300 Carbon Fiber Composite for the Eight Climatic Categories.....	11
2	A Comparison of the T_{kav} , RH_{kav} , F_T and F_{RH} values of Narmco 5208/T300 CF Composite and Nylon 612.....	12
3	Relative change of the rate of diffusion of moisture through (or into) a composite plate (q_1/q_2) as a function of relative coating thickness and permeability ratios.....	23
4	Month by month kinetic average moisture solubility and diffusion coefficient from weather data at Washington, D.C.....	18

ILLUSTRATIONS

Figure	Title	Page
1	EQUILIBRIUM CONCENTRATION OF MOISTURE IN NARMCO 5208 RESIN AS A FUNCTION OF TEMPERATURE AND RELATIVE HUMIDITY	28
2	ARRHENIUS PLOT OF MOISTURE DIFFUSION INTO HMS FIBER COMPOSITES (DETERMINED AT 33% RH)	29
3	CONCENTRATION DISTRIBUTION (MASTER PLOT) AT VARIOUS TIMES IN THE SHEET $-h < x < h$ WITH INITIAL UNIFORM CONCENTRATION C_0 AND SURFACE CONCENTRATION C_1 . NUMBERS ON CURVES ARE VALUES OF Dt/h^2 .	30
4	PLOT OF FRACTIONAL ABSORPTION OF ANY MATERIAL WITH FICKEAN BEHAVIOR VERSUS $(Dt/h^2)^{1/2}$ FOR PLATE GEOMETRY	31
5	AREAS OF OCCURRENCE OF CLIMATIC CATEGORIES	32
6	PERCENT MOISTURE UPTAKE OF A SIX PLY NARMCO 5208/T300 ($V_f = .7$) CARBON FIBER COMPOSITE CALCULATED FOR WASHINGTON, D.C. CLIMATIC CONDITION. (SOLID LINE: 3 HOURLY WEATHER DATA, *: FROM MONTHLY AVERAGES). THE 3-YEARLY CYCLE WAS REPEATED	33
7	PERCENT MOISTURE UPTAKE OF 6, 12, 18, 24, 30, 36, 42, AND 48 PLY 5208/T300 CF COMPOSITES (WASHINGTON, D.C. CONDITIONS). SMOOTH LINE: FROM 3-YEARLY AVERAGES (T_{kav} , RH_{kav}). FLUCTUATING LINE: FROM MONTHLY AVERAGES	34
8	PERCENT MOISTURE UPTAKE IN A 6 PLY NARMCO 5208/T300 CARBON FIBER COMPOSITE CALCULATED FOR WASHINGTON, D.C. CLIMATIC CONDITIONS (MONTHLY AVERAGES). STARTED AT VARIOUS TIMES OF THE YEAR	35
9	PERCENT MOISTURE UPTAKE IN AN 18 PLY NARMCO 5208/T300 CF COMPOSITE CALCULATED FOR WASHINGTON, D.C. CLIMATIC CONDITIONS (MONTHLY AVERAGES). STARTED AT VARIOUS TIMES OF THE YEAR	36
10	INTERNAL MOISTURE DISTRIBUTION IN A 6 PLY 5208/T300 COMPOSITE ($V_f = 0.7$) AFTER VARIOUS EXPOSURE TIMES, COMPUTED BY USING MONTHLY AVERAGES (SOLID LINES) AND 3-HOURLY READINGS (POINTS)	37
11	INTERNAL MOISTURE DISTRIBUTION IN A 6 PLY 5208/T300 COMPOSITE ($V_f = 0.7$) AFTER VARIOUS EXPOSURE TIMES, COMPUTED BY USING MONTHLY AVERAGES (SOLID LINES) AND 3 YEAR AVERAGE (POINTS)	38
12	INTERNAL MOISTURE DISTRIBUTION IN A NARMCO 5208/T300 CF COMPOSITE (36 PLYS) (WASHINGTON, D.C.) AFTER 1, 2, 3, 7, 8, 9, 15, 16, AND 17 YEARS (SOLID LINES: MONTHLY AVERAGES, POINTS: 3 YEARLY AVERAGES)	39

ILLUSTRATIONS (CONT)

Figure	Title	Page
13	TEMPERATURE VARIATION OF CF COMPOSITES UNDER DIRECT AND INDIRECT EXPOSURE TO SUN RADIATION; UNPAINTED, PAINTED, AND BONDED TO AN ALUMINUM FOIL, ON A CLEAR SUNNY DAY WITH SCATTERED CLOUDINESS; CLEAR AIR (AUG 20, 1976)	40
14	TEMPERATURE VARIATION OF COMPOSITES ON A CLEAR SUNNY BUT WINDY DAY (AUG 19, 1976)	41
15	TEMPERATURE VARIATION OF CF COMPOSITES ON A HOT, HUMID, HAZY DAY (AUG 25, 1976)	42
16	TEMPERATURE VARIATION OF CF COMPOSITES ON A CLOUDY AND RAINY DAY (AUG 27, 1976)	43
17	TIME TO REACH VARIOUS LEVELS OF THE RESPECTIVE EQUILIBRIUM CONCENTRATIONS AS A FUNCTION OF NUMBERS OF PLYS OF NARMCO 5208/T300 ($V_f = .70$) (THE THICKNESS IN CM IS OBTAINED BY MULTIPLYING THE PLY NUMBER WITH .01397)	44
18	SAMPLE COMPUTER OUTPUT	45
19	SAMPLE COMPUTER OUTPUT	46

INTRODUCTION

A commitment has been made by the Navy to use carbon fiber reinforced composites in future Naval aircraft as structural materials. Stringent requirements on structural integrity and durability prior to aircraft production provide further impetus to fuller understanding and resolution of the moisture/thermal environmental effects and their prediction in a real service environment.

This report is Part III of an investigation into the effects that moisture has on carbon fiber reinforced epoxy composites. In Part I and Part II we discussed diffusion, and changes in the matrix dominated strength properties as a function of the combined effect of moisture concentration and temperature. This report discusses the prediction of moisture uptake as a function of time and the corresponding internal distribution in carbon fiber composites in a real outdoor or service environment. Such knowledge is essential for the analysis of the concomitant changes in the elastic properties which will be discussed in a forthcoming report, and we also believe that it is essential for a theoretical explanation and prediction of the reversible strength degradation.

EXPERIMENTAL

For the experimental measurements of the moisture equilibrium concentrations in the composite matrix as a function of relative humidity and for the measurements of composite diffusion coefficients as a function of temperature, we refer to Part I of this report [1].

DISCUSSION

The subject to be discussed here is the diffusion, uptake, and internal distribution of moisture in a composite exposed to real outdoor environments under service and storage conditions. Other degradative mechanisms such as UV radiation damage or thermal spiking and mechanical fatigue will not be considered. There is no doubt that these latter degradation mechanisms may be superimposed in real service environments, and cannot be neglected; however, these

[1] J. M. Augl and A. E. Berger, "The Effect of Moisture on Carbon Fiber Reinforced Composites. I Diffusion." NSWC/WOL TR 76-7

mechanisms depend more on the structural application and have to be ascertained independently. We are presently investigating the effect that thermal and mechanical cycling has on the diffusion of moisture into the composite. These results shall be reported at a later date.

Also, the analysis of the effect that moisture (and its internal distribution) has on composite elastic constants will be discussed in a forthcoming report. The knowledge of the internal moisture distribution, however, is essential for such an analysis.

A. Prediction of Moisture Absorption and Internal Moisture Distribution In Organic Materials.

If one would know exactly the future environmental history of a given composite element, one could predict with a high degree of certainty what the moisture level and internal distribution of moisture would be at any time. All that is required is to solve Fick's second equation (1)

$$\frac{\partial c}{\partial t} = D_1 \left(v_f, T, c \right) \frac{\partial^2 c}{\partial \xi^2} + D_2 \left(v_f, T, c \right) \frac{\partial^2 c}{\partial \eta^2} + D_3 \left(v_f, T, c \right) \frac{\partial^2 c}{\partial \zeta^2} \quad (1)$$

Where c = concentration, t = time, and D_1, D_2, D_3 are the principal diffusion coefficients, the magnitude and direction of which are described by a rotational ellipsoid. As we have stated in Part I of this report the diffusion coefficients (D_1, D_2, D_3) depend on the volume fraction (v_f), on the temperature, and perhaps on the moisture concentration (depending on the matrix).

For a composite plate, where the edge effects can be ignored, equation (1) reduces to the one dimensional equation (2).

$$\frac{\partial c}{\partial t} = D_z \left(v_f, T, c \right) \frac{\partial^2 c}{\partial z^2} \quad (2)$$

where D_z is the diffusion coefficient vertical to the composite plane.

The boundary conditions are assumed such that moisture penetrates from both sides of the sheet, i.e., the concentration on the surface of the composite is equal to the solubility (= equilibrium concentration) of moisture in the composite, and the initial interior moisture distribution is known.

In a real outdoor environment the boundary conditions change continuously because the relative humidity (RH) changes. And, since the equilibrium concentration changes with the partial pressure

of moisture in the air so does the surface concentration on the sheet. Over a daily or seasonal RH cycle there will be absorption and desorption, but, the long-term net effect will be an absorption till equilibrium has been reached with the surroundings. Therefore, we can say that the final moisture equilibrium depends on some kind of RH average.

Also, the temperature changes continuously and so does the corresponding diffusion coefficient, which may be described by an Arrhenius equation

$$D = D_0 \exp (-E/RT) \quad (3)$$

where D_0 is a constant, E is the activation energy of diffusion, R is the ideal gas constant and T is the absolute temperature in $^{\circ}\text{K}$.

Assuming that we have experimentally determined the moisture equilibrium concentration as a function of RH and temperature (as in Figure 1) and the diffusion coefficient (as a function of temperature as in Figure 2, and if necessary, as a function of concentration), and, that we know what the environment will be (or has been), we are now in a position to calculate the moisture absorption and internal moisture distribution as a function of time.

The problem can be solved in two ways:

- a) by some averaging of temperature and humidity conditions
or
- b) by a finite difference approach where the environmental temperature and humidity changes are introduced in discrete finite time intervals and by solving the diffusion equation (which has been converted to a finite difference equation).

Both procedures will be described in some detail in the following.

B. Solution of the Diffusion Equation by a Temperature and Humidity Averaging Procedure.

- a) Series Solution.

If the RH and the temperature in the environment had the known constant values $C_1 = M(\text{RH}_1)$, and the initial moisture distribution had the uniform value C_0 , then the moisture uptake and internal distribution would be given immediately by equations (4a and 4b) [2].

[2] J. Crank, "Mathematics of Diffusion" Oxford (1956).

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[-D(2n+1)^2 \pi^2 t / 4h^2 \right] \quad (4a)$$

$$\frac{C-C_0}{C_1-C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \exp \left[-D(2n+1)^2 \pi^2 t / 4h^2 \right] \cos \frac{(2n+1)\pi x}{2h} \quad (4b)$$

where M_t = amount of moisture absorbed after a time t ; M_∞ amount of moisture absorbed after an infinite time, i.e., equilibrium concentration or solubility; h = half of the thickness of the composite sheet, and D corresponding to T_1 .

Figure 3 shows a reproduction of the solution from reference [2], in dimensionless coordinate. $X/h = 0$ corresponds to the composite midplane, and $(C-C_0)/(C_1 - C_0) = 1$ corresponds to the constant surface concentration in equilibrium with the surrounding RH. The $(Dt/h^2)^{1/2}$ parameter gives a master curve (Figure 4) which holds for all materials following Fickian diffusion. If M_t and M_∞ is replaced by the percent moisture concentration after time t and by the equilibrium percentage concentration respectively, one obtains directly the moisture uptake (in %) as a function of time and the problem is solved.

If we knew the "right" temperature and humidity averages of an environment where temperature and humidity changes continuously, we would also have the average solution for such an environment.

In other words the "right" averages T_{kav} and RH_{kav} are those that would give the "same" results had the composite been exposed to constant weather conditions with temperature = T_{kav} and humidity = RH_{kav} .

From inspection of equation (3) we see that one cannot use the arithmetic average temperature T_{av} since the diffusion coefficient is exponentially dependent on the temperature, i.e., for a given temperature cycle the diffusion rates at the higher temperatures, $T > T_{av}$, are more dominant than those at the lower temperatures $T < T_{av}$. Therefore, one has to use an average diffusion coefficient which is obtained by converting the temperature curve to a diffusion coefficient curve of which the average integral value (D_{kav}) is used for the calculation. (D_{kav} will be called the kinetic average diffusion coefficient and the corresponding temperature T_{kav} will be called the kinetic average temperature.) From equation (3) it is also easily seen that, the larger the temperature fluctuation is, the more is the deviation of T_{kav} from T_{av} , and T_{kav} is always larger or equal to T_{av} .

In a similar way we can show that it is not permissible to use the arithmetic average of the relative humidity cycle since the RH values over a daily cycle are generally lowest when the temperatures are highest, i.e., in a sample with a uniform internal distribution corresponding to the arithmetic average humidity there would be a higher rate of desorption during the hot part of the cycle than absorption during the cold part, thus there would be a net desorption. On the other hand, the rate of diffusion depends also on the concentration gradient, which is highest during the cold part of the cycle. This effect may be even more pronounced if the equilibrium concentration increases non linearly at high relative humidities (>85% RH). The determination of RH_{kav} will be discussed below under b.

Thus, one can establish correction factors F_T and F_{RH} for the temperature and relative humidity, which, multiplied with the arithmetic average temperature and humidity gives the kinetic average temperature and humidity respectively. The higher the temperature fluctuation over a daily or seasonal cycle the larger are F_T and F_{RH} . F_T and F_{RH} will therefore be material constants for a specific climatic (geographic) area (or, more generally, of a military hardware service cycle in a given geographic area).

These factors (F_T and F_{RH}) can be easily determined for various geographic locations or for climatic categories from meteorological data and now it becomes very easy, for engineering purposes, to estimate moisture absorption in organic materials without the use of high speed computers. (An example of such an engineering problem is described in reference [3])

b. Determination of F_T and F_{RH}

Since T_{av} and RH_{av} can be readily obtained from almanacs or encyclopedias, the knowledge of F_T and F_{RH} for various climatic categories may be all that is required for estimates in engineering diffusion problems for outdoor conditions.

For the composite material under consideration it is assumed that for any temperature value T one can obtain the corresponding diffusion coefficient for moisture $D = D(T)$ (e.g., from equation (3)), and, for each relative humidity value H , one can obtain the corresponding solubility (equilibrium percent by weight moisture) $M = M(H)$ (e.g., by interpolation of tabulated experimental values). We present an averaging procedure for obtaining values for T_{kav} and RH_{kav} given 8 evenly spaced temperature and relative humidity readings over a 24-hour period. The values of T_{kav} and RH_{kav} will, of course, depend on the material being considered; specifically they will depend

[3] J. M. Augl "Prediction of Moisture Absorption in the 5"54 HIFRAG Discarding Rotating Band for Various Climatic Environments." NSWC/WOL/TR 76-167

on the functional relationships $D(T)$ and $M(H)$. From the description of this case it should be clear how to apply this procedure to average any tabulated weather data (such as data at 1-hour or 3-hour intervals over a month or a year).

Let the 8 temperature and humidity values be denoted by T_1, T_2, \dots, T_8 and by H_1, H_2, \dots, H_8 , respectively. Let \bar{D} be a fixed positive number (for example, set $\bar{D} = D(293.15 \text{ }^\circ\text{K})$) and let \bar{T} be the temperature corresponding to \bar{D} (so $D(\bar{T}) = \bar{D}$). Now the change in moisture concentration throughout a composite plate after 3 hours of being at temperature T and whose surface during this time is maintained at moisture concentration $M(H)$ is exactly equal the change in moisture concentration throughout the same plate after $3 D(T)/\bar{D}$ hours of being at the temperature \bar{T} and whose surface during this time is maintained at moisture concentration $M(H)$. This follows quickly from changing the time scale in the diffusion equation $M_t = DM_{xx}$ (since if $\tau \equiv D(T)t/\bar{D}$ then $M_\tau = \bar{D}M_{xx}$).

Thus one can approximate the effect of the weather data given by the eight 3-hourly readings T_i, H_i ($i=1, \dots, 8$) by the following: let the composite be exposed for $\tau_1 \equiv 3D(T_1)/\bar{D}$ hours at temperature \bar{T} with surface moisture concentration $M(H_1)$, followed by exposure for $\tau_2 \equiv 3D(T_2)/\bar{D}$ hours at temperature \bar{T} with surface moisture concentration $M(H_2)$, and so on, ending with exposure for $\tau_8 \equiv 3D(T_8)/\bar{D}$ hours at temperature \bar{T} with surface moisture concentration $M(H_8)$. We approximate the latter situation by the case where the composite is exposed for $\tau \equiv (\tau_1 + \tau_2 + \dots + \tau_8)$ hours at temperature \bar{T} and with surface moisture concentration

$$M_{kav} \equiv (\tau_1 M(H_1) + \tau_2 M(H_2) + \dots + \tau_8 M(H_8)) / \tau. \quad (5)$$

As explained above, exposure for τ hours at temperature \bar{T} and with surface moisture concentration M_{kav} is exactly equivalent to exposure for 24 hours with diffusion coefficient

$$D_{kav} \equiv \bar{D} \cdot \tau / 24 \quad (6)$$

and with surface moisture concentration M_{kav} . Let T_{kav} be the temperature corresponding to D_{kav} (so $D_{kav} = D(T_{kav})$) and let RH_{kav} be the relative humidity corresponding to M_{kav} (so $M_{kav} = M(RH_{kav})$). Then exposure of the composite material to the weather data $\{T_i, H_i\}$ may be approximated by the situation of exposure to the constant weather condition temperature = T_{kav} , relative humidity = RH_{kav} for the same time period (which in this example was 24 hours). Numerical results obtained using this procedure are given in Tables 1 and 2.

Table 1. Average and Kinetic Average Temperature and Humidity Conditions and Kinetic Average Diffusion Coefficients of Narmco 5208/T300 Carbon Fiber Composite for the Eight Climatic Categories^a

Cat	Time of day	0	3	6	9	12	15	18	21	24	T _{av}	T _{kav}	(F _T) Factor	RH _{av}	RH _{kav}	(F _{RH}) Factor	D _{kav}
1	RH	100	100	100	95	95	95	100	100	100	75.0	75.0	1.00	97.5	97.5	1.00	3.93 E-9
	OF	nearly constant at 75°															
1'	RH	100	100	100	95	95	95	100	100	100	80.0	80.0	1.00	97.5	97.5	1.00	4.73 E-9
	OF	nearly constant at 80°															
2	RH	100	100	100	82	75	74	82	95	100	85.7	86.3	1.006	88.5	86.8	.981	5.98 E-9
	OF	80	79	78	87	94	95	90	83	80							
2'	RH	75	80	84	74	30	10	35	59	75	119.6	127.6	1.066	55.9	38.4	.687	2.42 E-8
	OF	98	94	91	117	150	160	142	105	98							
3	RH	82	90	79	66	63	64	68	75	82	93.5	93.9	1.004	73.4	72.4	.987	7.80 E-8
	OF	89	86	88	97	100	100	96	92	89							
3'	RH	75	80	84	74	30	10	35	59	75	119.6	127.6	1.066	55.9	38.4	.687	2.42 E-8
	OF	98	94	91	117	150	160	142	105	98							
4	RH	15	17	19	12	7	5	7	10	15	105.2	107.0	1.016	11.5	9.9	.864	1.24 E-8
	OF	95	94	91	101	115	125	116	105	95							
4'	RH	46	50	30	8	2	14	33	41	28	119.6	127.6	1.066	28	16.5	.589	2.42 E-8
	OF	98	94	91	117	150	160	142	105	98							
5	RH	72	85	83	63	28	23	36	54	72	87.9	90.5	1.030	55.5	46.2	.833	7.04 E-9
	OF	75	71	73	90	106	109	96	83	75							
5'	RH	41	46	50	30	10	5	14	33	41	106.4	116.0	1.109	28.6	17.4	.609	1.71 E-11
	OF	75	71	73	117	135	145	135	100	75							
6	RH	close to 100												100	100	1.000	7.00 E-11
	OF	-24	-25	-15	-5	-6	-6	-13	-19	-24	-16.5	-15.2	.923	100	100	1.000	4.45 E-11
6'	RH	close to 100												100	100	1.000	4.45 E-11
	OF	-29	-30	-30	-28	-19	-13	-20	-26	-29	-24.4	-23.6	.967	100	100	1.000	4.45 E-11
7	RH	close to 100												100	100	1.000	1.44 E-11
	OF	-49	-50	-50	-45	-35	-35	-39	-45	-49	-43.5	-42.6	.979	100	100	1.000	1.44 E-11
7'	RH	close to 100												100	100	1.000	1.44 E-11
	OF	-49	-50	-50	-45	-35	-35	-39	-45	-49	-43.5	-42.6	.979	100	100	1.000	1.44 E-11
8	RH	close to 100												100	100	1.000	3.24 E-12
	OF	-69	-70	-70	-69	-61	-60	-63	-66	-69	-66	-65.6	.993	100	100	1.000	3.24 E-12
8'	RH	close to 100												100	100	1.000	3.24 E-12
	OF	-69	-70	-70	-69	-61	-60	-63	-66	-69	-66	-65.6	.993	100	100	1.000	3.24 E-12

a) The first two lines in each category are the storage and the following 2 lines are the operational conditions (from AR-70-38). The D_{kav} refer to Narmco 5208/T300 CF composite (calculated from the experimentally determined diffusion coefficients).

Table 2. A Comparison of the T_{kav} , RH_{kav} , F_T and F_{RH} values of Narmco 5208/T300 CF Composite and Nylon G12.

Category	Narmco 5208/T300				Nylon 612			
	T_{kav}	F_T	RH_{kav}	F_{RH}	T_{kav}	F_T	RH_{kav}	F_{RH}
1	75.0	1.000	97.5	1.000	75.0	1.000	97.5	1.000
1'	80.0	1.000	97.5	1.000	80.0	1.000	97.5	1.000
2	86.3	1.006	86.8	.981	86.4	1.007	90.5	1.023
2'	127.6	1.066	38.4	.687	128.8	1.076	37.5	.672
3	93.9	1.004	72.4	.987	93.9	1.004	73.2	.997
3'	127.6	1.066	38.4	.687	128.8	1.076	37.5	.672
4	107.0	1.016	9.9	.864	107.2	1.019	9.7	.846
4'	127.6	1.066	16.5	.589	128.7	1.076	15.2	.541
5	90.5	1.030	46.2	.833	90.9	1.035	46.9	.845
5'	116.0	1.091	17.4	.609	117.3	1.103	16.4	.572
6	-15.2	.923	100	1.000	-15.0	.912	100	1.000
6'	-23.6	.967	100	1.000	-23.4	.961	100	1.000
7'	-42.6	.979	100	1.000	-42.5	.976	100	1.000
7''	-42.6	.979	100	1.000	-42.5	.976	100	1.000
8'	-65.6	.993	100	1.000	-65.5	.993	100	1.000
8''	-65.6	.993	100	1.000	-65.5	.993	100	1.000

c. Solution of the Diffusion Equation by a Finite Difference Method.

From meteorological stations one can obtain weather data (including temperature, RH, wind and sky conditions) in three-hourly intervals over many years on magnetic tapes. These data are quite suitable to be read directly by a high speed computer and can be used to solve the diffusion equation by a finite difference method in discrete three-hourly time steps over a period of several years, and assuming that such a multi-year weathercycle remains the same in the average if one takes multiples of it, the process can be repeated as often as necessary to obtain the final answer.

The finite difference method can, as well, be used to solve the diffusion equation when monthly or seasonal or yearly kinetic average temperatures and relative humidities have been obtained. The boundary data and diffusion coefficient in the moisture diffusion equation are then changed only every month (or season or year) instead of every three hours, and hence the numerical solution procedure takes much less computer time. In the case of Narmco 5208/T300 epoxy composites it will be seen that the results of 3-hourly data can be excellently approximated using monthly averages even with a relatively thin composite thickness (Figure 6).

We now describe the finite difference method used to solve the diffusion equation for moisture in a plate of composite material with thickness $2h$. The diffusion equation is

$$M_t = (D(t)M_x)_x \quad \text{for } 0 \leq x \leq 2h, t > 0$$

where $M(x,t)$ denotes the percent by weight of moisture in the composite (at location x and at time t), and D is the diffusion coefficient. Since D depends on temperature, and the variation of the temperature with time is assumed to be given, one may consider D to be directly a function of time. Both surfaces of the composite plate are assumed to be exposed to the same relative humidity conditions, so the moisture concentration $M(t,x)$ in the plate will be symmetric about the midplane $x=h$, and it is thus sufficient to solve the following diffusion problem:

$$M_t = (D(t)M_x)_x \quad \text{for } 0 \leq x \leq h, t > 0 \quad (7a)$$

$$M(x,t=0) = M^0(x) \quad \text{for } 0 \leq x \leq h \quad (7b)$$

$$M(x=0,t) = g(t) \quad \text{and} \quad M_x(x=h,t) = 0 \quad \text{for } t > 0 \quad (7c)$$

where the subscripts t and x symbolize partial differentiation with respect to time and direction vertical to the plane of the plate, and where $M^0(x)$ is the given initial moisture concentration within the plate (generally $M^0 \equiv 0$), and $g(t)$ is the known surface moisture concentration which is equal to the solubility of moisture in the composite corresponding to the (given) relative humidity at time t . The values $D(t)$ and $g(t)$ are determined from the given weather data (or from T_{kav} and RH_{kav} values which were obtained from the weather data).

The diffusion problem (7) can be solved numerically, using the standard implicit finite difference method which is described below. Let I be a positive integer, define $x_0=0$ and $x_I=h$, and pick points x_1, \dots, x_{I-1} such that $x_0 < x_1 < \dots < x_{I-1} < x_I$. For $i=1, \dots, I$ define $\Delta_i = x_i - x_{i-1}$, and choose a time step Δt . Let N denote the number of time steps to be taken (the final time at which an approximation to the moisture concentration in the composite is obtained is then $N \cdot \Delta t$). The numerical solution value approximating $M(x_i, n \cdot \Delta t)$ will be denoted by M_i^n (for $i=0, \dots, I$ and $n=0, \dots, N$). Define $M_i^0 = M^0(x_i)$ for $i=0, \dots, I$, and define $M_0^n = g(n \cdot \Delta t)$ for $n=0, \dots, N$. If values M_i^n , $i=0, \dots, I$, have been obtained approximating the moisture concentration in the plate at time $t^n \equiv n \cdot \Delta t$, then the approximate solution values M_i^{n+1} approximating the moisture profile at the next time level $t^{n+1} \equiv (n+1) \Delta t$ can be obtained by solving the following linear system of I equations:

$$\frac{M_i^{n+1} - M_i^n}{\Delta t} = \frac{2D(t^{n+1})}{\Delta_i + \Delta_{i+1}} \left[\frac{M_{i-1}^{n+1}}{\Delta_i} - \left(\frac{1}{\Delta_i} + \frac{1}{\Delta_{i+1}} \right) M_i^{n+1} + \frac{M_{i+1}^{n+1}}{\Delta_{i+1}} \right]$$

for $i = 1, \dots, I-1$ (8a)

and

$$\frac{M_i^{n+1} - M_i^n}{\Delta t} = \frac{2D(t^{n+1})}{\Delta_i^2} (M_{i-1}^{n+1} - M_i^{n+1}) \text{ at } i=I$$

(8b)

Note that (8b) results from defining $M_{I+1}^{n+1} = M_{I-1}^{n+1}$ and $\Delta_{I+1} = \Delta_I$ and letting $i=I$ in (8a). The average percent by weight moisture in the composite at a given time t^n is defined to be

$$\frac{1}{h} \int_0^h M(x, t^n) dx$$

(9)

and was numerically approximated by

$$\frac{1}{h} \sum_{i=1}^I \left(\frac{M_{i-1}^n + M_i^n}{2} \right) \Delta_i. \quad (10)$$

Further details on the numerical method, including choices of the spatial mesh (Δ_i) and the time step (Δ_t) and the method of solution of the linear equations (8) are given in Appendix A.

D. Eight Categories of Climatic Conditions

Guidelines for realistic considerations of climatic conditions in research, development, test and evaluation have been published by the Army under Army Regulation AR 70-38, July 1969. This report divided the earth's climatic conditions into eight climatic categories:

- Category 1, wet-warm
- Category 2, wet-hot
- Category 3, humid-hot coastal desert
- Category 4, hot-dry
- Category 5, intermediate hot-dry
- Category 6, intermediate cold
- Category 7, cold
- Category 8, extreme cold

A reproduction of the world map indicating these climatic areas from AR 70-38 is shown in Figure 5. For all categories, a representative daily temperature and humidity cycle is given for "operational" and "storage and transit" conditions. We have calculated the D_{kav} and RH_{kav} of Narmco 5208/T300 for all eight categories for the operational and storage conditions (Table 1) and compared these values with the D_{av} values corresponding to the average temperature (T_{av}) and the average relative humidity RH_{av} . The ratios of these values give the F_T and F_{RH} factors. The way these correction factors should be used is to look up the yearly temperature and humidity averages of a particular environment, then determine to which climatic category it will belong. Then the averages are multiplied by the corresponding F_T and F_{RH} factors. The T_{kav} and RH_{kav} values thus obtained are used as pseudo constant temperature and humidity conditions.

It should be remembered that the F_T and F_{RH} factors depend on the climatic condition and on the material (i.e., on the slope of the $\log D$ vs. $1/T$ curve and on the equilibrium concentration curve). The effect of the climatic category on these factors, however, is much more pronounced, as can be seen from Table 2 where we compared the T_{kav} , RH_{kav} and the F_T and F_{RH} of Narmco 5208/T300 CF composite with Nylon 612 which is a totally different material.

The T_{kav} can be considered equal for all practical purposes, but also the RH_{kav} 's are surprisingly close. It appears therefore that these F_T and F_{RH} correction factors can be used for moisture diffusion problems in most organic materials as a first approximation. In tropical areas, such as the Panama Canal Zone, there is little difference between seasons, and the temperature fluctuations between day and night are so small that $T_{kav} \approx T_{av}$ and $RH_{kav} \approx RH_{av}$.

E. Limitation of the Averaging Procedure

a) Moisture Absorption.

An averaging procedure may, by its very nature, be insensitive to fluctuations. The fluctuations in moisture content, caused by seasonal temperature and humidity changes in the environment, are obviously stronger in thin composite plates than in thick ones. While a calculation using variable boundary conditions at short time intervals will give realistic fluctuations in moisture uptake, an averaging procedure will give only smooth curves.

Examples are given in Figures 6 and 7. Figure 6 shows a computer printout of moisture uptake for a 6-ply Narmco 5208/T300 composite laminate if it had been exposed at Washington, D.C., under climatic condition between 1972 to 1975 (this 3 yearly cycle was repeated).

The solid line was obtained by supplying the computer with 3 hourly temperature and humidity data and the stars represent an averaging over each month of the year.

One can see that an averaging over monthly periods is almost as good as 3-hourly data inputs. It requires however considerably less computer time.

The repeat cycle of 36 months is clearly visible which reflects that there are visible differences also in the yearly climatic changes.

The thicker the composite, the less pronounced are these fluctuations as shown in Figure 7. These curves show the moisture uptake of 6, 12, 18, 24, 30, 36, 42 and 48 ply laminates (.01397 cm per ply).

The smooth curves were obtained by using a 3-yearly average while the oscillating curves were obtained from monthly averages.

For 24-ply laminates it is quite sufficient to use long-term average data of T_{kav} and RH_{kav} .

Also, as one might expect in temperate zones the largest amount of moisture is absorbed during the summer months, where the average temperatures are highest. Figures 8 and 9 show computer printout for 6- and 18-ply laminates respectively if such composites would

have been exposed starting with January, May and September 1972. Such details can, of course, not be observed if yearly averages would have been used. These differences are significant only during the initial moisture uptake.

b) Internal Moisture Distribution

Kinetic average temperature and moisture conditions can be used to obtain the time history of the internal moisture distribution within a composite exposed to variable weather conditions. The results of using monthly kinetic averages (see Table 4) to calculate the moisture distribution within 6 plies (half thickness = .04191 cm.) of Narmco 5208/T300 with fiber volume fraction = .7 agree very well with the values obtained by running the corresponding 3 hourly weather data, except (as to be expected) for a thin layer near the surface which reflects what the last several hourly readings happen to have been: see Figure 10 in which the solid lines join the values obtained at the mesh points of the finite difference method used to solve the diffusion problem with month by month kinetic averages, and in which the values obtained when using 3 hourly weather data are plotted as individual points.

For this thin laminate, the result of using the constant moisture boundary condition and diffusion coefficient corresponding to the 3 year kinetic average of the weather data ($M_{kav} = .82975$, $D_{kav} = 5.556E-11$) is not a good approximation to the actual moisture uptake (see Figure 11 in which the lines are as in Figure 10 while the individual points were obtained using the 3 year kinetic average). In both Figure 10 and 11 a solid line is plotted at $.82975 = M_{kav}$, and curves are plotted at 28 and 45 months. When using the monthly kinetic averages, the weather readings for 1972-1974 were continually repeated, and in this thin composite the moisture profiles became virtually 3 year-periodic. After 28 months, the maximum and minimum moisture profiles (when using month by month kinetic averages) occur at 28 and 45 months, respectively, and all other profiles lie in between these two curves.

For a thicker laminate, using the 3 year kinetic average produces a reasonably good approximation (Figure 12). Since the kinetic average was taken over a 3 year period, one would expect the best approximation to occur at 3 year intervals (i.e. at multiples of the period over which the averaging was done). Here the approximation (away from the boundary) at other times is almost as good. In Figure 12 moisture profiles after 1,2,3,7,8,9,15,16, 17 years in 36 plies (half thickness = .25146 cm.) of Narmco 5208/T300 with fiber volume fraction = .7 are given. The lines were obtained using month by month kinetic averages while the points were obtained using the 3 year kinetic average.

TABLE 4

**MONTH BY MONTH KINETIC AVERAGE MOISTURE SOLUBILITY AND DIFFUSION
COEFFICIENT FROM WEATHER DATA AT WASHINGTON, D.C.**

FOR EACH MONTH THE 3-HOURLY WEATHER DATA HAS BEEN CONVERTED (USING THE METHOD DESCRIBED IN THIS REPORT) TO EQUIVALENT AVERAGES FOR EXPOSURE OVER A 30 DAY TIME PERIOD (NARMCO 5208/T300 WITH FIBER VOLUME FRACTION EQUAL .7). THIS EXPOSURE OF THIS COMPOSITE TO THE WEATHER CONDITIONS DURING EACH MONTH IS APPROXIMATELY EQUIVALENT TO EXPOSURE TO THE CORRESPONDING CONSTANT AVERAGE CONDITIONS FOR A DURATION OF 30 DAYS.

MOISTURE SOLUBILITY (PERCENT BY WEIGHT)	DIFFUSION COEFFICIENT (CM*CM/SEC)	YEAR	MONTH
.9005190E+00	.2611587E-10	72	1
.8170750E+00	.2216612E-10	72	2
.7301196E+00	.3353042E-10	72	3
.7390433E+00	.4440660E-10	72	4
.8673660E+00	.6390483E-10	72	5
.9058252E+00	.7338817E-10	72	6
.9161317E+00	.9583120E-10	72	7
.8874992E+00	.9162142E-10	72	8
.9208647E+00	.7537843E-10	72	9
.8424243E+00	.4819722E-10	72	10
.8633999E+00	.3353145E-10	72	11
.9282614E+00	.3015068E-10	72	12
.7630026E+00	.2561955E-10	73	1
.7698729E+00	.2212300E-10	73	2
.8817909E+00	.3985569E-10	73	3
.7904717E+00	.4681851E-10	73	4
.8240859E+00	.6103103E-10	73	5
.8798575E+00	.9069834E-10	73	6
.8175871E+00	.1021234E-09	73	7
.8470329E+00	.1025200E-09	73	8
.8057607E+00	.8409489E-10	73	9
.7716061E+00	.6131747E-10	73	10
.7268787E+00	.4084501E-10	73	11
.8175299E+00	.2918202E-10	73	12
.8410242E+00	.3021490E-10	74	1
.6765142E+00	.2404313E-10	74	2
.6777355E+00	.3797676E-10	74	3
.6732737E+00	.5280847E-10	74	4
.8003374E+00	.6707123E-10	74	5
.8586486E+00	.7733809E-10	74	6
.7585552E+00	.1031040E-09	74	7
.9021245E+00	.9706892E-10	74	8
.8823868E+00	.7521015E-10	74	9
.7683954E+00	.5053943E-10	74	10
.7626207E+00	.3990357E-10	74	11
.63838E+00	.2990110E-10	74	12

F. Additional Corrections for Exposure to Direct Sun Radiation.

So far we have taken temperatures reported in weather data. This would mean that the composite is completely protected from sun (or even sky radiation).

Unpainted carbon fiber composites that are exposed to direct sun radiation can become considerably warmer than the surrounding air temperature, and therefore, the diffusion rate is also higher than one would calculate from the temperatures of the surrounding air. It is important to estimate the error in predicting the moisture absorption in a composite if one only uses the temperature or humidity data from a particular outdoor exposure site.

For this purpose we have exposed four CF-composite panels outdoors.

Each panel was mounted horizontally on a piece of polypropylene foam and had a thermocouple in its center. Three panels were exposed to direct sun radiation (#1 uncoated, #2 painted white, #3 bonded to a thin aluminum foil). One reference sample #4 was shielded from the sun radiation by placing it inside a wooden box, open at the opposite side of the sun. The temperatures were recorded simultaneously (day and night) for several weeks.

Four typical temperature profiles are shown in Figures 13 to 16. These represent a clear sunny day; a clear sunny but windy day; a hot, humid, hazy day; and a cloudy, rainy day.

The observed differences are quite remarkable. The differences in temperature between the unprotected samples covered from and exposed to sun radiation can be 40-50°F. The white painted sample was somewhat cooler than the sample coated on both sides with an aluminum foil. Even the unexposed samples absorbed enough scattered radiation to become slightly warmer than the reference thermocouple not connected to a composite (see Figure 13-16). A clear day with blue sky showed a greater temperature difference than a hazy day. A clear but windy day had a somewhat cooling effect. And the least difference was observed on a cloudy, rainy day.

If one had calculated a kinetic average diffusion coefficient D_{kav} (corresponding to the air temperature), then the calculated amount for the moisture absorption of the sun exposed samples could be off by a factor of 2. Thus an airplane with CF composites inside a hanger or outside on a runway would absorb different amounts of moisture. For refined estimates such correction factor should not be neglected in predicting real environmental effects.

Thus, if unpainted carbon fiber composites are exposed to direct sun radiation, then one also should know the sky conditions and

the fractional times the composite is exposed to these conditions. The diffusion coefficient corrected for sun radiation is given by (11)

$$D_{kavr} = D_{kav} (2.05f_{cs} + 1.64f_{cw} + 1.47f_{hh} + 1.14f_{cr} + f_p) \quad (11)$$

where f_{cs} , f_{cw} , f_{hh} , f_{cr} , and f_p are the fractional times the composite is exposed to clear sunny sky, clear sunny sky but with wind, humid and hazy conditions, cloudy rainy conditions, and fully protected from sun and sky radiation. The constant 2.05, 1.64, etc., were taken from the experimentally determined values for unpainted panels. (It should be remembered that in the D_{kav} values the correction factor for the climatic category is already included.) So that the whole procedure may be shown schematically by

$$\text{look up } \left\{ \begin{array}{c} RH_{av} \\ T_{av} \end{array} \right\} \xrightarrow[\text{climatic category}]{\text{corr. for}} \left\{ \begin{array}{c} RH \times F_{RH} \\ T_{av} \times F_T \end{array} \right\} \rightarrow \left\{ \begin{array}{c} RH_{kav} \\ D_{kav} \end{array} \right\} \xrightarrow[\text{radiation}]{\text{corr. for}} \left\{ \begin{array}{c} RH_{kav} \\ D_{kavr} \end{array} \right\}$$

For storage conditions where only the air temperature governs the materials temperature, this reduces to $D_{kavr} = D_{kav}$.

If the temperature fluctuations over daily and seasonal periods are small, then $D_{kav} = D_{av}$ and $RH_{kav} = RH_{av}$.

G. Effect of Coatings as a Moisture Barrier.

While organic coatings give a definite protection against UV radiation, we do not expect that they will be of great benefit as moisture barriers. Some of the highly fluorinated or chlorinated hydrocarbons such as Teflon, polyvinylidene fluoride, and polyvinylidene chloride may perhaps reduce the rate of moisture permeation into the composite slightly, but will not prevent it.

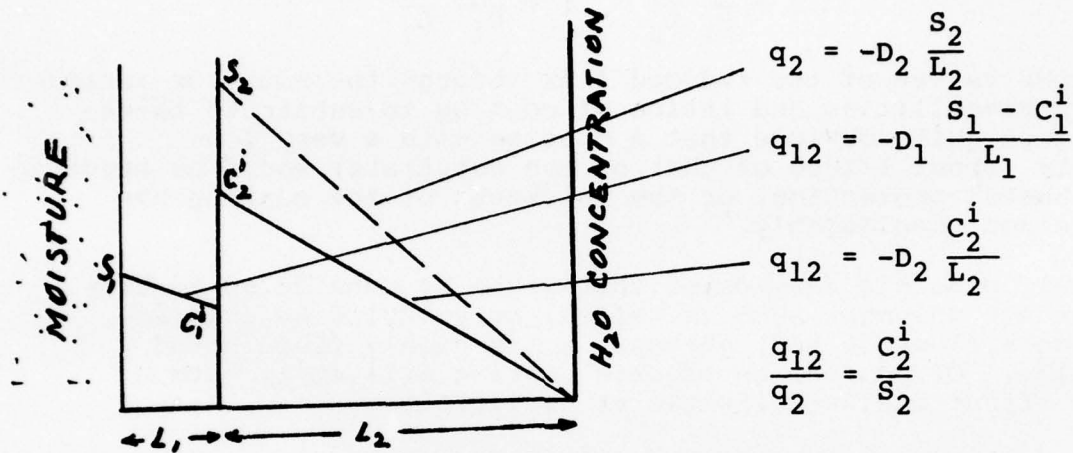
In order to estimate the effect of a particular coating one needs to know the diffusion coefficient or the permeabilities of the coating film. The moisture permeability (P) is given by (12)

$$P = SD \quad (12)$$

where S = equilibrium concentration or solubility of moisture, and D = diffusion coefficient.

The effective change in the flux of moisture through a unit surface between an uncoated and a coated sheet of material can be easily visualized by considering a steady state flux through such a sheet where on one side the humidity is kept at some constant

value and on the other side it is kept essentially at zero. Let us call substance (1) as the coating and substance (2) as the protected substrate. At the surface of the coating the moisture concentration is $C_0 = S_1$ (where S_1 is the equilibrium moisture concentration or solubility). The concentrations on both sides of the interface (i) are not the same, but are given by the distribution coefficient $C_2/C_1 = k$ which have the same ratio as the solubilities, i.e., $S_2/S_1 = k$. The internal concentration distribution of moisture is then indicated by the sketch below,



where q_2 is the flux without coating and q_{12} is the flux throughout the coated plate; C_1^i and C_2^i are the concentrations at the interface, S_1 and S_2 are the solubilities, L_1 and L_2 are the corresponding thicknesses and D_1 and D_2 are the diffusion coefficient of substances (1) and (2) respectively. Since at the steady state the flux is the same throughout the slab, one obtains

$$D_1 \frac{S_1 - C_1^i}{L_1} = D_2 \frac{C_2^i}{L_2}$$

Using permeabilities $P_1 = S_1 D_1$ and $P_2 = S_2 D_2$, one obtains further

$$\frac{P_1 S_1}{S_1 L_1} - \frac{P_1 C_1^i}{S_1 L_1} = \frac{P_2 C_2^i}{S_2 L_2}$$

$$C_2^i = \frac{P_1 k S_1 L_1 S_2 L_2}{L_1 (P_1 S_2 L_2 + P_2 k S_1 L_1)}$$

Now the reduced flux due to the coating can be calculated from the ratio.

$$\begin{aligned} \frac{q_{12}}{q_2} &= \frac{C_1^i}{S_2} = \frac{P_1 k S_1 L_2}{(P_1 S_2 L_2 + P_2 k S_1 L_1)} \\ &= \frac{1}{1 + \frac{P_2 L_1}{P_1 L_2}} \quad \text{or} \quad \frac{1}{1 + \frac{kD_2 L_1}{D_1 L_2}} \end{aligned} \quad (13)$$

Table 3 shows values of the reduced flux through the slab for various ratios of permeabilities and ratios of coating to substrate thicknesses. It is quite obvious that a coating with a very low permeability (about 1/1000 of that of the substrate) would be required to give a useful protection, or the thickness of the coating has to be increased considerably.

The only possible candidates that might be considered to have some effect are polymers such as teflon, polyvinylidene chloride, polyvinylidene fluoride and, perhaps, a few highly fluorinated polymer films. Of course, an organic coating will still have a protective effect against ultraviolet radiation.

Metal coating, on the other hand, would be sufficient even in very thin films to protect the composite from moisture. In addition, metal coatings would also give added lightning strike protection.

H. Engineering Examples.

Example 1.

Determine the moisture uptake (in percent) of Narmco 5208/T300 epoxy composites with varying numbers of plies.

The thickness for a commercial ply of 5208/T300 in a fabricated laminate is approximately .01347 cm (.0055 inches). The diffusion coefficients of a composite with a fiber volume fraction of .70 has been measured or can be calculated 1, and the temperature dependence is given in Figure 2. The solubility profile of moisture in Narmco 5208 is given in Figure 1. Using these data and the 3-hourly weather data of Washington, D.C. (from 1972-1974) the following three yearly averages were determined as described under C.

$$\begin{aligned} T_{av} &= 58.19^\circ\text{F} & T_{kav} &= 62.31^\circ\text{F} \\ D_{Tav} &= 4.818 \text{ E-11 cm}^2/\text{sec} & D_{kav} &= 5.556 \text{ E-11 cm}^2/\text{sec} \end{aligned}$$

Table 3. Relative change of the rate of diffusion of moisture through (or into) a composite plate (q_{12}/q_2) as a function of relative coating thickness and permeability ratios.

P_2/P_1 \ L_1/L_2	0.001	0.005	0.01	0.05	0.1
1000	.50	.167	.091	.02	.01
500	.67	.285	.167	.038	.02
100	.91	.67	.50	.167	.091
50	.95	.80	.67	.285	.167
10	.99	.95	.91	.67	.50
5	.995	.975	.95	.80	.67

$$\begin{array}{ll}
 RH_{av} = 64.15\% & RH_{kav} = 64.45\% \\
 M_{RHav} = .8259\% & M_{RHkav} = .8297\% \\
 F_T = 1.0707 & F_{RH} = 1.0046
 \end{array}$$

Where M_{RHav} and M_{RHkav} are the equilibrium concentrations of moisture in the composite corresponding to 64.15% and 64.45% of relative humidity, the other symbols are the same as defined before.

Figure 7 shows a computer printout of the percent moisture uptake of 6, 12, 18, 24, 30, 36, 42 and 48 ply Narmco 5208/T300 composite. The smooth lines were obtained by the averaging method using 3-yearly T_{kav} and RH_{kav} values and the irregularly shaped lined were obtained by using monthly kinetic averages in the finite difference method.

Example 2.

Prepare a diagram that gives the fraction of the equilibrium concentration of moisture in a laminate as a function of number of plies (or thickness) and time for the same composite as described in Example 1. The same experimental data were used as in Example 1.

The results is shown in Figure 17 which allows a quick estimate for the moisture uptake of a Narmco 5208/T300 ($V_f = .7$) composite for the climatic conditions of Washington D.C. for any number of plies. If the diffusion coefficient can be considered as concentration independent, then this graph is applicable for any average relative humidity (RH_{kav}) (with the understanding that the equilibrium concentration is RH dependent). For instance, a 20-ply 5208/T300 CF composite would take 6, 16, 39, 76 and 118 months to reach 25, 40, 60, 80 and 90 percent respectively of its equilibrium moisture concentration (which, for Washington, D.C. is .8275% by weight). Such engineering diagrams can be readily given for any desired environment.

I. Expansion to other Organic Materials and to Military Hardware in Service Environment.

The approach described in this report can, of course, be easily expanded to other organic materials. It is necessary to measure the moisture equilibrium concentration profile and the diffusion coefficient as a function of temperature. More complex shapes of components can be usually broken down into simpler configurations or the general diffusion equation in two or three dimensions has to be solved by finite difference methods.

For service environments a realistic mission profile is required. Let us qualitatively discuss an example.

What is the moisture absorption of an aircraft wing skin made of CF composite? In addition to the skin thickness, the composite diffusion coefficient as a function of temperature, the moisture equilibrium concentration profile and the local T_{kav} and RH_{kav} one requires knowledge about a projected aircraft history. For instance, fraction of time standing unprotected on the airfield, fraction of time in the hangar, fraction of time in the air, fraction of time under supersonic skin heating.

High altitude subsonic flight will contribute very little to diffusion because of the low temperatures. Supersonic flights may contribute significantly if a.) the composite is thin and b.) the skin temperature is high (see exponential effect of T on D). However, it is expected that the major contribution comes from the fraction of time the aircraft is standing unprotected in the field.

The program described in this report can be easily modified to incorporate such conditions.

CONCLUSIONS

1. Two analytic methods have been described to model the moisture uptake and internal distribution in fiber reinforced organic composites in real outdoor environments. Required for the calculations are the diffusion coefficients of the composites as a function of temperature and the moisture equilibrium concentrations as a function of the relative humidity.

2. The first method is simple and can be applied without the use of a high speed computer. It uses average temperatures and average humidities combined with correction factors that are specific for certain climatic categories or geographic areas and, to a lesser degree, dependent on the material. This method gives smooth curves that average out seasonal changes.

3. The second method is exact but requires one to three hourly weather data over a period of several years and it also requires access to a high speed computer. It assumes that the data (of several years) will be representative for the prediction.

4. Further corrections were introduced if the temperature effect of direct sun radiation is of interest.

5. The program can be readily expanded to include various profiles of military hardware mission environments.

ACKNOWLEDGEMENT

The authors would like to thank Messrs M. Stander and C. Bersch of the Naval Air Systems Command for their interest and support of this work.

SYMBOLS

C_0, C_1, C_1^i, C_2^i	various expressions of moisture concentration
D	diffusion coefficient
D_{av}	diffusion coefficient corresponding to the average temperature
D_{kav}	diffusion coefficient corresponding to the kinetic average temperature
D_{kavr}	diffusion coefficient corresponding to the kinetic average temperature including sun radiation effects
F_{RH}	factor, which multiplied with the average relative humidity, gives the kinetic average humidity
F_T	factor, which multiplied with the average temperature, gives the kinetic average temperature
f_{cr}	fractional time of exposure to cloudy-rainy conditions
f_{cs}	fractional time of exposure to clear, sunny sky conditions
f_{cw}	fractional time of exposure to clear, sunny sky, with windy conditions
f_p	fractional time of exposure protected from direct sun radiation.
h	half of the composite plate thickness
k	distribution coefficient
l, L	thickness of composite
M	moisture concentration
M_t	moisture concentration at time t
M_∞	equilibrium moisture concentration
M_{kav}	moisture equilibrium concentration corresponding to the kinetic average relative humidity.

SYMBOLS Cont.

P	permeability
q	flux
RH_{av}	average relative humidity
RH_{kav}	kinetic average relative humidity
S	solubility
t, τ	time
T	temperature
V_f	volume fraction of fibers in the composite

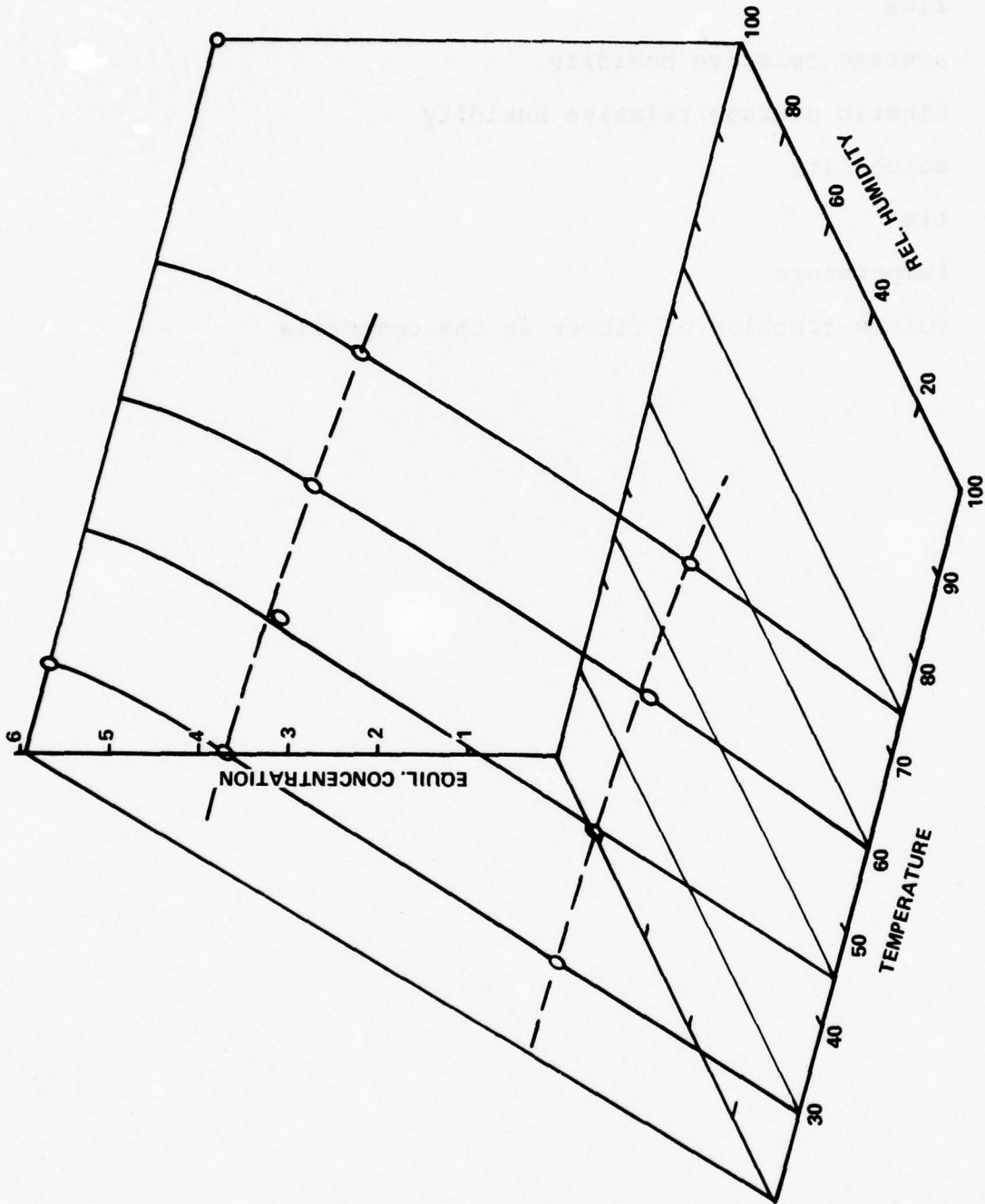


FIG. 1 EQUILIBRIUM CONCENTRATION OF MOISTURE IN NARMC0 5208 RESIN AS A FUNCTION OF TEMPERATURE AND RELATIVE HUMIDITY

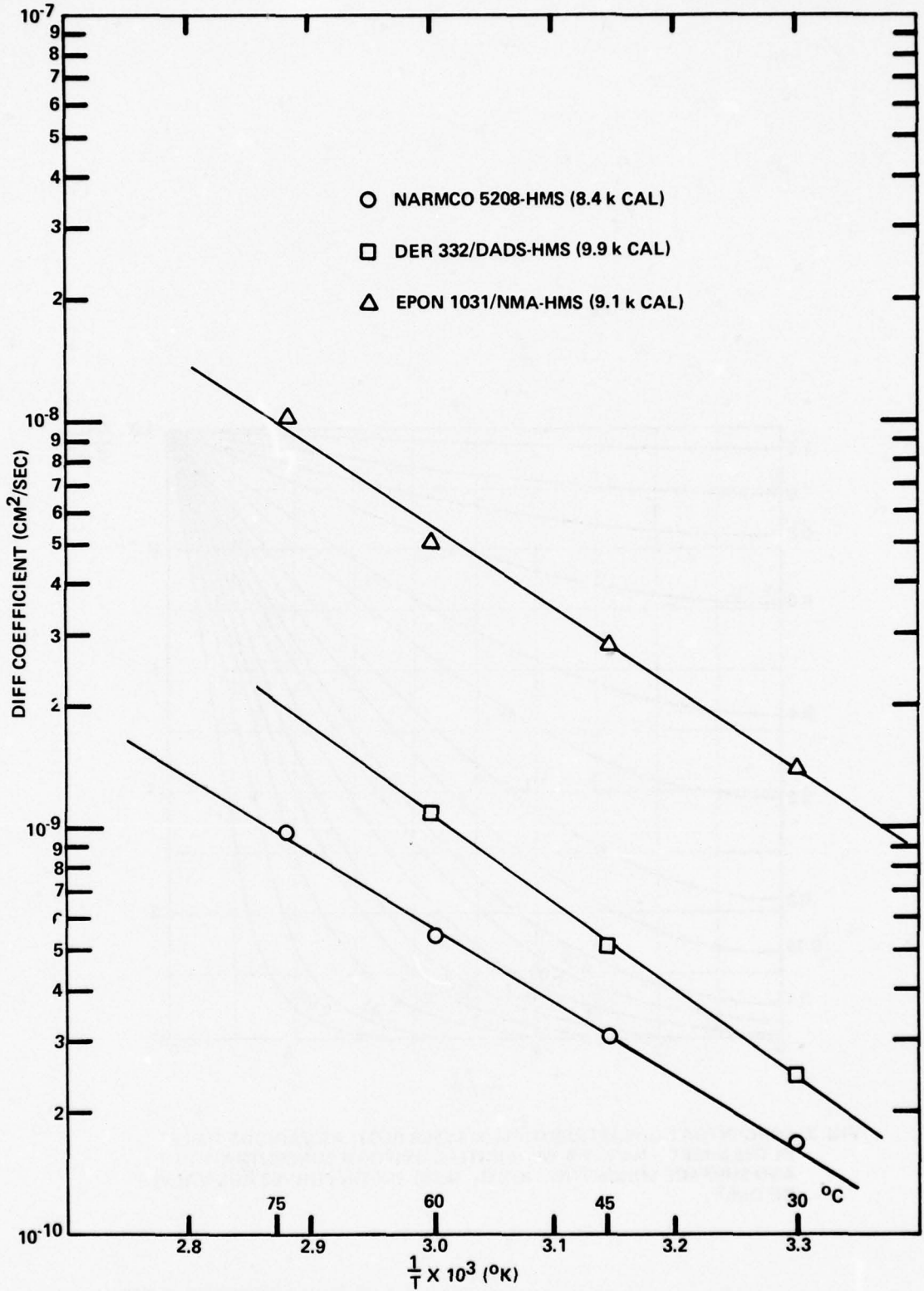


FIG. 2 ARRHENIUS PLOT OF MOISTURE DIFFUSION INTO HMS FIBER COMPOSITES (DETERMINED AT 33% RH)

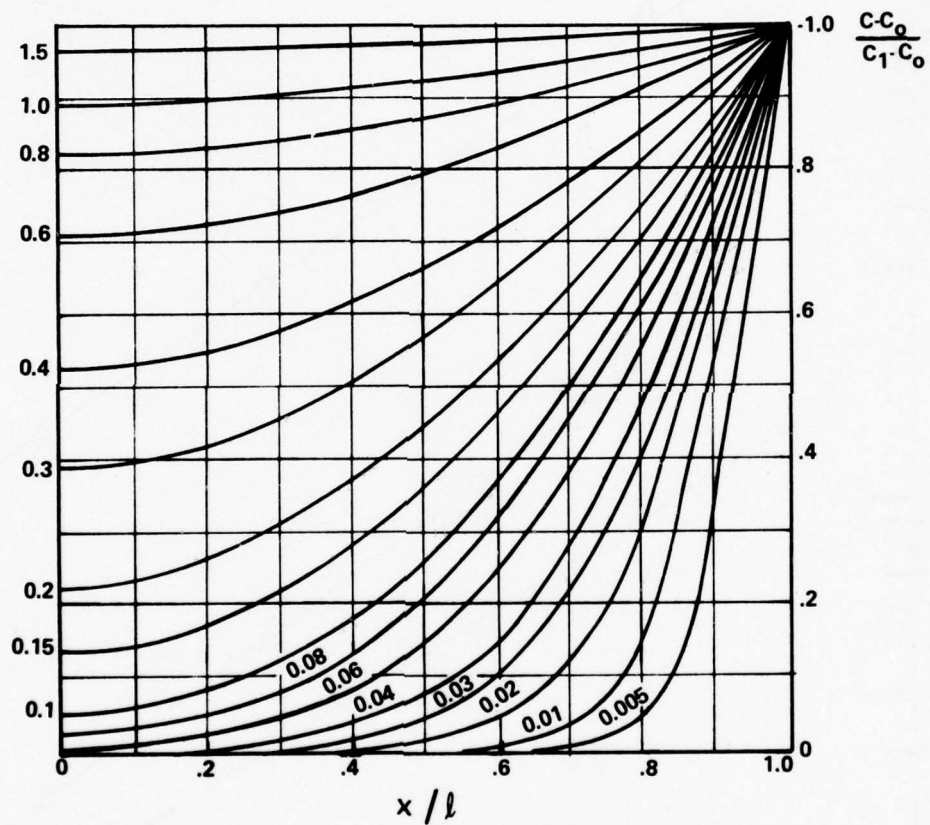


FIG. 3 CONCENTRATION DISTRIBUTION (MASTER PLOT) AT VARIOUS TIMES IN THE SHEET $-h < X < h$ WITH INITIAL UNIFORM CONCENTRATION C_0 AND SURFACE CONCENTRATION C_1 . NUMBERS ON CURVES ARE VALUES OF Dt/h^2 .

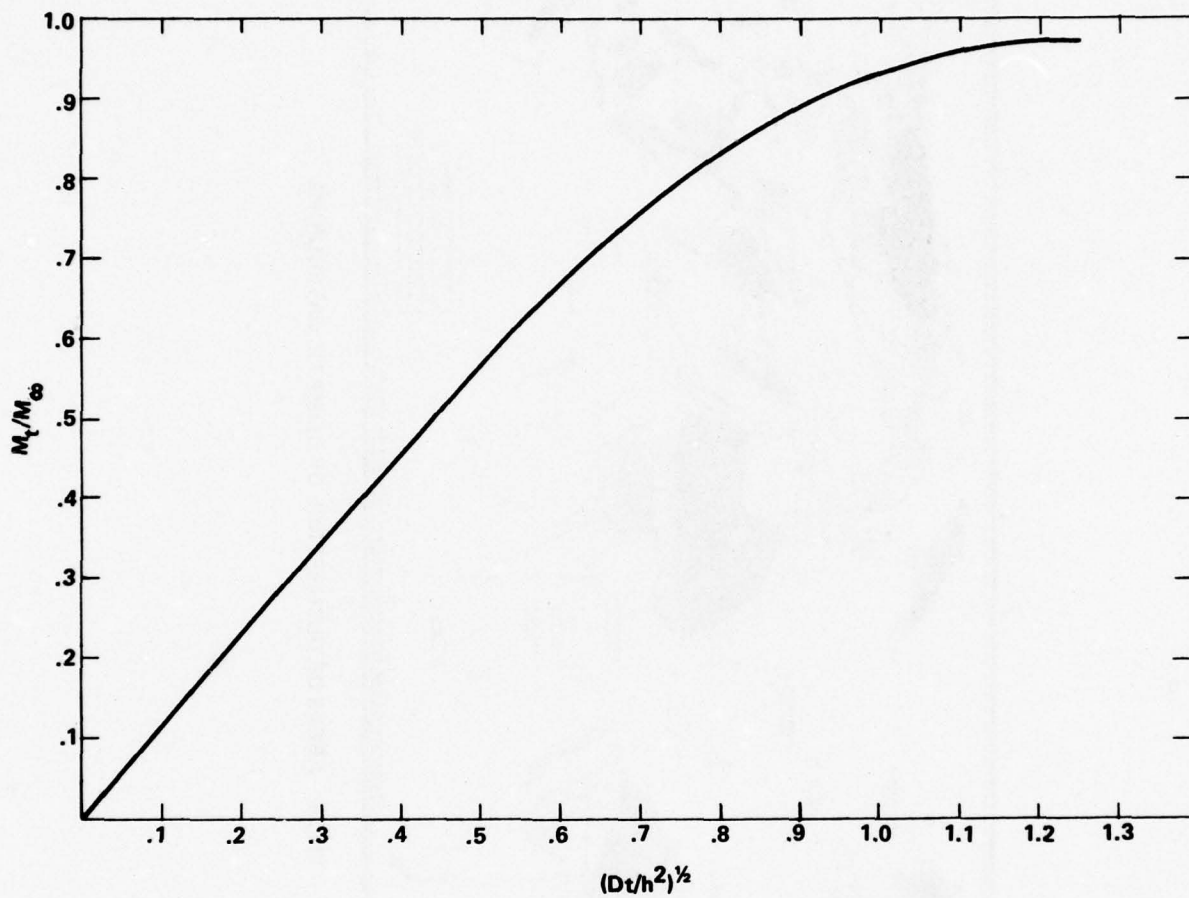


FIG. 4 PLOT OF FRACTIONAL ABSORPTION OF ANY MATERIAL WITH FICKEAN BEHAVIOR VERSUS $(Dt/h^2)^{1/2}$ FOR PLATE GEOMETRY

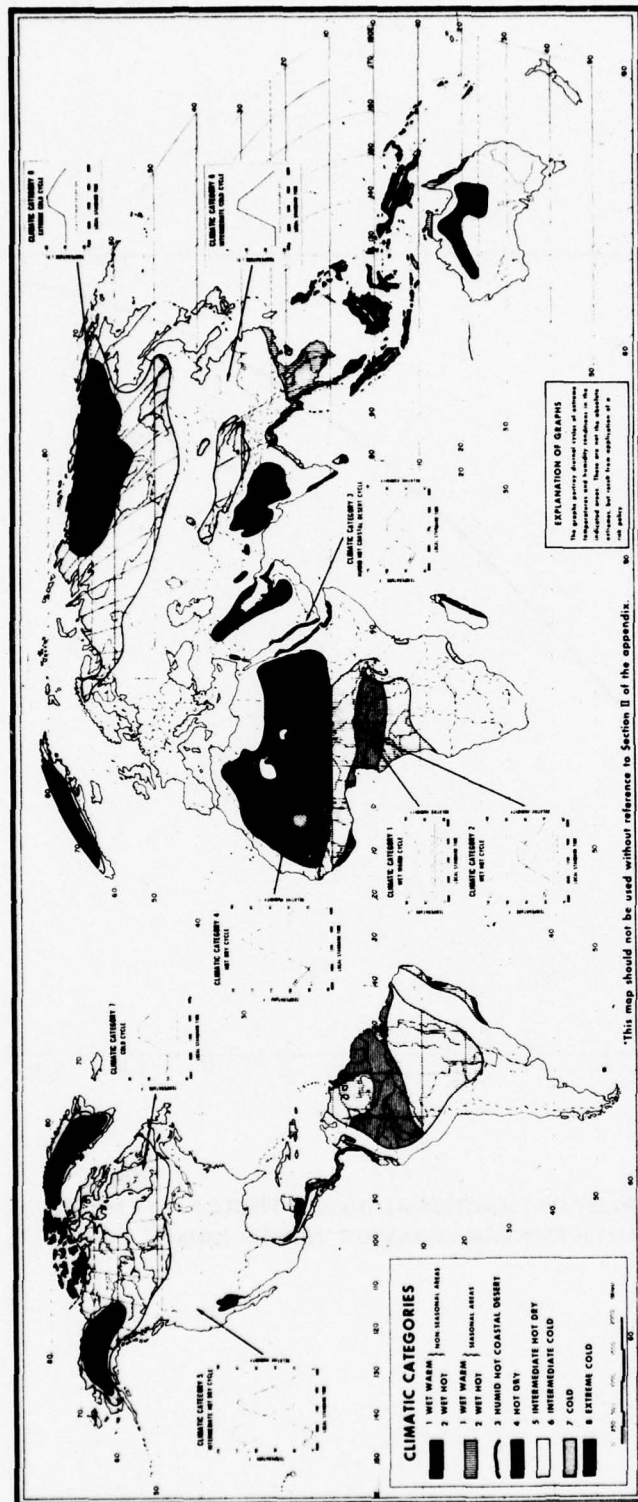


FIG. 5 AREAS OF OCCURRENCE OF CLIMATIC CATEGORIES.

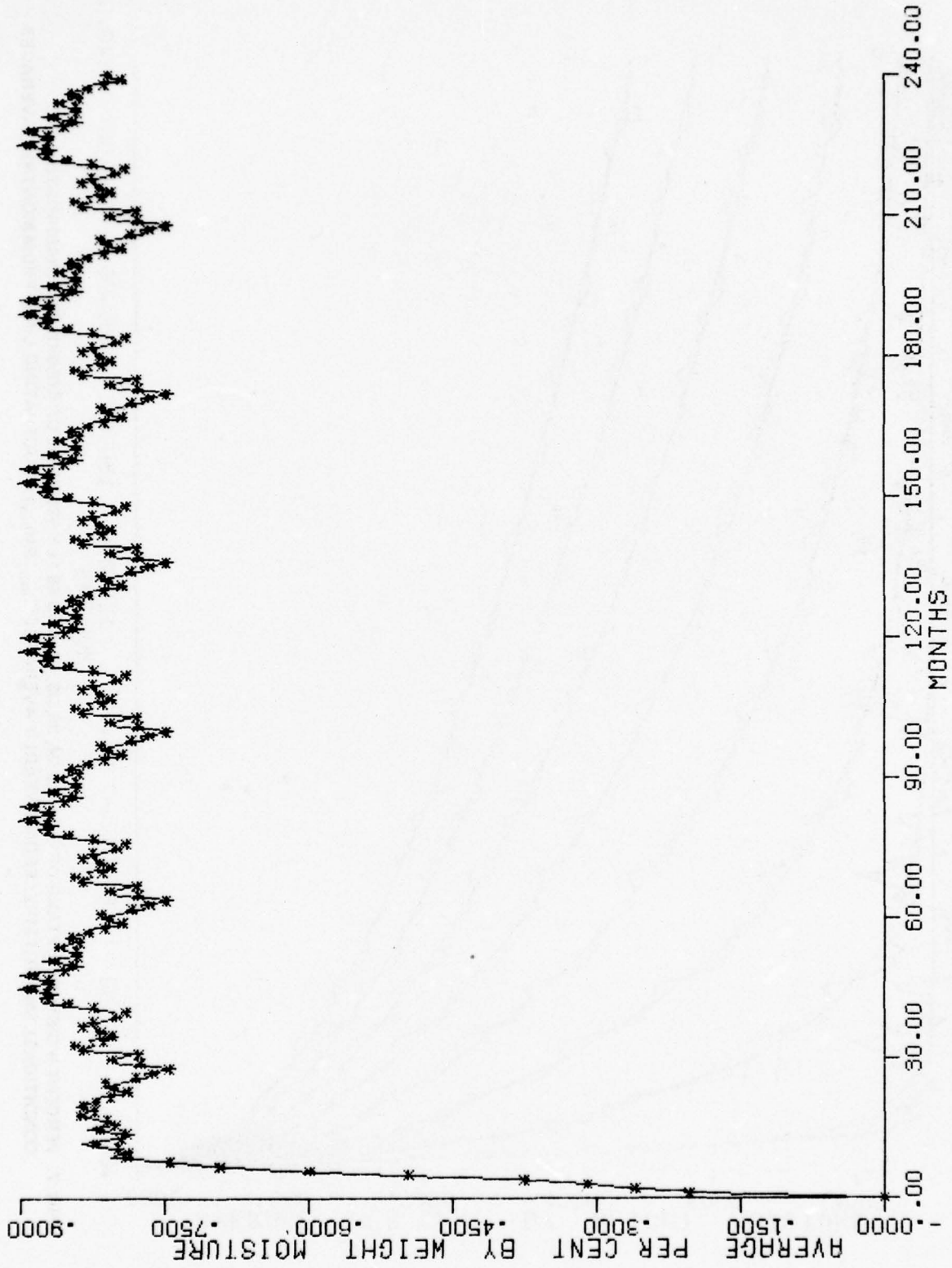


FIG. 6 PERCENT MOISTURE UPTAKE OF A SIX PLY NARMCO 5208/T300 ($V_f=7$) CARBON FIBER COMPOSITE CALCULATED FOR WASHINGTON, D.C. CLIMATIC CONDITION. (SOLID LINE: 3 HOURLY WEATHER DATA, * : FROM MONTHLY AVERAGES). THE 3-YEARLY CYCLE WAS REPEATED.

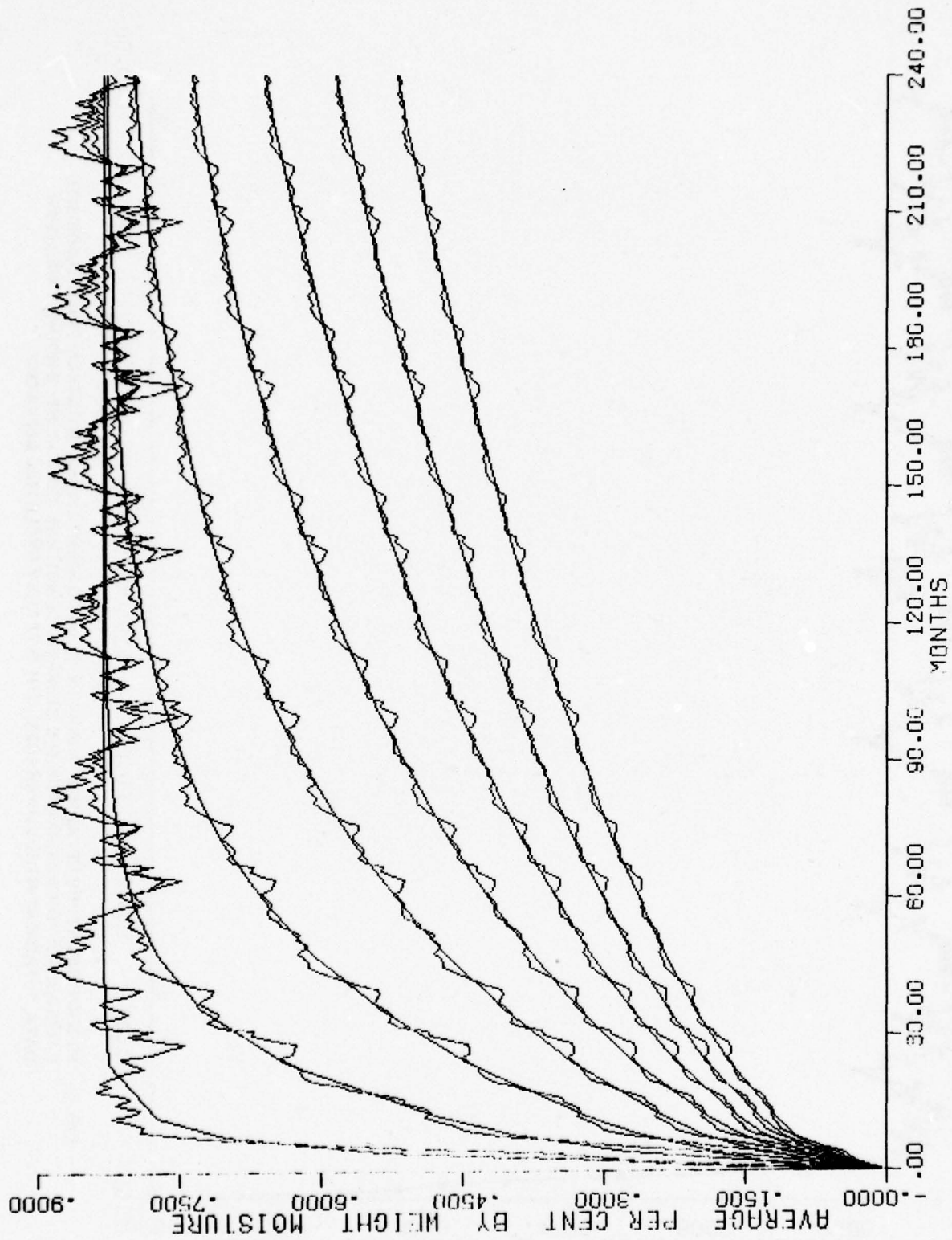


FIG. 7 PERCENT MOISTURE UPTAKE OF 6, 12, 18, 24, 39, 36, 42, AND 48 PLY 5208/T300 CF COMPOSITES (WASHINGTON, D.C. CONDITIONS). SMOOTH LINE: FROM 3-YEARLY AVERAGES (T_{kav} , RH_{kav}). FLUCTUATING LINE: FROM MONTHLY AVERAGES.

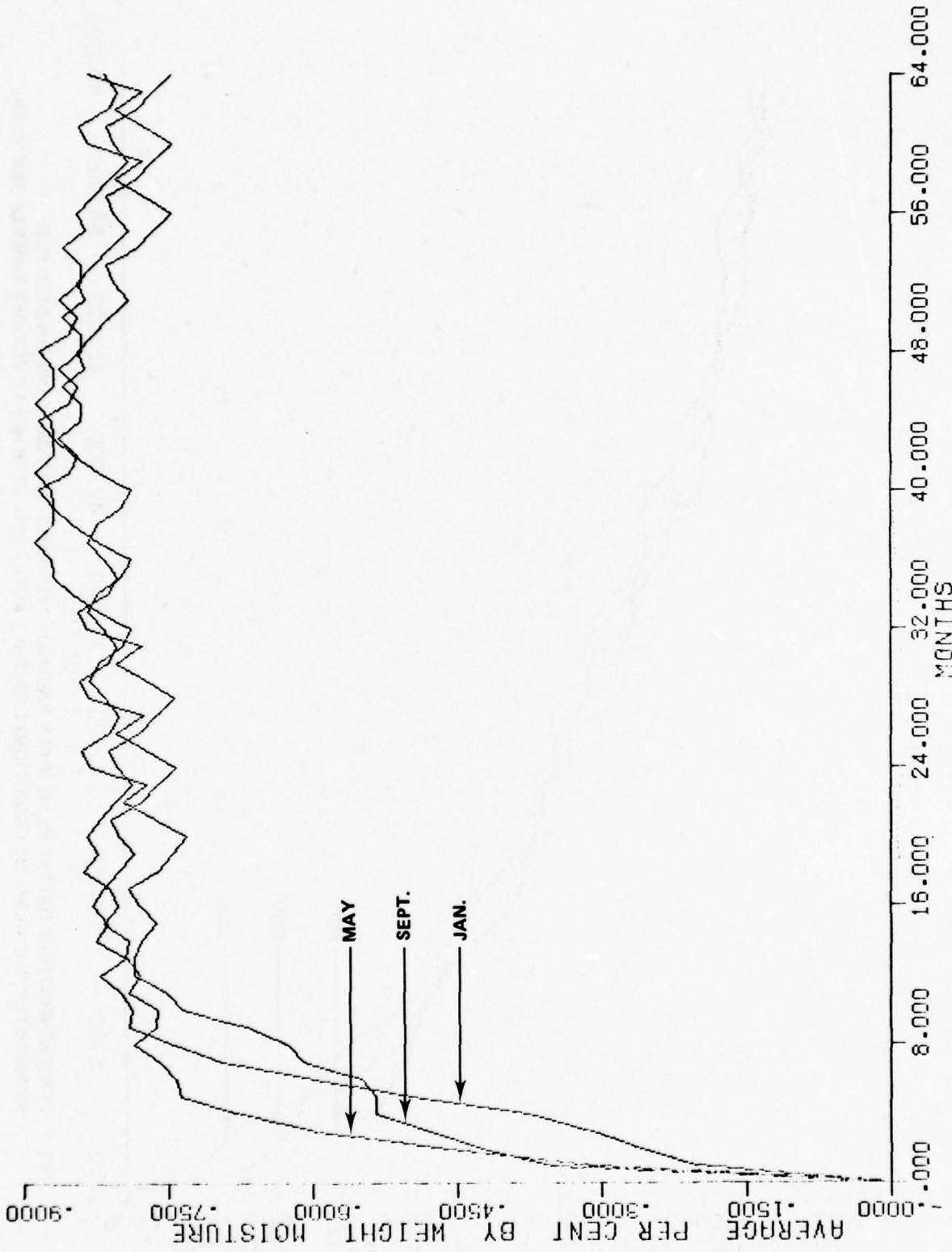


FIG. 8 PERCENT MOISTURE UPTAKE IN A 6 PLY NATMCO 5208/T300 CARBON FIBER COMPOSITE CALCULATED FOR WASHINGTON D.C. CLIMATIC CONDITIONS (MONTHLY AVERAGES). STARTED AT VARIOUS TIMES OF THE YEAR.

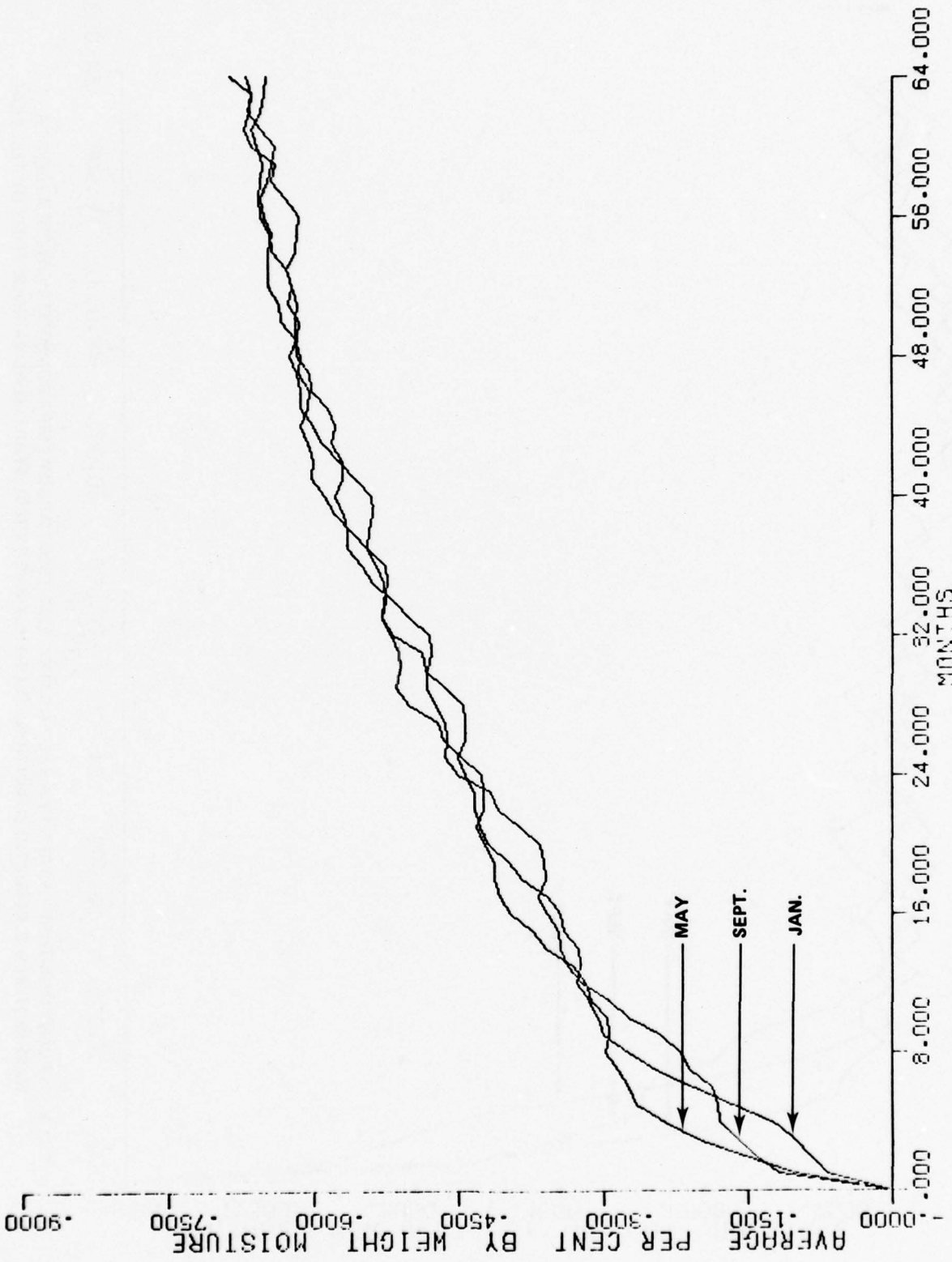


FIG. 9 PERCENT MOISTURE UPTAKE IN AN 18 PLY NARMCO 5208/T300 CF COMPOSITE CALCULATED FOR WASHINGTON, D.C. CLIMATIC CONDITIONS (MONTHLY AVERAGES). STARTED AT VARIOUS TIMES OF THE YEAR.

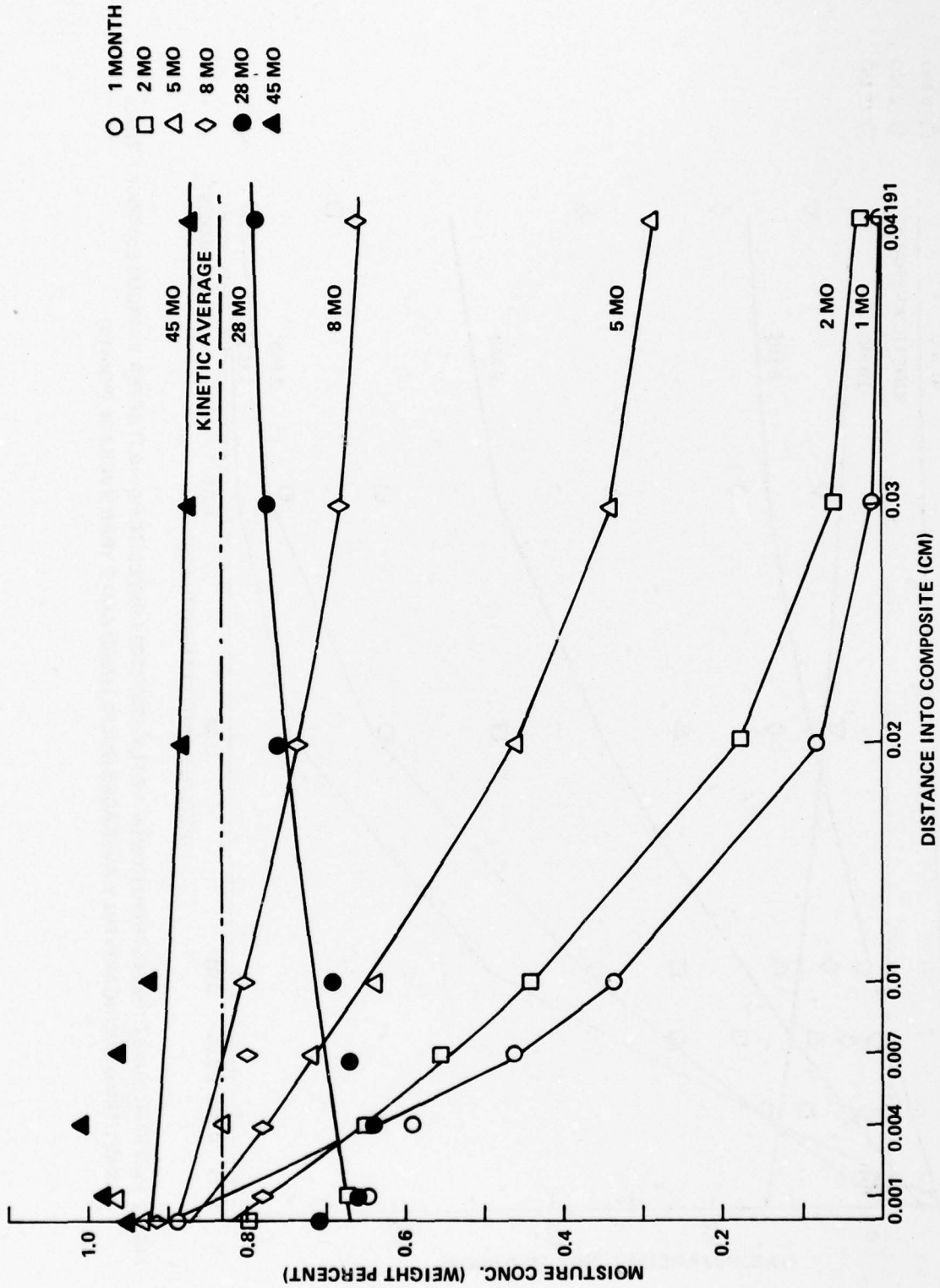


FIG. 10 INTERNAL MOISTURE DISTRIBUTION IN A 6 PLY 5208/T300 COMPOSITE ($V_f = 0.7$) AFTER VARIOUS EXPOSURE TIMES, COMPUTED BY USING MONTHLY AVERAGES (SOLID LINES) AND 3-HOURLY READINGS (POINTS)

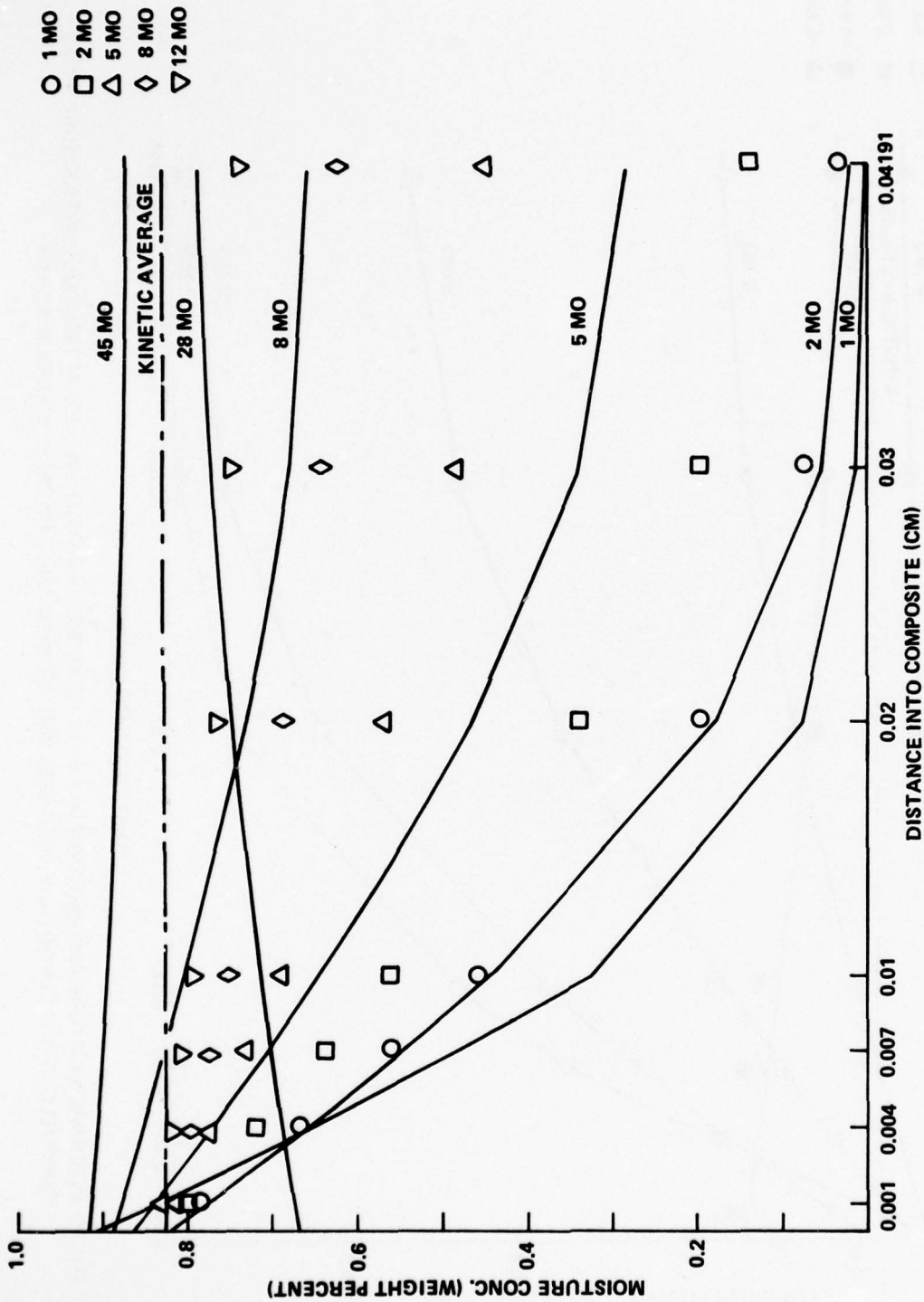


FIG. 11 INTERNAL MOISTURE DISTRIBUTION IN A 6 PLY 5208/T300 COMPOSITE ($V_f = 0.7$) AFTER VARIOUS EXPOSURE TIMES, COMPUTED BY USING MONTHLY AVERAGES (SOLID LINES) AND 3 YEAR AVERAGE (POINTS)

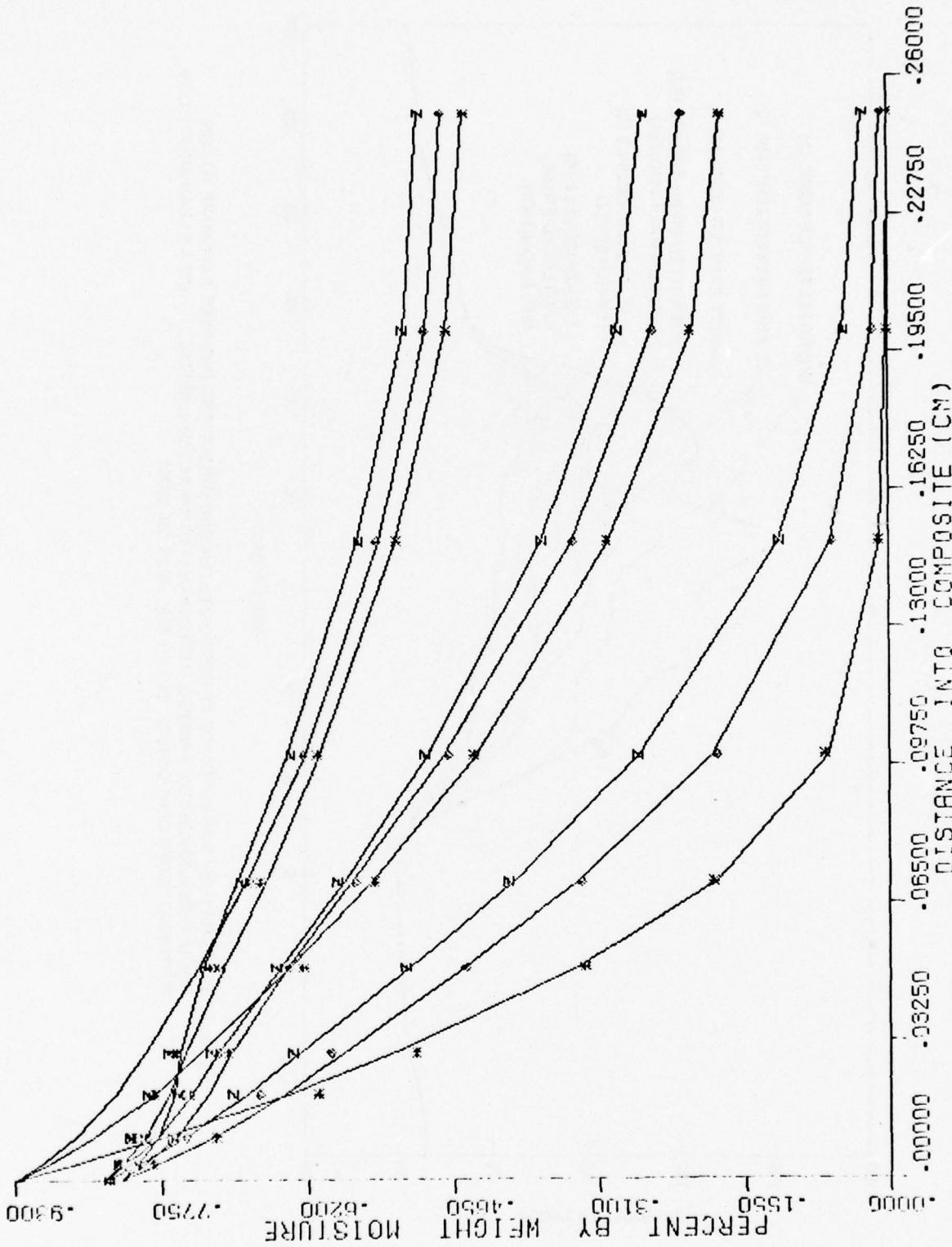


FIG.12 INTERNAL MOISTURE DISTRIBUTION IN A NARMCO 5208/T300 CF COMPOSITE (36 PLYS) (WASHINGTON, D.C.) AFTER 1, 2, 3, 7, 8, 9, 15, 16, AND 17 YEARS (SOLID LINES: MONTHLY AVERAGES, POINTS: 3 YEARLY AVERAGES).

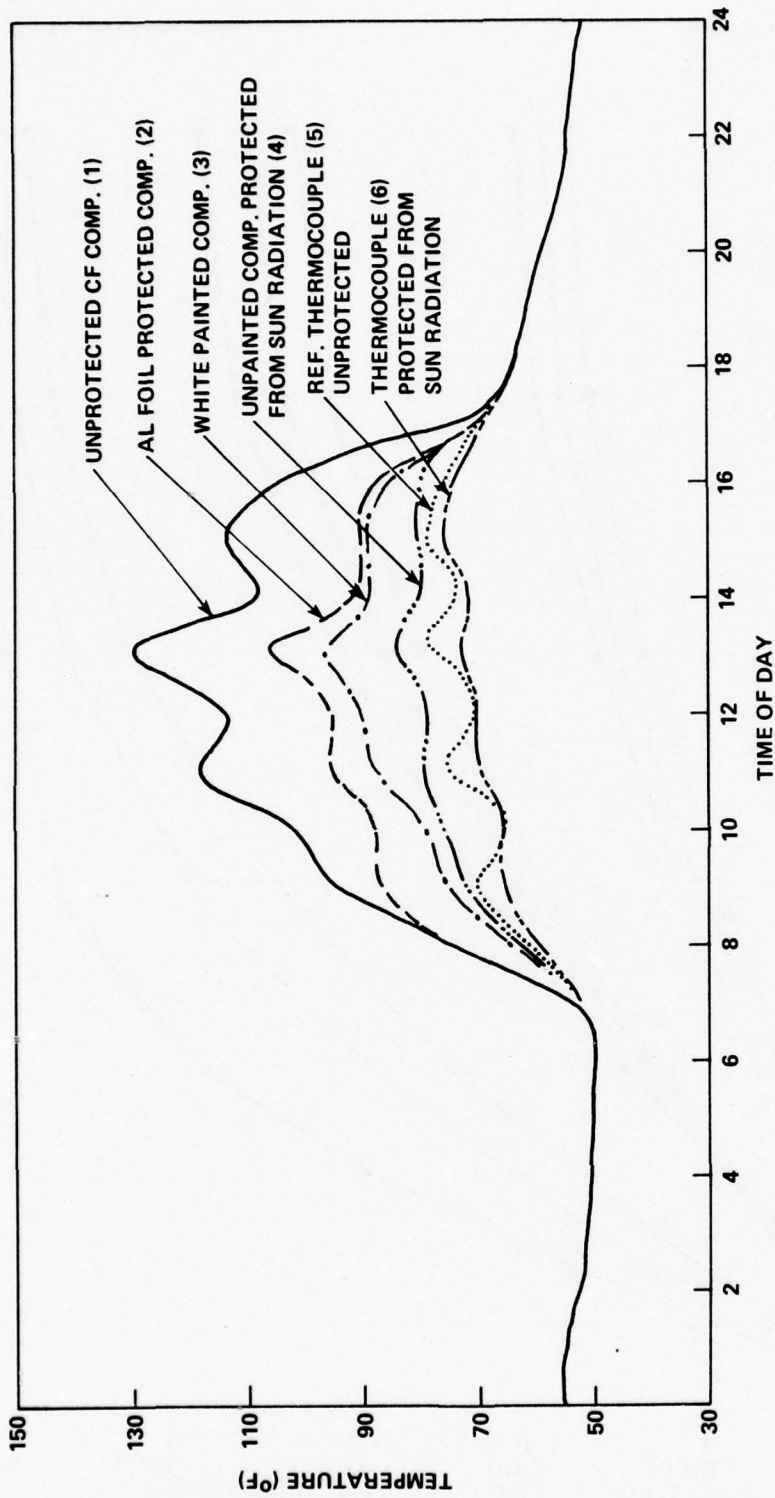


FIG. 13 TEMPERATURE VARIATION OF CF COMPOSITES UNDER DIRECT AND INDIRECT EXPOSURE TO SUN RADIATION; UNPAINTED, PAINTED, AND BONDED TO AN ALUMINUM FOIL, ON A CLEAR SUNNY DAY, WITH SCATTERED CLOUDINESS; CLEAR AIR. (AUG. 20, 1976)

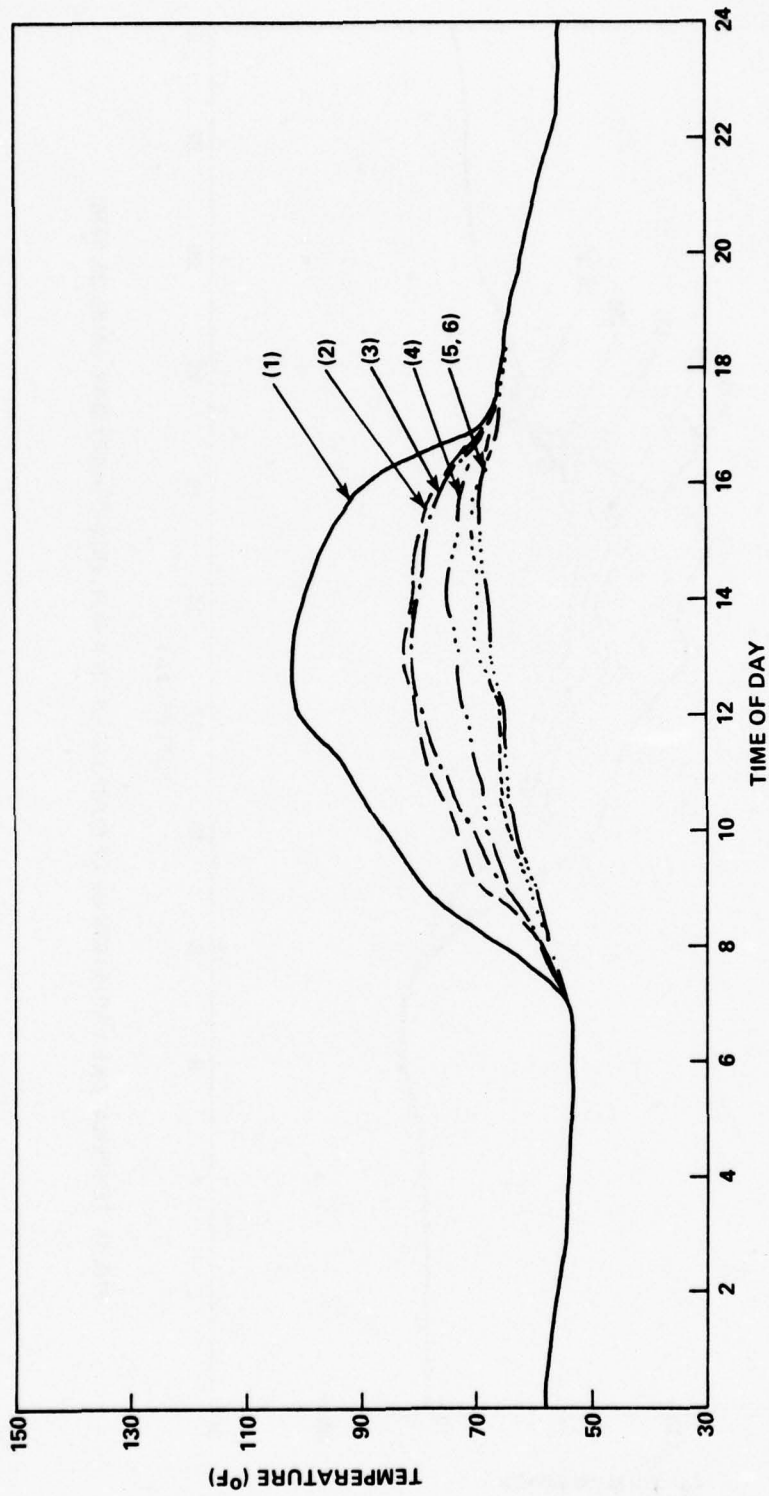


FIG. 14 TEMPERATURE VARIATION OF COMPOSITES ON A CLEAR SUNNY BUT WINDY DAY. (AUG. 19, 1976)

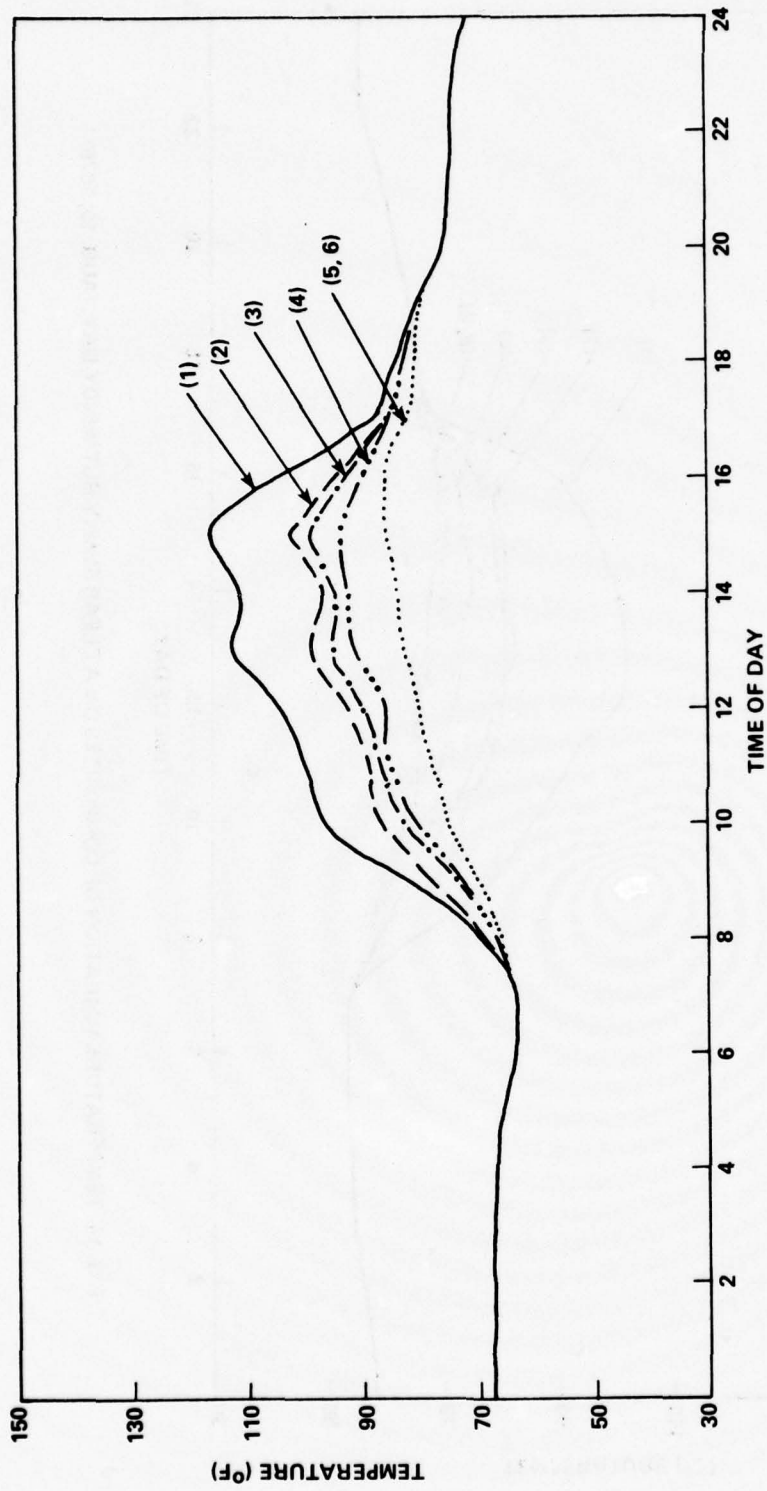


FIG. 15 TEMPERATURE VARIATION OF CF COMPOSITES ON A HOT, HUMID, HAZY DAY. (AUG. 25, 1976)

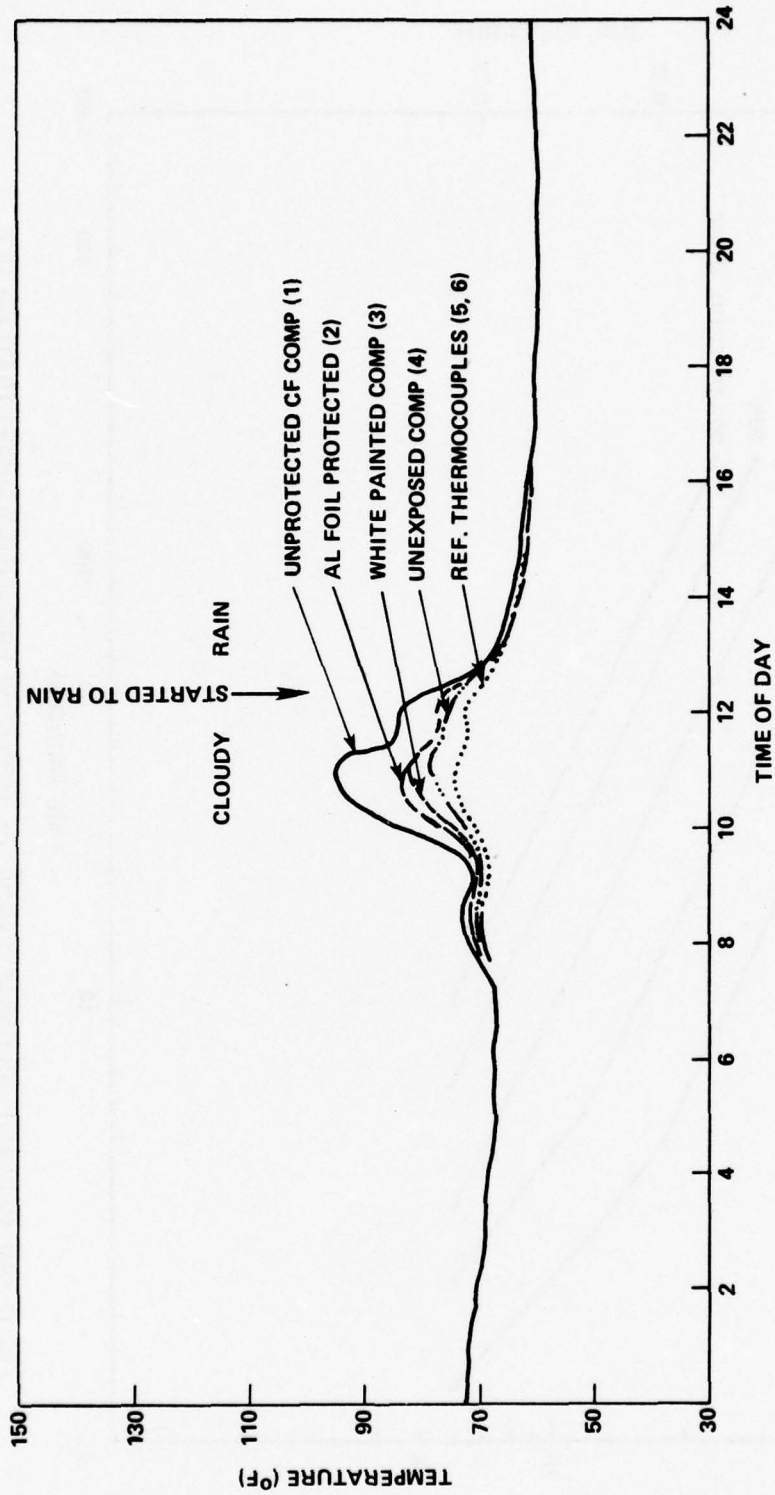


FIG. 16 TEMPERATURE VARIATION OF CF COMPOSITES ON A CLOUDY AND RAINY DAY. (AUG. 27, 1976)

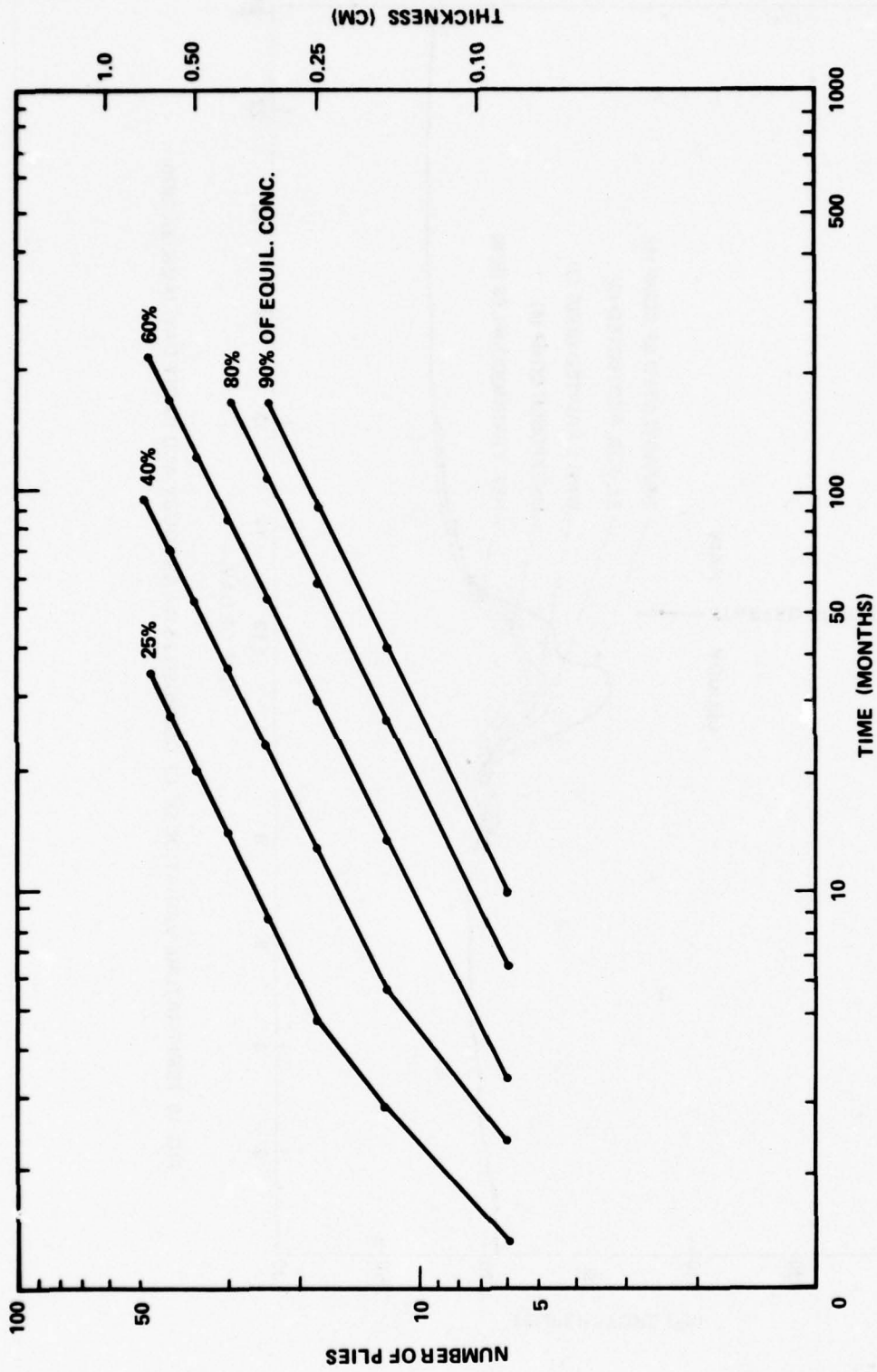


FIG. 17 TIME TO REACH VARIOUS LEVELS OF THE RESPECTIVE EQUILIBRIUM CONCENTRATIONS AS A FUNCTION OF NUMBERS OF PLYS OF NARMCO 5208/T300 ($V_f = .70$) (THE THICKNESS IN CM IS OBTAINED BY MULTIPLYING THE PLY NUMBER WITH .01397)

SOLVE DIFFUSION EQUATION ON INTERVAL 0 TO XFINAL= 2.0000000E-01
 NUMBER OF X-INTERVALS= 10 TOTAL NUMBER OF TIME STEPS= 4800

TIME STEP DT= 1.2960000E+05

DXELE= .1000000E-02 .3000000E-02 .3000000E-02
 .3000000E-02 .1000000E-01 .1000000E-01 .2000000E-01
 .5000000E-01 .5000000E-01 .5000000E-01

T= 0. D= 1.0000000E+00 JCYCL= 0
 END OF MONTH NUMBER 0 AVE PH BDY CONDITION DURING MONTH= 0.

X=	0.00000	.00100	.00400
UH=	0.	0.	0.
X=	.00700	.01000	.02000
UH=	0.	0.	0.
X=	.03000	.05000	.10000
UH=	0.	0.	0.
X=	.15000	.20000	
UH=	0.	0.	

THE INTEGRAL I FROM XINIT TO XFINAL OF U= 0.
 I/XFINAL= 0.

FIG. 18 SAMPLE COMPUTER OUTPUT

```

T= 2.592000E+06      D= 2.6115870E-11      JCYCL=      20
END OF MONTH NUMBER  1      AVE RH BDY CONDITION DURING MONTH= .9005190E+00
X= 0.00000          .00100          .00400          .00700          .01000          .02000
UH= 9.0051900E-01  8.3554034E-01  6.4364457E-01  4.6972495E-01  3.2363105E-01  7.6361605E-02
X= .03000          .05000          .10000          .15000          .20000
UH= 1.0811629E-02  2.9467913E-04  1.4752575E-04  1.0255485E-04  .9587214E-11
THE INTEGRAL I FROM XINIT TO XFINAL OF U= 8.5013691E-03
I/XFINAL= 4.2506846E-02

T= 5.184000E+06      D= 2.2166120E-11      JCYCL=      40
END OF MONTH NUMBER  2      AVE RH BDY CONDITION DURING MONTH= .8170750E+00
X= 0.00000          .00100          .00400          .00700          .01000          .02000
UH= 8.1707500E-01  7.7699237E-01  6.5763915E-01  5.4358288E-01  4.3834270E-01  1.7088189E-01
X= .03000          .05000          .10000          .15000          .20000
UH= 4.4557787E-02  2.3875366E-03  2.8418308E-05  2.7738867E-07  4.6426069E-09
THE INTEGRAL I FROM XINIT TO XFINAL OF U= 1.0877600E-02
I/XFINAL= 5.4388002E-02
    
```

FIG. 19 SAMPLE COMPUTER OUTPUT

Appendix A.

Numerical Solution of the Moisture Diffusion Equationa. Finite Difference Equations.

We first give a derivation for the finite difference equations (8) used to obtain an approximate solution to the diffusion equation (7). Define $t^{n+1} = (n+1)\Delta t$. The following approximations are used:

$$\frac{M_i^{n+1} - M_i^n}{\Delta t} \approx M_t(x_i, t^{n+1}) \quad (A1)$$

$$D(t^{n+1}) \frac{M_{i+1}^{n+1} - M_i^{n+1}}{\Delta_{i+1}} \approx D(t^{n+1}) M_x \left(\frac{x_{i+1} + x_i}{2}, t^{n+1} \right) \quad (A2a)$$

$$D(t^{n+1}) \frac{M_i^{n+1} - M_{i-1}^{n+1}}{\Delta_i} \approx D(t^{n+1}) M_x \left(\frac{x_i + x_{i-1}}{2}, t^{n+1} \right) \quad (A2b)$$

$$\left(\frac{\Delta_i + \Delta_{i+1}}{2} \right)^{-1} \left[D(t^{n+1}) M_x \left(\frac{x_{i+1} + x_i}{2}, t^{n+1} \right) - D(t^{n+1}) M_x \left(\frac{x_i + x_{i-1}}{2}, t^{n+1} \right) \right] \\ \approx \left(D(t) M_x \right)_x \text{ at } (x_i, t^{n+1}) \quad (A2c)$$

Equation (A1) accounts for the left side of (8a) while (A2c) with (A2a) and (A2b) yield the right side of (8a). Because of the boundary condition $M_x(h, t) = 0$, or more basically, because the solution of the original problem is symmetric about the midplane $x = h$, one may define the approximate solution value M_{I+1}^{n+1} at the point X_{I+1} (with

$x_{I+1} \equiv x_I + \Delta_I = h + \Delta_I$) to be $M_{I+1}^{n+1} \equiv M_{I-1}^{n+1}$. The choice of x_{I+1} gives $\Delta_{I+1} = \Delta_I$, and then equation (8a) is defined for $i=I$ and reduces to (8b).

b. The Linear Equations.

The structure of the linear system of I equations given by (8) for determining M_i^{n+1} ($i=1, \dots, I$) will now be described. Recall that M_i^n ($i=0, \dots, I$) and M_0^n ($n=0, \dots, N$) are defined by the given initial data $M^0(x)$ and by the given boundary data $g(t)$, respectively.

Multiplying both sides of (8a) by $(\Delta_i + \Delta_{i+1})/2$ produces

$$\frac{\Delta_i + \Delta_{i+1}}{2\Delta t} (M_i^{n+1} - M_i^n) = D(t^{n+1}) \left\{ \frac{M_{i-1}^{n+1}}{\Delta_i} - \left(\frac{1}{\Delta_i} + \frac{1}{\Delta_{i+1}} \right) M_i^{n+1} + \frac{M_{i+1}^{n+1}}{\Delta_{i+1}} \right\} \quad (A3)$$

Equation (A3) at $i=1$ has the form

$$A_{1,1} M_1^{n+1} + A_{1,2} M_2^{n+1} = F_1$$

where

$$A_{1,1} = \frac{\Delta_1 + \Delta_2}{2\Delta t} + D(t^{n+1}) \left(\frac{1}{\Delta_1} + \frac{1}{\Delta_2} \right), \quad A_{1,2} = \frac{-D(t^{n+1})}{\Delta_2}, \quad (A4a)$$

$$\text{and } F_1 = \frac{(\Delta_1 + \Delta_2) M_1^n}{2\Delta t} + \frac{D(t^{n+1})}{\Delta_1} M_0^{n+1}.$$

Equation (A3) for i in the range 2 through $I-1$ has the form

$$A_{i,i-1} M_{i-1}^{n+1} + A_{i,i} M_i^{n+1} + A_{i,i+1} M_{i+1}^{n+1} = F_i$$

where

$$A_{i,i-1} = \frac{-D(t^{n+1})}{\Delta_i}, \quad A_{i,i} = \frac{\Delta_i + \Delta_{i+1}}{2\Delta t} + D(t^{n+1}) \left(\frac{1}{\Delta_i} + \frac{1}{\Delta_{i+1}} \right),$$

$$A_{i,i+1} = \frac{-D(t^{n+1})}{\Delta_{i+1}}, \quad \text{and } F_i = \frac{(\Delta_i + \Delta_{i+1}) M_i^n}{2\Delta t}. \quad (A4b)$$

Multiplying both sides of (8b) by $\Delta_I/2$ produces the equation

$$A_{I,I-1} M_{I-1}^{n+1} + A_{I,I} M_I^{n+1} = F_I$$

where

$$A_{I,I-1} = \frac{-D(t^{n+1})}{\Delta_I}, \quad A_{I,I} = \frac{\Delta_I}{2\Delta t} + \frac{D(t^{n+1})}{\Delta_I},$$

$$\text{and } F_I = \frac{\Delta_I M_I^n}{2\Delta t}. \quad (\text{A4c})$$

Considering A to be an I by I matrix (entries of A which have not been specified in equation (A4) are defined to be zero), and considering M^{n+1} and F to be vectors of length I, the equations (A4), which are equivalent to (8), have the form

$$AM^{n+1} = F. \quad (\text{A5})$$

The matrix A and vector F in (A5) are those which result from solving (7) by using the finite element method (fully implicit in time) with linear elements and with lumping of the mass matrix (by using the trapezoidal rule) [4], and this is the linear system of equations which was solved in our computer program to obtain M^{n+1} .

c. Evaluation of A and F in Equation A5.

The entries of A and F depend on the time step Δt , the spatial mesh (i.e., the Δ_i), the value $D(t^{n+1})$, the value M_0^{n+1} , and the known approximate solution values M_i^n at the previous time level. Choices for Δt and the Δ_i will be discussed later. The diffusion coefficient $D t^{n+1}$ depends on the temperature at time t^{n+1} while M_0^{n+1} is the equilibrium concentration (solubility) of moisture in the composite corresponding to the relative humidity at t^{n+1} . Thus $D(t^{n+1})$ and M_0^{n+1} depend on the weather data and on the particular composite material being considered.

It is assumed that a relationship of the form (3) holds relating the diffusion coefficient (D) of the composite being studied to the temperature (T), so then for some constants α and β

[4] G. Strang and G. Fix, An Analysis of the Finite Element Method, Prentice Hall, Englewood Cliffs, 1973.

$$\ln(D) = \alpha + \beta \frac{1}{T} \quad (A6)$$

and thus $\ln(D)$ is a linear function of $1/T$. The constants α and β can be determined from experimental measurements such as given in Figure 2. For example, for Narmco 5208/T300 with a fiber volume fraction of .7; at $T = 348.15$ °K the value of D was found to be $1.11 \text{ E-}9 \text{ cm}^2/\text{sec}$ while at $T = 303.15$ °K the measured value of D was $1.21 \text{ E-}10 \text{ cm}^2/\text{sec}$. From these values one determines that $\alpha = -5198.1$ and $b = -5.6883$. It is assumed that from the weather data (or from a kinetic average of the weather data) a subroutine is available to obtain the temperature value (T^{n+1}) and the relative humidity value (RH^{n+1}) to be used at time t^{n+1} . Then

$$D(t^{n+1}) = \exp\left(\alpha + \beta/T^{n+1}\right).$$

The equilibrium concentration (g) of moisture at a given relative humidity value (RH) was found by linearly interpolating experimental measurements. The solubility of moisture in the composite was taken to be independent of the temperature (c.f. Figure 1). For example, for Narmco 5208/T300 with a fiber volume fraction of .7, linear interpolation of the following values was used: (RH=0, M=0), (RH=80%, M=1.03% by weight H₂O), (RH=100%, M=1.37%) (c.f. Figure 1). In this way M_0^{n+1} was obtained from RH^{n+1} . The computer program used to evaluate A and F in (A5) is a much more general finite element code and so is not reproduced here, as the evaluation of the A and F given in (A4) is relatively straightforward. An example of the determination of T^{n+1} and RH^{n+1} from given weather data will be discussed later. Having A and F, it remains to solve the linear system (A5) to obtain M^{n+1} .

d. Solution of the Linear System $AM^{n+1} = F$.

The structure of the matrix A in equation (A5) is tridiagonal in that for each row i of A, the only nonzero entries are the diagonal element $A_{i,i}$ together with $A_{i-1,i}$ (when $i \neq 1$) and $A_{i,i+1}$ (when $i \neq I$). To solve $AM^{n+1} = F$ we factored the matrix A (by Gaussian elimination) into the form LU where L and U are tridiagonal, L is lower triangular (i.e., $L_{i,j} = 0$ when $i < j$), U is upper triangular (i.e., $U_{i,j} = 0$ when $i > j$), and all the diagonal elements ($L_{i,i}$) of L are equal 1 (see for example Section 3.2 of Chapter 2 of [5]). The equation $AM^{n+1} = F$ is then $LUM^{n+1} = F$. Defining $Z = UM^{n+1}$, one solves $LZ = F$ for Z, and then one solves $UM^{n+1} = Z$ to obtain M^{n+1} . Since A is tridiagonal and A is strictly diagonally dominant (i.e., $A_{i,i} > \sum_{j \neq i} |A_{i,j}|$ for $i=1, \dots, I$), the determination of L and U can be done as in the subroutine TRIDEC given below⁵. The

[5] E. Isaacson and H. B. Keller, Analysis of Numerical Methods, John Wiley & Sons, New York, 1966.

solution of $LZ = F$ and of $UM^{n+1} = Z$ is done in the routine TRISOL given below. In these routines: NROWS denotes the number of unknowns (I); the vectors $AL(i)$, $AD(i)$, and $AR(i)$ ($i=1, \dots, I$) are defined in terms of the matrix A by $AL(i)=A_{i-1,i}$; $AD(i)=A_{i,i}$; and $AR(i) = A_{i,i+1}$ (note $AL(1)$ and $AR(I)$ are never used in TRIDEDEC or in TRISOL); RTSIDE is the right-hand side (F); and SOLN is the answer (M^{n+1}).

From equation (A4) it is seen that the matrix A and vector F in (A5) depend on the time, and thus we now rewrite (A5) as

$$A^{n+1} M^{n+1} = F^{n+1} \quad (A7)$$

Note that the time dependence of A^{n+1} is due entirely to the $D(t^{n+1})$ term. Thus if $D(t^{n+1}) = D(t^n)$ then $A^{n+1} = A^n$ and so the decomposition of A^{n+1} into the form LU (as done in TRIDEDEC) is the same as that for A^n and hence need not be repeated. Thus the use of a constant average kinetic temperature (which gives a corresponding average kinetic diffusion coefficient) over a period of time will save computing time because the matrix A need not be recalculated and decomposed as long as $D(t)$ stays fixed (only the formation of F^{n+1} , and the solution for M^{n+1} performed in TRISOL need be done at each step).

e. Outline of Computer Program.

We now give an outline of the structure of the computer program that was used to solve the diffusion problem (7). The choice of Δt and the spatial mesh (Δ_i), and an example of a routine which provides weather data will be given below. The user must supply: (1) a weather data subroutine which will produce the sequence of temperature and relative humidity values to be used - these could be given directly by meteorological data or by a kinetic average of weather data (as discussed earlier in this report); (2) a diffusion coefficient subroutine which will obtain the diffusion coefficient of the composite under study corresponding to any given temperature value; and (3) a moisture solubility subroutine which will obtain the equilibrium moisture concentration corresponding to a given relative humidity value. The computer program has a SETUP phase which reads in necessary parameters, and a MAIN phase which, given approximate solution values M_i^n at time $t^n \equiv n\Delta t$, produces the approximate solution values M_i^{n+1} at the next time level $t^{n+1} = (n+1)\Delta t$.

Outline of Computer Program

SETUP

1. read in: h , Δt , I , Δ_i ($i=1, \dots, I$), N = number of time steps to be taken, and interval of printout

2. set $x_0=0$, $x_I=h$, $x_i = x_{i-1} + \Delta_i$ ($i=1, \dots, I-1$)
3. read in initial concentration profile M_i^0 ($i=0, \dots, I$), M_i^0 is the percent by weight of moisture at point x_i
4. check that $\sum_i \Delta_i = h$
5. print out the variables that have been read in

MAIN at each time step:

1. set $t^{n+1} = (n+1)\Delta_t$ and find the temperature T^{n+1} and the relative humidity RH^{n+1} using the weather data subroutine
2. use the diffusion coefficient subroutine to find the diffusion coefficient $D(t^{n+1})$ corresponding to T^{n+1} and use the moisture solubility subroutine to find the equilibrium moisture concentration M_O^{n+1} corresponding to RH^{n+1}
3. form the matrix A^{n+1} (see equations (A7) and (A4)) and then decompose A^{n+1} into $A^{n+1} = LU$ by calling TRIDEC (skip this step if: $D(t^{n+1}) = D(t^n)$ and $n > 0$)
4. form F^{n+1} (see equations (A7) and (A4))
5. solve $A^{n+1} M^{n+1} = F^{n+1}$ for M^{n+1} by calling TRISOL
6. check if should do printout of solution values at t^{n+1} , if so, printout t^{n+1} , M_i^{n+1} , calculate average percent by weight moisture (10), etc.
7. if $n+1=N$ stop, otherwise set $n=n+1$ and go back to step (1) of

MAIN

Samples of Computer outputs are shown in Figures 18 and 19.

DISTRIBUTION

	Copies
Office of Director of Defense Research and Engineering Washington, D.C. 20301 Attn: Mr. J. Persh, OAD/ET	1
Commander Naval Air Systems Command Washington, D.C. 20361 Attn: AIR 52032 (C. Bersch) AIR 53032D (M. Stander) AIR 320A (T. Kearns)	1 1 1
Commander Naval Sea Systems Command Washington, D.C. 20360 Attn: SEA 0352 (M. Kinna) SEA 9921 (Hawver) SEA 033 SEA 035 SEA 09G32 SEA 03B	1 2 1 1 2 1
Office of Naval Research 800 Quincy Street Arlington, Virginia 22217 Attn: Code 472 (Dr. G. Neece) Code 470 (Dr. Edward I. Salkovitz) (Dr. E. J. Wynne)	1 1 1
Office of Naval Research 495 Summer St. Boston, MA 02210 Attn: Dr. L. Peebles	1
Director Naval Research Laboratory Washington, D.C. 20375	2

UNCLASSIFIED
NSWC/WOL/TR 77-13

DISTRIBUTION (Cont.)

	Copies
Commander Naval Weapons Center China Lake, California 93555 Attn: Code 533	2
Director of Development Army Material Command Graveley Point Washington, D.C. 20316	1
Commanding Officer Picatinny Arsenal Plastic Technical Evaluation Center Dover, New Jersey 07801 Attn: A. M. Anzalone	1
Commanding Officer U. S. Army Mobility Equipment R & D Laboratory Fort Belvoir, Virginia 22060 Attn: Technical Library	1
Air Force Materials Laboratory Wright-Patterson Air Force Base Ohio 45433 Attn: Technical Library	1
Commanding Officer Army Materials and Mechanics Research Center Watertown, Massachusetts 02172 Attn: Library	1
Army Materials and Mechanics Research Center Watertown, MA 02172 Attn: R. Sacher	1
J. Illinger	1
N. Schneider	1
G. Thomas	1
S. Wentworth	1
Commander, David W. Taylor Naval Ship Research and Development Center Carderock Library, Code 5641 Bethesda, Maryland 20032	1

UNCLASSIFIED
NSWC/WOL/TR 77-13

DISTRIBUTION (Cont.)

	Copies
Commander Naval Ship Research and Development Center Annapolis Laboratory Annapolis, Maryland 21402 Attn: Code 2841 (W. Klemens)	1
Defense Documentation Center Cameron Station Alexandria, Virginia 22314	12
Commander Naval Underwater Systems Center Newport, Rhode Island 02840 Attn: LA151, Technical Library	5
Director Naval Avionics Facility Indianapolis, Indiana 46218 Attn: Code 713 (F. Gahimer) Code 750 (Library)	1 1
Commander Naval Air Development Center Warminster, Pennsylvania 18974 Attn: F. S. Williams W. Fegyna R. Trobacco Code 302	1 1 1 1
NASA Langley Research Center Mail Stop 226 Langley Station Hampton, Virginia 23365 Attn: Dr. Norman Johnston	1
Harry Diamond Laboratories Washington, D.C. 20438 Attn: Library	1
Battelle Columbus Laboratories 505 King Avenue Columbus, Ohio 43201 Attn: Mr. W. Pfeifer	1

UNCLASSIFIED
NSWC/WOL/TR 77-13

DISTRIBUTION (Cont.)

	Copies
Boeing Commercial Airplane Co. P. O. Box 3707 M/S 73-43 Seattle, Washington 98124 Attn: J. T. Quinlivan	1
Effects Technology, Incorporated 5383 Hollister Avenue Santa Barbara, California 93105 Attn: Mr. M. Graham Mr. E. Steele	1 1
Kaman Sciences Corporation P. O. Box 7463 Colorado Springs, Colorado 80933 Attn: Mr. J. C. Nickell	1
KTECH Corporation P. O. Box 160 Goleta, California 93017 Attn: Mr. D. V. Keller	1
Lockheed Missiles and Space Company P. O. Box 504 Sunnyvale, California 94088 Attn: Mr. A. Mietz Mr. C. May	1 1
KTECH Corporation 911 Pennsylvania, Northeast Albuquerque, New Mexico 87110 Attn: Larry Lee	1
Lockheed-Georgia Company Dept. 72-26 Zone 28 Marietta, Georgia 30060 Attn: Walter S. Cremens	1
Los Alamos Scientific Laboratory Los Alamos, New Mexico 87544 Attn: Dr. J. Taylor	1
Prototype Development Associates, Inc. 1740 Garry Avenue, Suite 201 Santa Ana, California 92705 Attn: Dr. John Slaughter	1

UNCLASSIFIED
NSWC/WOL/TR 77-13

DISTRIBUTION (Cont.)

	Copies
Southern Research Institute 2000 Ninth Avenue, South Birmingham, Alabama 35205 Attn: Mr. C. D. Pears Mr. James R. Brown	1 1
Systems, Science, and Software P. O. Box 1620 La Jolla, California 92037 Attn: Dr. G. A. Gurtman	1
United Research Center East Hartford, Connecticut 06601 Attn: D. A. Scola	1
Materials Science Corporation Blue Bell, Pennsylvania 19422 Attn: B. W. Rosen	1
Rockwell International Aircraft Division Los Angeles, California 90009 Attn: Dr. D. Y. Konishi	1
Advanced Technology Center, Inc. P. O. Box 6144 Dallas, Texas 75222 Attn: D. H. Petersen	1
Brunswick Corporation 4300 Industrial Avenue Lincoln, Nebraska 68503 Attn: Ray Nuss	1
General Dynamics Convair Division P. O. Box 80847, San Diego, CA 92138 Attn: W. G. Scheck	1
McDonnell Aircraft Co. P. O. Box 516 St. Louis, MO 63166 Attn: M. P. Renieri (Bldg. 34) G. D. Renieri (Bldg. 106)	1 1

UNCLASSIFIED
NSWC/WOL/TR 77-13

DISTRIBUTION (Cont.)

Copies

R & D Associates
P. O. Box 3580
Santa Monica, CA 90403
Attn: R. A. Field

1

TO AID IN UPDATING THE DISTRIBUTION LIST
FOR NAVAL SURFACE WEAPONS CENTER, WHITE
OAK LABORATORY TECHNICAL REPORTS PLEASE
COMPLETE THE FORM BELOW:

TO ALL HOLDERS OF NSWC/WOL/TR 77-13
by J. M. Aug1, Code WR-31

DO NOT RETURN THIS FORM IF ALL INFORMATION IS CURRENT

A. FACILITY NAME AND ADDRESS (OLD) (Show Zip Code)

NEW ADDRESS (Show Zip Code)

B. ATTENTION LINE ADDRESSES:

C.

REMOVE THIS FACILITY FROM THE DISTRIBUTION LIST FOR TECHNICAL REPORTS ON THIS SUBJECT.

D. NUMBER OF COPIES DESIRED _____

**DEPARTMENT OF THE NAVY
NAVAL SURFACE WEAPONS CENTER
WHITE OAK, SILVER SPRING, MD. 20910**

**OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE, \$300**

**POSTAGE AND FEES PAID
DEPARTMENT OF THE NAVY
DOD 316**



**COMMANDER
NAVAL SURFACE WEAPONS CENTER
WHITE OAK, SILVER SPRING, MARYLAND 20910**

ATTENTION: CODE WR-31