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LIFE ASSURANCE OF COMPOSITE STRUCTURES

VOLUME I. MOISTURE EFFECTS
FORT WORTH DIVISION OF GENERAL DYNAMICS

MAY 1975

TECHNICAL REPORT AFML-TR-75-51, VOLUME I

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ERRATA SHEET

AFML-TR-75-51
LIFE ASSURANCE OF COMPOSITE STRUCTURES
Volume I, Moisture Effects

Section VII, CONCLUSIONS, p. 89, 4th paragraph should read as follows:

"Some desorption occurs when a laminate is exposed to the elevated temperatures of supersonic service. However, moisture content eventually climbs to an equilibrium value despite twice weekly supersonic service. In fact, such exposures to 300°F supersonic service peak temperatures cause permanent changes in the subsequent moisture diffusion behavior of T300/5208. Periodic exposures to a thermal spike having a peak temperature of 300°F increase moisture absorptivity. The absorptivity coefficient was doubled by such exposures. All of the absorbed moisture was removed by drying at 180°F; however, the diffusion behavior was permanently changed. Exposure to sub-zero temperatures, on the other hand, caused no changes in diffusion behavior."

Unclassified

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Composites, Graphite-Epoxy, Life Assurance, Humidity, Moisture Diffusion, Supersonic Heating Effects, Accelerated Conditioning, Environmental Simulation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Volume I describes tests that were conducted to determine rates and extent of moisture absorption by graphite-epoxy composites. Procedures were developed for accelerating moisture exposures so that years of environmental service could be simulated within a few months. An empirical math model was developed which can predict moisture absorption behavior under realistic or accelerated exposure conditions. Tests also were conducted to determine

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20. ABSTRACT (Continued)

whether aircraft flight conditions cause changes in moisture absorption behavior. These investigations show that graphite-epoxy composites absorb moisture until an equilibrium level is reached which is proportional to relative humidity. Simulated flight conditions do not cause significant drying of the laminates. In fact, brief exposures (4-5 minutes) to supersonic heating temperatures cause significant increases in the amount and rate of subsequent moisture absorption. Subsonic temperatures, however, cause no detectable change in diffusion behavior.

FOREWORD

The work reported in this final report, which is designated Report No. AFML-TR-75-51, Vol. 1, was performed under Contract F33615-73-C-5104, Task No. 698CW. This contract with General Dynamics' Fort Worth Division (P. O. Box 748, Fort Worth, Texas 76101) was accomplished under the technical direction of Mr. A. W. Davis of the Air Force Materials Laboratory, Advanced Development Division, Wright-Patterson Air Force Base, Ohio. All work was accomplished between July 1973 and February 1974.

Mr. R. V. Wolff served as General Dynamics' program manager. Mr. E. L. McKague, Jr. was technical task leader over the moisture effects investigations, which are reported in this volume. Mr. J. E. Halkias and Mr J. D. Reynolds were the test engineers for the moisture effects studies.

This technical report was submitted in February 1975. It has been reviewed and is approved.

A. W. Davis	R. A. Mollicone, Maj. USAF
Project Engineer	Program Manager
Advanced Development Division	Advanced Development Division
Air Force Materials Laboratory	Air Force Materials Laboratory
Wright-Patterson AFB, Ohio	Wright-Patterson AFB, Ohio

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS
(CONTINUED)

LIST OF ILLUSTRATIONS (CONTINUED)

LIST OF ILLUSTRATIONS
(CONTINUED)

LIST OF ILLUSTRATIONS
(CONTINUED)

LIST OF TABLES

SECTION I

INTRODUCTION

The objective of this program was to demonstrate that the lifetime characteristics of a composite component can be predicted from the lifetime characteristics of its elements.

The basic approach was to test selected wing structural elements under random fatigue loading with superimposed environmental conditions simulating actual service conditions. Then, the performances of these wing elements, which represented the critical areas of the composite wing box demonstration component, were used to predict the test performance of the wing box.

Sufficient testing was planned to validate the ability to determine service-life characteristics of the component based on statistical analyses of elemental specimens.

The program was divided into the following phases:

Phase I - Element Characterization

Phase II - Reliability Prediction

Phase III - Component Characterization

Phase IV - Life Assurance Correlation.

One of the main problems in Phase I was determining how to simulate actual environmental service conditions. Accounting for environmental factors meant that the effects of months or years of actual service exposures would have to be condensed into a period of several weeks.

The effects of elevated or lowered temperatures during flight loadings could be accounted for easily by appropriate temperature cycling during the time-compressed random fatigue loadings. Therefore, the problem was centered on simulating the atmospheric moisture effects an element would experience during a lifetime of service.

An important corallary objective of this program was to characterize moisture imbibition by graphite-epoxy composites in non-xeric environments. This characterization was to lead to the development of a method by which the effects of realistic exposure to atmospheric moisture could be studied by compressing years of exposure to service environments into several weeks of laboratory exposure.

A part of this characterization was to determine if static and dynamic laboratory conditioning methods differ significantly. As used here, static conditioning means any of a variety of hygrothermal exposures (exposure to a specific combination of constant humidity and constant temperature). Dynamic conditioning means changing humidity and temperature conditions that might be required to simulate "real life."

The determination, per se, of moisture effects upon specific mechanical properties was not a major objective of the program. However, some tests of mechanical effects caused by moisture were conducted. These included tests of 0° flexural strength, short beam shear strength, flexural creep behavior, and bolt bearing strength. All of these properties were determined as a function of absorbed moisture content.

This volume, Volume I, of this final report presents all of the data developed concerning moisture effects. This includes the studies of moisture absorption and desorption, mechanical effects, and accelerated exposure investigations.

SECTION II

TEST MATERIALS, SPECIMEN DESIGN, AND FABRICATION

A graphite-epoxy material system was used for all of the investigations in this program. The reinforcing fiber was a high-strength, intermediate-modulus graphite fiber manufactured by Union Carbide Corporation. It is identified as Thornel 300 and abbreviated to T300. The fiber is a continuous, 3000-end, untwisted yarn that is made from a polyacrylonitrile (PAN) precursor. The resin matrix was a high-temperature, modified-epoxy system identified as 5208 epoxy resin. It is produced by the Narmco Materials Division of Whittaker Corporation, which also impregnates the fibers with the resin. The resin impregnated, collimated fiber system is identified as T300/5208 graphite-epoxy. It is supplied with a nominal resin content of 40% by weight and has a volatile content of less than 1% by weight. The typical time-temperature relationship for resin gellation in the prepreg is shown in Figure 1.

Four panels were laid up using T300/5208 graphite-epoxy from Batch 30, Rolls 6 and 7. The material met the requirements of Fort Worth Specification FMS-2023, Type III, Form C. Acceptance test values are shown in Table I. Each panel was 12 inches long in the 0° reference direction; panel widths varied as required to obtain the necessary number of test specimens. Each of the four panels contained a different number of plies, which were oriented to form $[0_2/\pm45]$ laminates for three panels containing 8, 16, and 24 plies. The fourth panel contained only ±45 plies and was only 4 plies thick.

These laminate orientations were selected to simulate actual aircraft panels and to minimize the surface waviness that sometimes occurs with a unidirectional orientation. The test panel lay-up sequences are identified in Table II.

The four test panels provided all of the test specimens used in the moisture effects studies with the exception of the specimens used to determine bolt bearing strength. The graphite-epoxy test skins for the bolt bearing specimens were taken from a 20-ply (±45) laminate made from Batch 55 of T300/5208. Acceptance test values for Batch 55 are shown in Table III. These values also met the requirements of Fort Worth Specification FMS-2023, Type III, Form C (Reference 1).

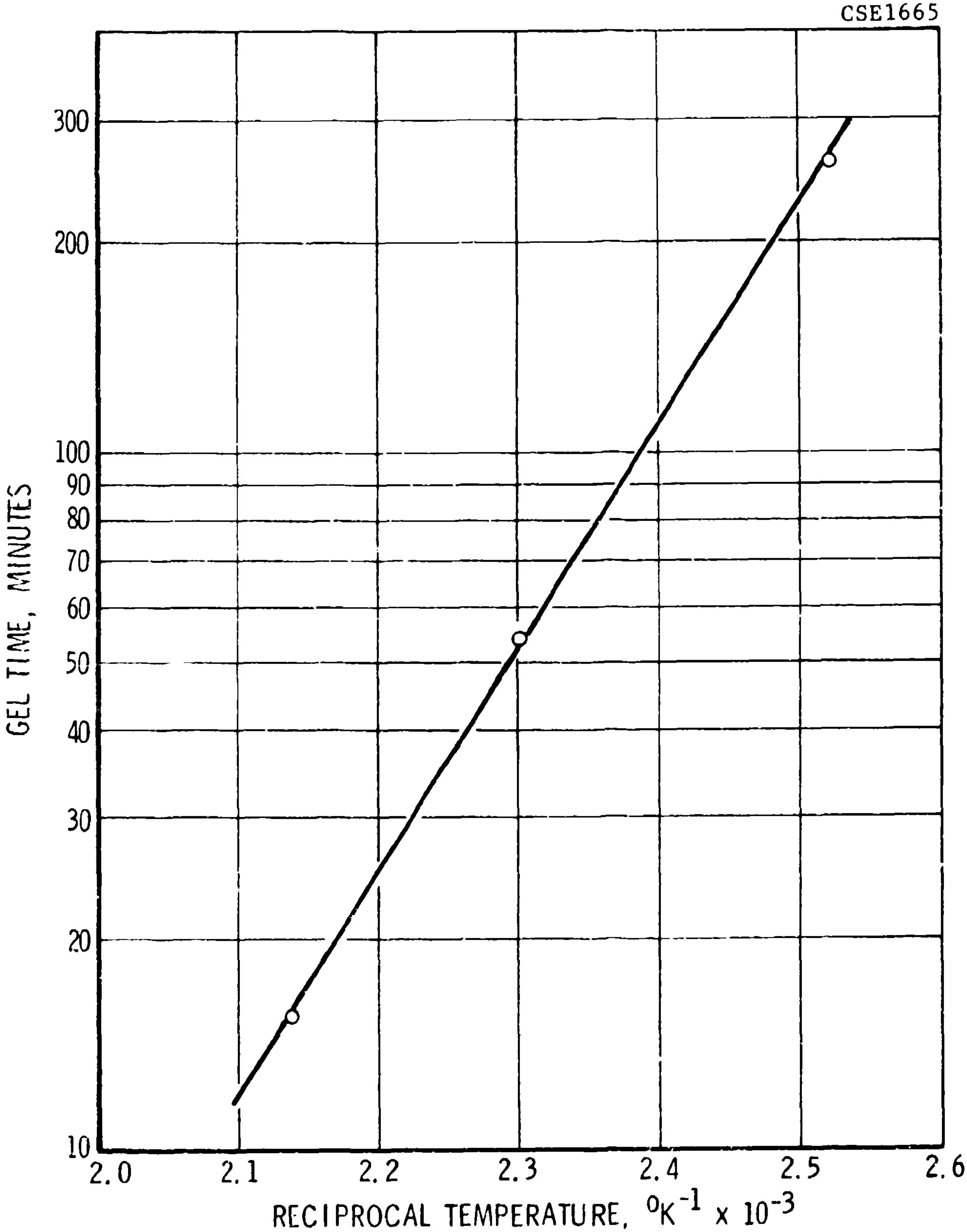


Figure 1 Resin Gellation Characteristics of T300/5208 Graphite-Epoxy

Table I

BATCH 30* ACCEPTANCE TEST VALUES

Property	75°F	350°F
0° Flex Strength, psi x 10^3	285.1	223.4
0° Flex Modulus, psi x 10^6	22.0	20.3
90° Flex Strength, psi x 10^3	13.7	7.8
Horizontal Shear Strength, psi x 10^3	16.7	9.4
0° Tensile Strength, psi x 10^3	222.0	-
0° Tensile Modulus, psi x 10^6	20.8	-
0° Ultimate Strain, μ-inch/inch	10,020	-
90° Tensile Strength, psi x 10^3	5.87	-
90° Tensile Modulus, psi x 10^6	1.42	-
90° Ultimate Strain, μ-inch/inch	4,230	
Ply Thickness, inch	0.0058	

* T300/5208 (Narmco)

Table II

TEST PANEL LAY-UP SEQUENCE

Orientation	Plies Per Panel		
+45			
-45	4 Plies		
-45			
+45			
0			
+45			
-45			
0	8 Plies		
0			
-45			
+45			
0			
0			
-45		16 Plies	
+45			
0			
0			24 Plies
-45			
+45			
0			
0			
-45			
+45			
0			
0			
-45			
+45			
0			

Table III

BATCH 55* ACCEPTANCE TEST VALUES

Property	75°F	350°F
0° Flex Strength, psi x 10^3	258.6	219.5
0° Flex Modulus, psi x 10^6	20.5	19.9
90° Flex Strength, psi x 10^3	12.2	7.2
Horizontal Shear Strength, psi x 10^3	17.2	8.7
0° Tensile Strength, psi x 10^3	165.8	-----
0° Tensile Modulus, psi x 10^6	20.2	-----
0° Ultimate Strain, μ-inch/inch	7780	-----
90° Tensile Strength, psi x 10^3	8.0	-----
90° Tensile Modulus, psi x 10^6	1.43	-----
90° Tensile Strain, μ-inch/inch	5480	-----
Ply Thickness, inch	0.0054	

*T300/5208 (Narmco)

After each panel was laid up, it was cured in accordance with Fort Worth Specification FPS-2021, Reference 2. Immediately after the panels were cured, they were placed into desiccated storage until time for specimen cutting and testing. After the specimens were cut they were immediately returned to desiccated storage. An indicating desiccant was used for all such storage periods.

Tests were conducted to verify that the laminates represented good quality. These tests included determinations of resin content and mechanical property tests. The resin contents of the laminates were found to be as follows:

Number of Plies	Resin Content, %
4	31.1
8	29.2
16	32.7
24	30.7

Resin contents were determined using a sulfuric acid/hydrogen peroxide digestion method per FMS-2023, Reference 1. Mechanical property tests consisted of 0° flex and short beam (horizontal) shear strength determinations on the 16-ply laminate only. These strength values are shown in Table IV.

After the 4-, 8-, 16-, and 24-ply panels had been cured, each was cut to yield numerous rectangular specimens. Each specimen was nominally 0.50 inch wide and 3.00 inches long. These specimens, for all four panel thicknesses, were used for moisture absorption and desorption tests. Part of the specimens from the 16-ply laminate were used for mechanical tests. These were tests of flexural strength retention after various periods of moisture exposure. The tests were, in essence, 0° flexural strength tests even though the specimens were not unidirectionally reinforced. These specimens were tested in accordance with the 0° flex test method defined in FMS-2023.

Other rectangular specimens were cut from the 16-ply and 4-ply laminates. The 16-ply specimens were cut and tested mechanically in accordance with FMS-2023 requirements for short beam shear strength determination. The 4-ply laminate was cut to yield tiny rectangular specimens for use in determining flexural creep behavior. These specimens were nominally 0.25 inch long by 0.050 inch wide.

Table IV

LAMINATE PROPERTIES*

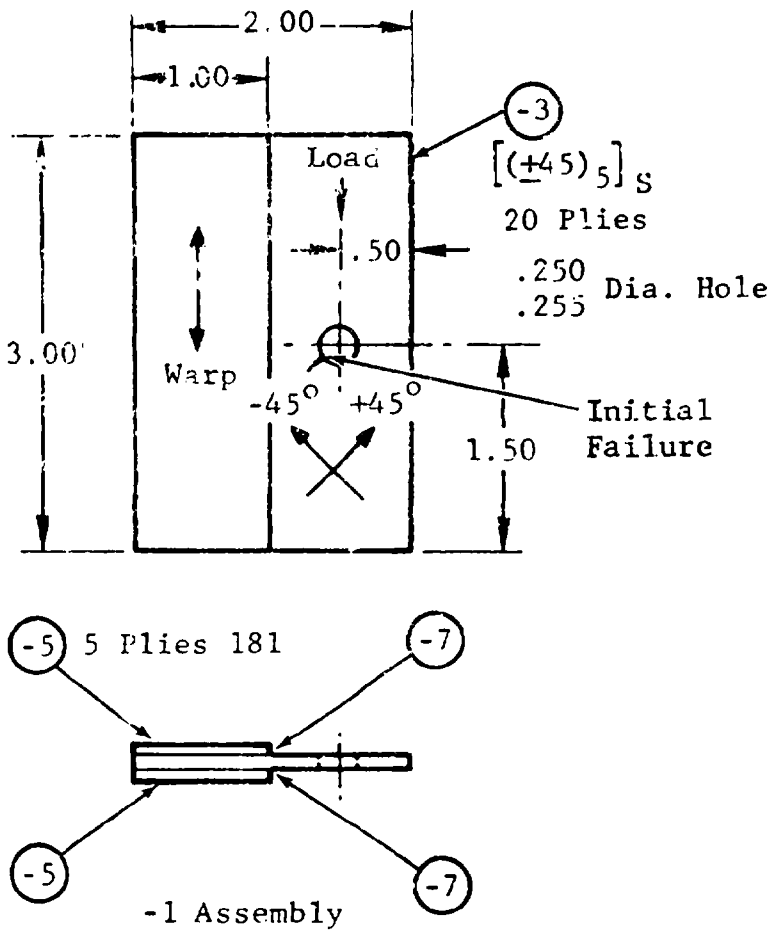
Property	75°F	350°F
0° Flex Strength, psi x 10^3	155.6	139.5
	132.7	142.2
	153.1	133.6
	137.8	134.2
	146.8	133.4
Average	145.2	136.6
Std Dev, %	6.7	2.9
0° Flex Modulus, psi x 10^6	12.6	11.7
	10.9	10.7
	12.5	10.7
	9.8	11.5
	11.3	10.6
Average	11.4	11.0
Std Dev, %	10.2	4.7
Horizontal Shear Strength, psi x 10^3	10.6	7.5
	11.1	6.7
	11.5	7.0
	12.4	7.1
	11.3	7.1
Average	11.4	7.1
Std Dev, %	5.8	4.0

* Initial Dry Condition on $[0_2 / \pm 45]$ Laminates

After the various specimens were cut, they were numbered, weighed, and measured. Then, they were returned to desiccated storage.

The 20-ply (± 45) laminate was processed to yield bolt bearing specimens, also identified as Type I specimens. Figure 2 shows the details of dimension, construction, and orientation of these specimens. The finished specimens were 2 by 3 inches with 1- by 3-inch glass tabs bonded on both sides of one edge of the graphite-epoxy skin. A 1/4-inch-diameter hole was drilled through the center of the base portion of the graphite-epoxy. The specimens were designed to be loaded with a pin, simulating a bolt through the hole, bearing downward along the reference warp axis. This load was reacted by gripping the specimen along the 3-inch side in the bonded glass reinforced doubler area. Figure 3 shows the static test setup used for the bolt bearing static strength determinations. Figure 4 illustrates the positioning of the reusable clip gage used in developing load/deflection traces.

CSE 1291



		Description	Material
AR	-7	Adhesive	FMS 1013
2	-5	Doubler	FMS 1023 CL II Style 181
1	-3	Skin	FMS 2023 Type III
	-1	Part Number	
420	Quantity Required		

2. Process and Quality Control of -1 & -5 per FPS 2002, Omit 7.2.2.1 & 7.2.2.2

1. Process and Quality Control of -3 per FPS 2021, Omit Para. 3.1-3.5

Figure 2 Bolt Bearing Specimen

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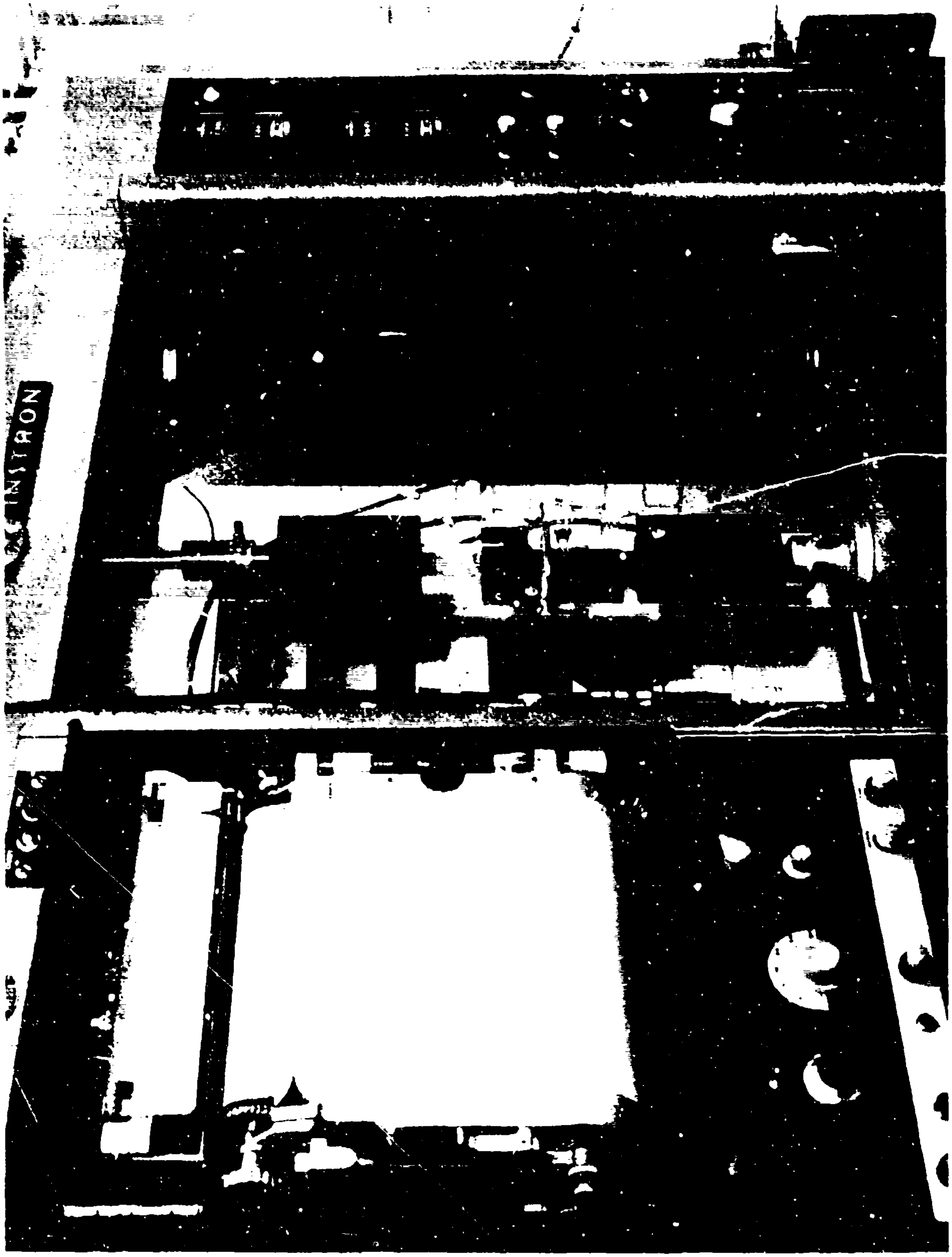

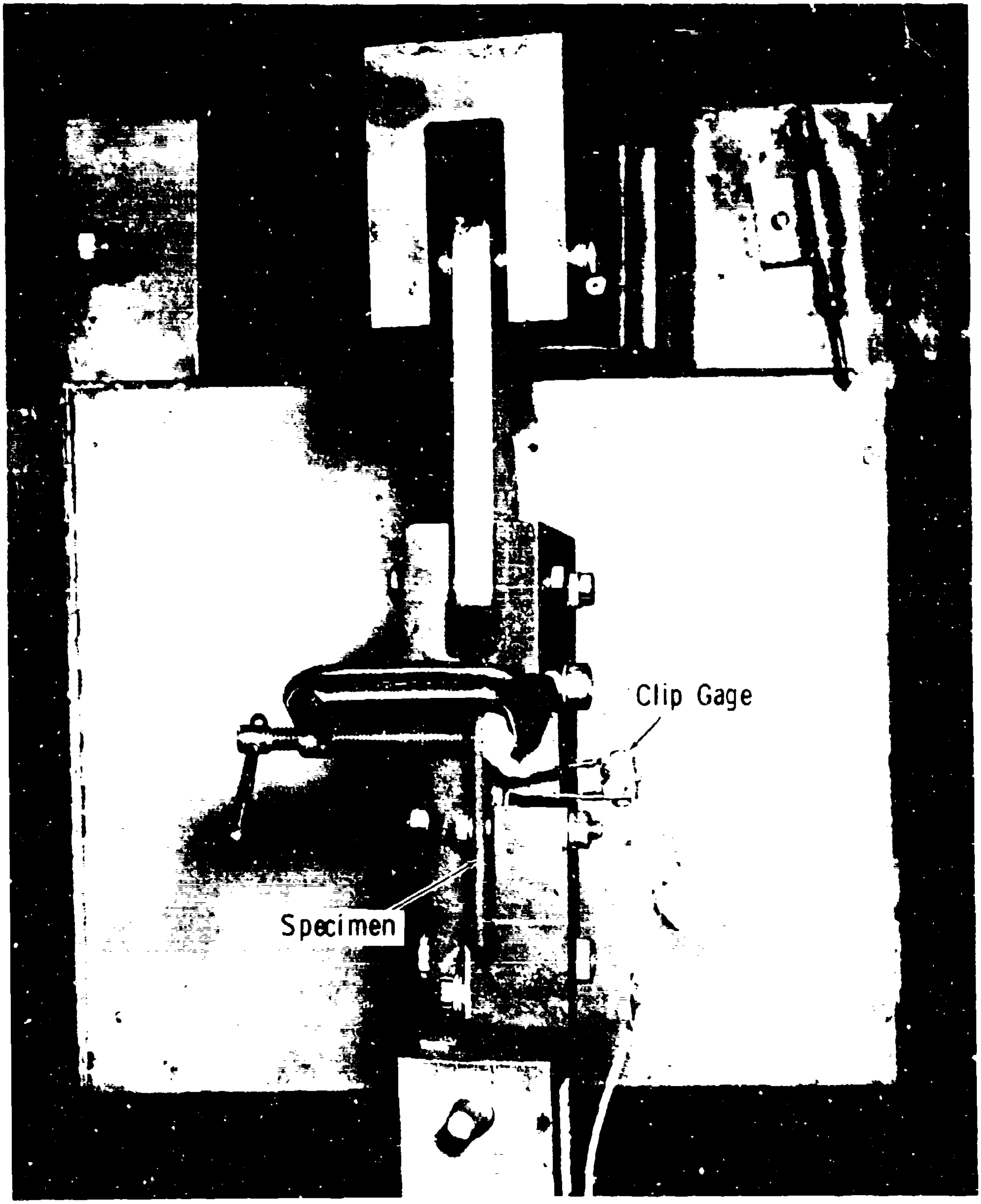

Figure 4 Reusable Clip Gage Installation, Bolt Bearing Specimen

SECTION III

HYGROTHERMAL EXPOSURES

Tests were conducted to characterize the behavior of graphite-epoxy in hygrothermal environments. This was the first test condition for determining moisture absorption behavior because a hygrothermal environment (constant humidity at constant temperature) is easy to establish in the laboratory.

The hygrothermal environments that were established involved temperatures that ranged from 75°F to 212°F. The values of humidity ranged from essentially zero (<1%) to 100%. The absence of humidity at any temperature technically constitutes a hygrothermal environment. However, it is a special condition that has meaning only for preservation of the moisture-free state for some period or for desorption of moisture following an exposure to some level of humidity. Therefore, desorption behavior is discussed in a section following discussion of absorption. Then, the analysis of data and development of an empirical diffusion model are discussed.

3.1 DIFFUSION BEHAVIOR

Moisture absorption was characterized by exposing unstressed specimens from each of the four panel thicknesses (4, 8, 16, and 24 plies) to 16 different hygrothermal environments. These environments were made up of various combinations of temperature and humidity, as shown in Table V.

Table V EXPOSURE MATRIX FOR HYGROTHERMAL ABSORPTION

Exposure Temp., °F	Relative Humidity, %				
	15	45	75	98	100
75	X	X	X	X	X
120		X	X	X	X
150		X	X	X	
180		X	X	X	
212					X

Immersion in water was used to simulate a relative humidity of 100%. These conditions were added later in the investigation to demonstrate that water immersion at less than 212°F is equivalent to a 100% relative humidity.

Various saturated salt solutions were used to create the other humidity values. These solutions were held by sealable glass chambers, which were kept at the selected temperatures. Ovens provided the 120°F, 150°F, and 180°F temperatures. The 212°F temperature was provided by a hot plate, and the 75°F temperature was provided by the ambient laboratory temperature. The saturated solutions and the relative humidity that each provided (Reference 3) are shown in Table VI.

Table VI RELATIVE HUMIDITIES PROVIDED BY SATURATED SOLUTIONS

Solution	Relative Humidity, %
Lithium chloride (LiCl)	15
Chromium Trioxide (CrO_3)	45
Sodium Chloride (NaCl)	75
Lead Nitrate ($PbNO_3$)	98

Racks were used to hold the unstressed composite specimens in the humidified, stagnant air space above the saturated solutions. Water-immersed specimens merely rested on the bottom of water-filled beakers. Periodically, specimens of all four thicknesses were removed from the hygrothermal environments, and their weights were recorded.

3.1.1 Fick's Law

Diffusion of moisture into polymeric materials follows Fick's law of diffusion. For one-dimensional diffusion, the general equation is

$$\partial c/\partial t = D\partial^2 c/\partial x^2 \qquad (1)$$

where, c = concentration;
t = time;
D = diffusion coefficient; and
x = distance.

The solution to this differential equation yields the following relationship for a flat plate absorbing vapor through both faces (Reference 4):

$$F = (4/\ell)\ (Dt/\pi)^{\frac{1}{2}} \tag{2}$$

where, F = fraction of equilibrium moisture content;
ℓ = plate thickness, cm;
D = diffusion coefficient, cm^2/sec; and
t = exposure time, sec.

The form of this solution shows that moisture content changes in proportion to the square root of exposure time. For a given exposure time, absorption is inversely proportional to plate thickness.

Because of the relationship between absorbed moisture and exposure time, all weight change data has been plotted as a function of the square root of exposure time. For convenience in interpreting the data, one day was used as the unit of exposure time.

3.1.2 Experimental Results

Four rectangular specimens, 0.50 inch by 3.00 inch (0° flex size), of each panel thickness were exposed to each hygrothermal environment. After each of several exposure periods, the specimens were removed briefly from the test environment for weighing. These weight data were converted to values of moisture content, expressed as a percentage of the initial, moisture-free specimen weight.

3.1.2.1 Absorption

The relationships of moisture content (%) to square root of exposure time (days$^{1/2}$) is shown in Figure 5 for 4-ply specimens exposed to various humidities at room temperature. These data include exposures to all five test humidities: 15, 45, 75, 98, and 100% relative humidity (R.H.). The averages and ranges of moisture contents for each group of four specimens are shown. Figure 5 shows that the 4-ply specimens gain weight in all five humidities and asymptotically approach equilibrium levels. Higher values of relative humidity cause higher equilibrium moisture levels.

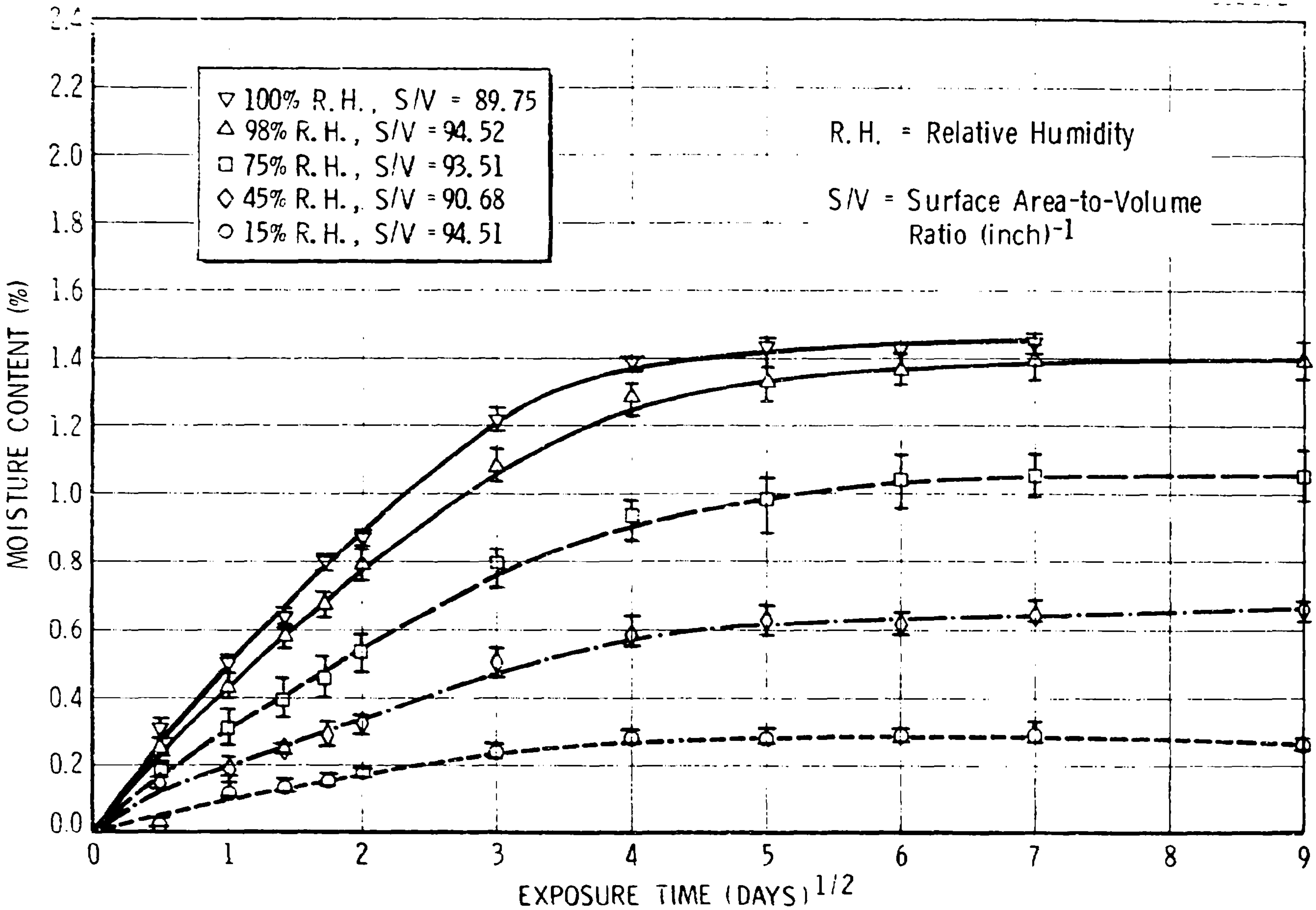

Figure 5 Moisture Absorption - 4 Ply Laminate at 75° F

As shown previously, the fraction of equilibrium moisture content defined by Fick's Law is inversely proportional to thickness. However, the 0° flex sized specimens used in this test are dimensionally different than a large area plate. To compensate for these dimensional differences, the ratio of surface area to volume (S/V) has been used for all analyses. Values of S/V for each laminate are shown in the figures. Units of S/V are $inch^{-1}$. As the width and length of a 0° flex specimen increase to approach the dimensions of a large-area flat panel, the value of S/V approaches that given by twice the reciprocal of panel thickness.

Figure 6 shows data for 8-ply specimens exposed to the five relative humidities at 75°F. The behavior is similar to that shown in Figure 5 except that it takes a little longer to approach equilibrium. In Figure 7, moisture content (%) versus square root of exposure time ($days^{\frac{1}{2}}$) is shown for 16-ply-thick 0° flex specimens exposed to humidity at 75°F. The character of these data differs from that shown in Figures 5 and 6 because longer times are required to approach equilibrium. The 16-ply data are essentially linear with $(time)^{\frac{1}{2}}$ during the total exposure duration, which was 81 days. Similarly, linear data are shown in Figure 8 for 24-ply laminate specimens exposed at room temperature.

The range of data points has been shown only for Figure 5 because the range diminishes significantly as specimen thickness increases. The plotted data points in the other figures are averages of four specimens.

Data for 4-, 8-, 16-, and 24-ply-thick specimens exposed to humidity at 120°F are shown in Figures 9 through 12, respectively. Exposure to 15% was not performed for this and other elevated temperatures, and exposure to 100% was given only to 4-ply specimens. Again, the asymptotic approach to equilibrium is evident in the 4- and 8-ply laminates; however, the rate of approach to equilibrium is more rapid. The 16-ply laminates exposed at 75°F displayed linear behavior, but the 16-ply specimens exposed at 120°F displayed nonlinearity. However, the 24-ply specimens are linear through 81 days of exposure at both temperatures.

Data for specimens exposed to humidity at 150°F are shown in Figure 13 through 16. The rate of approach to equilibrium is more rapid than that found in the specimens exposed at 120°F. At 150°F exposure, the 24-ply laminates exhibit nonlinearity in weight gain versus square root of days. The data in Figures

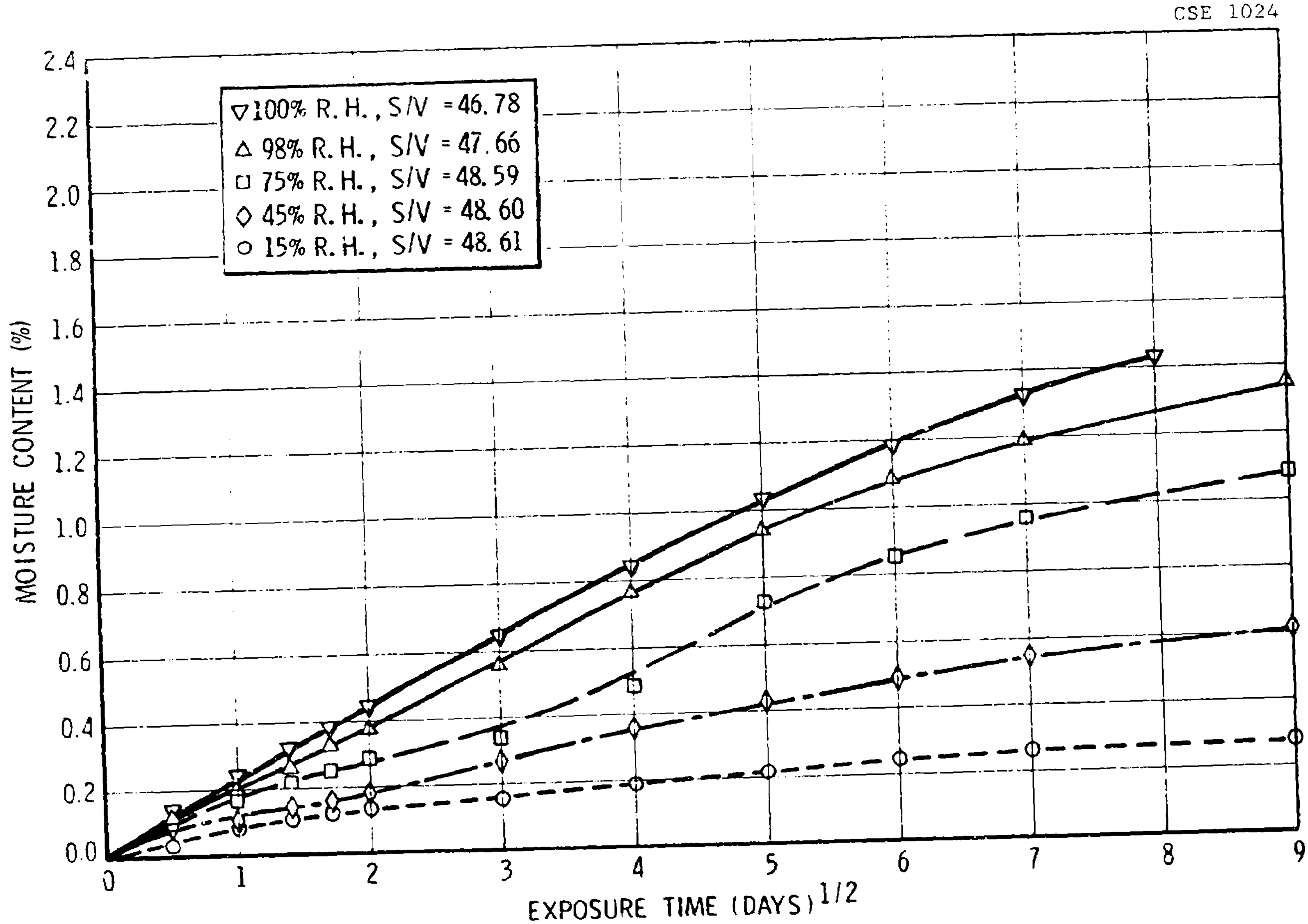

Figure 6 Moisture Absorption - 8 Ply Laminate at 75°F

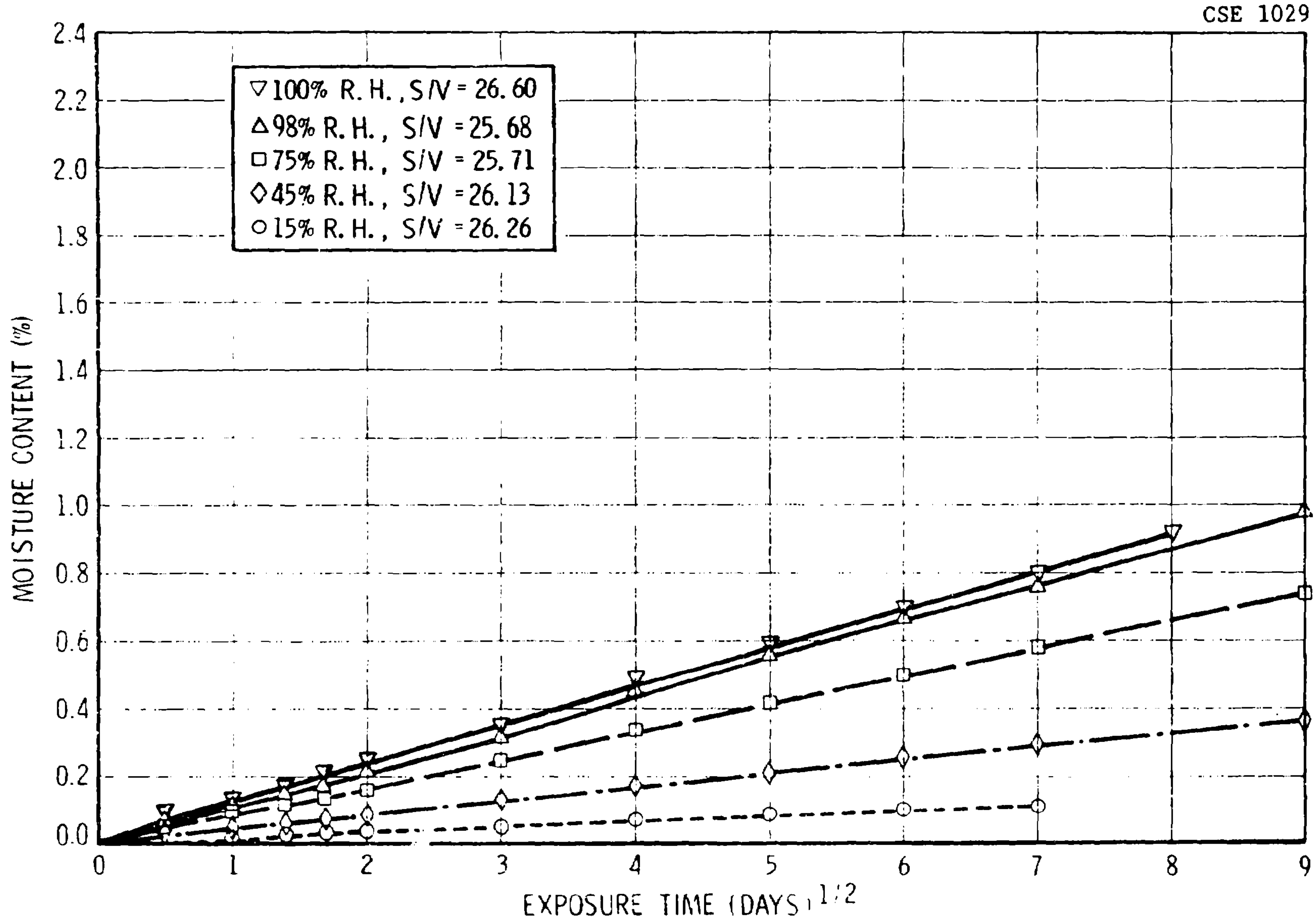

Figure 7 Moisture Absorption - 16 Ply Laminate at 75°F

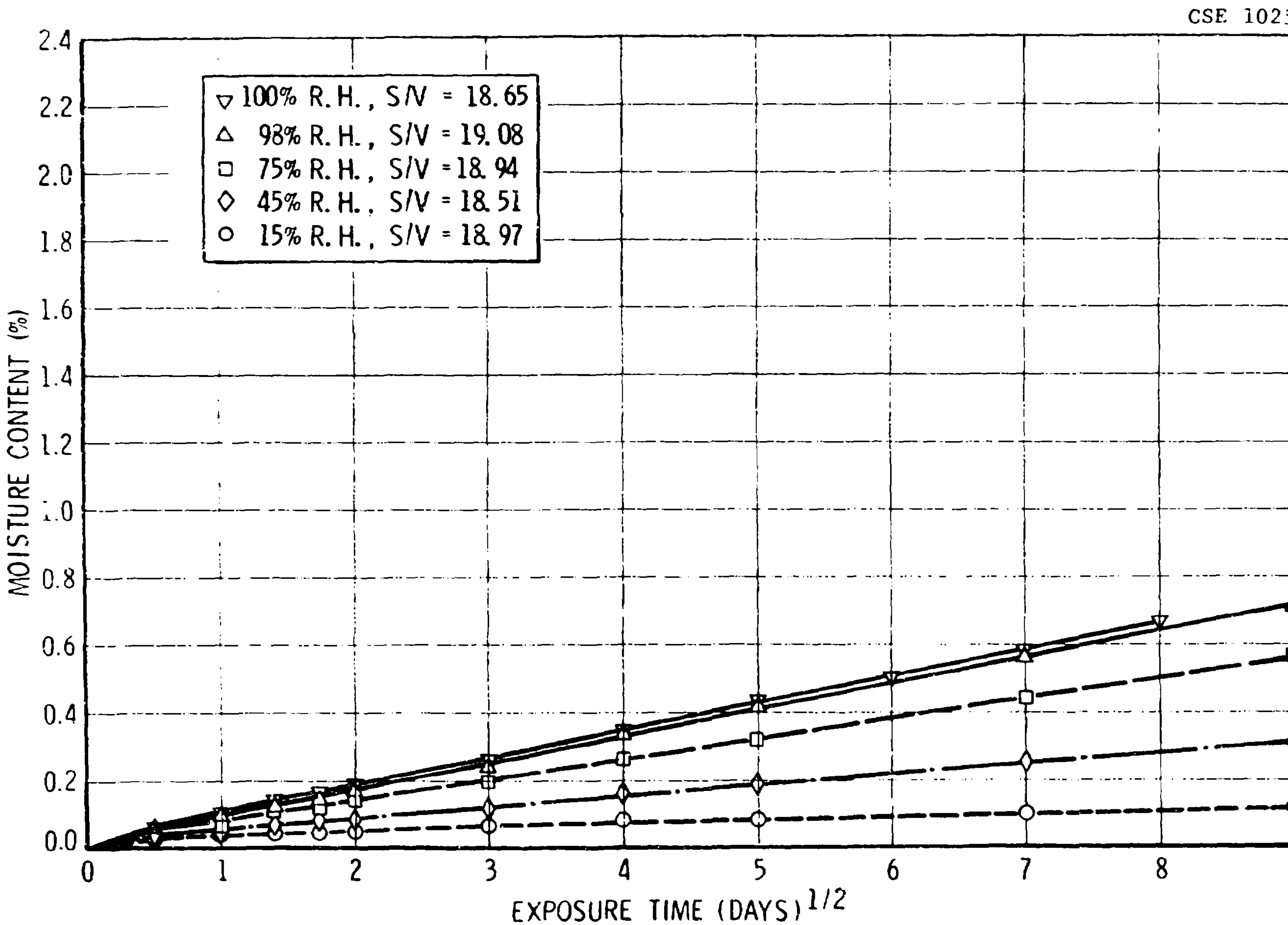

Figure 8 Moisture Absorption - 24 Ply Laminate at 75°F

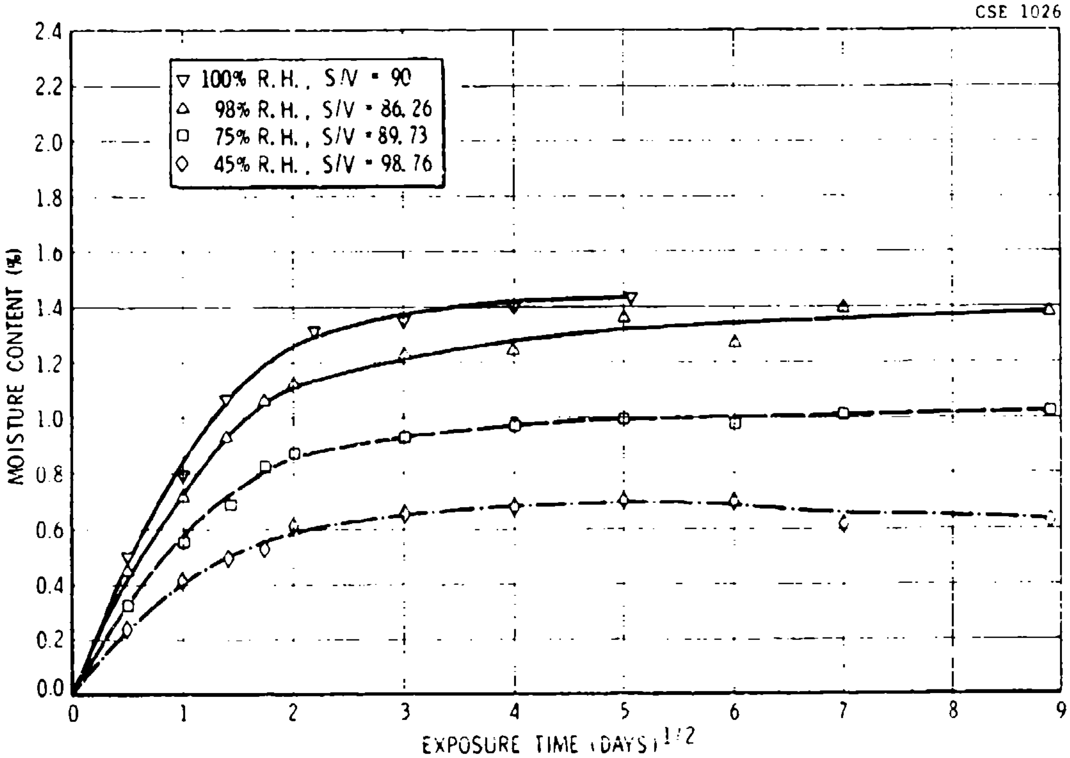

Figure 9 Moisture Absorption - 4 Ply Laminate at 120°F

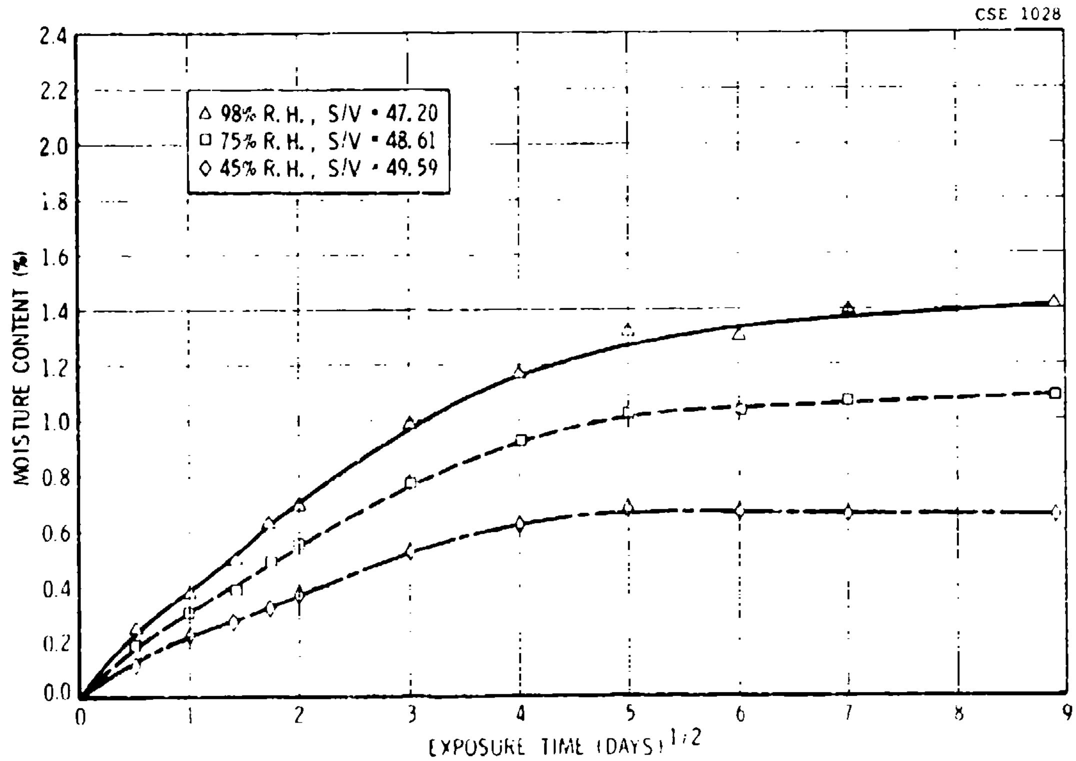

Figure 10 Moisture Absorption - 8 Ply Laminate at 120°F

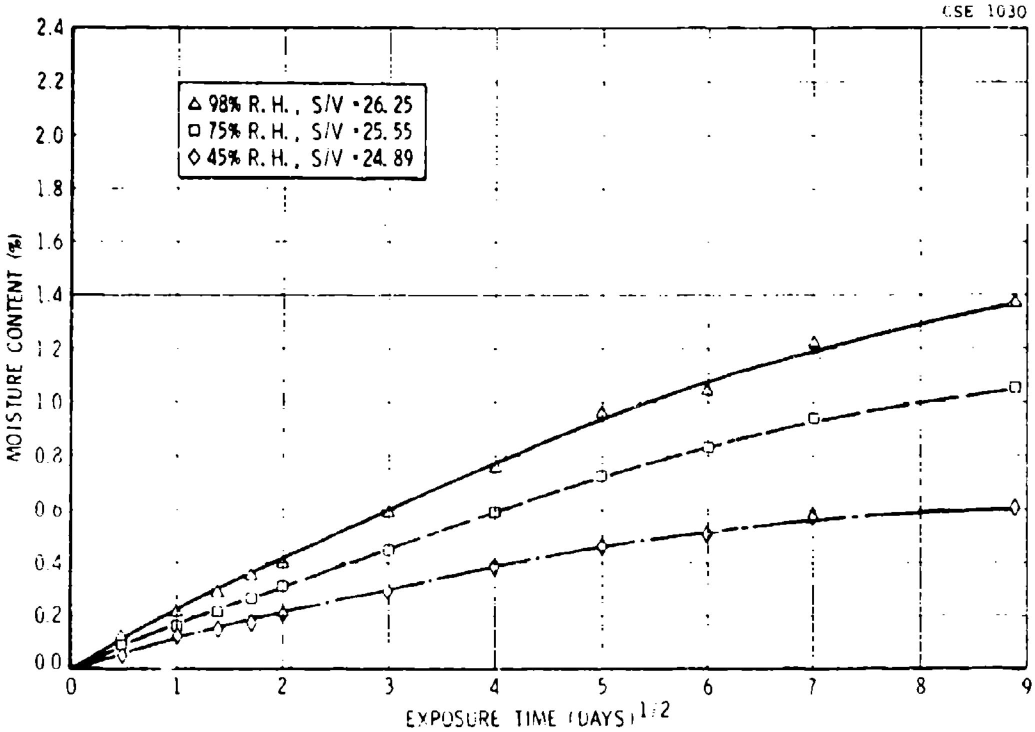

Figure 11 Moisture Absorption - 16 Ply Laminate at 120°F

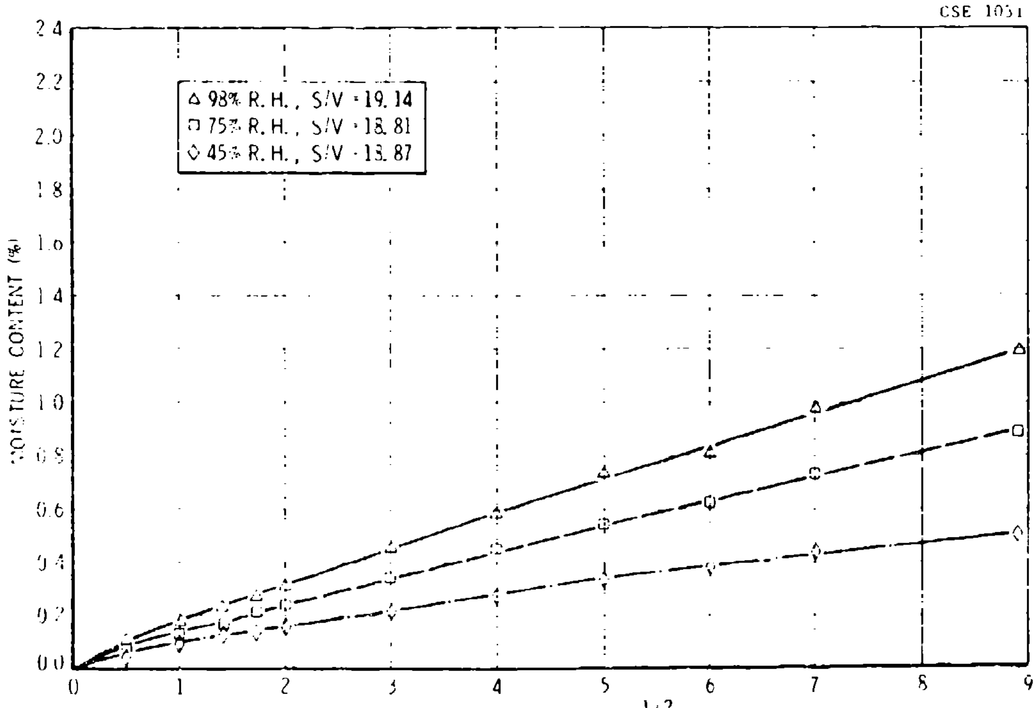

Figure 12 Moisture Absorption - 24 Ply Laminate at 120°F

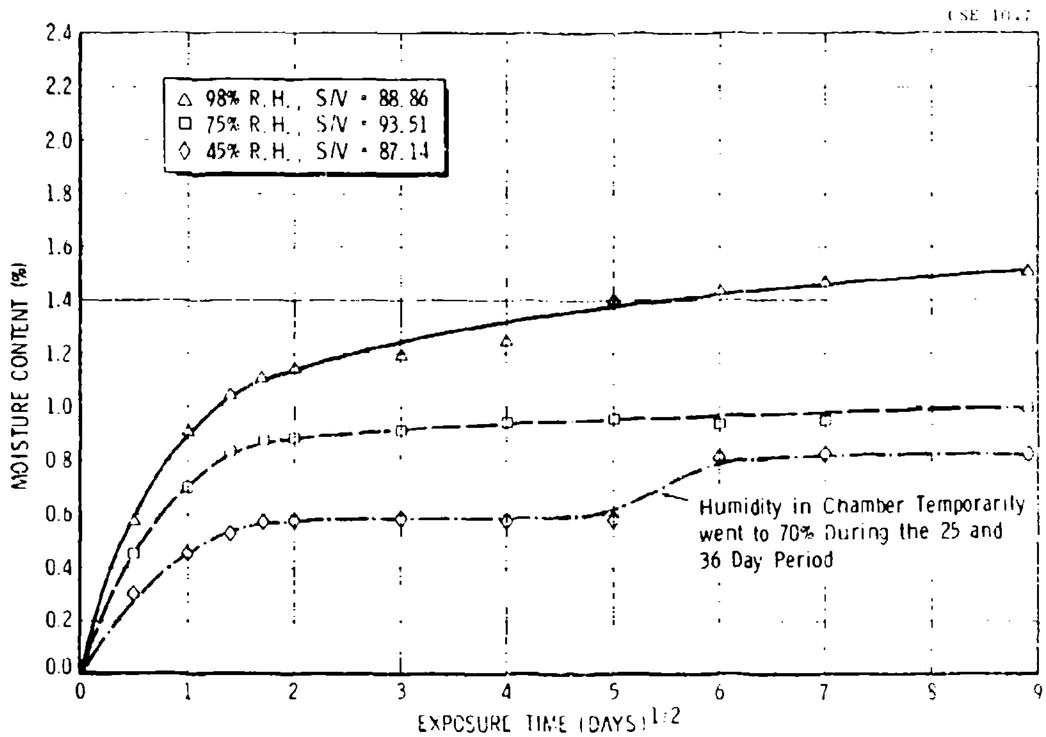

Figure 13 Moisture Absorption - 4 Ply Laminate at 150°F

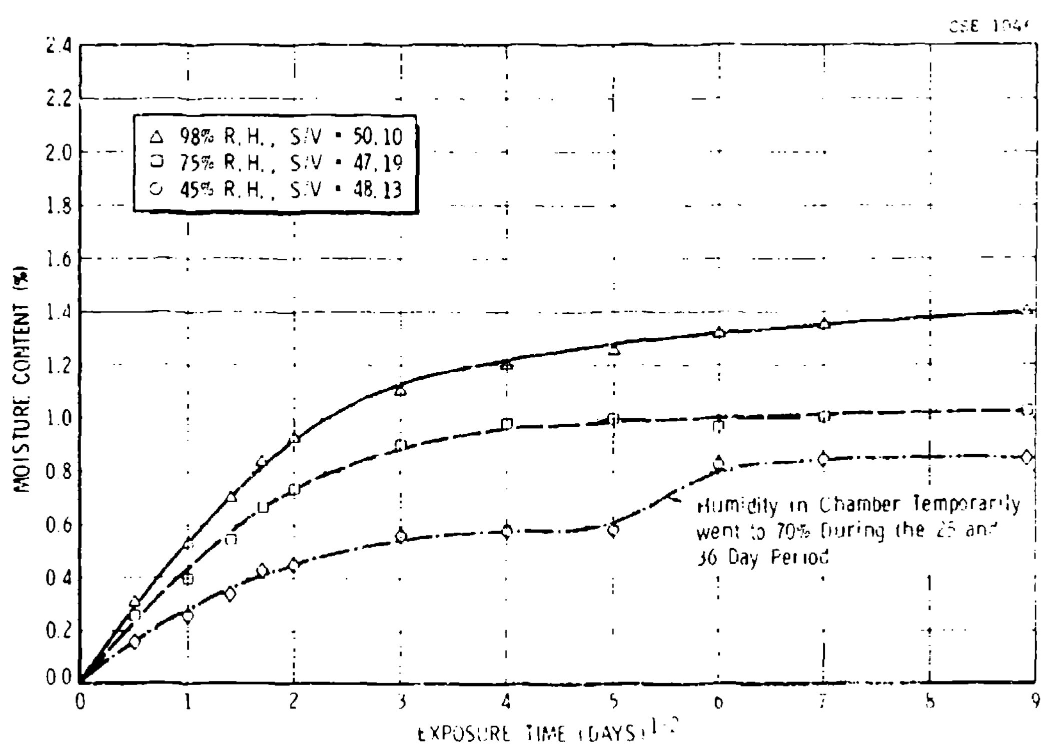

Figure 14 Moisture Absorption - 8 Ply Laminate at 150°F

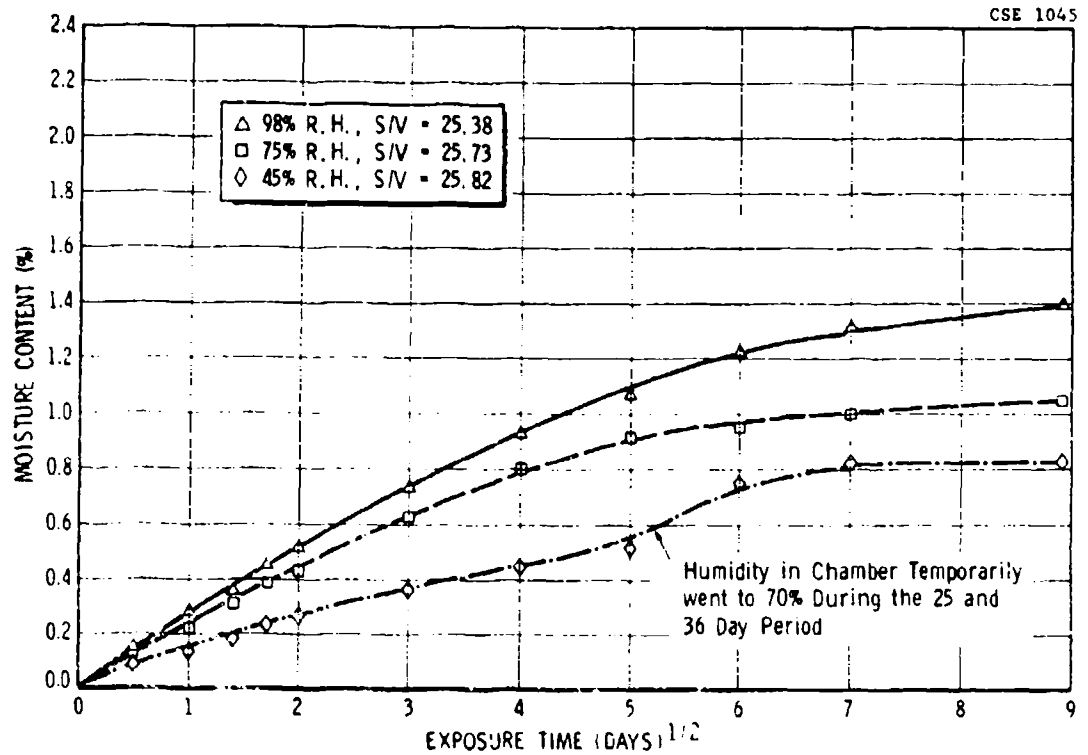

Figure 15 Moisture Absorption - 16 Ply Laminate at 150°F

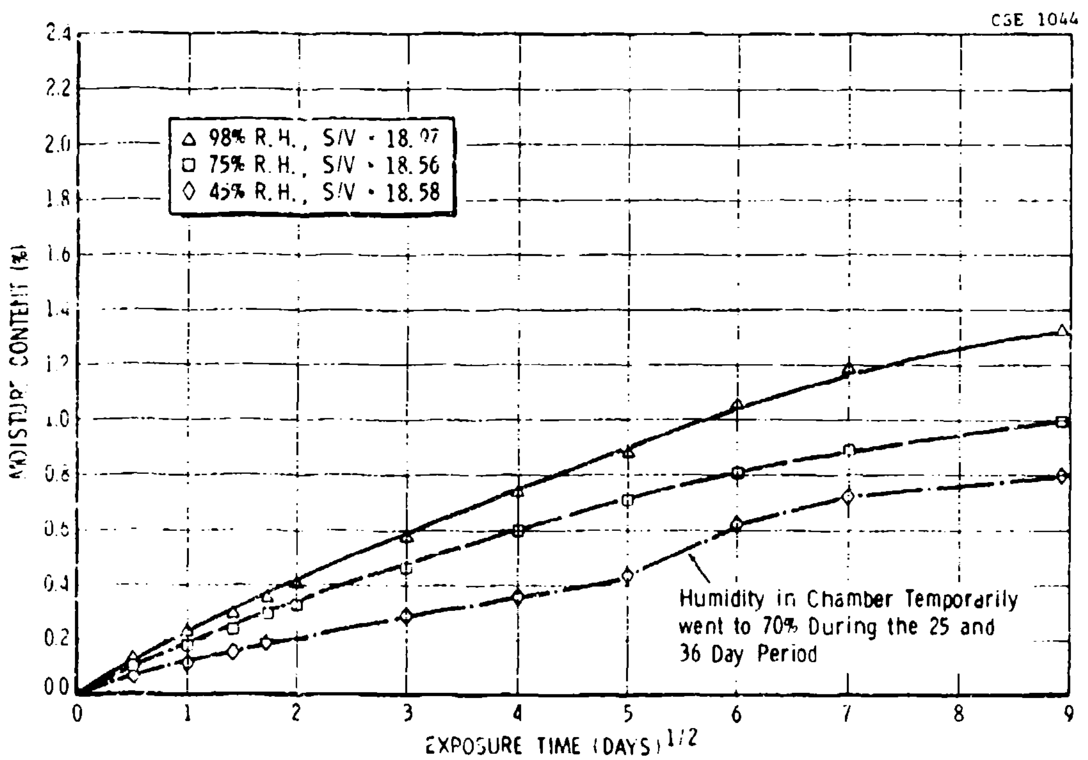

Figure 16 Moisture Absorption - 24 Ply Laminate at 150°F

17 through 20 indicate the relationships of weight gain and exposure time for specimens exposed to humidity at 180°F. This data displays a more rapid approach to equilibrium than did the 150°F data. Also, nonlinearity in the thicker laminates is more evident.

In Figure 21, weight gain data are summarized for all four laminate thicknesses that were hygrothermally exposed to 98% at 75°F. These are the same data that are presented in Figures 5 through 8, except that data ranges are shown for all four thicknesses. This illustrates the narrowing of range as thickness increases. The figure also shows that the linearity of the thicker specimens sharply contrasts with the nonlinear character of the thinner specimens.

In Figures 22 through 24, the absorption behavior at 98% is similarly regrouped for all four thicknesses exposed to 120, 150, and 180°F, respectively. These data show that all laminate thicknesses approach the same level of moisture equilibrium at all three exposure temperatures. Similar behavior is observed when the data for 75% and 45% exposures are examined, except that the equilibrium level is lower.

Immersion in boiling water produces different results. The 1.4 to 1.5% moisture content is quickly reached. Thereafter, the moisture level slowly climbs; it reaches the 2.0% level within 64 days without achieving equilibrium. These data are illustrated in Figure 25.

The maximum equilibrium levels that are observed in these laminate data agree with TGA test data. For each of the 13 hygrothermal environments, 4-ply specimens were TGA tested to determine maximum moisture contents. Each TGA specimen was heated at 320°C/min. in a Perkin-Elmer thermogravimetric analyzer until a temperature of 171°C (340°F) was reached. Then, the specimens were held isothermally while weight loss versus time was recorded. Total percentage weight loss was determined after the specimen reached apparent equilibrium.

The relationship of equilibrium moisture content to relative humidity is shown in Figure 26. Mean values and the range of values are shown. This data clearly shows that the equilibrium amount of hygrothermally absorbed moisture is a function of concentration, or partial pressure, of the water vapor.

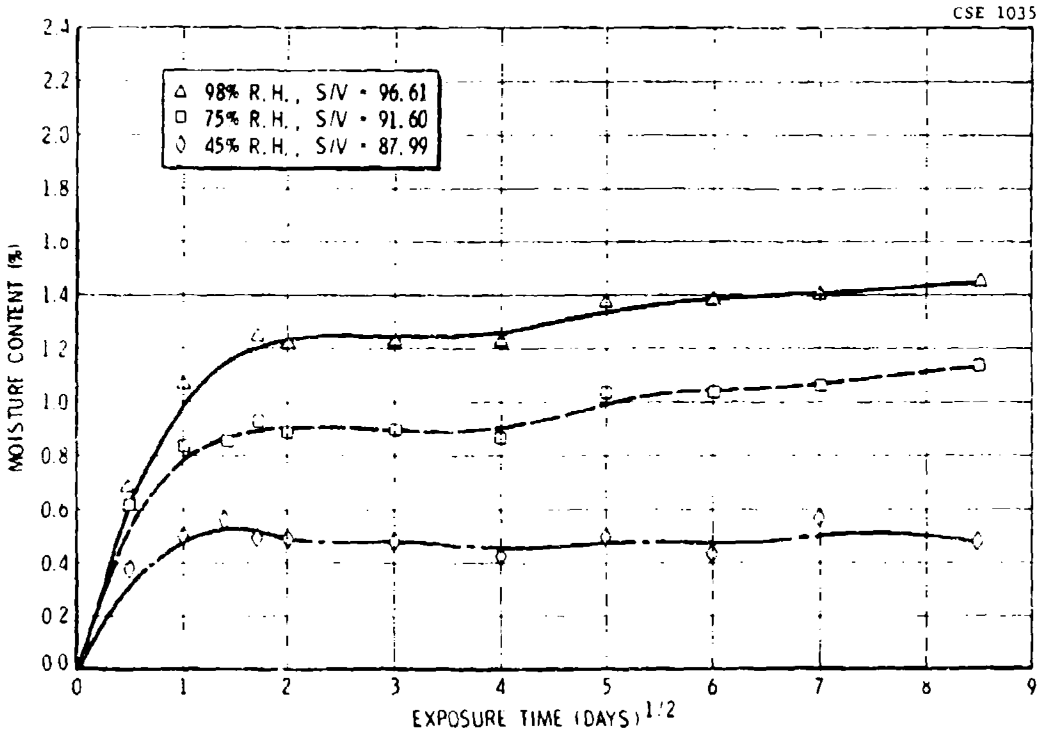

Figure 17 Moisture Absorption - 4 Ply Laminate at 180°F

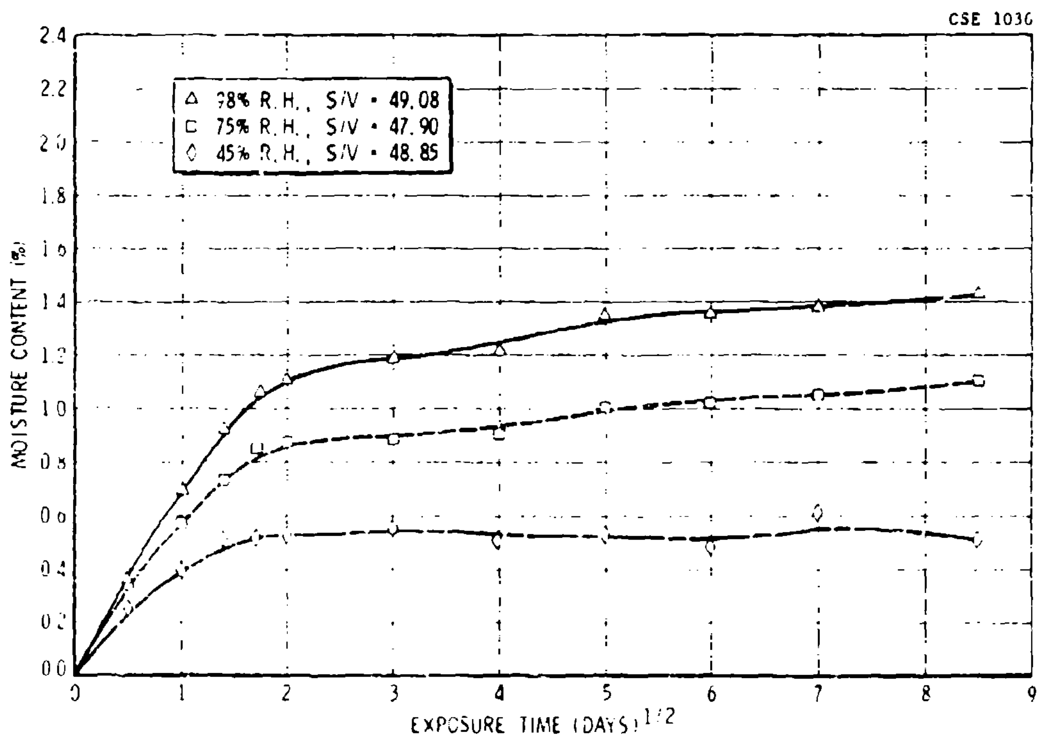

Figure 18 Moisture Absorption - 8 Ply Laminate at 180°F

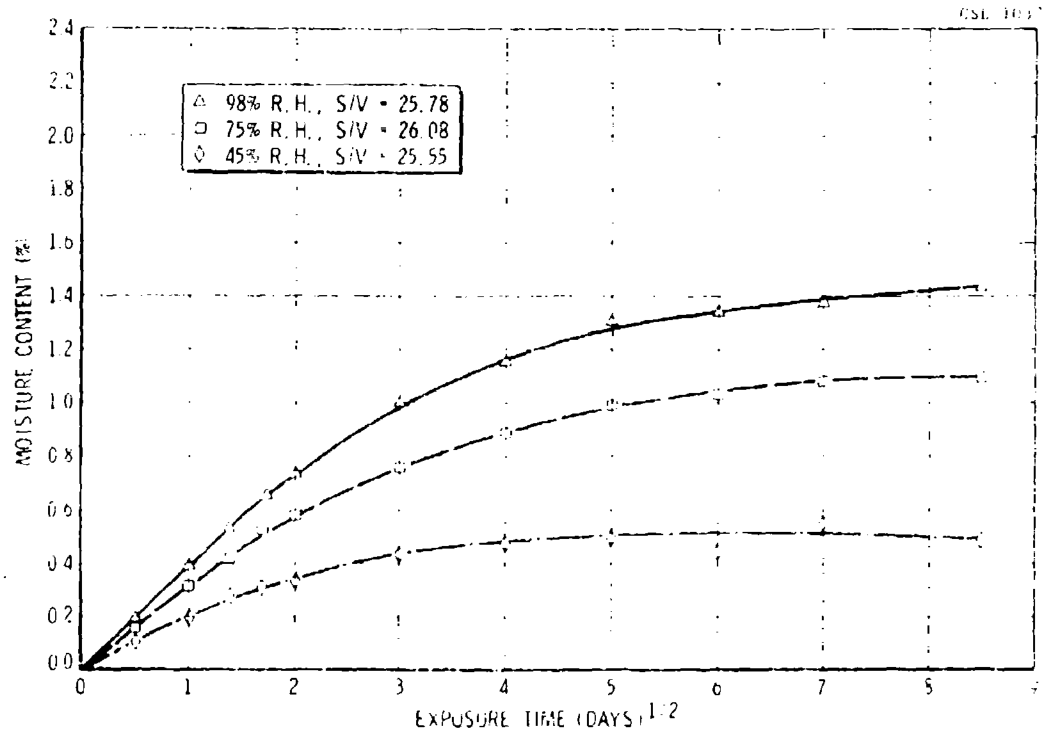

Figure 19 Moisture Absorption - 16 Ply Laminate at $180^{\circ}F$

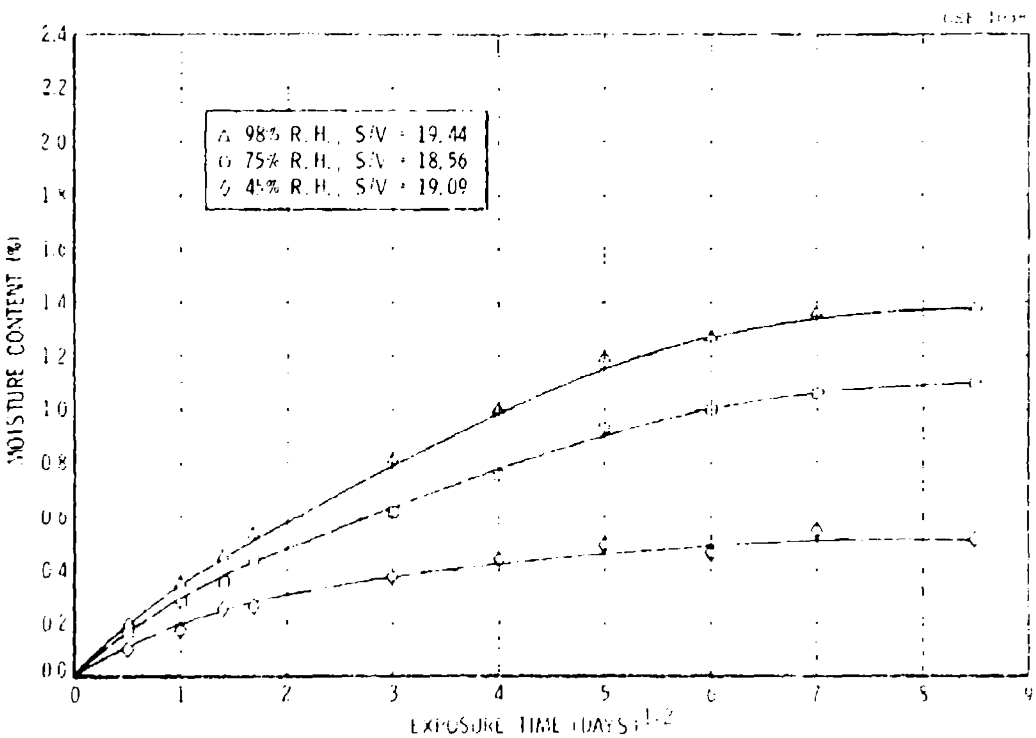

Figure 20 Moisture Absorption - 24 Ply Laminate at $180^{\circ}F$

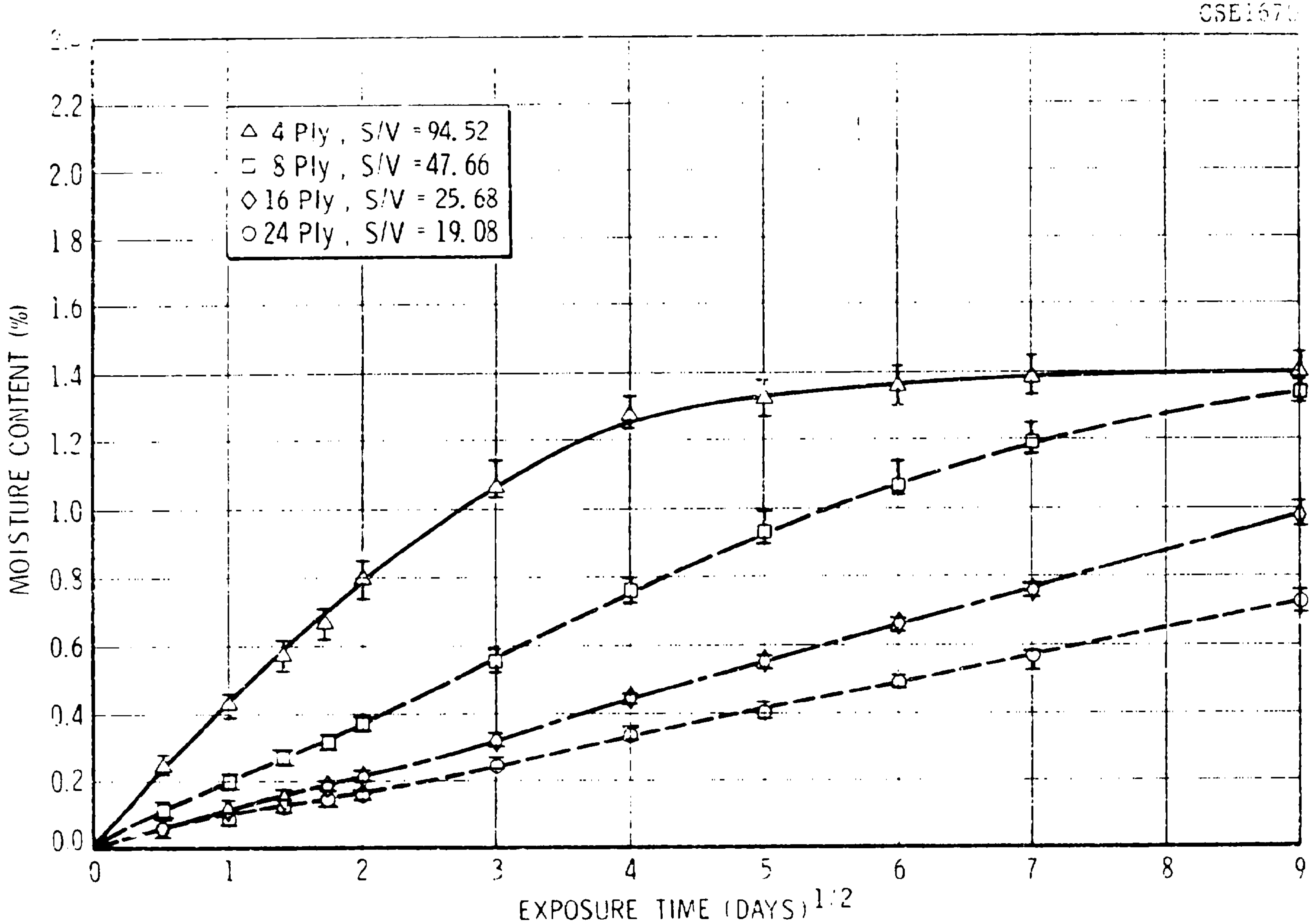

Figure 21 Moisture Absorption - 98% RH 75°

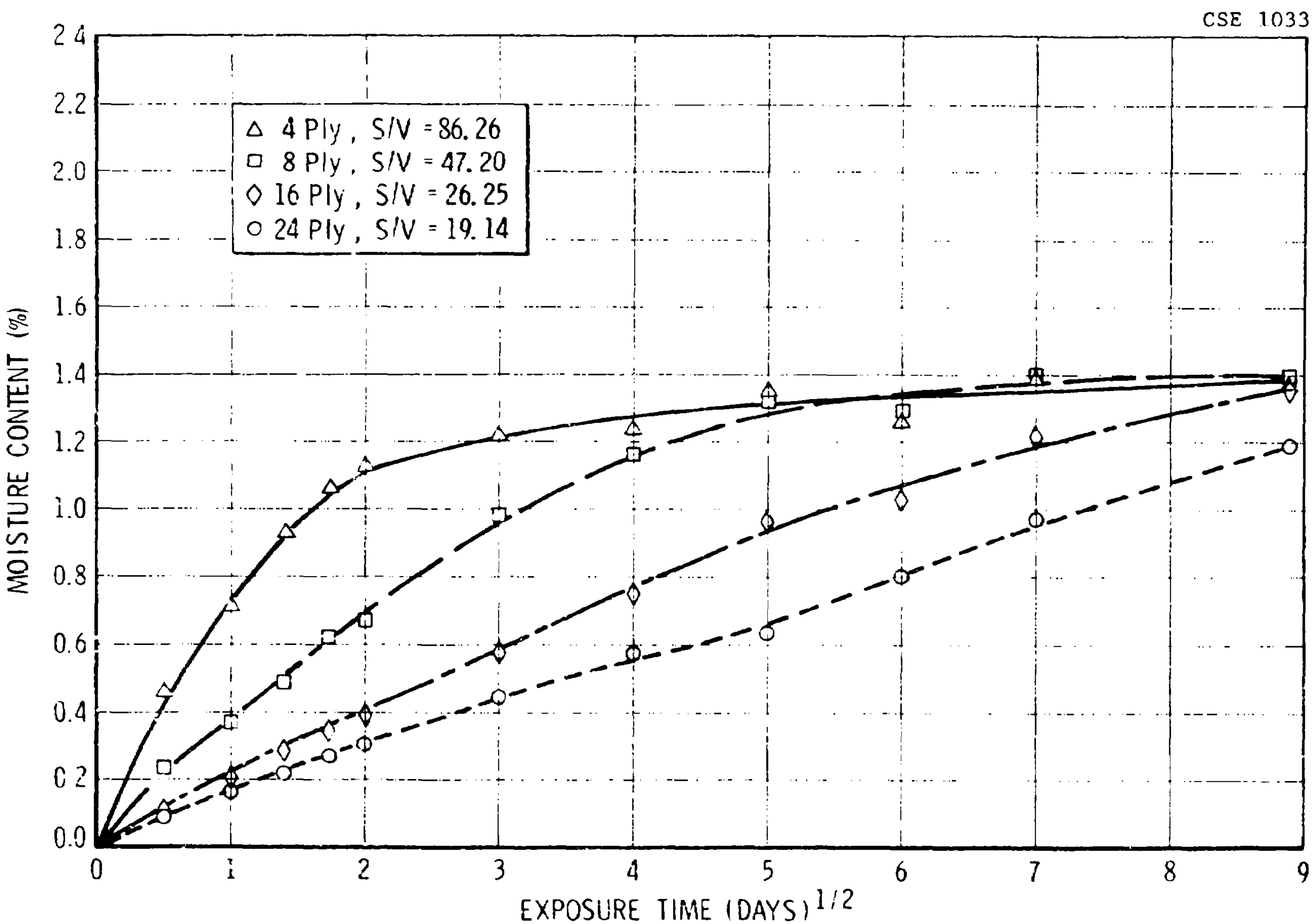

Figure 22 Moisture Absorption - 98% R.H. - 120°F

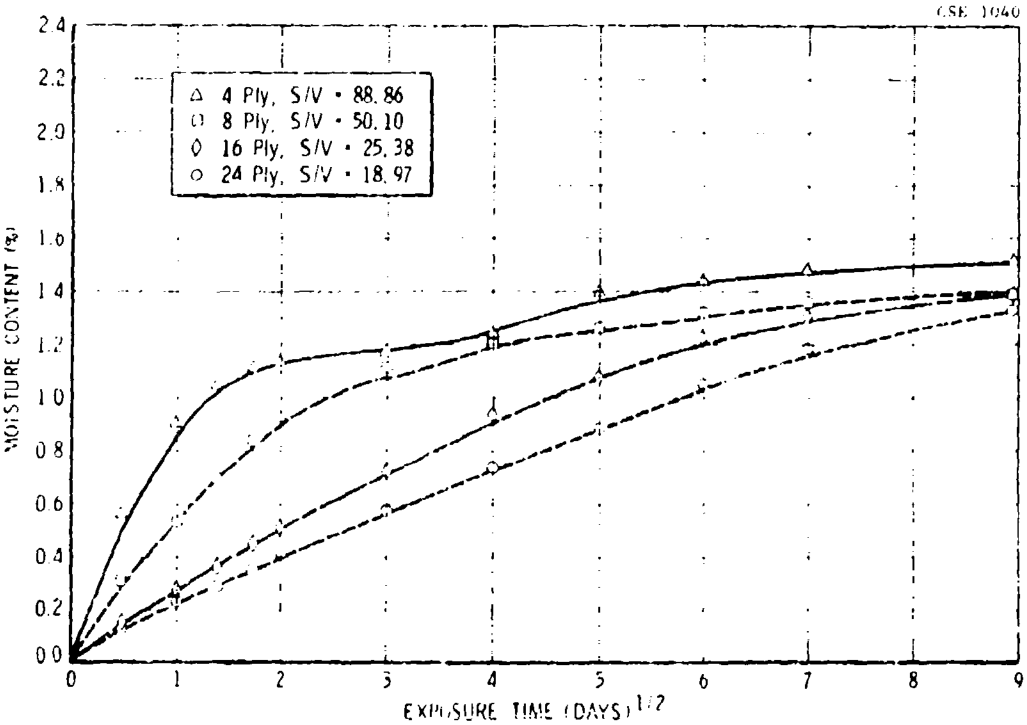

Figure 23 Moisture Absorption - 98% R.H. - 150°F

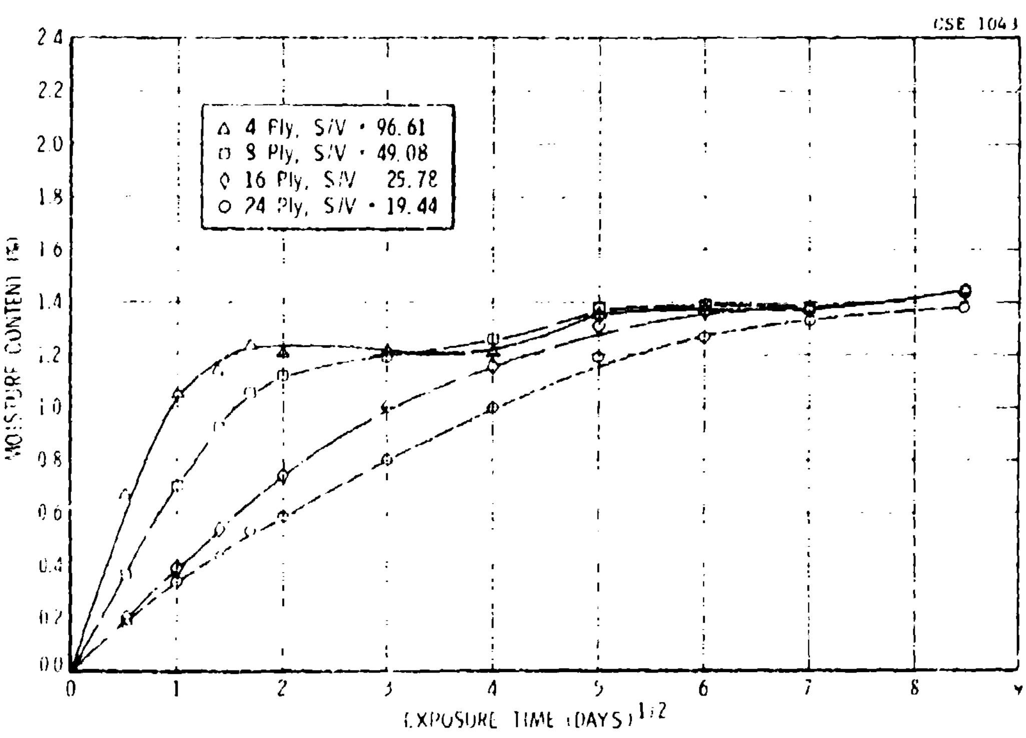

Figure 24 Moisture Absorption - 98% R.H. - 180°F

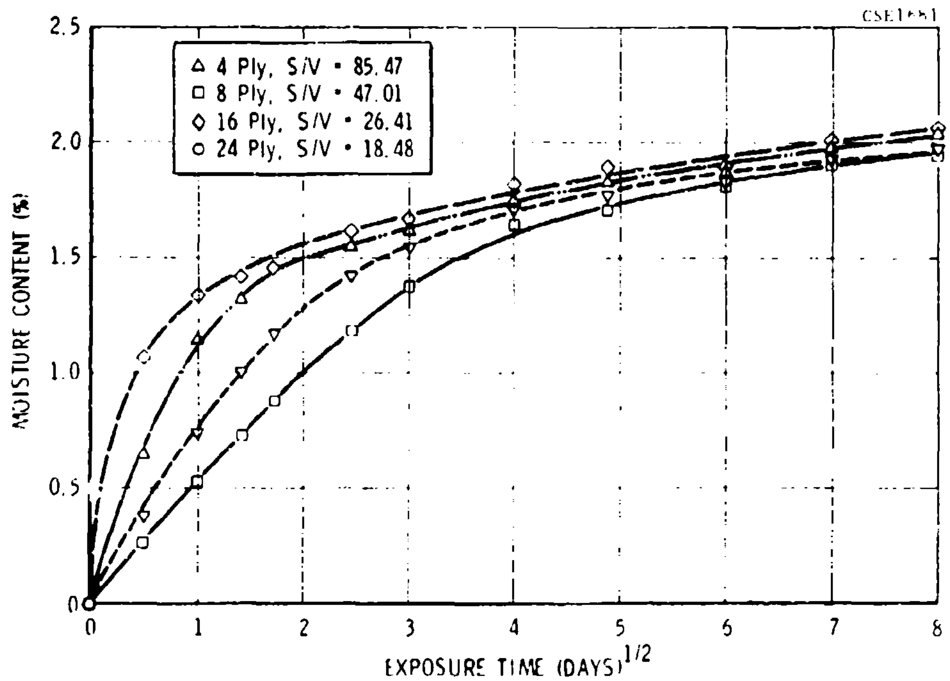

Figure 25 Moisture Absorption - Boiling Water

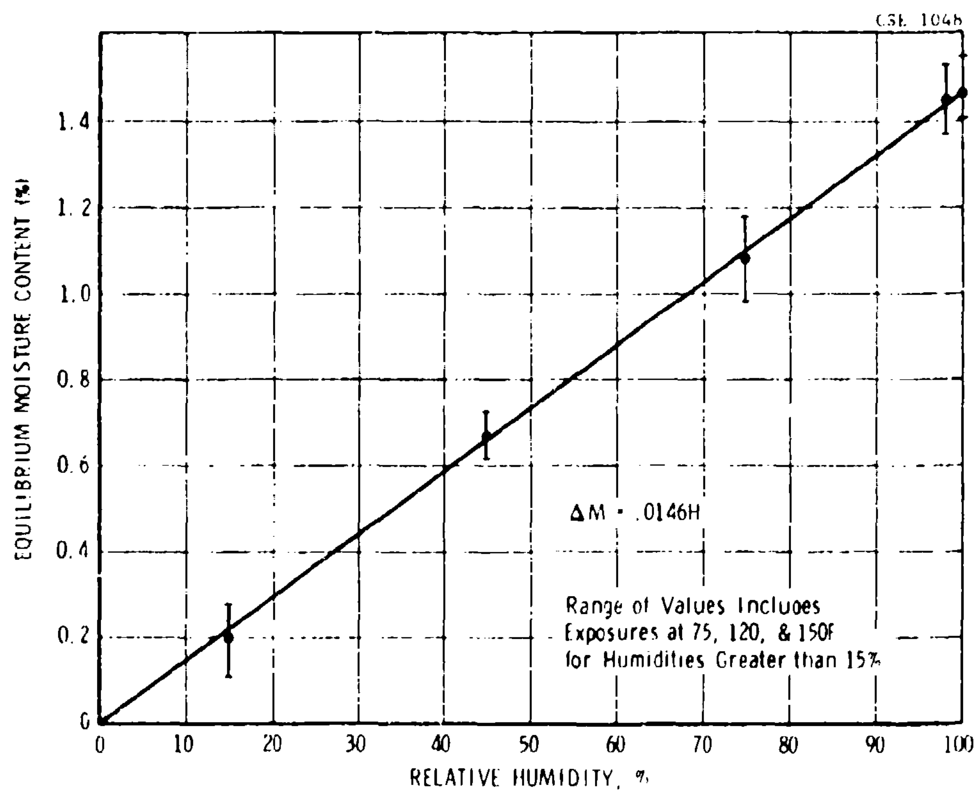

Figure 26 Maximum Absorption Levels for Different Humidities

A different presentation of the hygrothermal data is shown in Figures 27 through 29. In these figures, the effects of temperature upon absorption rates are illustrated for 4-ply specimens exposed to 45, 75, and 98%, respectively. As shown in these figures, increasing temperature increases absoption rates at all humidities. The range of values is shown in Figure 29 to illustrate that temperature does not affect the variability of the results.

As shown in Figure 30, weight gain is linear with surface area-to-volume ratio for short exposure periods. At longer exposure periods, the specimens with high S/V values (the thinner specimens) reach saturation earlier than specimens with low S/V values.

3.1.2.2 Desorption

Laminates that had absorbed known amounts of water during exposures to humidity were dried at 180°F and 250°F in circulating air ovens. The percentage of weight lost was determined after each of various drying periods. Since elevated temperatures accelerate diffusion, hours were used as the unit of exposure time instead of days for measuring the drying periods.

In Figure 31 the relationships between weight loss and exposure time are shown for laminates that were dried at 180°F. Laminates of all four thicknesses (4, 8, 16, and 24 plies) were tested. The moisture content (percent of specimen weight) differed for each of the laminates at the start of drying. Each data point represents the average for four specimens.

Drying rates at 250°F are shown in Figure 32 for four laminate thicknesses. As expected, the rate of weight loss is greater at 250°F than at 180°F.

The character of these desorption data is similar to that observed for absorption. That is, weight loss versus square root of exposure time provides curve shapes that are similar to those of the absorption data.

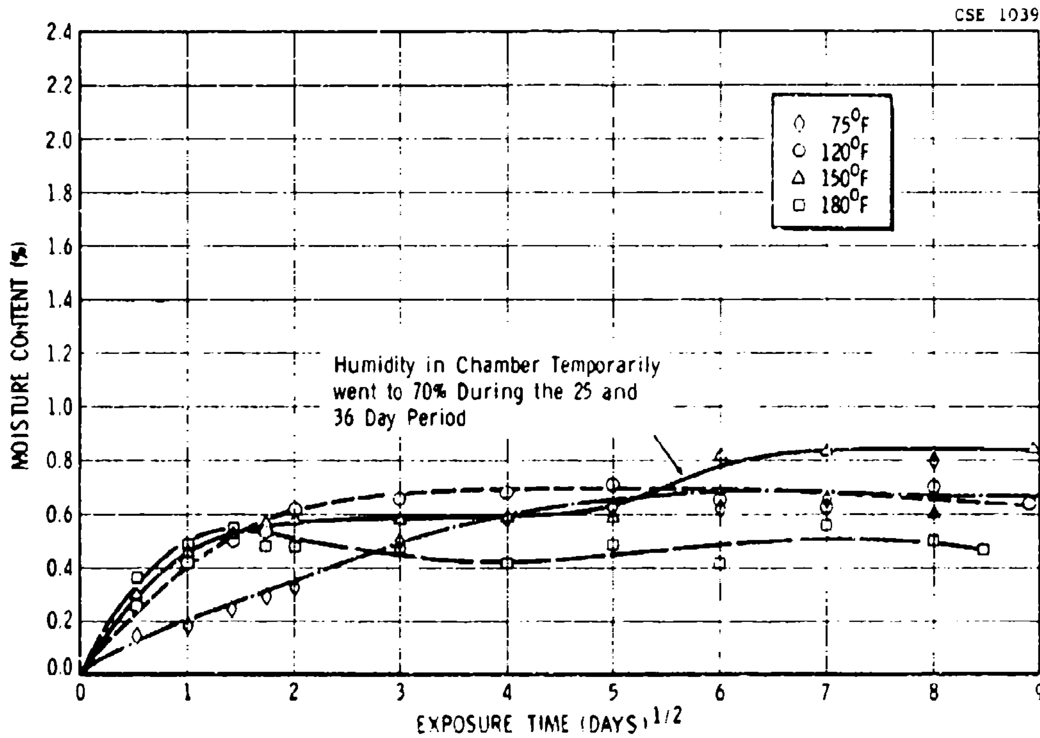

Figure 27 Moisture Absorption - 4 Ply Laminate at 45% R.H.

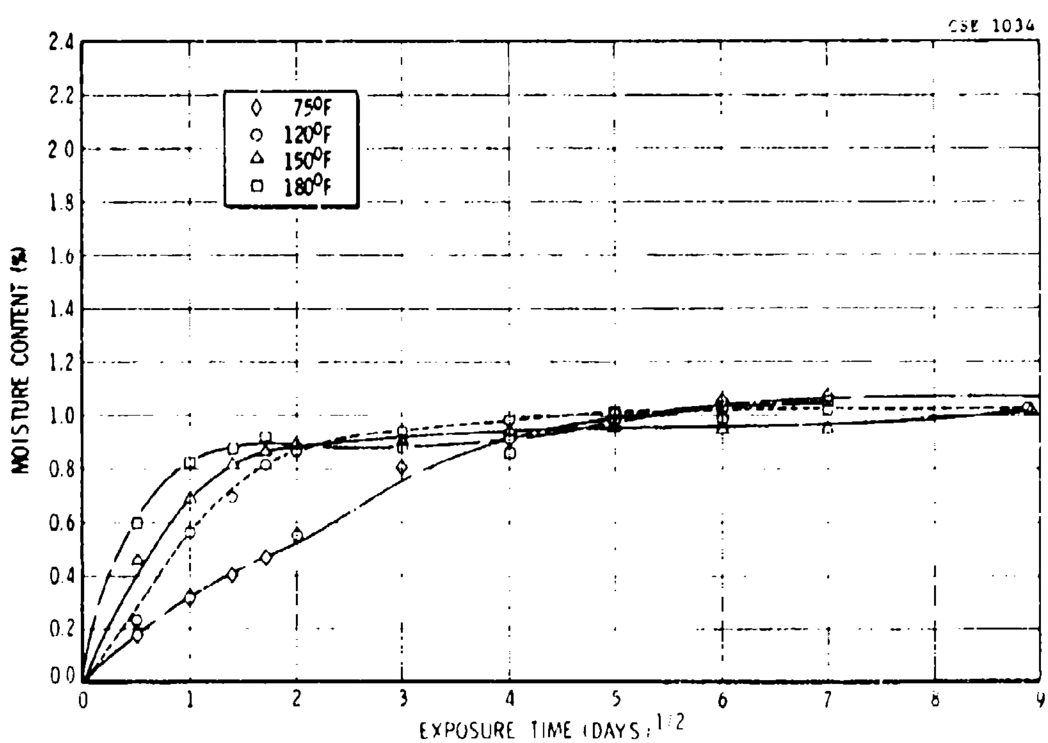

Figure 28 Moisture Absorption - 4 Ply Laminate at 75% R.H.

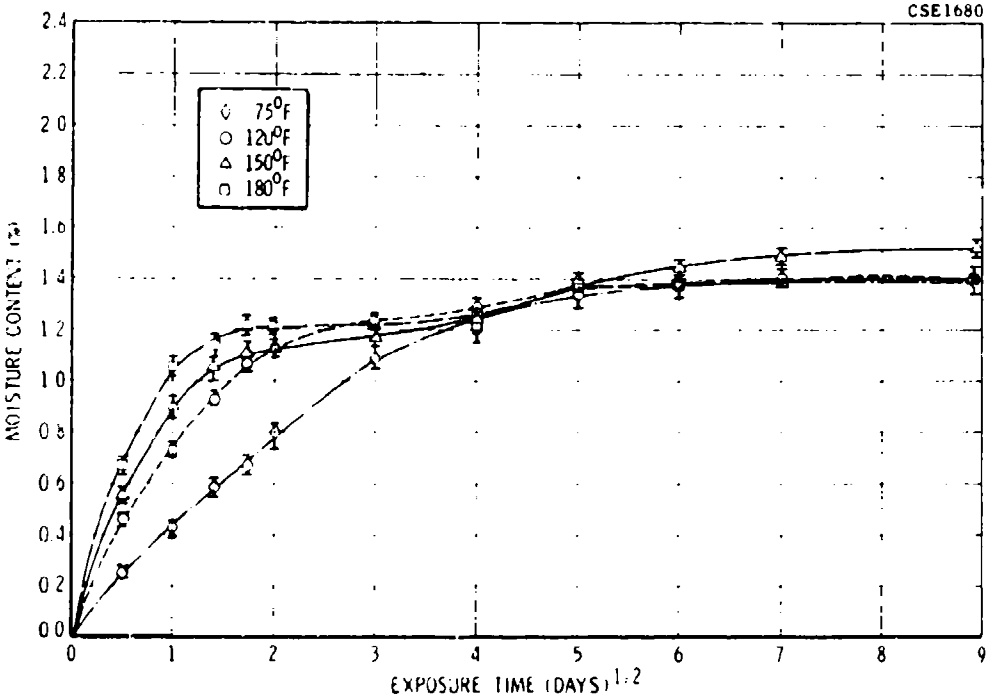

Figure 29 Moisture Absorption - 4 Ply Laminate at 98% R.H.

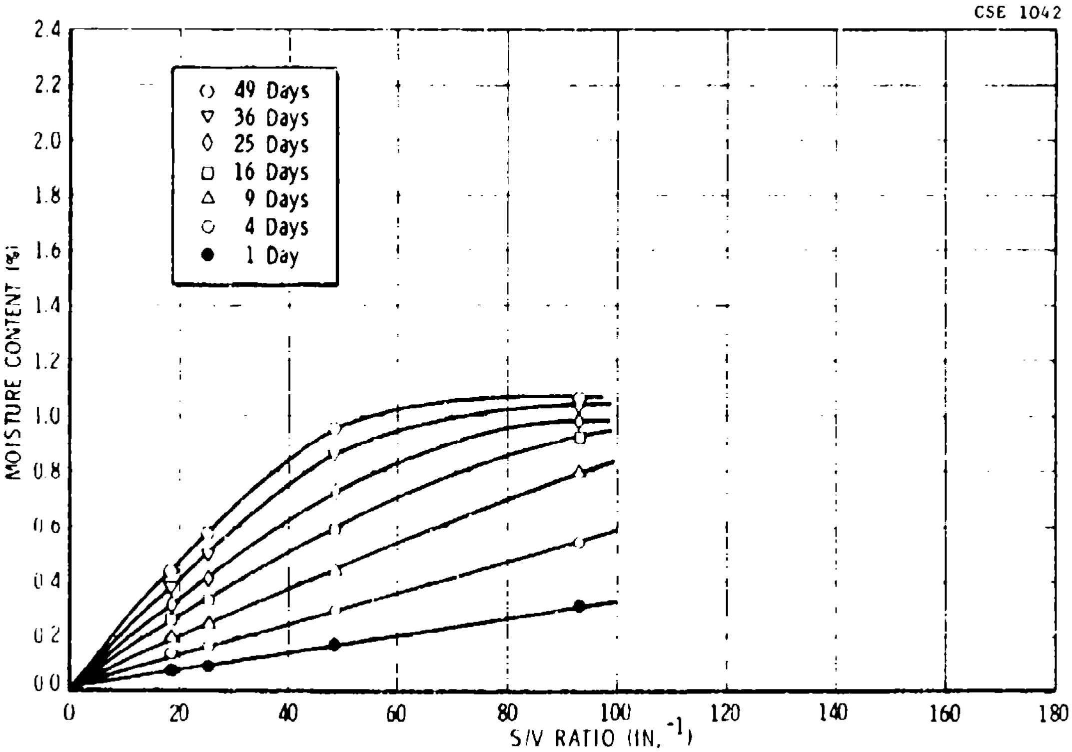

Figure 30 Effects of Geometry on Moisture Absorption

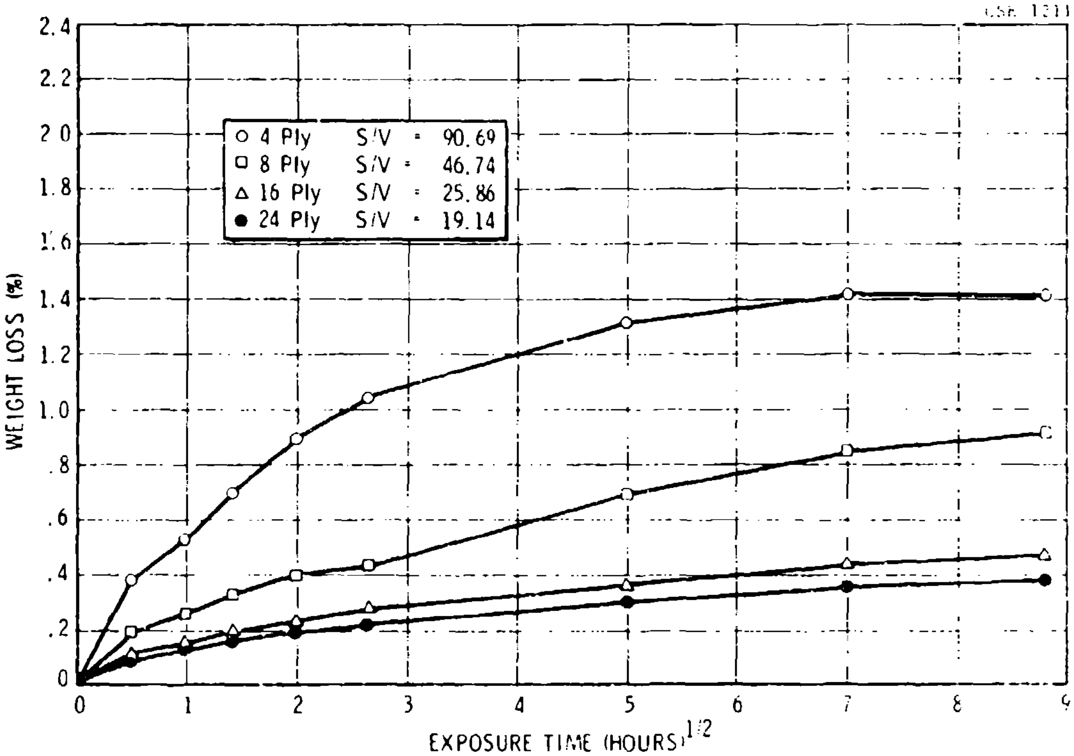

Figure 31 Moisture Desorption at 180°F

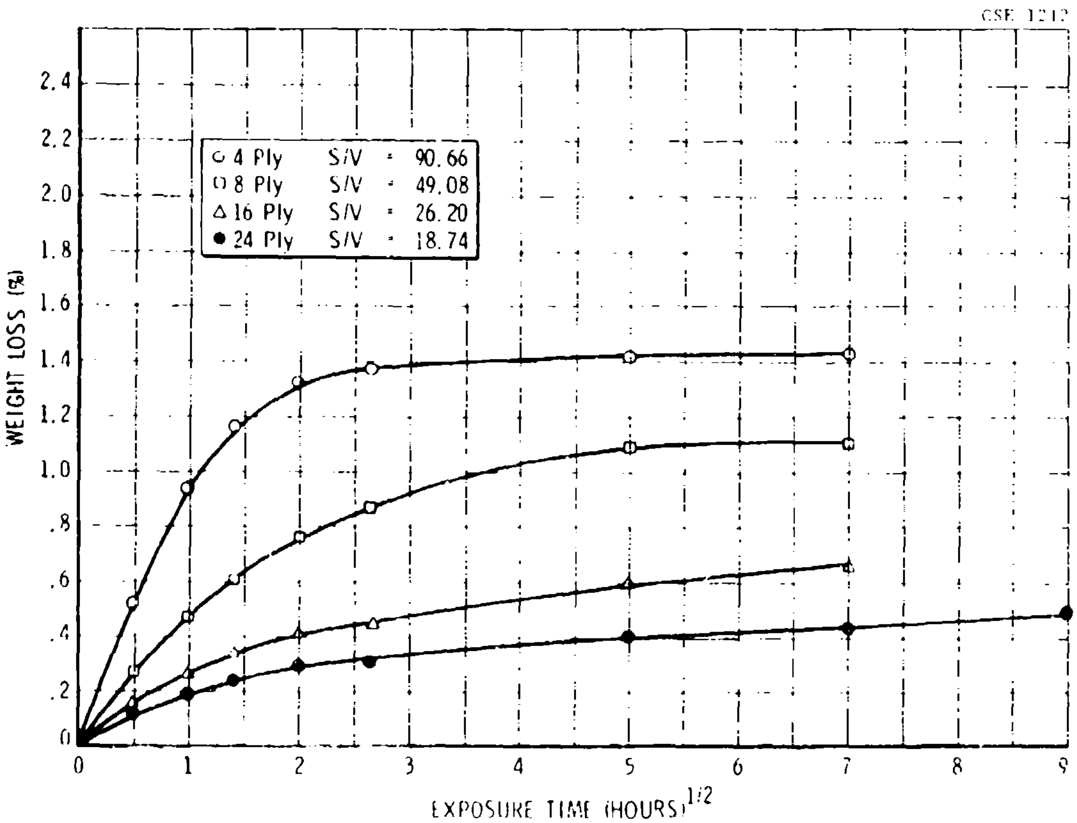

Figure 32 Moisture Desorption at 250°F

3.2 DIFFUSION MODEL

Analysis of all of the hygrothermal absorption data shows that the linear representation of absorption, Equation (2), does not adequately characterize the absorption behavior. It does not describe the nonlinear approach to equilibrium moisture content. However, this behavior is described by a slightly different form of Equation (2):

$$F = \tanh\left(4/\ell\,(Dt/\pi)^{1/2}\right). \qquad (3)$$

As time approaches infinity, the absorption fraction, F, approaches 1.0. Even so, Equation (3), cannot be used easily for general situations. Therefore, further modifications were made.

First, the absorption fraction, F, can be expressed as the moisture content, M, at some time dividied by the equilibrium moisture content. As shown in Figure 5, the equilibrium moisture content varies with the relative humidity of the exposure. In fact, the equilibrium moisture content is a linear function of relative humidity, as was shown in Figure 26. Therefore,

$$F = M/(AH) \qquad (4)$$

where H = relative humidity, %;
A = absorptivity coefficient.

From Figure 26, the value of A is 0.0146 for the T300/5208 graphite-epoxy test laminates.

Next, the overall diffusion coefficient, D, was expressed to show the temperature dependence of diffusion (Reference 4):

$$D = D_o \exp(-E/RT) \qquad (5)$$

where, D_o = permeability index, cm^2/sec;
E = activation energy for diffusion, cal/gm;
R = universal gas constant = 1.986 cal/gm-^oK; and
T = exposure temperature, ^oK.

Using the experimental data with Equations (3) and (4) combined, values of D were computed for each test temperature, and these are shown in Figure 33. Then, it is simple to determine the values of D_o and E. For the T300/5208 graphite-epoxy material,

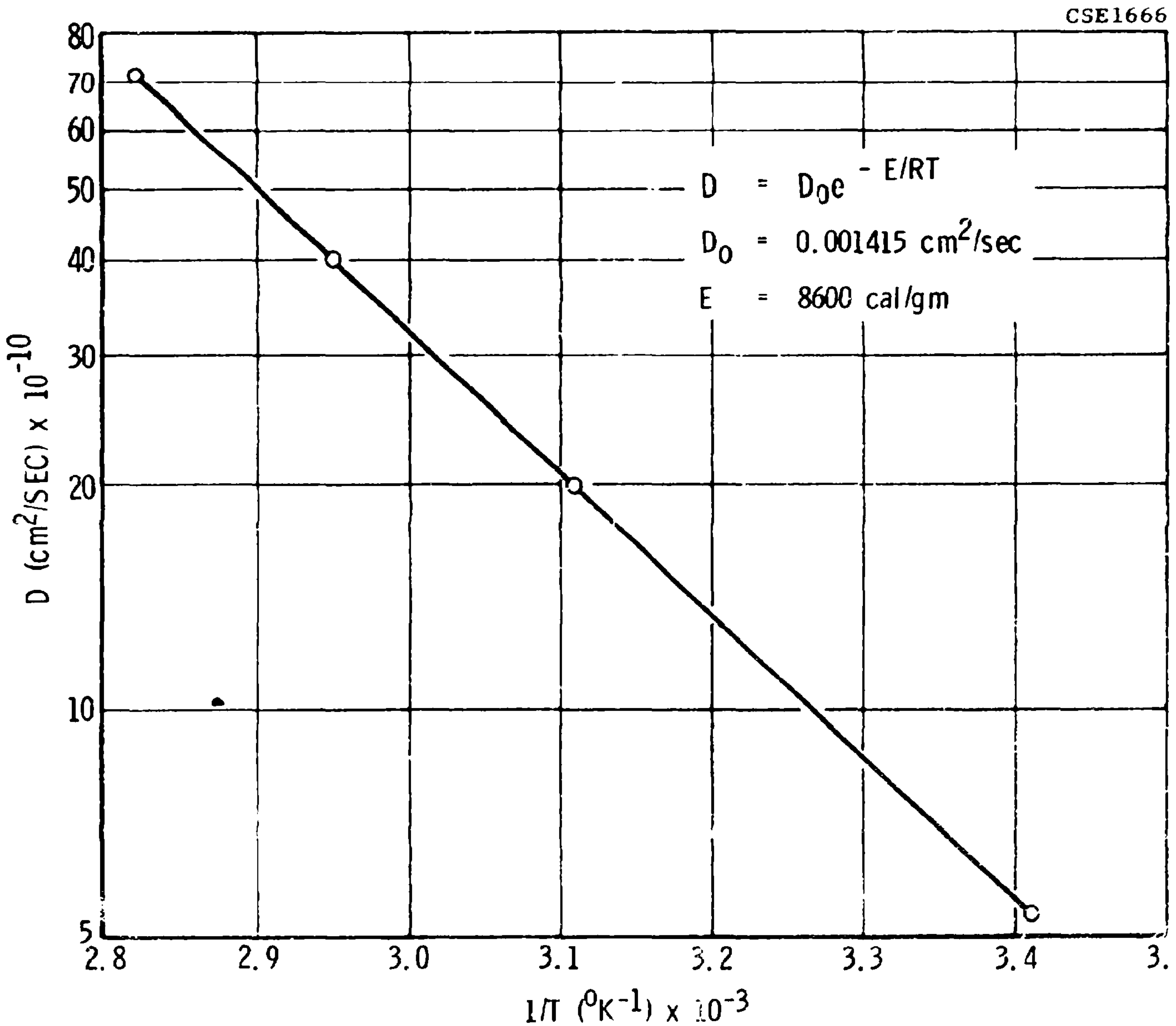

Figure 33 Relationship of Overall Diffusion Coefficient (D) to Exposure Temperatures

the permeability index, D_o, was calculated to be 0.001415 cm^2/sec. The activation energy for diffusion, E, was calculated to be 8600 cal/gm.

As mentioned earlier, the specimens used in this experiment were dimensionally different than a large area plate. Therefore, each specimen's surface area-to-volume ratio (S/V) was doubled and used instead of $4/\ell$. (As the width and length of a specimen approach the dimensions of a large-area flat panel, the value of S/V approaches that given by twice the reciprocal of panel thickness. Hence, 2 S/V will equal $4/\ell$.)

Finally, a term was added to allow consideration of an initial moisture content, M_i. This would be necessary for desorption and for changing humidity conditions. Therefore, the final model for diffusion is given by

$$M = M_i + (AH - M_i)\tanh\left((2S/V)(D_o \exp(-E/RT)t/\pi)^{1/2}\right). \quad (6)$$

A calculator program was written for use in computing values of M for incrementally increasing values of t. Input information for the program consists of all other parameters so that other materials may be considered and so that any temperature/humidity combination can be evaluated. Output is a plot of moisture content, %, versus square root of exposure time.

Figure 34 is a calculator plot for a 24-ply laminate exposed to 98% at 180°F. The figure also includes experimental data for four specimens in this hygrothermal environment. The form of the model correlates well with the form of the data. Similar comparison of the model with experimental data are shown in Figures 35 through 37 for other combinations of thickness, humidity, and temperature.

Desorption is also described by the model, but the value of the permeability index, D_o, must be increased over that used for absorption. This is illustrated by Figure 38, which presents experimental data for desorption of 4-ply laminates at 180°F. The theoretical curve given by the model for D_o = 0.001415 cm^2/sec (determined from the absorption data) does not conform with this data. The permeability index must be increased to D_o = 0.0049 cm^2/sec to achieve a reasonable fit with the data. Figures 39 through 41 similarly show that D_o = 0.0049 better describes desorption whether the laminate is thicker or whether the drying temperature is 250°F.

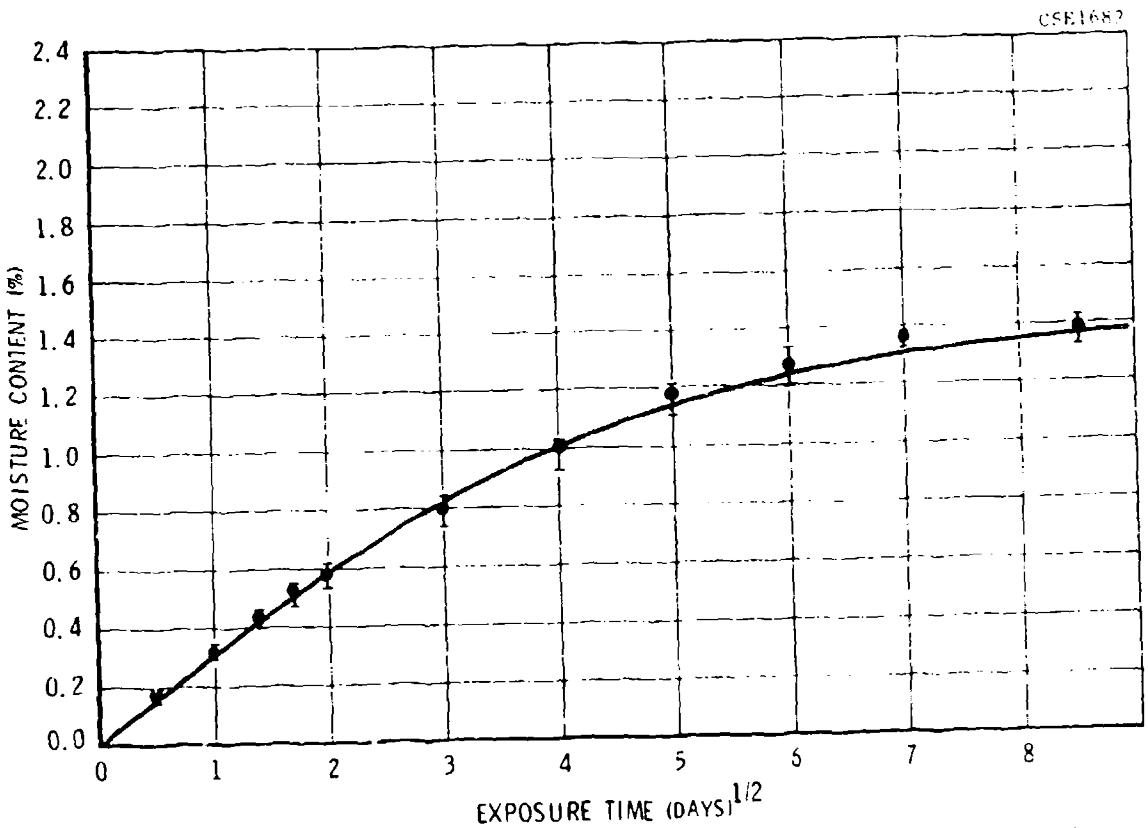

Figure 34 Comparison of Calculated and Experimental Moisture Contents - 24-Ply Laminate in 98% R.H. at 180°F

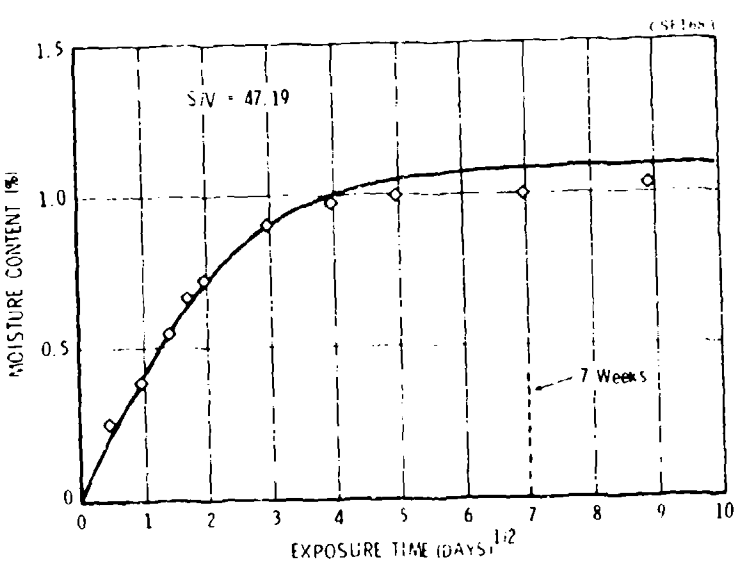

Figure 35 Calculated and Experimental Moisture Contents - 8-Ply Laminate in 75% R.H. at 150°F

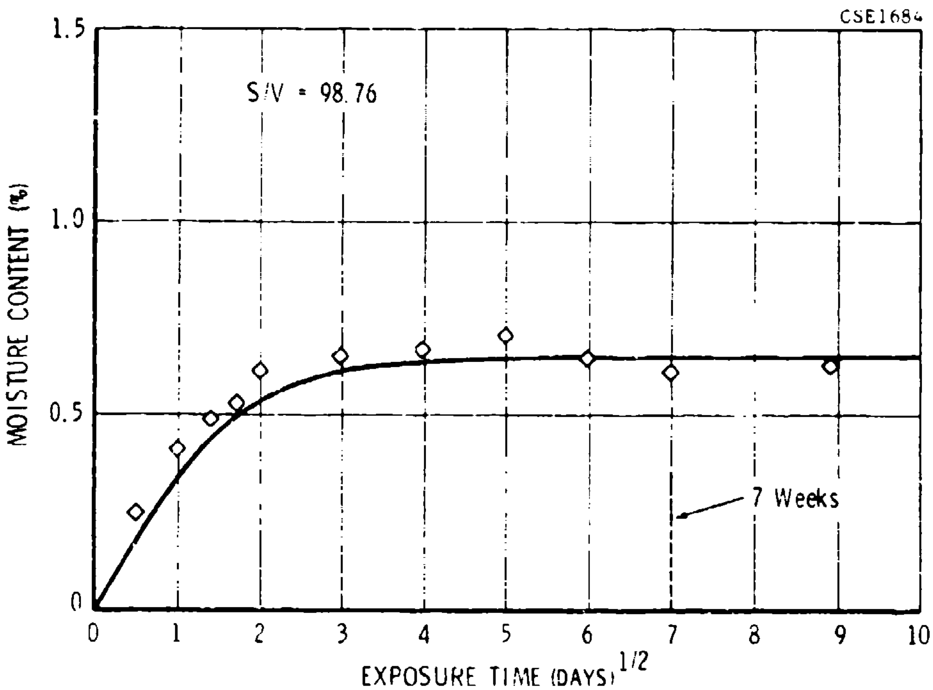

Figure 36 Calculated and Experimental Moisture Contents - 4-Ply Laminate in 45% R.H. at 120°F

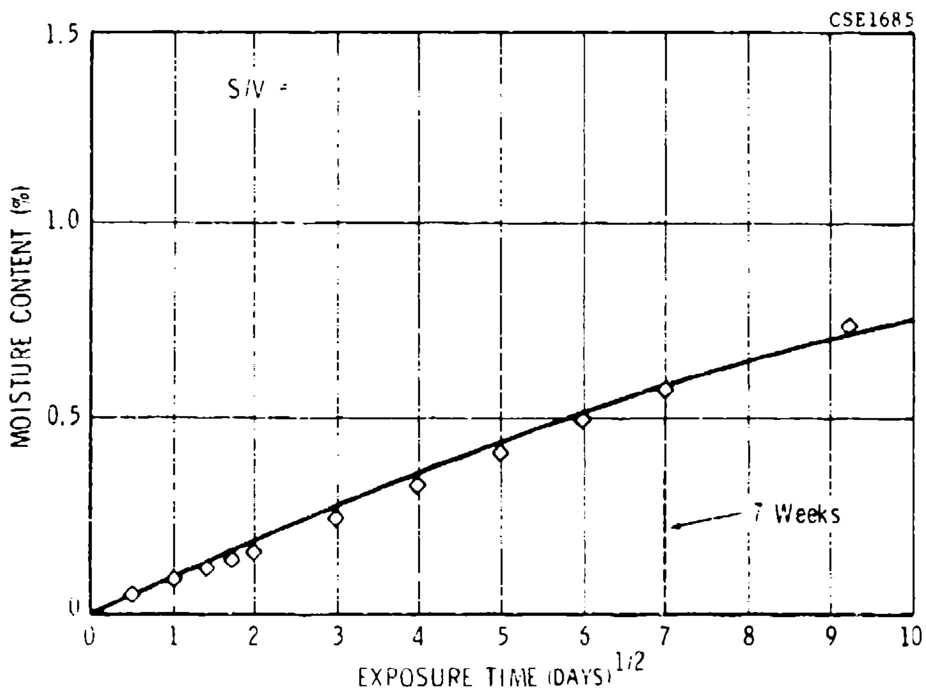

Figure 37 Calculated and Experimental Moisture Contents - 16-Ply Laminate in 75% R.H. at 75°F

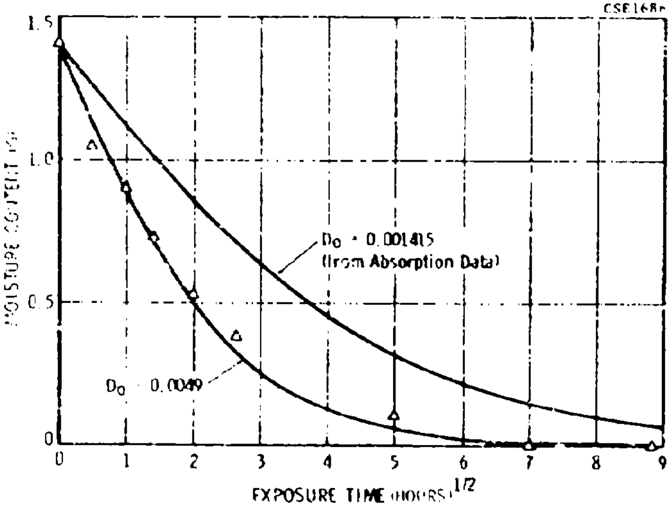

Figure 38 Calculated and Experimental Desorption at 180°F - 4-Ply Laminate

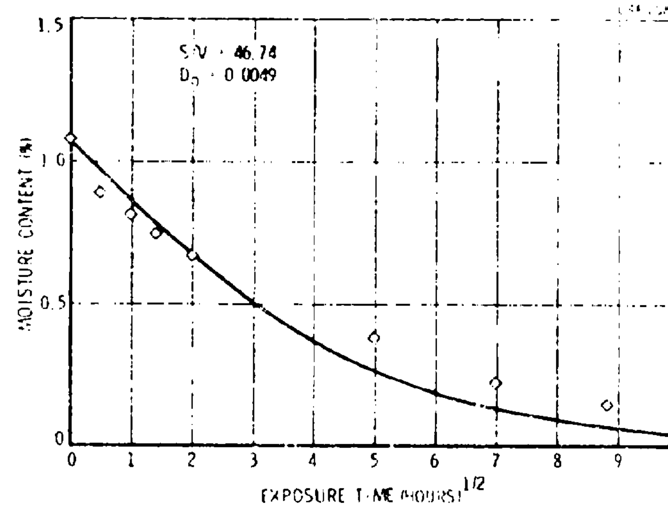

Figure 39 Calculated and Experimental Desorption at 180°F - 8-Ply Laminate

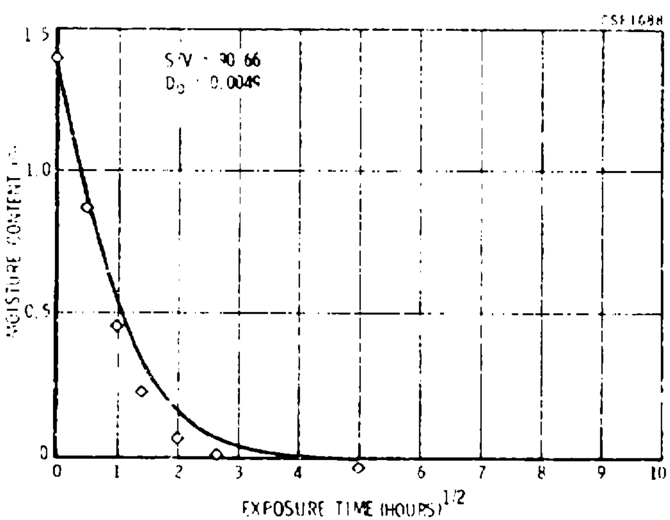

Figure 40 Calculated and Experimental Desorption at 250°F - 4-Ply Laminate

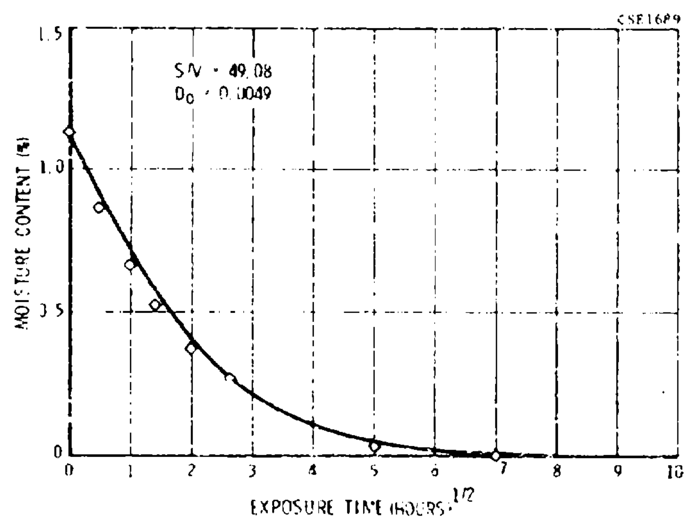

Figure 41 Calculated and Experimental Desorption at 250°F - 8-Ply Laminate

The unit of desorption time used was $(\text{hours})^{\frac{1}{2}}$ instead of $(\text{days})^{\frac{1}{2}}$. The combination of high temperature acceleration of diffusion and a higher apparent permeability index make this a more convenient scale.

The unexpected larger value of the permeability index did not apply to data for drying at 75°F. Four rectangular specimens of the 4-ply laminate were placed into 98% relative humidity at 75°F for 9 days. Then the specimens were removed and placed into a desiccator at 75°F. Figure 42 compares theoretical (calculated from the model) and experimental data for both absorption and desorption. The desorption part of the profile was predicted by using the computed 9-day absorption value of M for M_i, setting H = 0, and resetting t to 0. The permeability index value was $D_o = 0.001415$ for both segments of the data. The close fit of the curve and data suggests that the permeability index is increased only by elevated temperatures. However, it is unusual for drying at 180°F and at 250°F to produce approximately the same values of the permeability index, i.e., $D_o = 0.0049\ cm^2/sec$.

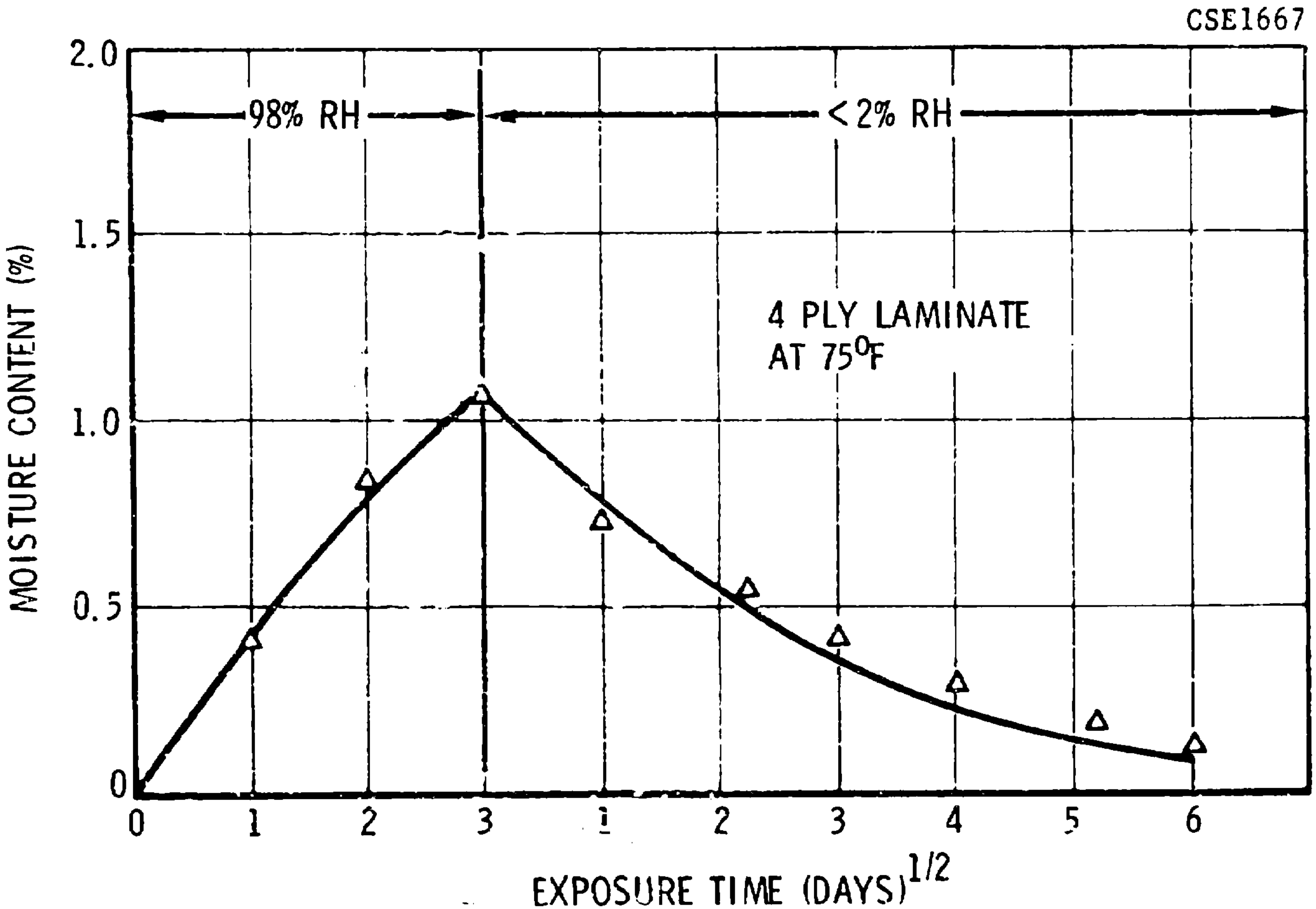

Figure '2 Calculated and Experimental Moisture Content - 4 Ply Laminate for 9 Days Exposure to 98% RH at 75°F Followed by Desiccation at 75°F

SECTION IV

DYNAMIC EXPOSURES

Hygrothermal environments are simple to establish and maintain. Therefore, they represent a desirable class of conditions for experimental studies of environmental effects. However, actual-use conditions seldom, if ever, involve constant humidity at constant temperature. Dynamic, or changing, environmental conditions create the possibility of synergistic and unexpected effects. Therefore, some investigations were begun to determine dynamic environmental behavior.

Tests were conducted to determine the behavior of graphite-epoxy exposed to changing environmental conditions. Specimens were tested for behavior under conditions of progressively increasing and decreasing humidities. In addition, a "real life" environmental cycle was developed and used to evaluate dynamic exposure effects upon the composite.

4.1 CHANGING HUMIDITY

Tests were conducted at 75°F to determine weight change behavior of T300/5208 exposed to increasing and decreasing humidity. Four 0° flex specimens for each of the four material thicknesses (4, 8, 16, and 24 plies) were weighed after 0, 1, 4, and 9 days in 20% relative humidity. After the ninth day, these specimens and four additional dry specimens were placed into a 45% relative humidity environment. These eight specimens of each thickness were weighed after 1, 4, and 9 days of exposure. Then, these specimens were placed successively into 75% and 98% relative humidity and weighed after 1, 4, and 9 days in each.

The weight gain experienced by the 4-ply specimens during this cycle is shown in Figure 43. After only one day of exposure, the moisture content of the new specimens at a given humidity "caught up" with the moisture content of specimens soaked for nine days at the next lower humidity.

Similar data for 8-, 16-, and 24-ply specimens are shown in Figures 44 through 46, respectively. For all 4-ply thicknesses, moisture content quickly converged to the same values as new specimens were added to those already exposed to lower humidity.

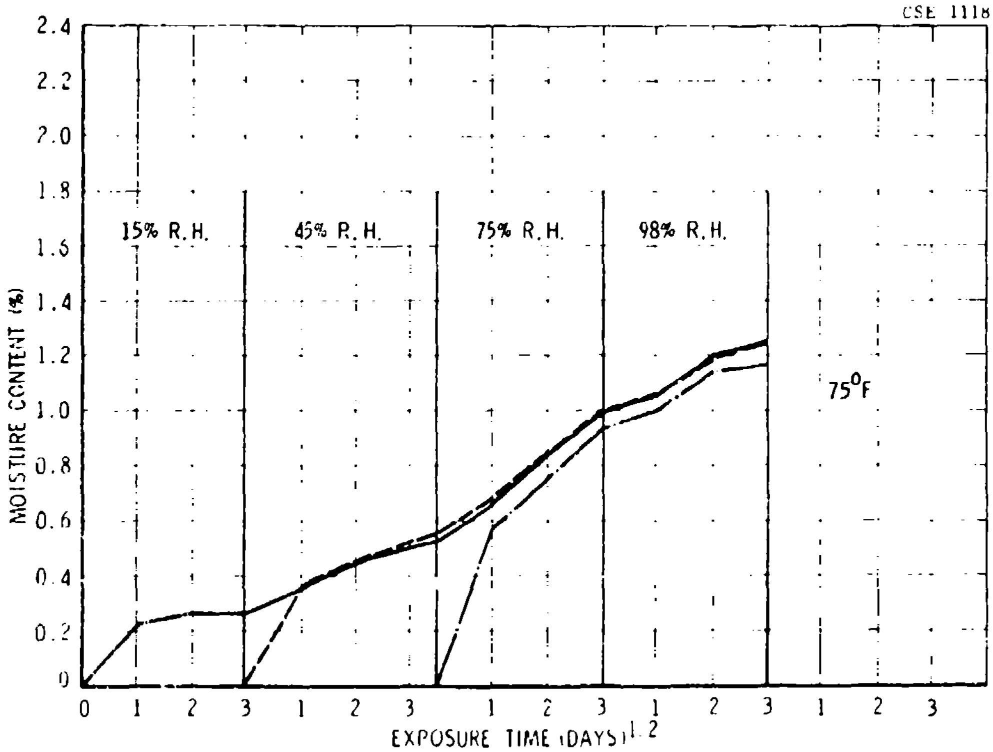

Figure 43 Effects of Increasing Humidity - 4 Ply Laminate

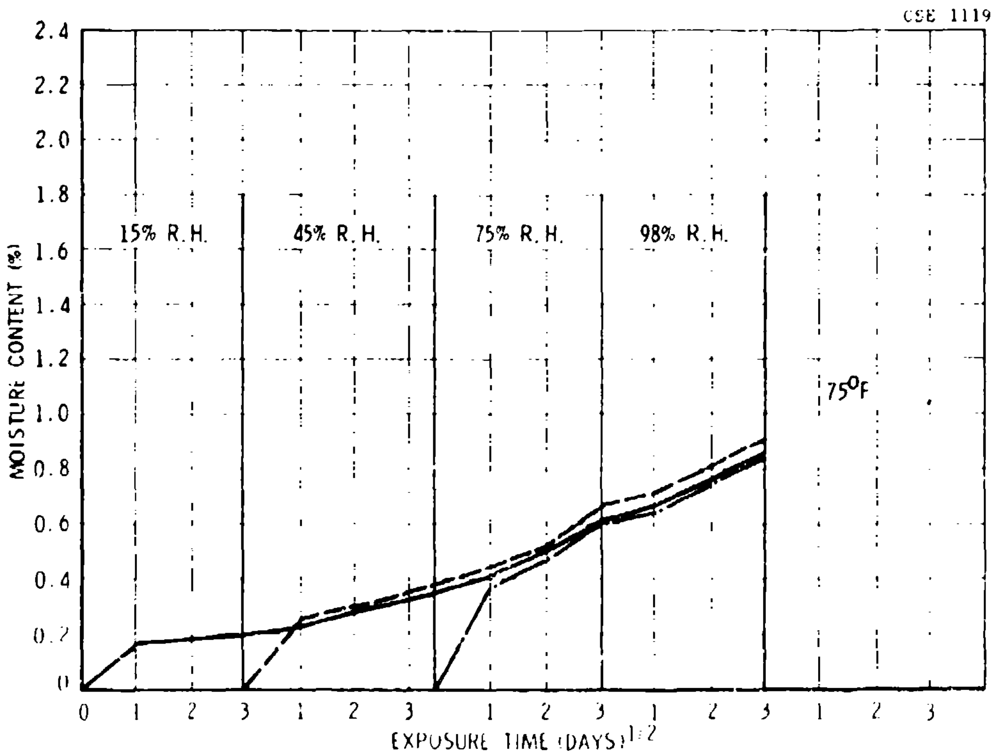

Figure 44 Effects of Increasing Humidity - 8 Ply Laminate

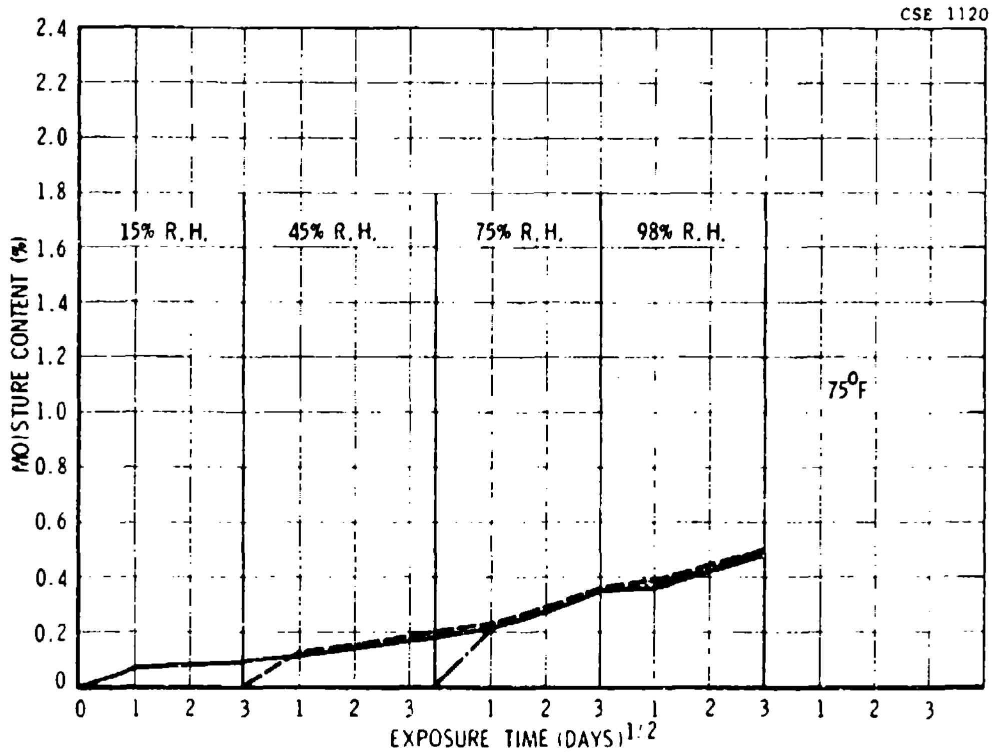

Figure 45 Effects of Increasing Humidity - 16 Ply Laminate

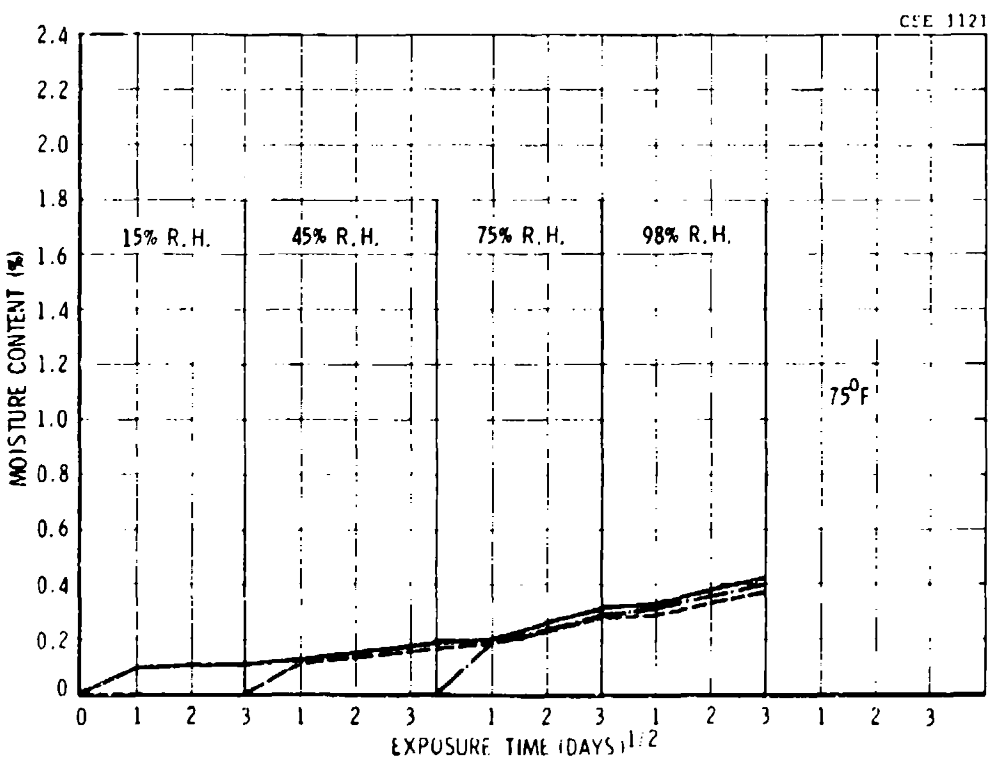

Figure 46 Effects of Increasing Humidity - 24 Ply Laminate

This test procedure was repeated in reverse, beginning with exposure to 98% relative humidity at 75°F. Then, the specimens were progressively moved to lower humidities, ending with exposure to 15% relative humidity. The same numbers of specimens and the same weighing intervals were used. These data for 4-, 8-, 16-, and 24-ply specimens are summarized in Figures 47 through 50, respectively.

Figure 51 compares moisture contents predicted by the model discussed in Subsection 3.2 with experimental values for sequentially increasing humidity exposures. The data in this figure are from Figure 44. The mismatch for the 15% relative humidity exposure may have been due to experimental difficulty in getting specimens into the chamber without raising the chamber humidity.

Figure 52 compares predicted and experimental moisture contents for sequentially diminishing humidities. These experimental data are from the 8-ply exposures summarized in Figure 48.

4.2 "REAL LIFE" ENVIRONMENTAL CYCLE

A realistic or "real life" environmental cycle was developed for the study of changing environmental effects. This cycle was modeled, as nearly as practical, around a flight training program with aircraft based at Homestead AFB, Florida.

Environmental studies of the Homestead AFB area showed that for approximately eight months each year the mean temperature is approximately 75°F and the relative humidity averages approximately 75% (Reference 5). These studies also showed that rain falls approximately 15 hours each week. Based upon F-111 crew training schedules, it was assumed that an aircraft would average four flights per week. Two of these flights were assumed to be YF-16 "Mission I" flights (Reference 6) involving both subsonic cruise and supersonic dash segments. The other two flights were assumed to be "Mission II" flights (Reference 6) involving only subsonic conditions. A "real life" environmental test cycle was developed as a result of these findings and assumptions. This cycle is shown in Table VII. The supersonic segment of the Mission I profile involves heating at 1.5°F/sec. to an apex temperature of 300°F. At the apex temperature, cooling begins and proceeds at 1.0°F/sec. until 75°F is reached. There are no constant-temperature holds above 75°F at any point

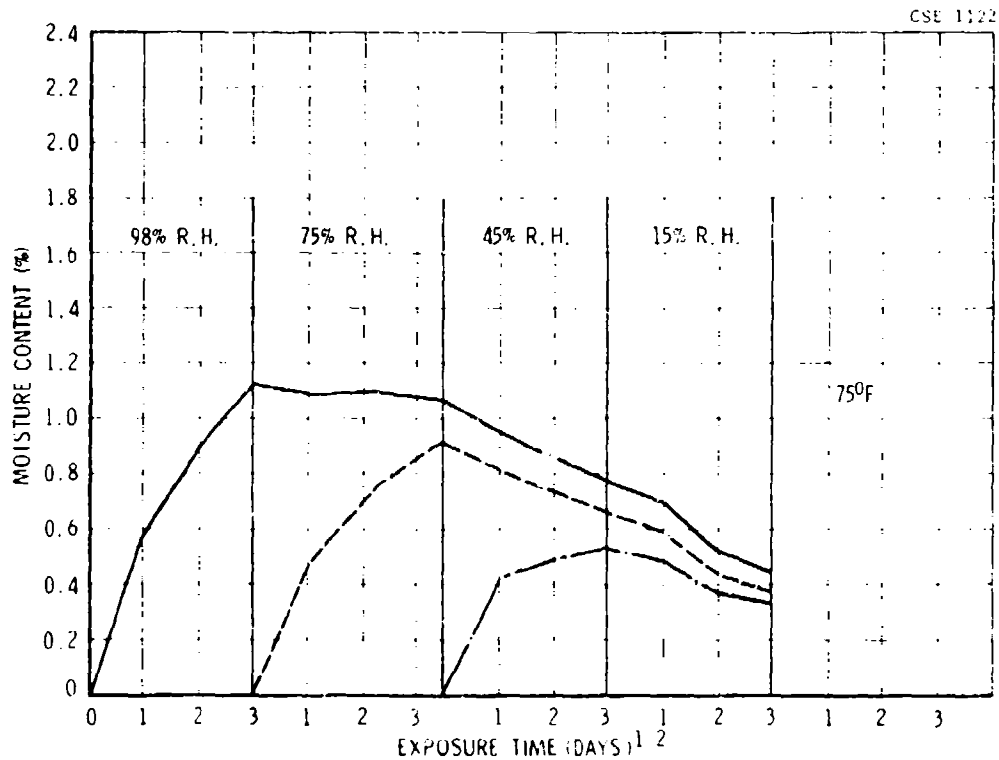

Figure 47 Effects of Decreasing Humidity - 4 Ply Laminate

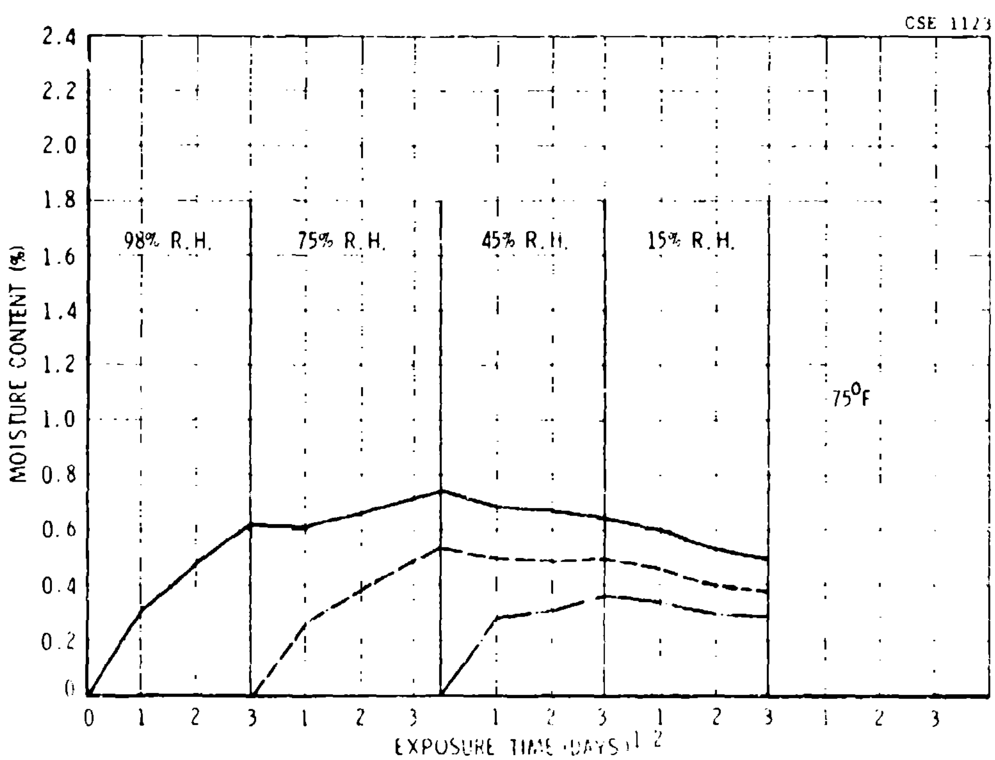

Figure 48 Effects of Decreasing Humidity - 8 Ply Laminate

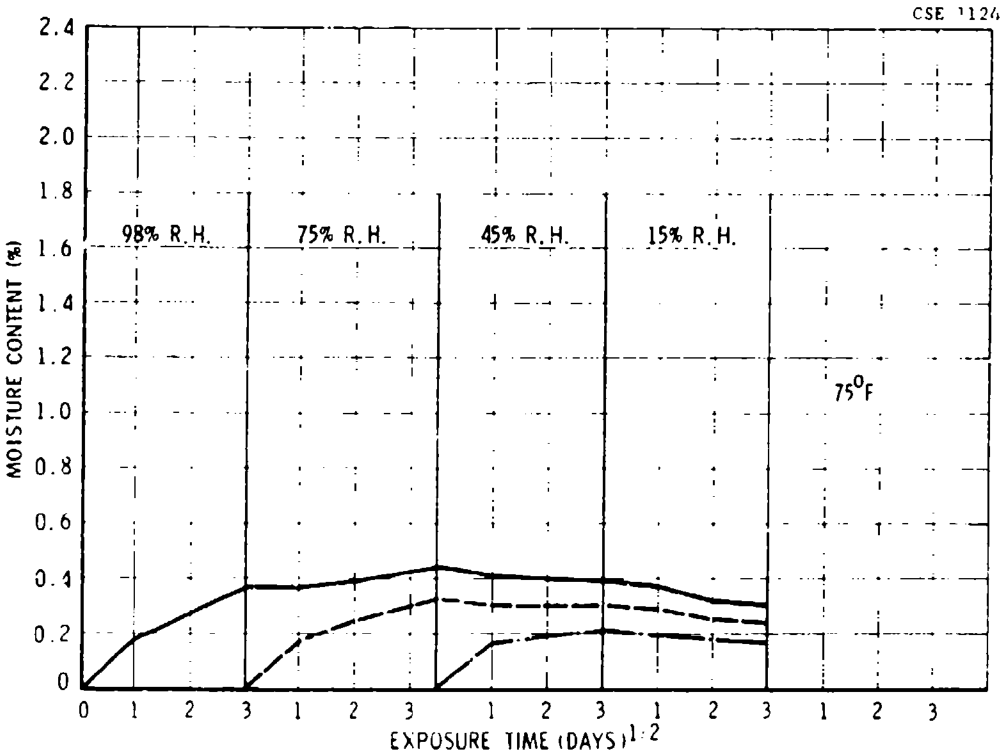

Figure 49 Effects of Decreasing Humidity - 16 Ply Laminate

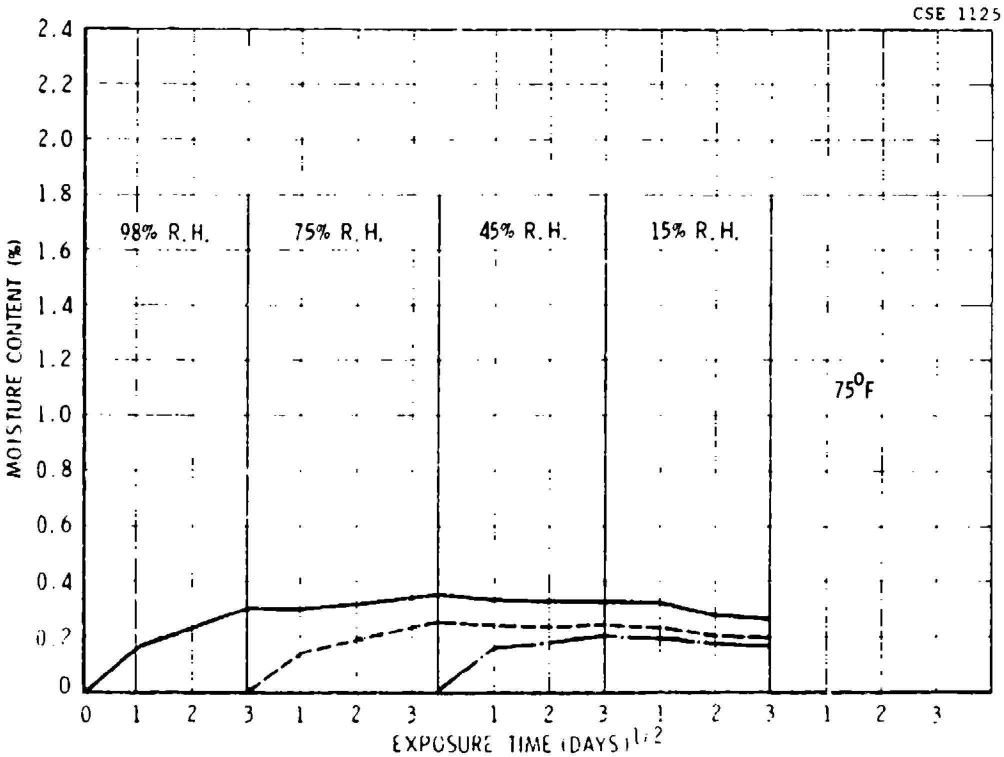

Figure 50 Effects of Decreasing Humidity - 24 Ply Laminate

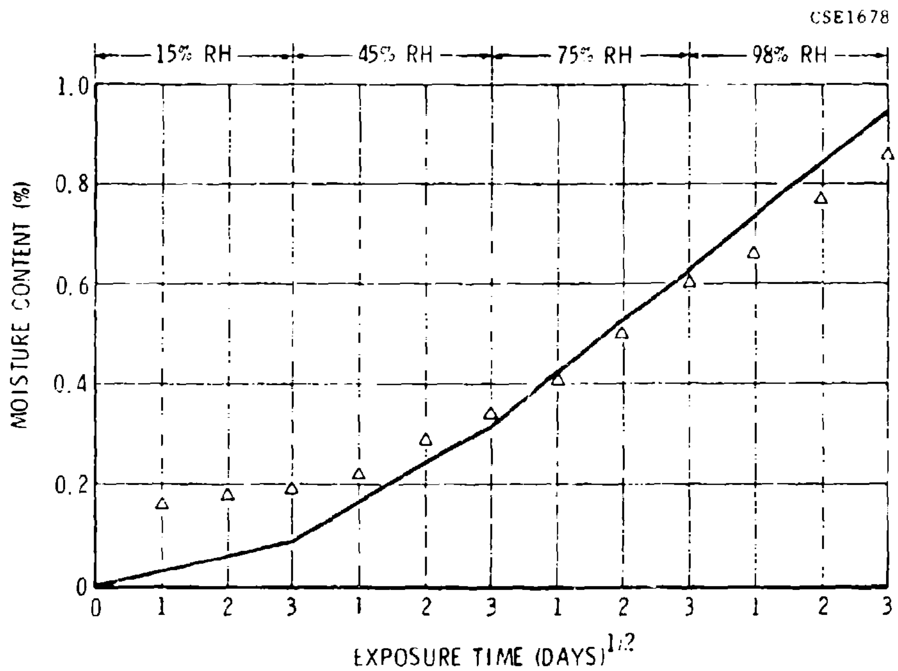

Figure 51 Comparison of Calculated and Experimental Moisture Contents - 8-Ply Laminate After 1, 4, and 9 Days at 75^{o}F in Sequentially Increasing Humidities

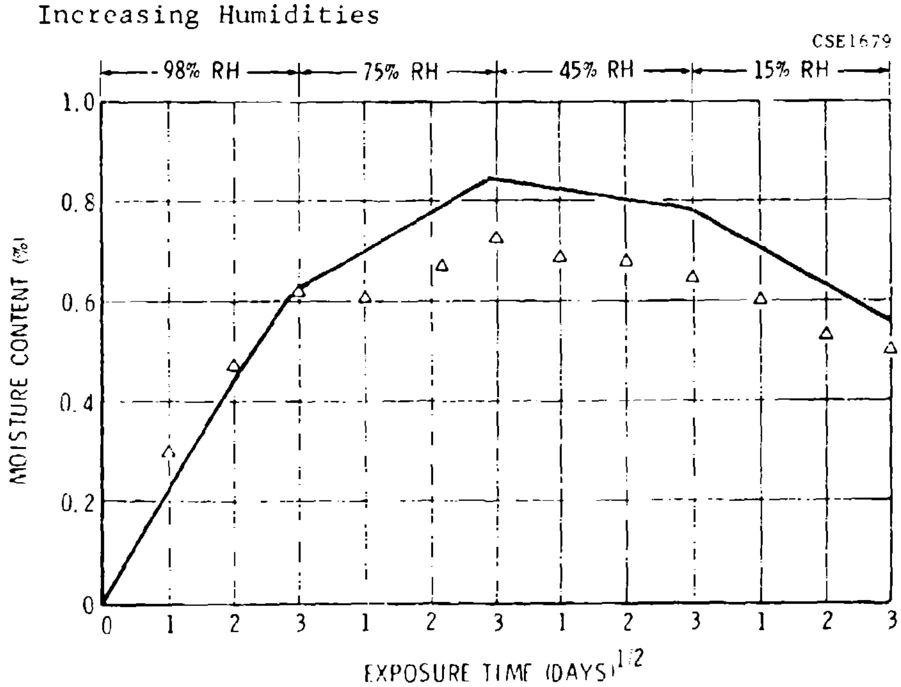

Figure 52 Comparison of Calculated and Experimental Moisture Contents - 8-Ply Laminate at 75^{o}F After 1, 4, and 9 Days in Sequentially Decreasing Humidities

Table VII "REAL LIFE" ENVIRONMENTAL CYCLE

Mondays and Thursdays:

(1) 75% RH @ 75°F for 18.5 Hours; Weigh
(2) 3-1/2 Hours "Rainfall"*; Wipe Dry; Weigh
(3) -65°F for 90 Minutes; Put into Desiccator at R.T. for 10 Minutes
(4) Weigh; Return to 75% RH @ 75°F

Tuesdays and Fridays:

(1) 75% RH @ 75°F for 19.5 Hours; Weigh
(2) 3-1/2 Hours "Rainfall"; Wipe Dry; Weigh
(3) -15°F for 45 Minutes
(4) Put into Heating Tube and Heat to 300°F @ ~ 1.5°F/Sec; Cool to R.T. @ ~ 1.0°F/Sec
(5) Weigh; Return to 75% RH @ 75°F

Wednesdays:

(1) 75% RH @ 75°F for 23-3/4 Hours
(2) Weigh; Return to 75% RH @ 75°F

Saturdays and Sundays:

(1) 75% RH @ 75°F for 24 Hours Each Day

*Immersion in Agitated Water at 75°F

in the "real-life" cycle. This heating spike is identical to the one selected for real time fatigue tests of Type I specimens and of the box beam component in this program.

Four-ply laminates were subjected to the "real life" environmental cycle shown in Table VII. The moisture content relationship to weeks of exposure to the "real life" cycle is shown in Figure 53. Data points for the major segments of the cycle are identified. These major segments are

1. Ground-based humidity exposure
2. Ground-based "rainfall"
3. Mission II flight profile
4. Mission I flight profile.

These data show that the moisture content due to "real life" exposures oscillates within an ascending band, which approaches an equilibrium level. The Mission II flight profile, which involves only subsonic conditions, has a barely perceptible drying effect. The Mission I flight profile has a much greater drying effect, but the drying is not sufficient to remove all of the absorbed moistured.

The band of moisture contents versus exposure times for 4-, 8-, 16-, and 24-ply laminates is shown in Figures 54 through 57, respectively. The 4-ply data in Figure 54 is the same as that shown in Figure 53; it is presented again to show the same format as that used for the thicker laminates in Figure 53 through 57.

The trend is similar for all four laminates. Moisture content climbs within a band of values and approaches an equilibrium level. As was the case with hygrothermal absorption, the thicker laminates approach equilibrium at a slower rate than do the thinner laminates.

The behavior of the laminates exposed to the "real life" environmental cycle appear similar to the behavior in hygrothermal environments. However, there are two important differences. First, the equilibrium moisture level is higher than that observed in the hygrothermal tests. Even at 100% relative humidity, the nominal hygrothermal equilibrium level is only about 1.46%. As indicated by the 4- and 8-ply data in Figures 54 and 55, the equilibrium level for the "real life" cycle is approximately 2.2%.

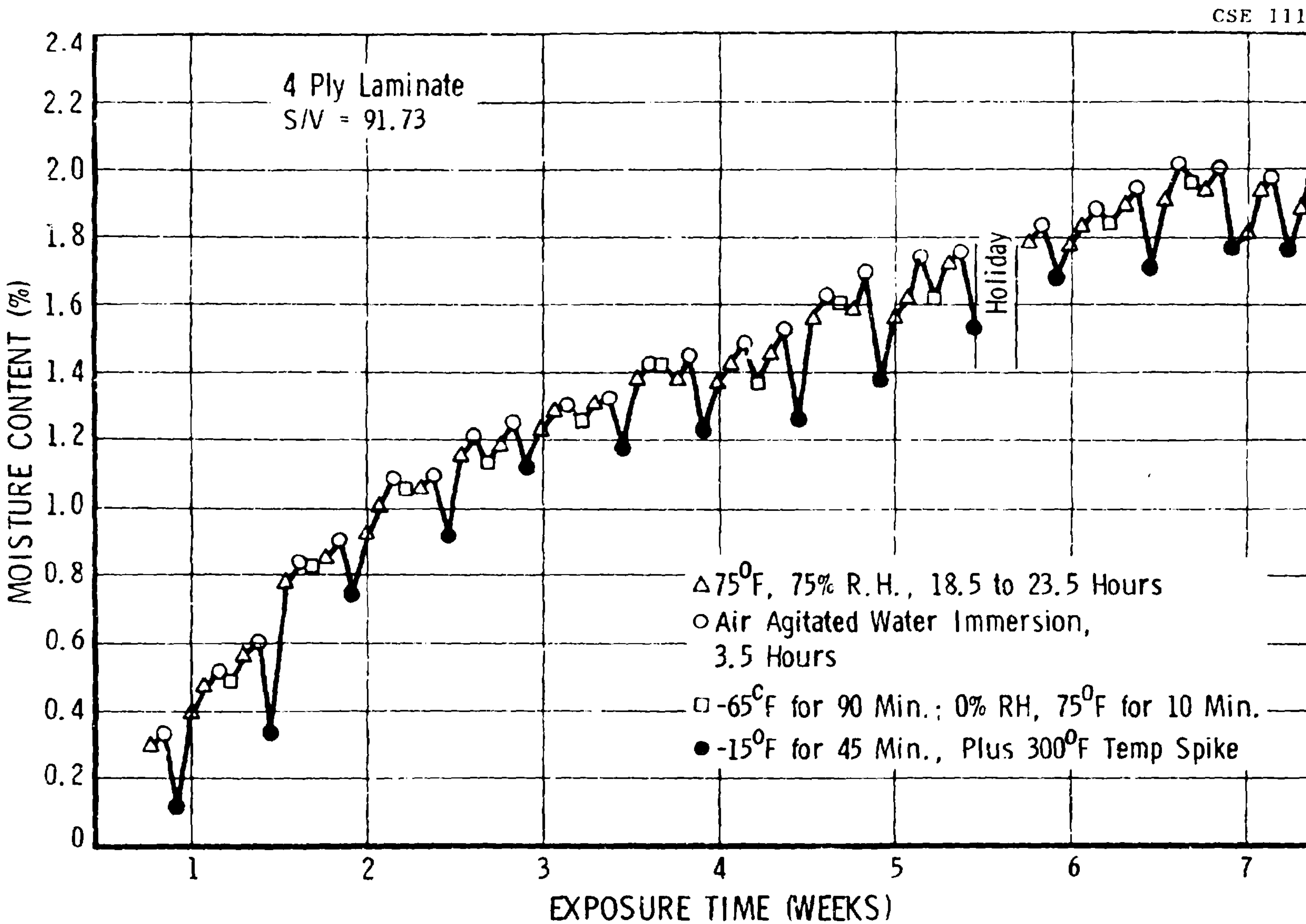

Figure 53 Effects of "Real Life" Environmental Cycle

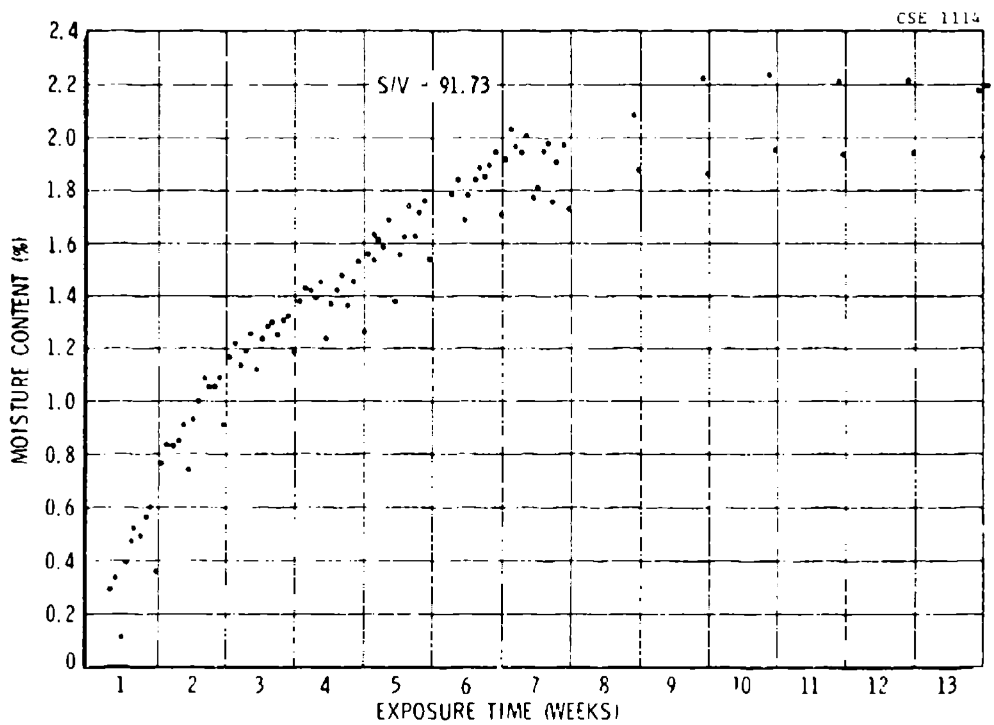

Figure 54 "Real Life" Environmental Cycle - 4 Ply Laminate

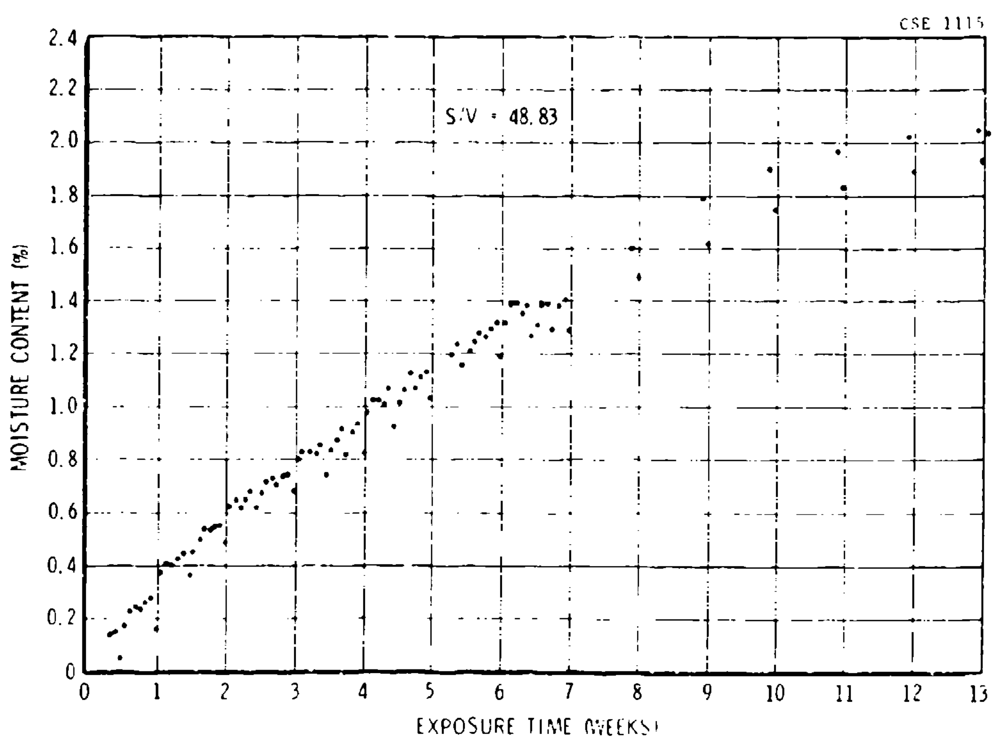

Figure 55 "Real Life" Environmental Cycle - 8 Ply Laminate

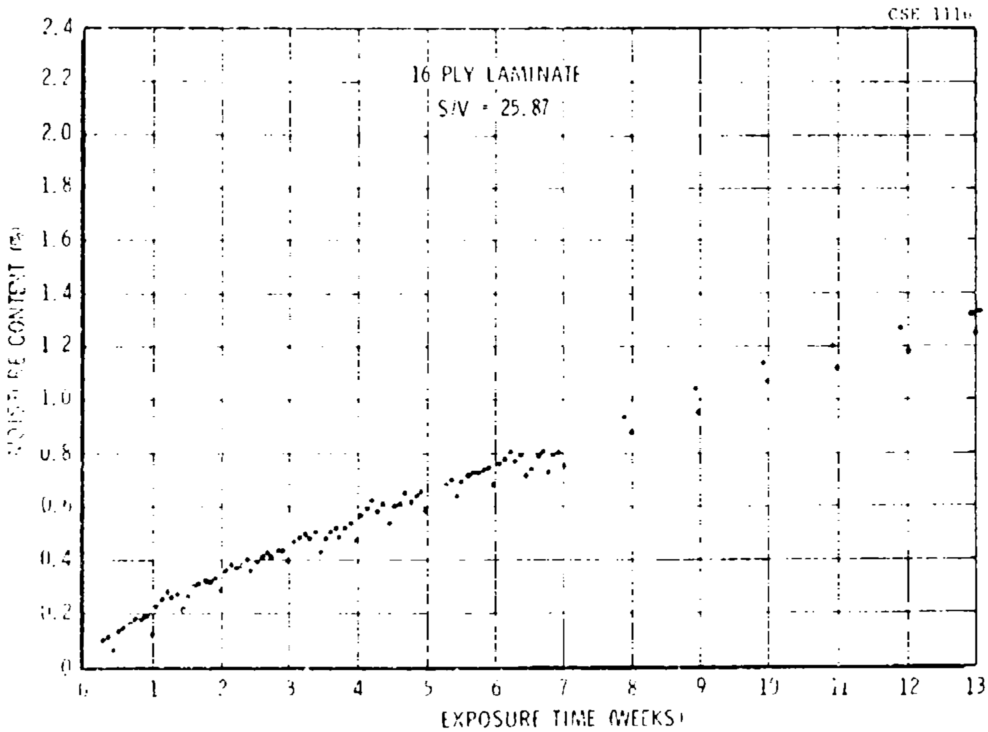

Figure 56 "Real Life" Environmental Cycle - 16 Ply Laminate

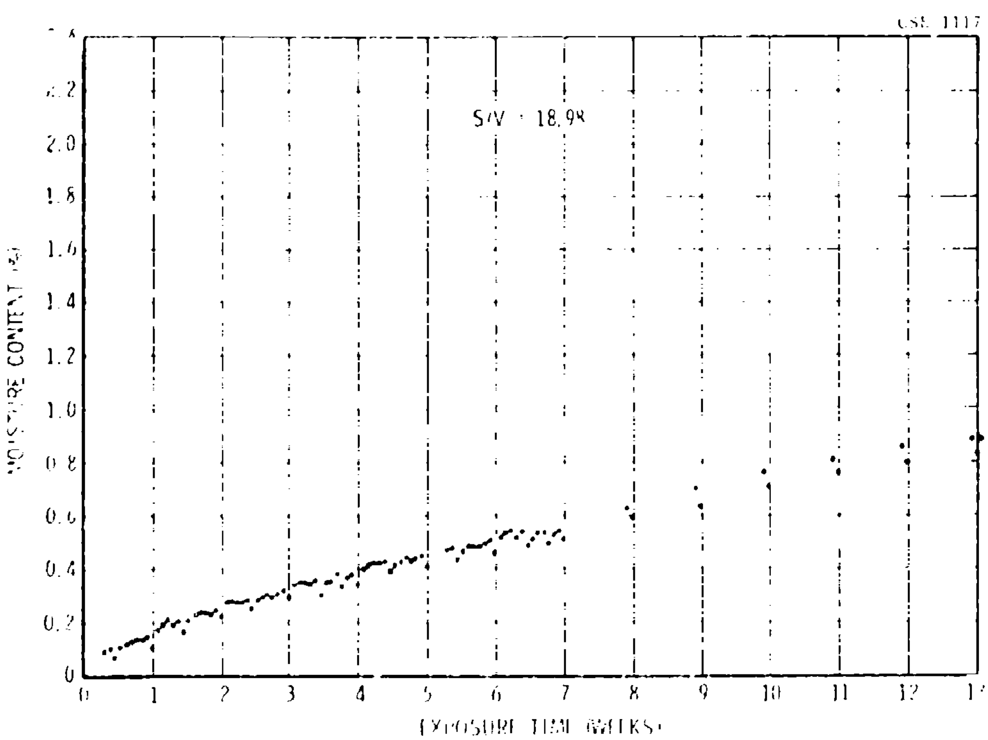

Figure 57 "Real Life" Environmental Cycle - 24 Ply Laminate

The other difference is revealed when the "real life" cycle moisture content data are plotted against square root of exposure time. These relationships are shown in Figure 58. For convenience, only the data points for one common point in each week's cycle have been plotted. These plots show an increasing rate of absorption after a linear segment that occurs during the first two weeks. Hygrothermal absorption does not include this increasing rate segment; it is linear until decreasing rates begin as equilibrium is approached. Figure 59 compares the behavior of an 8-ply laminate for the "real life" and the hygrothermal exposures, where the hygrothermal condition is 75% relative humidity at 75°F.

4.3 "REAL LIFE" CYCLE COMPONENTS

Tests were conducted to determine the factor(s) causing the "real life" environmental cycle to behave differently than the hygrothermal cycles. Specimens from the 4- and 8-ply laminates were immersed in water at room temperature; this simulated a hygrothermal environment of 100% relative humidity at 75°F. Control specimens were subjected to no other environment. The weight-versus-time behavior of these control specimens was almost identical to that previously observed for hygrothermal specimens exposed to similar conditions. Three other groups of specimens were also immersed in water, but each group was also subjected to one of the following three conditions:

1. Once-daily exposure to -65°F for 90 minutes, then warmed to 75°F in a desiccator for 10 minutes.
2. Once-daily exposure to temperature spike, 75°F up to 300°F at 1.5°F/sec with cooling to 75°F at 1.0°F/sec.
3. Combination of 1 and 2.

The data from these test series for the 4- and 8-ply specimens are shown in Figures 60 and 61, respectively. As shown in these figures, exposure to -65°F had no effect on the absorption behavior of the laminates. These data coincide almost exactly with the hygrothermal absorption data.

However, exposure of the specimens to the supersonic heating spike profile produced increased absorption rates and equilibrium levels. The combination of the heating spike and the -65°F exposure produced behavior identical to that found for the heating spike alone.

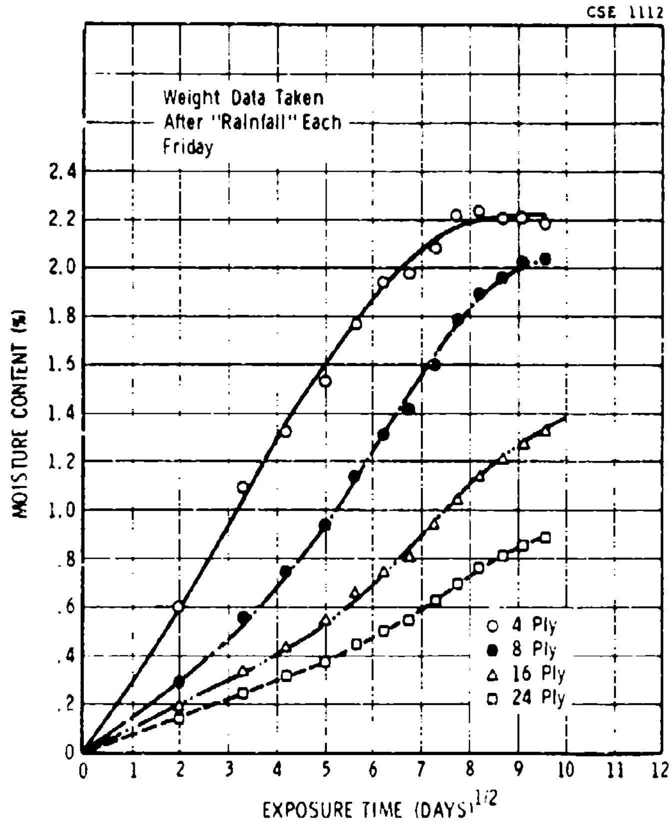

Figure 58 Weight Gain Versus Square Root of Exposure Time for "Real Life" Environmental Cycle

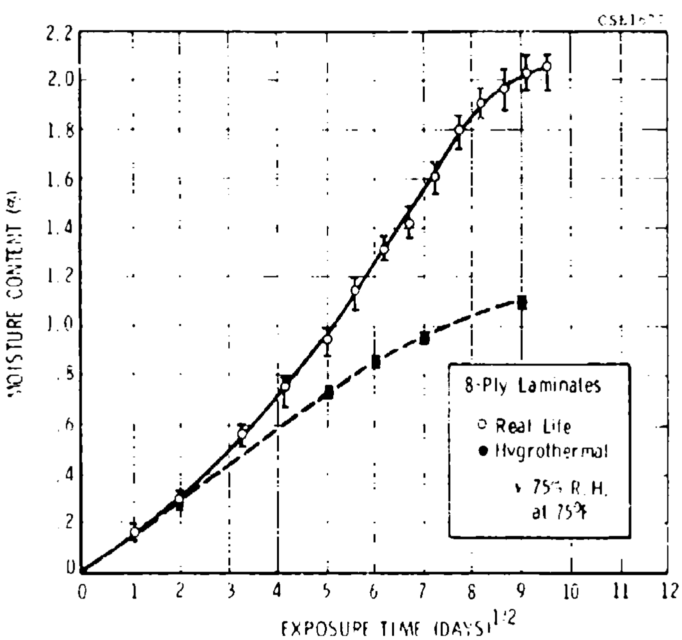

Figure 59 Comparison of "Real Life" and Hygrothermal Absorption Behavior

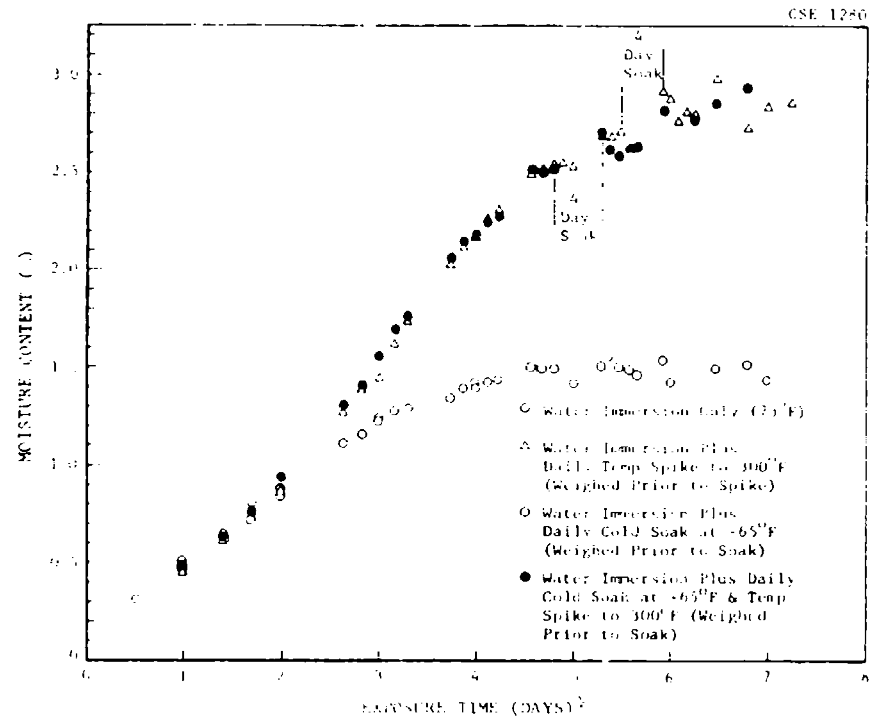

Figure 60 Effect of Realistic Exposure Components Upon Absorption Behavior, 4-Ply Laminate

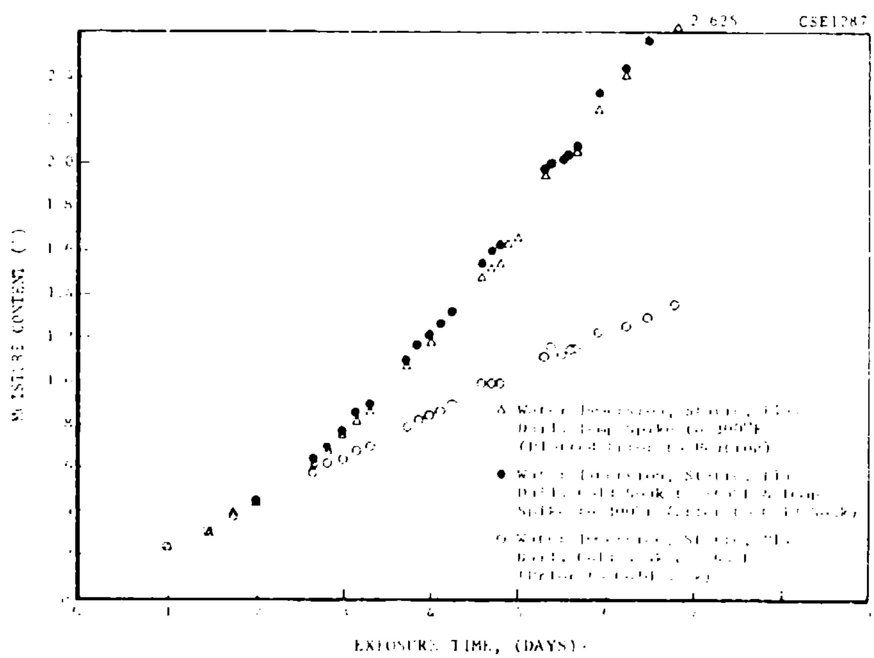

Figure 61 Effect of Realistic Exposure Components Upon Absorption Behavior, 8-Ply Laminate

The equilibrium level produced by the heating spike appears to be something over 3.0%. This shows that the concentration, or relative humidity, determines the amount absorbed, just as it did in the hygrothermal test series. (Equilibrium level in the "real life" cycle was 2.2%, occurring with 75% relative humidity baseline versus the 100% baseline for this test series). Figure 62 shows the equilibrium moisture contents for exposures to these conditions and to 45% relative humidity. For comparison, the relationship for hygrothermal exposures is shown.

After apparent equilibrium was reached, the daily heating spikes were discontinued. The specimens, which had gained about 3% by weight, were left immersed in 75°F water. Both gained a small amount in weight (approximately 0.2%).

These spiked specimens then were dried in a 180°F circulating air oven to determine if the absorbed moisture would be lost or if only the portion of the moisture equal to the hygrothermal absorption would be lost. As shown in Figure 63, all of the moisture was desorbed.

These specimens were again immersed in 75°F water and weight gain was recorded periodically. The specimens gained weight rapidly and approached equilibrium levels about equal to their moisture content before they were dried. The weight gain profiles for the 4-ply specimens after drying and before drying (water immersion plus heating spike) are given in Figure 64. The hygrothermal profile for unspiked specimens is also shown in this figure. This data shows that some permanent changes in the composite material occurred as a result of exposures to the supersonic heating spikes. These changes affected the values of both the absorptivity coefficient, C, and the inherent diffusion (or permeability) coefficient, D_O, of the mathematical model (Equation 6 in Subsection 3.2).

Unspiked specimens were also dried in a 180°F circulating air oven following hygrothermal equilibrium in 75°F water. After the specimens were dried, they were replaced in 75°F water. The original and post-drying absorption profiles for 4-, 8-, and 16-ply laminates are compared in Figure 65. Absorption rates appear unaffected by the oven drying; however, the absorptivity coefficient appears to have been increased slightly. This result is surprising in view of the apparently higher permeability index applicable during drying at 180°F (see Subsection 3.2).

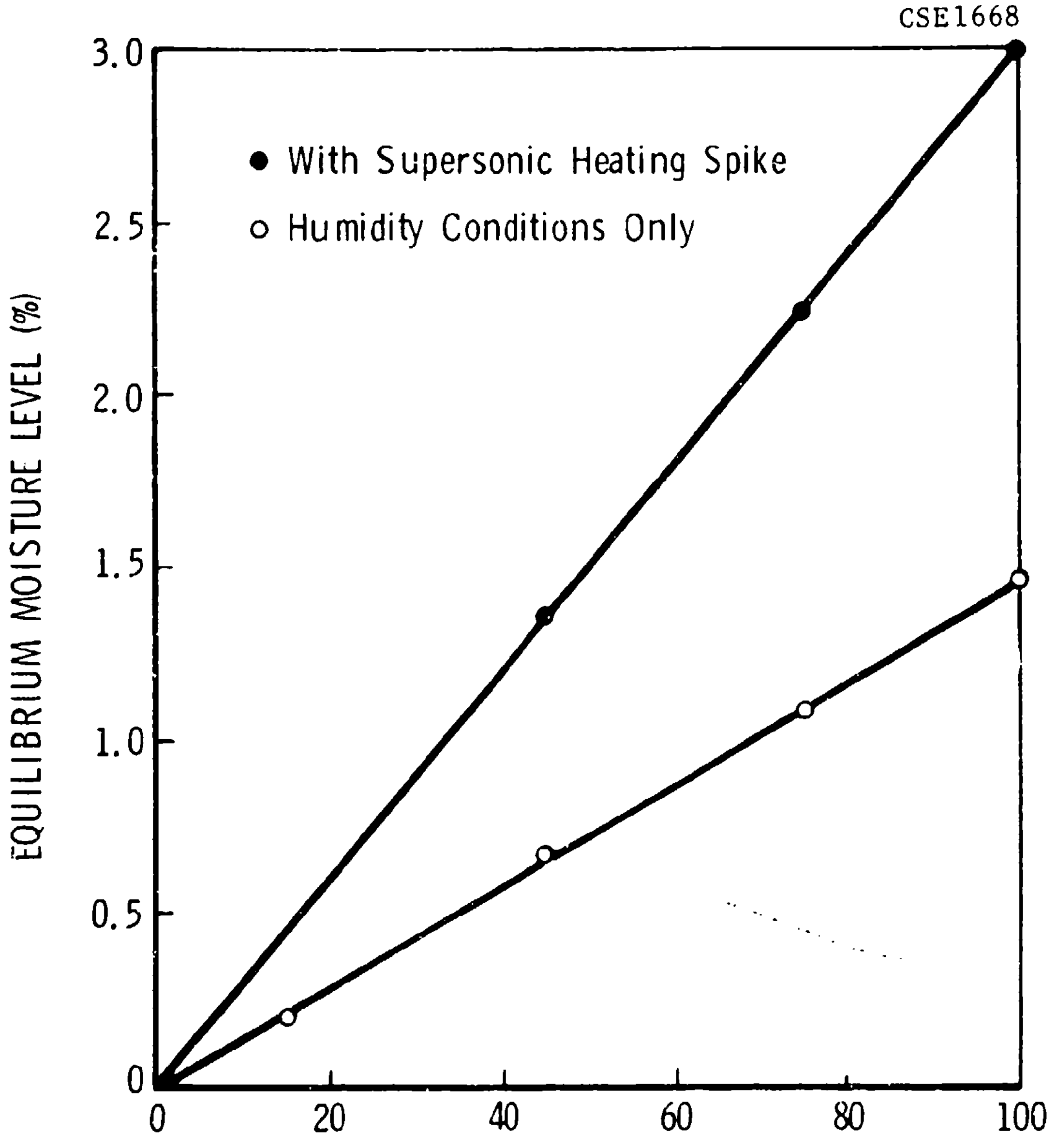

Figure 62 Equilibrium Moisture Levels-Effects of Supersonic Heating Spike

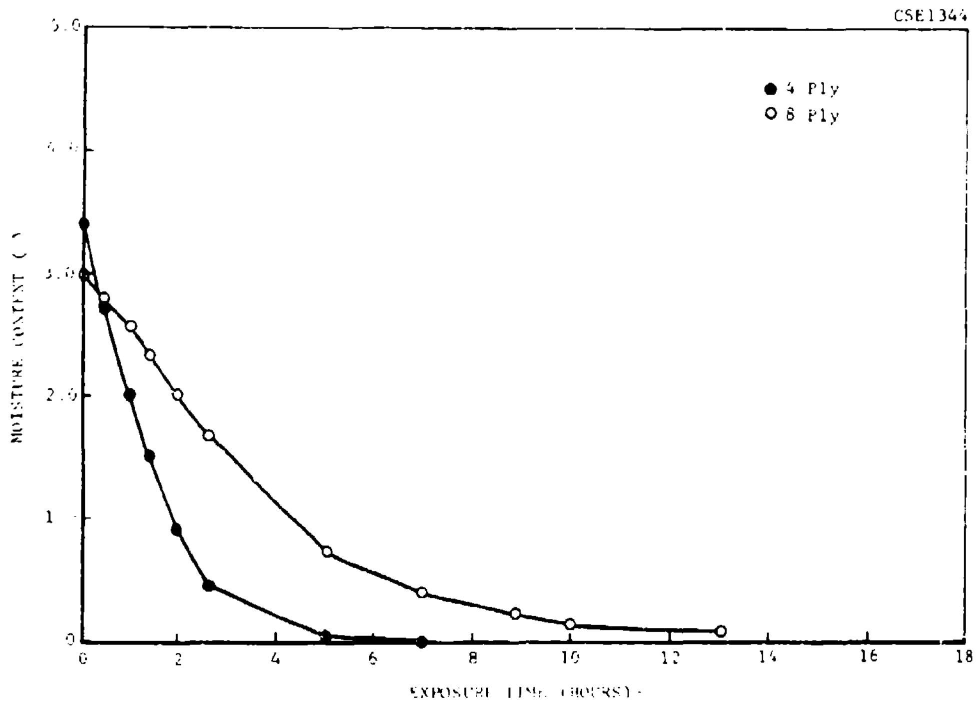

Figure 63 Desorption at $180^{\circ}F$, 0% R.H. After Absorption Due to Spiking

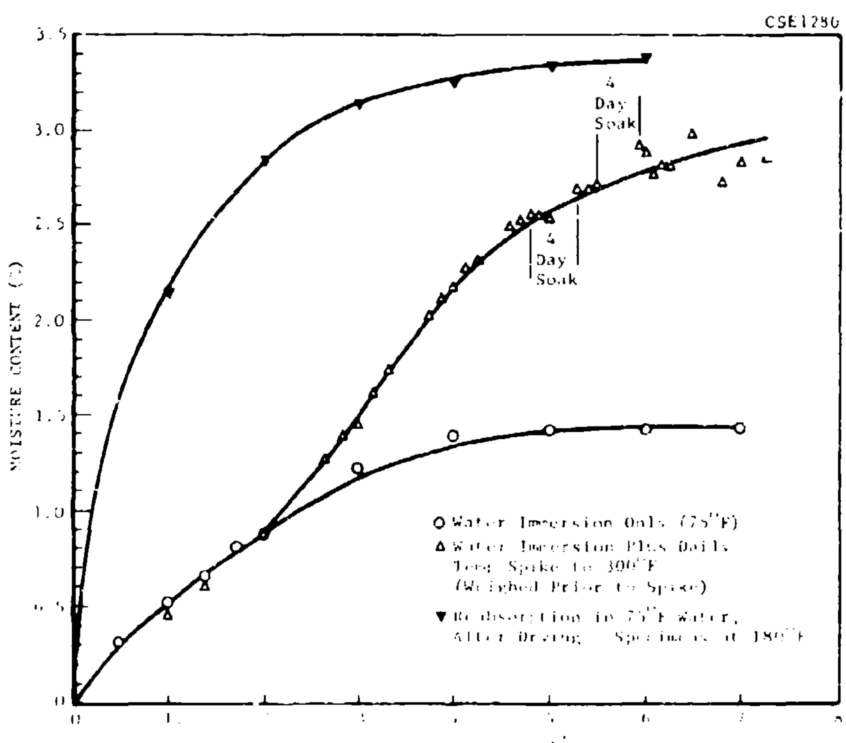

Figure 64 Comparison of Reabsorption Behavior - 4-Ply Laminate

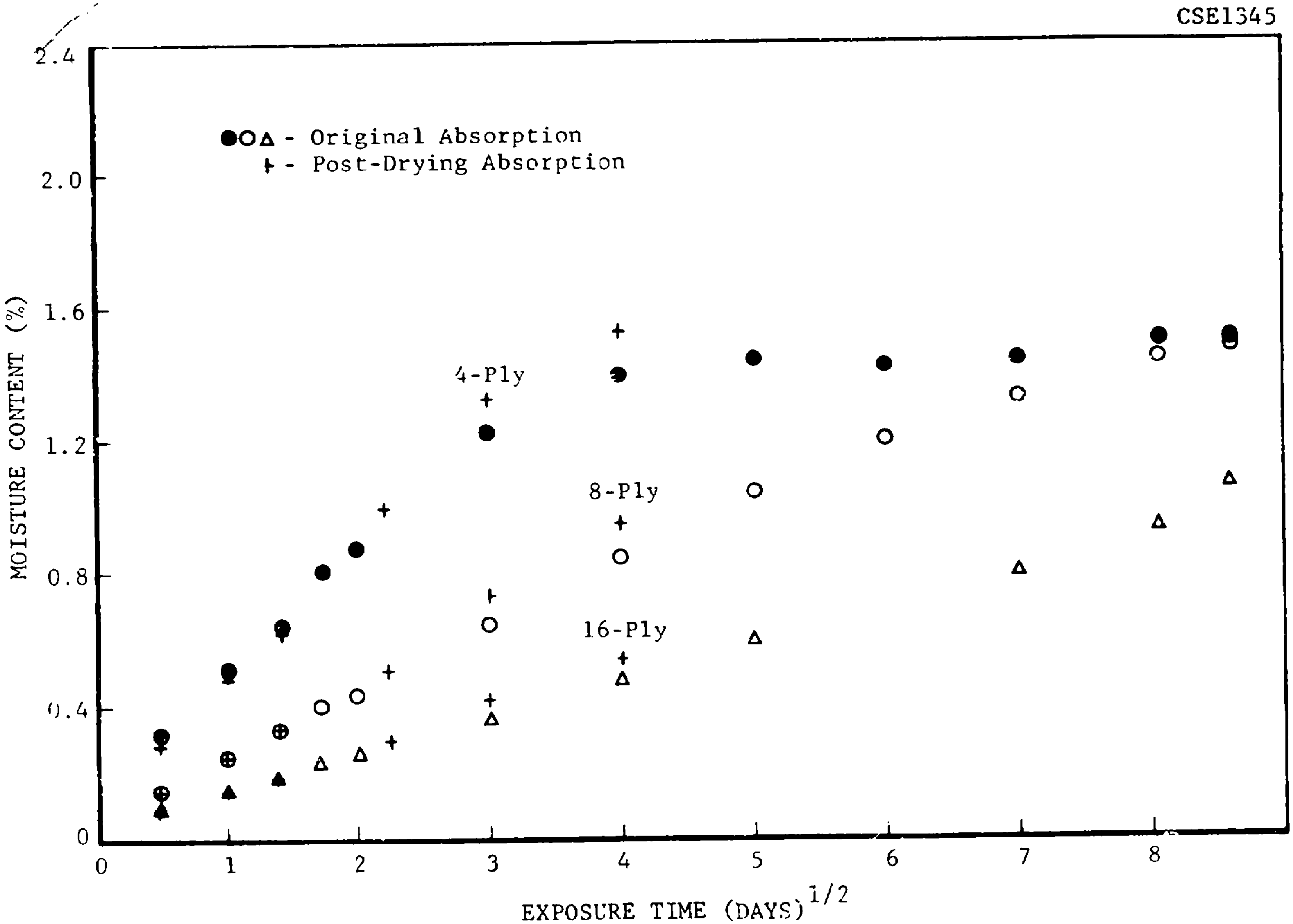

Figure 65 Effect of 180°F Drying of Hygrothermal Specimens Upon Reabsorption in 75°F Water

Altogether, these experiments showed that the supersonic heating profile causes material changes that result in a much higher level of absorbed moisture. However, since supersonic flight occurs at some altitude, the possibility was considered that this conclusion might not be valid for actual flight conditions. Specifically, the possibility was considered that the combination of supersonic heating and reduced pressure due to altitude might cause much faster loss of moisture during the heating.

A special test was conducted to determine if this would happen. This test involved a repeat of laminate exposures to a hygrothermal environment followed by a daily temperature spike exposure. The difference was that the temperature spikes were applied to the specimens in an altitude chamber at a simulated altitude of 30,000 feet. As shown in Figure 66, the same behavior occurred which had been observed with the "real life" environment specimens. In fact, the rate of weight gain was slightly greater. This probably was the result of a slightly lowered mass heating effect resulting from the lower air density at the simulated altitude.

The effect of individual spikes was studied after it was confirmed that supersonic heating spikes cause increases in absorbed moisture. Specimens from the 4-ply laminate were hygrothermally exposed to water immersion at 120°F. After the specimens reached an equilibrium moisture content of 1.55%, they were exposed to one supersonic heating spike. This reduced the moisture content to approximately 1.20%. Then, the specimens were again immersed in 120°F water. Periodic weighings showed that equilibrium was reached within 9 days, but it was reached at a highe moisture content (almost 1.80%). At that point, the specimens were exposed to a second heating spike, weighed, and re-immersed in 120°F water. Again, equilibrium was reached within 9 days' this time it was reached at a moisture content of about 2.10%. Then the specimens were exposed to a third heating spike.

This cycle was continued until 12 heating spikes had been applied. Figure 67 shows the moisture content (%) relative to square root of exposure time (days)$^{\frac{1}{2}}$, beginning after the original hygrothermal equilibrium was reached. These data show that the first 9 spikes cause a rapid doubling of the equilibrium moistur level. The 10th through 12th spikes also caused an increase, but the rate of increase diminished greatly.

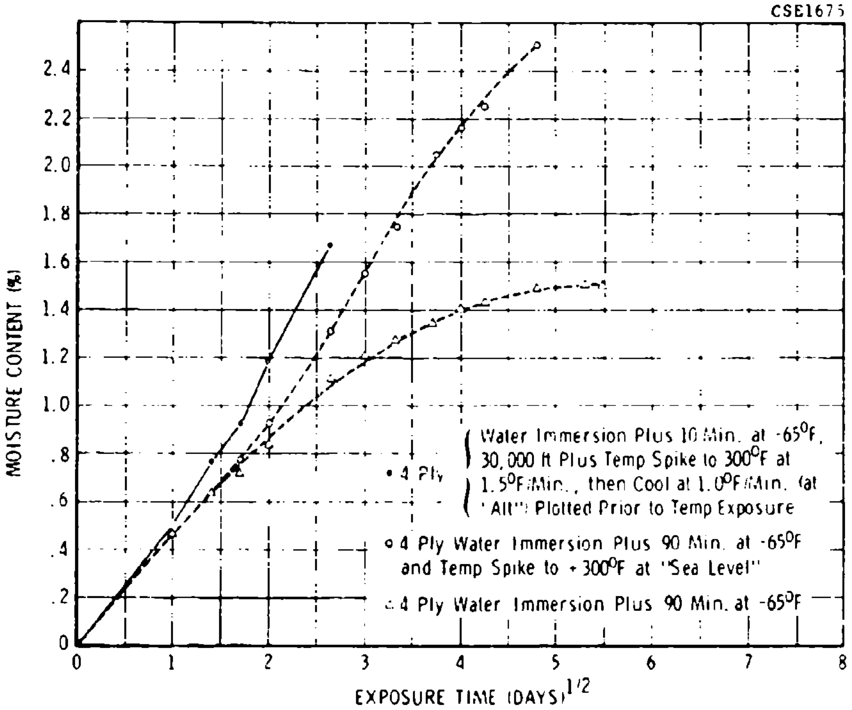

Figure 66 Effect of Simulated Altitude and Spike

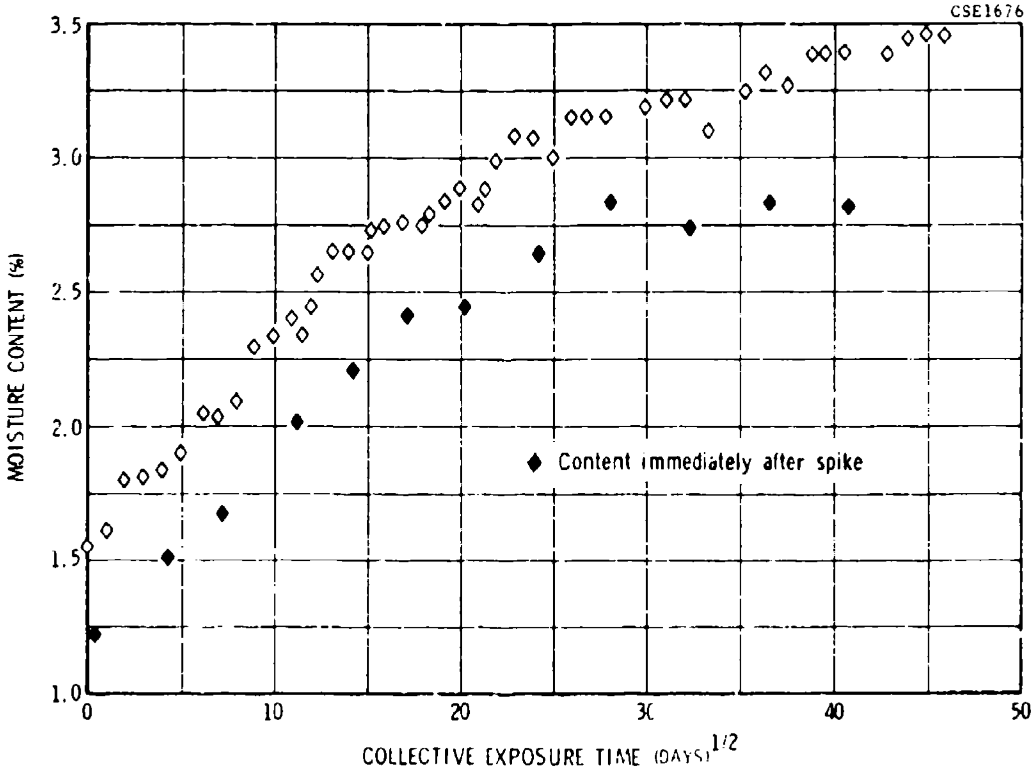

Figure 67 Effect of Single Spikes Upon Moisture Content

SECTION V

MECHANICAL EFFECTS

There were two major objectives of the moisture investigations. One was to gain understanding of moisture diffusion in composites. The other was to learn to apply this knowledge to the rapid simulation of actual environmental service conditions. Rigorous determination of mechanical effects was not a goal. However, several series of tests were conducted to determine some mechanical effects. Effects of moisture content were established for 0° flexural strength, short beam shear strength, and bolt bearing strength. Flexural creep behavior was also determined.

5.1 0° FLEX AND SHORT BEAM SHEAR STRENGTHS

Tests of 0° flex and short beam shear strengths were conducted early in the program before learning of the effects of supersonic dash simulation on absorption behavior. Therefore, all data for these two properties were obtained from specimens that had been hygrothermally exposed.

Sixteen-ply specimens were exposed to 98% relative humidity at 75°F, 120°F, and 150°F for various periods of time. Then, they were weighed and tested to determine the relationships of 0° flex strength and short beam shear strength to absorbed moisture content. These specimens were taken from the $[0_2/(\pm45)]_2$ laminates. Tests were conducted at both room temperature and 350°F.

The residual strength, as a fraction of the original room temperature dry strength, versus moisture content is shown in Figure 68. A similar relationship for short beam shear strength is shown in Figure 69. The mechanical property values of the room temperature dry specimens are shown in Table IV. These data show that at room temperature the plasticization of the resin can be slightly beneficial. However, at elevated temperature, progressive strength losses result from increased amounts of absorbed moisture.

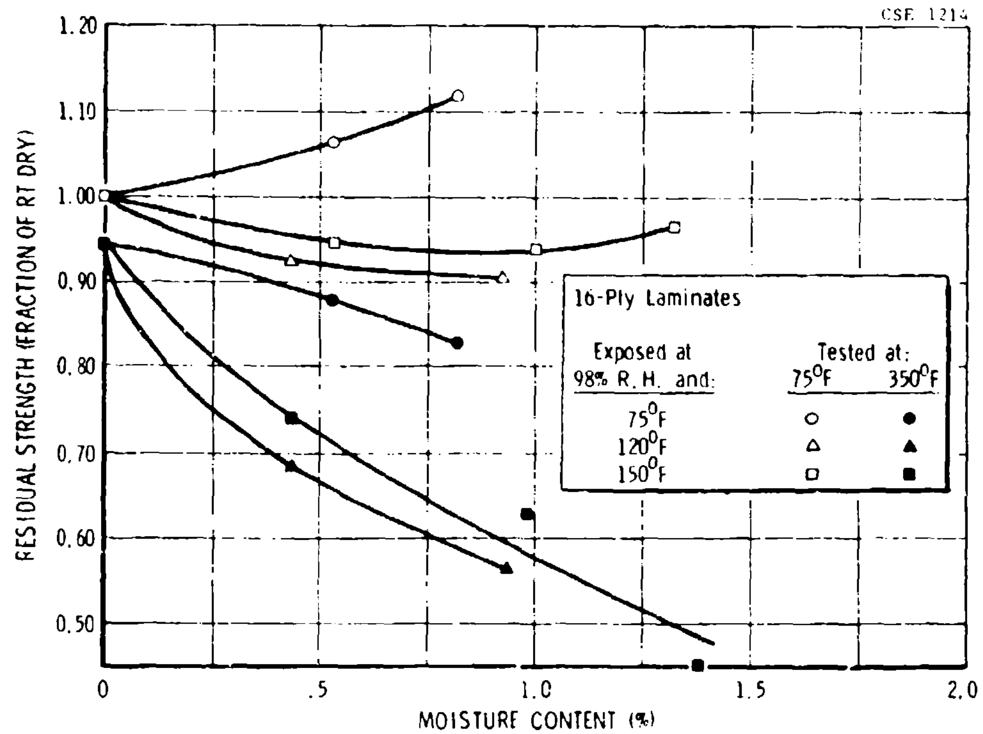

Figure 68 Effect of Hygrothermally Absorbed Moisture Upon 0° Flexural Strength

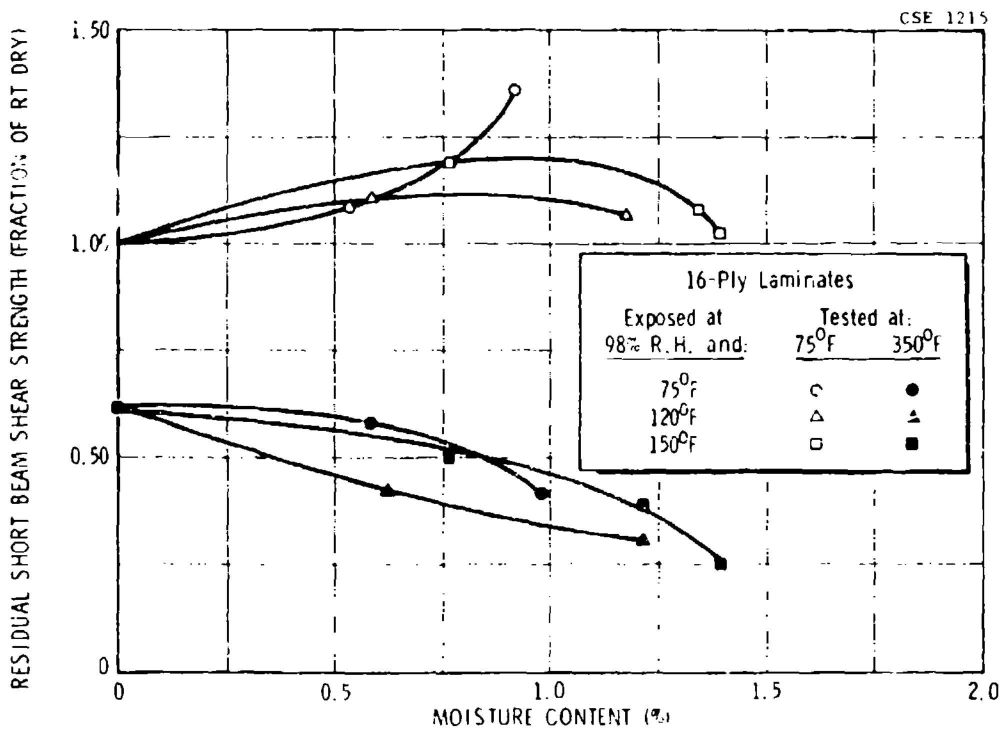

Figure 69 Effect of Hygrothermally Absorbed Moisture Upon Horizontal Shear Strength

5.2 BOLT BEARING STRENGTH

Tests were conducted to determine the effects of moisture content upon bolt bearing strength. These tests were conducted at temperatures of 75°F, 200°F, and 300°F. At each of these temperatures, tests were conducted for five moisture contents. These five contents were 0 and, approximately, 0.3%, 0.9%, 1.4%, and 1.7% by weight. Moisture was absorbed during exposures to the "real life" cycle, except that the background humidity was 98% instead of 75%.

The bolt bearing specimen, also referred to as the Type I specimen, is described in Figure 70. The specimen is a (± 45) graphite-epoxy laminate gripped along a side having glass doublers. It is loaded through a 1/4-inch-diameter hole in the center of the other side.

Figure 71 shows the ratio of static strength for each moisture content to the static strength of dry (0% moisture) specimens at the same temperature. This shows both the temperature reduction and the effect of moisture content. The results show that increasing temperature is more severe than increasing moisture content. They also show that a small amount of moisture (up to 0.6%) is beneficial to bolt bearing strength

Further details on the Type I specimens are presented in Volume II of this final report. This includes values of bolt bearing strength for the reference dry condition at each test temperature.

5.3 FLEXURAL CREEP BEHAVIOR

Thermomechanical analysis (TMA) tests were conducted to determine the extent of flexural creep after various periods of moisture exposure. These tests were conducted on five groups of environmentally conditioned specimens. These groups are

1. 98% relative humidity at 75°F
2. 98% relative humidity at 150°F
3. Water immersion at 75°F under 35 atmospheres of pressure
4. 75°F water immersion plus daily cold soak at -65°F
5. 75°F water immersion plus daily supersonic heating spike.

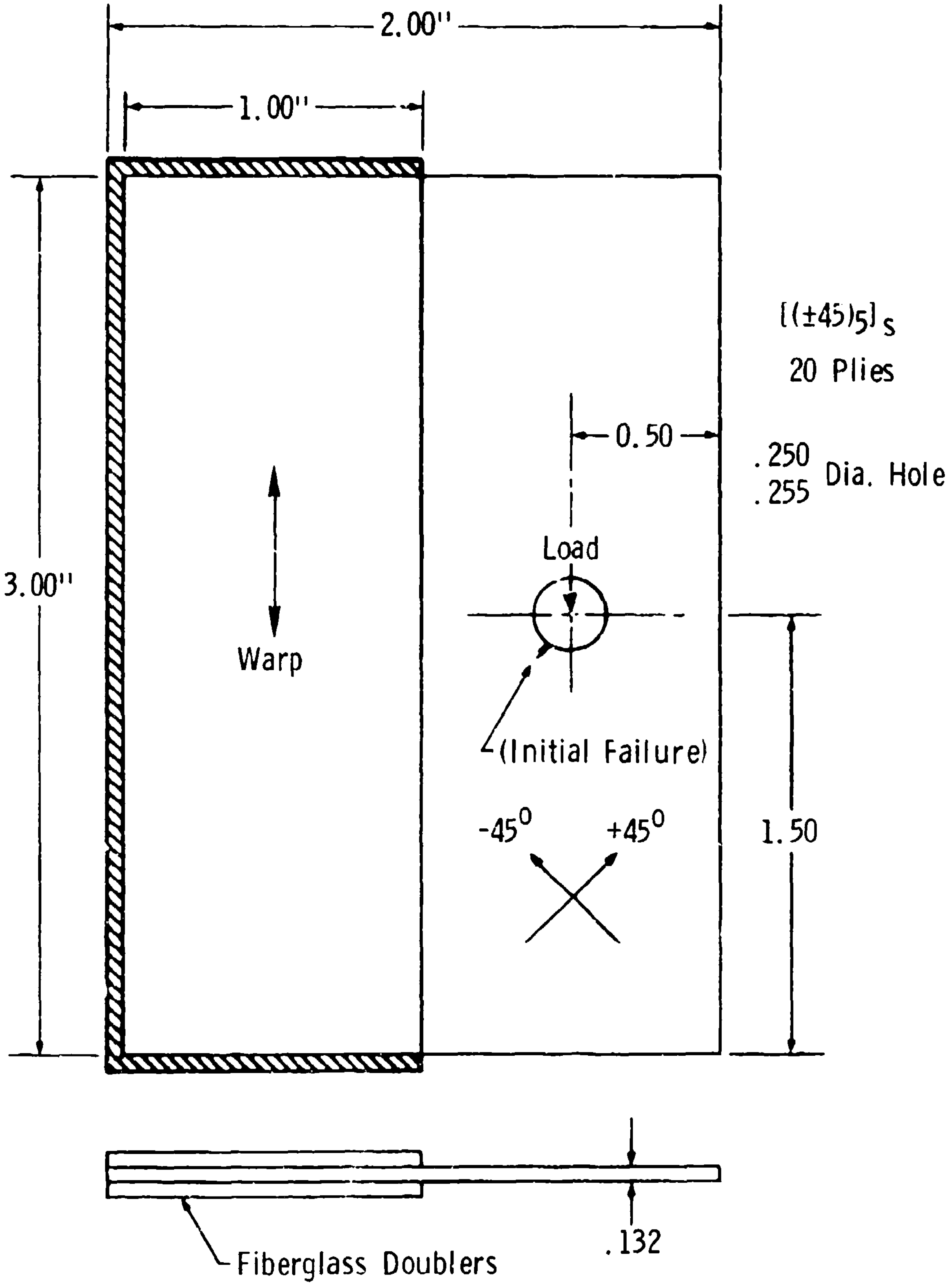

Figure 70 Bolt Bearing Specimen Configuration

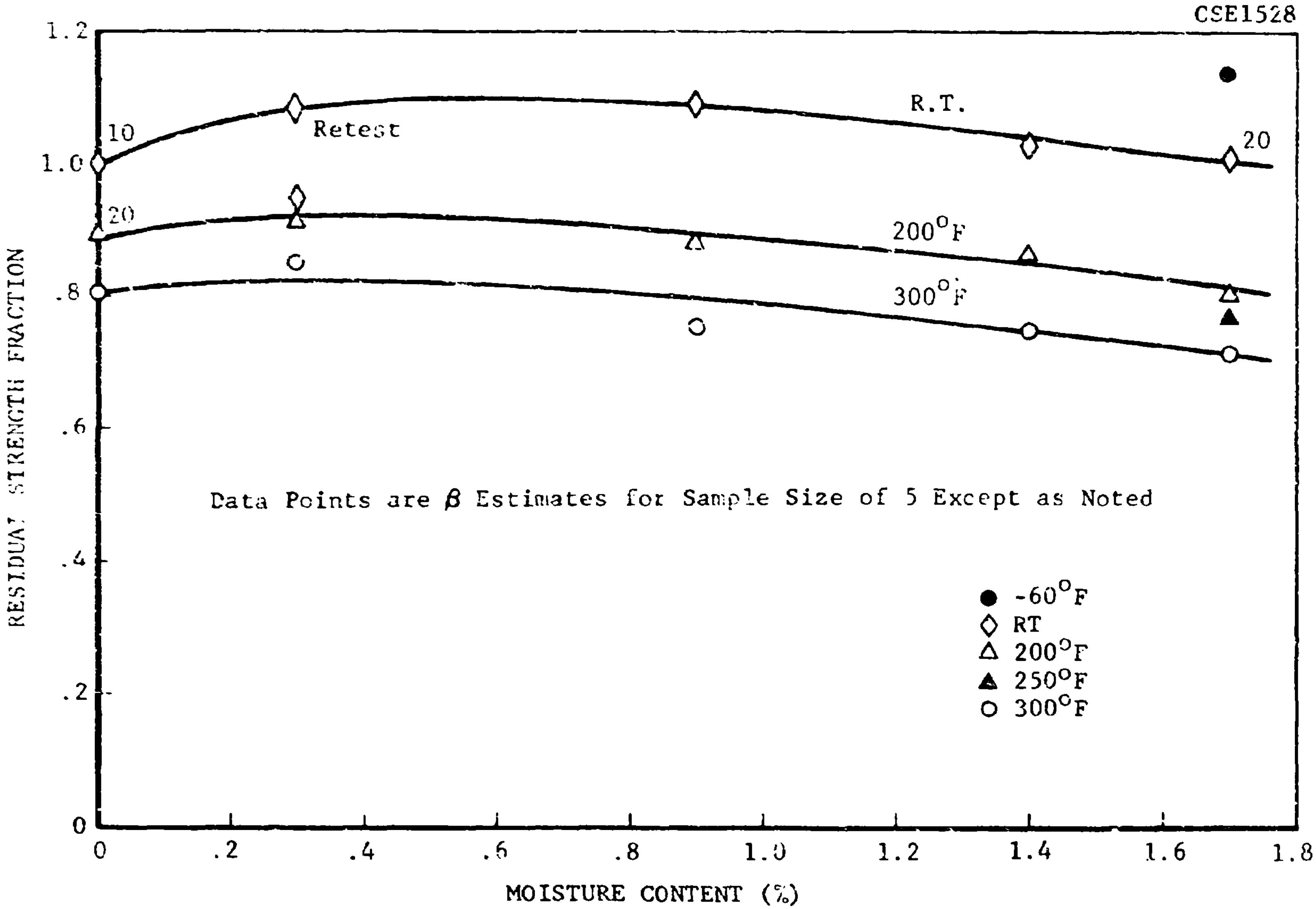

Figure 71 Bolt Bearing Static Strength as a Function of Laminate Moisture Content

The TMA tests were conducted using a Perkin-Elmer TMS-1 instrument. This instrument provides a sensitive measure of certain temperature-dependent properties of materials. It is capable of measuring dimensional changes (relative to expansion) or viscoelastic changes (relative to softening or creep behavior) of a composite material as a function of temperature and time. The test specimen, up to 0.25 by 0.25 inch by any thickness from a few mils up to 0.50 inch, is supported by the bottom of an open-sided quartz tube. One of several different probe extensions made of quartz is vertically oriented in the instrument so that one end rests on top of the test specimen. A weight tray on top of the probe assembly can be loaded to provide a downward force. This force remains essentially constant over a wide range of probe displacements because the probe assembly is suspended by a float that is totally immersed in a high density, low viscosity fluid. The core of a sensitive linear variable differential transformer is mounted on the shaft of the probe assembly and causes an electrical signal to be input to a recorder when there is any motion of the probe tip relative to the sample tube platform. The instrument is sensitive to specimen movements of as little as 40-microinch/inch. A furnace assembly that fi[illegible]ound the specimen tube together with a control unit can be use[illegible] to raise the specimen temperature from ambient to 700°C at rates ranging from 0.625° to 80°C/min. The specimen may be held isothermally at any temperature within the range and can be cooled at a controlled rate. Figure 72 is a photograph of the probe, furnace, and housing assembly.

The TMA procedure that has been developed involves a measur[illegible]nt of viscoelastic behavior revealed in a flexural creep mode. A small rectangular piece of composite is loaded in three-point flexure using a bevel-ended quartz probe and a double-knife-edged quartz support fixture. The flexural fixture, probe, and a tested specimen housed in the quartz support tube are shown in Figure 73. The test specimen is typically 0.250 by 0.0[illegible] 0.017 inch, and it is supported over a 0.200 inch span.

With the beveled probe in place, the weight tray is loaded to provide an initial 5000 psi flexural stress in the test specimen. The furnace is preheated to 250°F and then raised into position. Deflections of the test specimen are recorded as the test time increases.

The initial 5000 psi stress, applied at room temperature, caused small amounts of creep in specimens exposed to humidity. [illegible]ever, specimens with little or no moisture content showed no r[illegible] temperature [illegible]p.

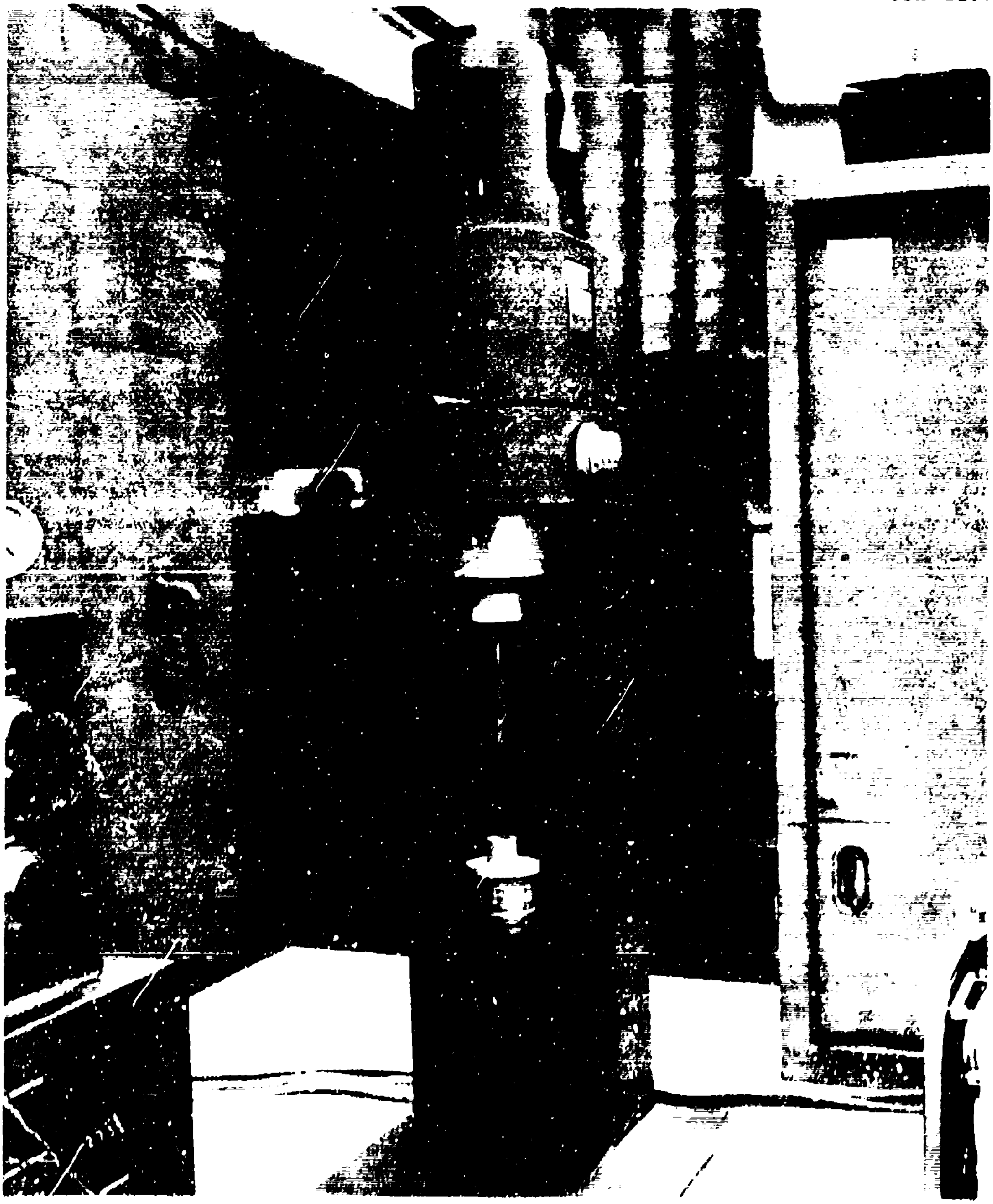

Figure [illegible]. Thermomechanical Analyzer

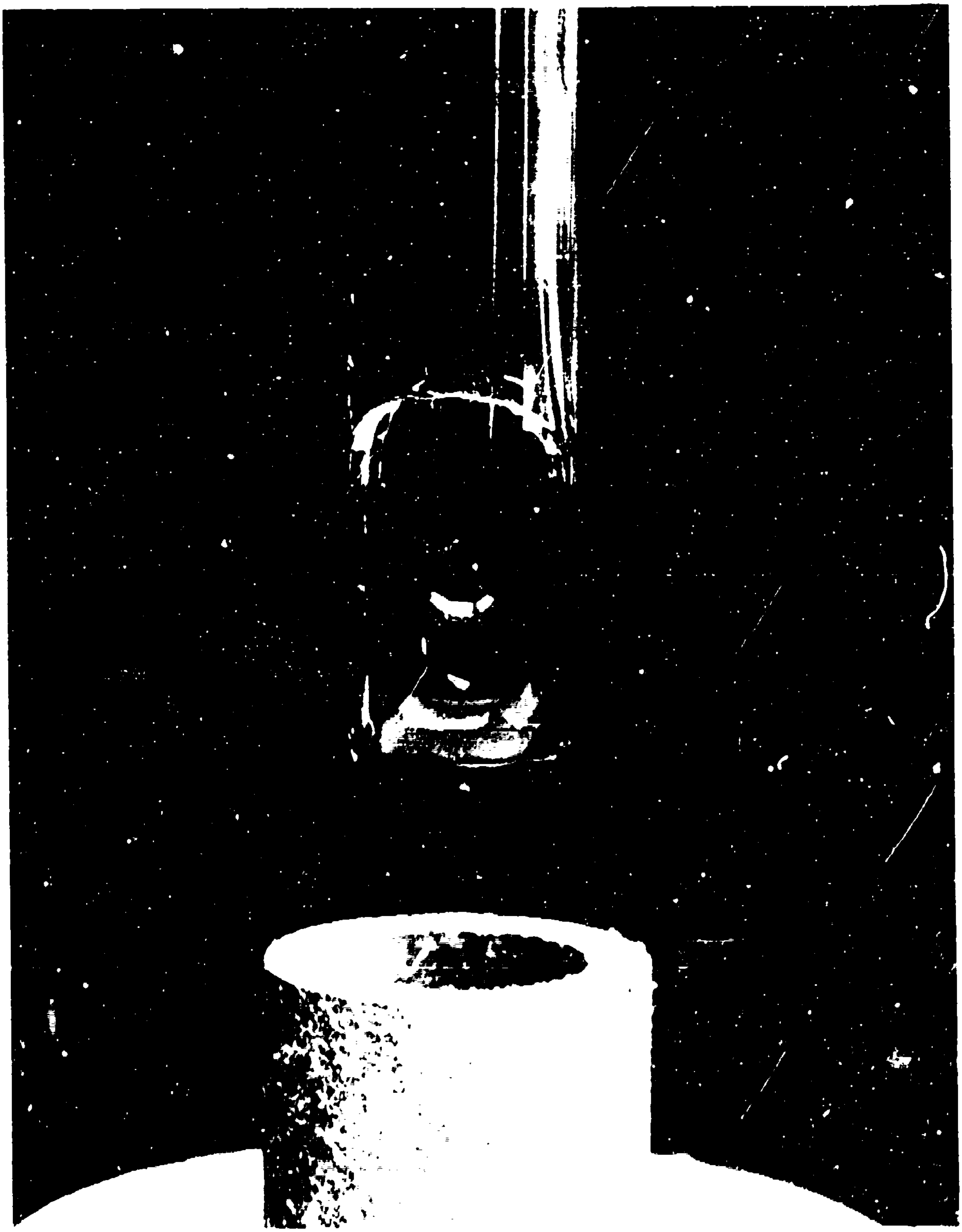

Figure 73 TMA Electrode Assembly and Tested [illegible]

The relationship between exposure time (days)$^{\frac{1}{2}}$ and extent of flexural creep that occurred in 15 minutes at 250°F is shown in Figure 74. These data show that absorbed moisture changes the viseoelastic behavior of the resin in the composite and acts like a plasticizer. Increasing concentrations produce increasing creep. As the concentration approaches equilibrium, the extent of flexural creep approaches a limit. This limit is approximately 1.8 mils of creep. Not shown in Figure 74 is a value of 1.8 mils obtained after a year of exposure to 98% relative humidity at 75°F.

Figure 75 shows the relationship of flexural creep to moisture content. The moisture contents were determined by thermogravimetric analysis (TGA) of companion specimens.

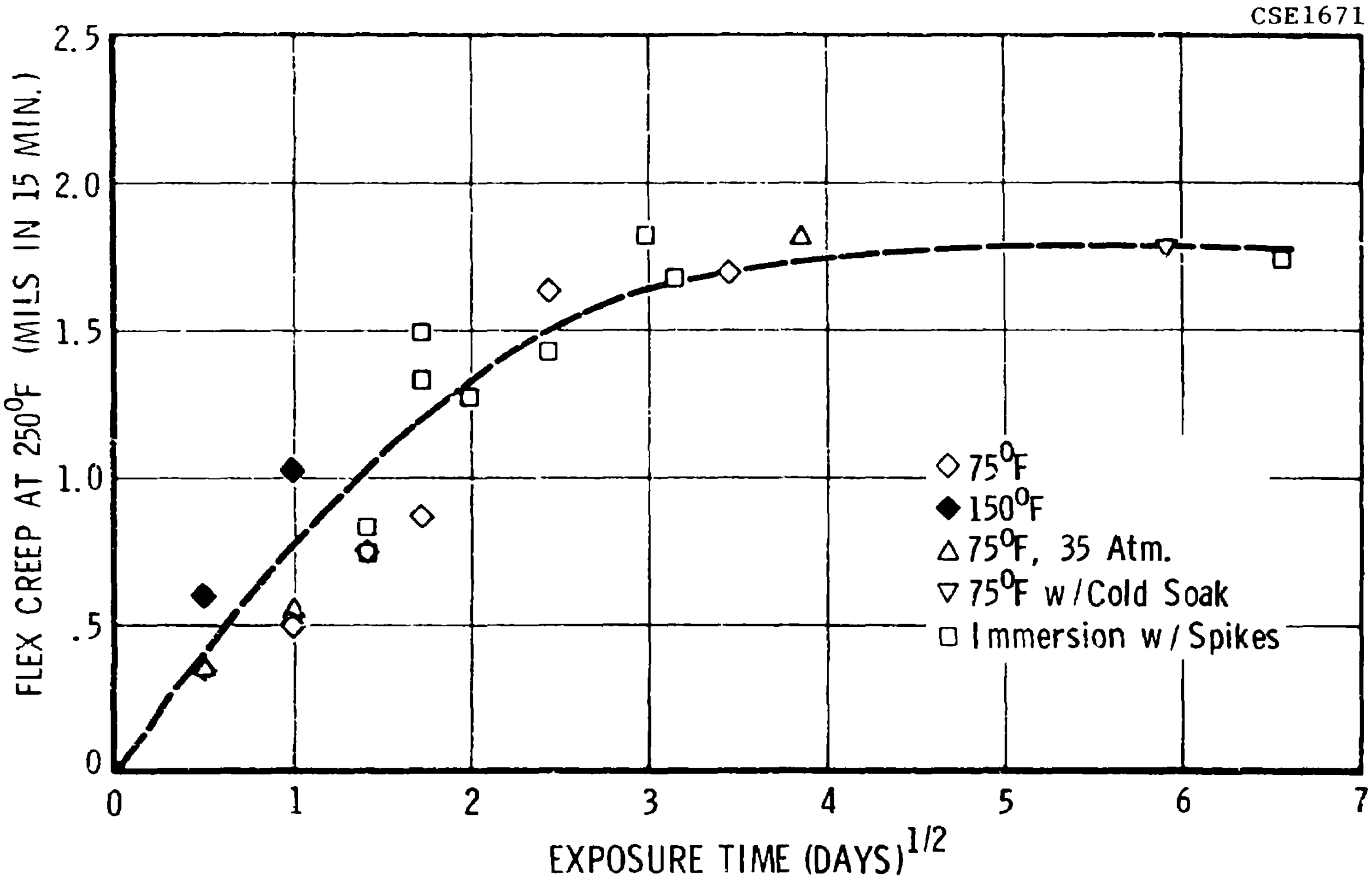

Figure 74 Flexural Creep vs. Exposure Time

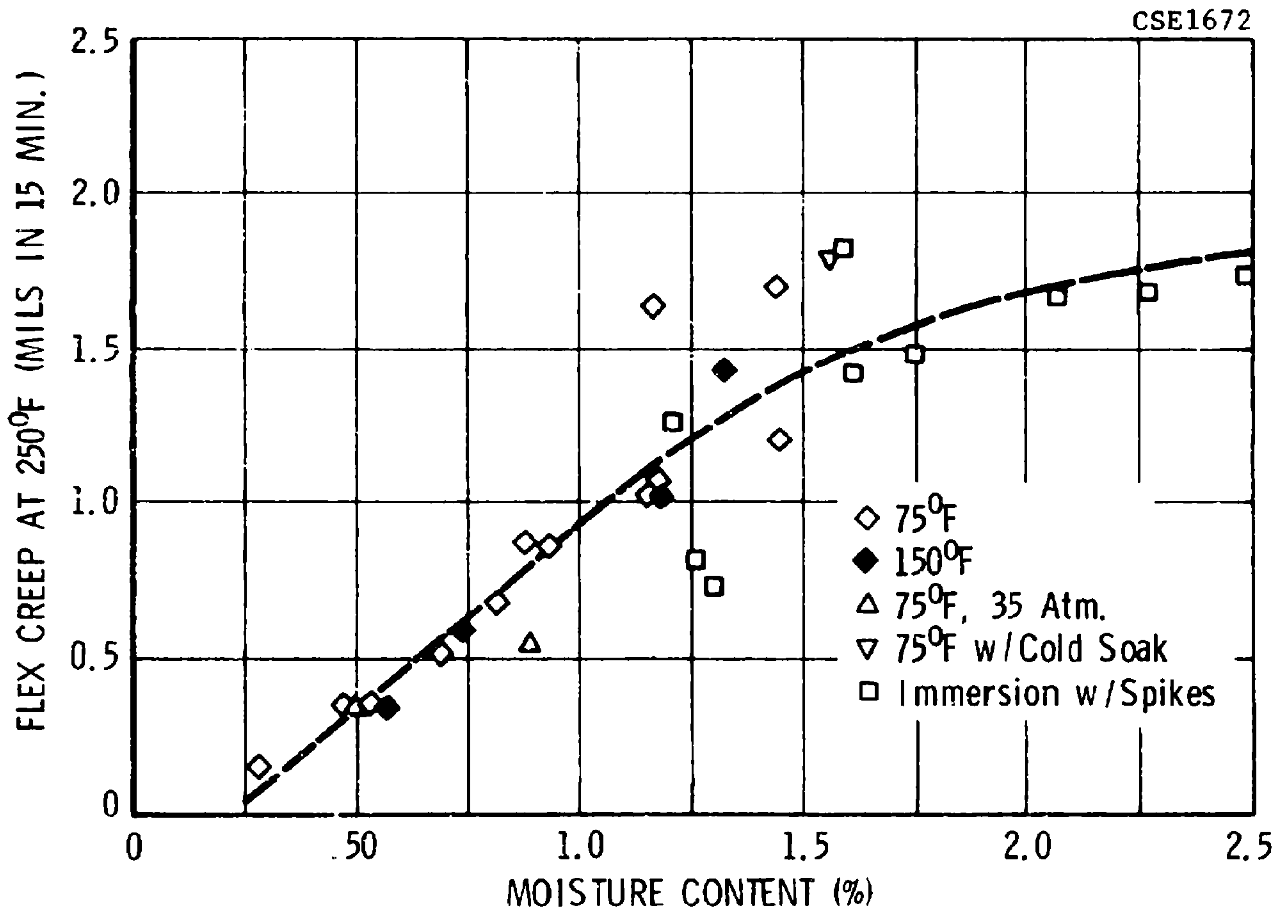

Figure 75 Relationship of Flexural Creep and Moisture Content

SECTION VI

ACCELERATED EXPOSURE AND TESTING

Years of exposure to service environments must be condensed into several weeks of laboratory exposure. Without such time shortening, realistic component tests would not be economically feasible. Similarly, realistic random fatigue testing must be accelerated in time.

Therefore, the first objective of these moisture investigations was to establish the best method to use in accelerating moisture absorption in composite structures. The second objective was to evaluate ways to maintain moisture during accelerated random fatigue testing.

6.1 EXPOSURE

The diffusion process that had been observed, based on theory, was thought to be controlled by the partial pressure of the water vapor and by its kinetic energy. Therefore, increases in hydrostatic pressure were not expected to increase the diffusion rate. Two experiments were conducted to confirm this.

Specimens from the 4-ply laminate were immersed in room temperature water. This group served as a control group. Two other groups of specimens were immersed in water in a pressurized container. One specimen container was pressurized to 10 atmospheres and the other to 35 atmospheres. Periodically the specimens were removed, wiped dry, and weighed. Figure 76 shows that absorption rate remains constant over the range from 1 to 35 atmospheres.

The investigations described in Section III showed that raising temperature and relative humidity both shorten the time to achieve a given level of bulk moisture content. However, conditioning at temperatures greater than 212°F was judged to be too costly. This was true because above 212°F concentration, or effective relative humidity, diminishes with increasing temperature unless atmospheric pressure is allowed to increase with temperature. The effective relative humidity for tempera-

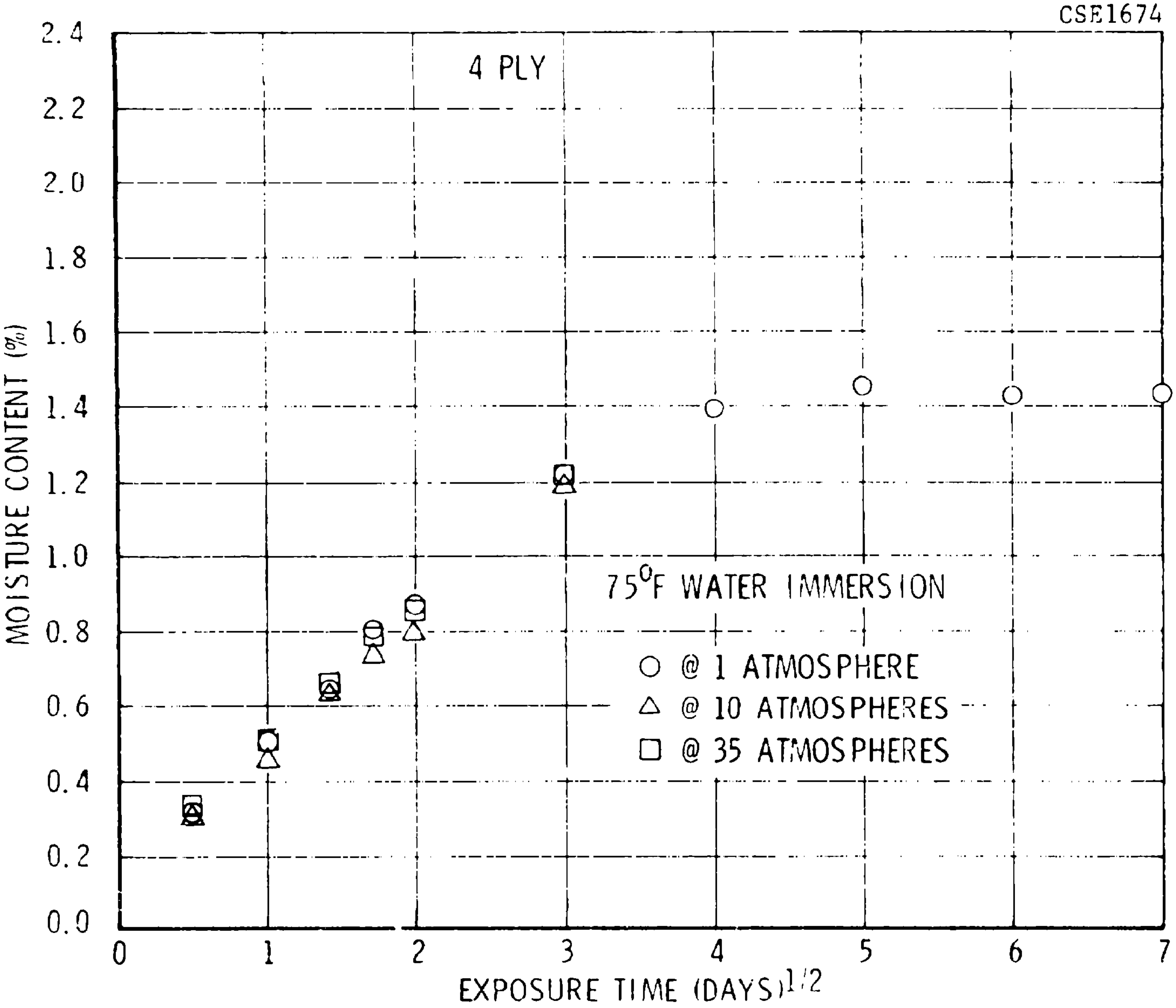

Figure 76 Effect of Hydrostatic Pressure on Absorption

above 212°F, assuming constant pressure of 14.7 psia, is given in Figure 77. This was confirmed by exposing specimens to pressurized steam at 300°F followed by exposure to 300°F steam at 14.7 psi. The results are summarized in Figure 78.

Based on these results, 212°F was the highest practical temperature at which conditioning could be performed. However, anomalous behavior in boiling water suggested that some lower temperature should be used. Since behavior at 180°F was similar to that at lower temperatures, this temperature was selected as the upper limit for exposure.

Altogether, these test results pointed to accelerated environmental conditioning at high humidity (95 to 100%), high temperature (180°F), and ambient pressure. Therefore, it remained only to determine the most economical chamber or apparatus for providing such exposure.

Two concepts were evaluated. One involved immersing the specimens in 180°F water, and the other involved exposing them to 180°F steam. Steam exposure was found to be more economical of these two concepts. It was also found that hot air easily could be delivered to the chamber at a controlled rate that would allow simulation of the thermal spike. Then, this spike could be achieved without removing the structural components. Therefore, a steam cabinet was constructed. The accelerated exposure cycle selected involved continuous exposure to 180°F steam with daily exposures to a hot-air thermal spike. This spike, to a peak temperature of 300°F, was like the spike described in Section IV.

6.2 TESTING

Fatigue testing of box beam components was conducted while the surrounding air temperature was cycled. Temperature varied in direct proportion to a real-time supersonic flight profile (Mission I). Subsonic portions of the Mission I profile were on a compressed time scale. The representation of an entirely subsonic mission (Mission II) was also on a compressed time scale. Runway time was deleted from the accelerated service simulation.

In a random fatigue test, the sequencing of Mission I and Mission II profiles varied. However, on the average, each hour of accelerated testing involved five Mission I profiles and

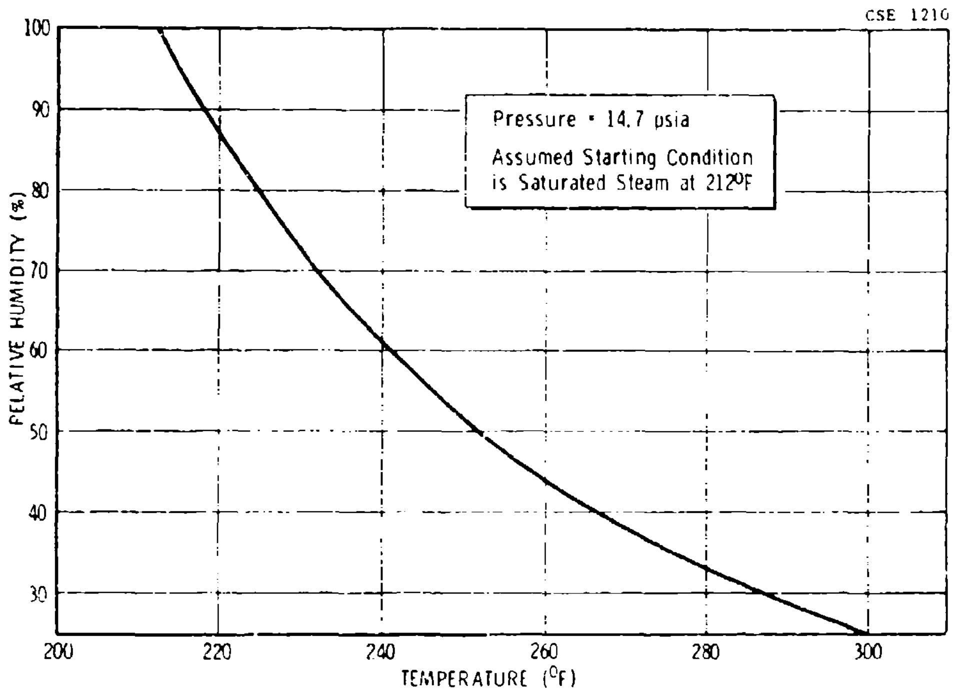

Figure 77 Theoretical Maximum Effective Humidity at High Temperature

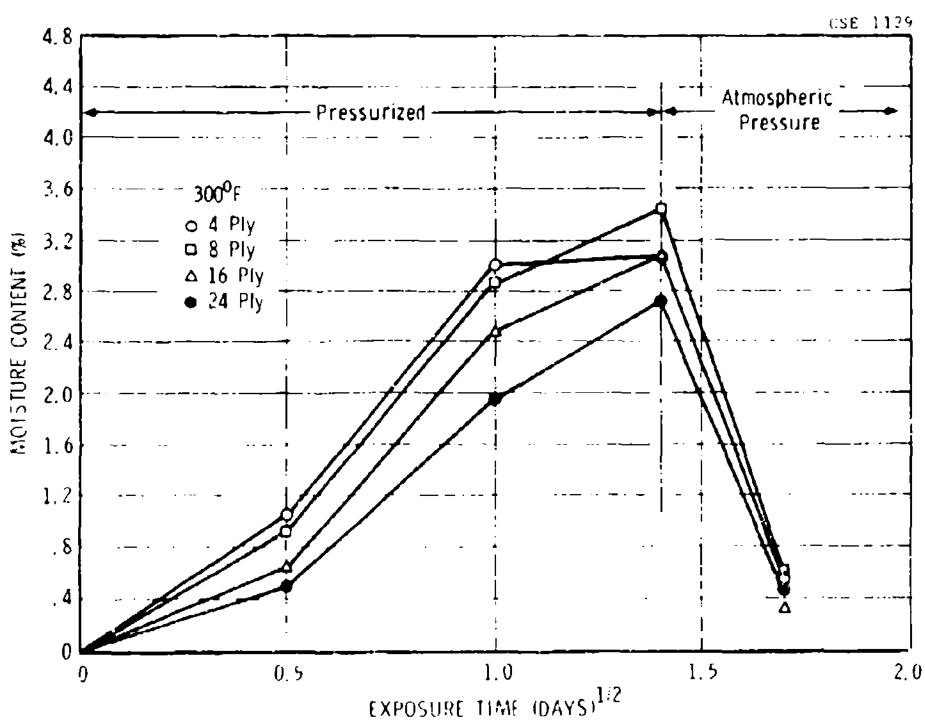

Figure 78 Effects of Steam Exposure on Initially Dry Laminates

two Mission II profiles. The temperature cycling which, on the average, was experienced during each hour of accelerated testing is illustrated in Figure 79.

Testing had to progress on a two-shift-per-day basis to satisfy schedule requirements. An equivalent 0.5 lifetime was achieved during three weeks of quasi-real-time testing.

As discussed in Subsection 6.1, incorporating the effects of humidity into this fatigue cycle required pre-test conditioning of the box beams. The box beam components had to be in a moisture-saturated condition before fatigue testing because each supersonic heating spike caused some moisture to be lost. Therefore, during the fatigue test itself, moisture exposure was required merely to maintain some level of absorbed moisture.

Tests were conducted to determine how the moisture content in the box beams would fluctuate during testing. Several 24-ply specimens were hygrothermally saturated at 180°F and 100% relative humidity. Then, these specimens were subjected to a series of 80 consecutive supersonic heating spikes. With an average of five Mission I profiles per hour, this represented 16 hours, or two shifts, of accelerated fatigue testing per day. Subsonic temperature segments were not used because they do not cause desorption.

All specimens were weighed after each block of 80 spikes. Then, they were exposed to 98% relative humidity at 180°F for 8 hours. This represented humidity exposure during the third shift to replace desorbed moisture. It also represented the highest temperature that was practical and easy to achieve with steam expanded into a relatively large chamber (each box beam was 7 feet long). After the fifth block of heating spikes, the 180°F/98% relative humidity exposure was continued for 56 hours instead of 8 hours. This represented humidification during the weekend. This cycle was continued through the equivalent of three weeks of accelerated fatigue testing. The moisture content in the specimens at the beginning and at the end of each "day's" testing is shown in Figure 80.

As discussed in Section IV, the real-life environmental cycle caused changes in the absorptivity and inherent diffusion coefficients of the T300/5208 material. Therefore, a test was started to simulate the effects of the accelerated test when the starting moisture content represented the real-life saturation levels.

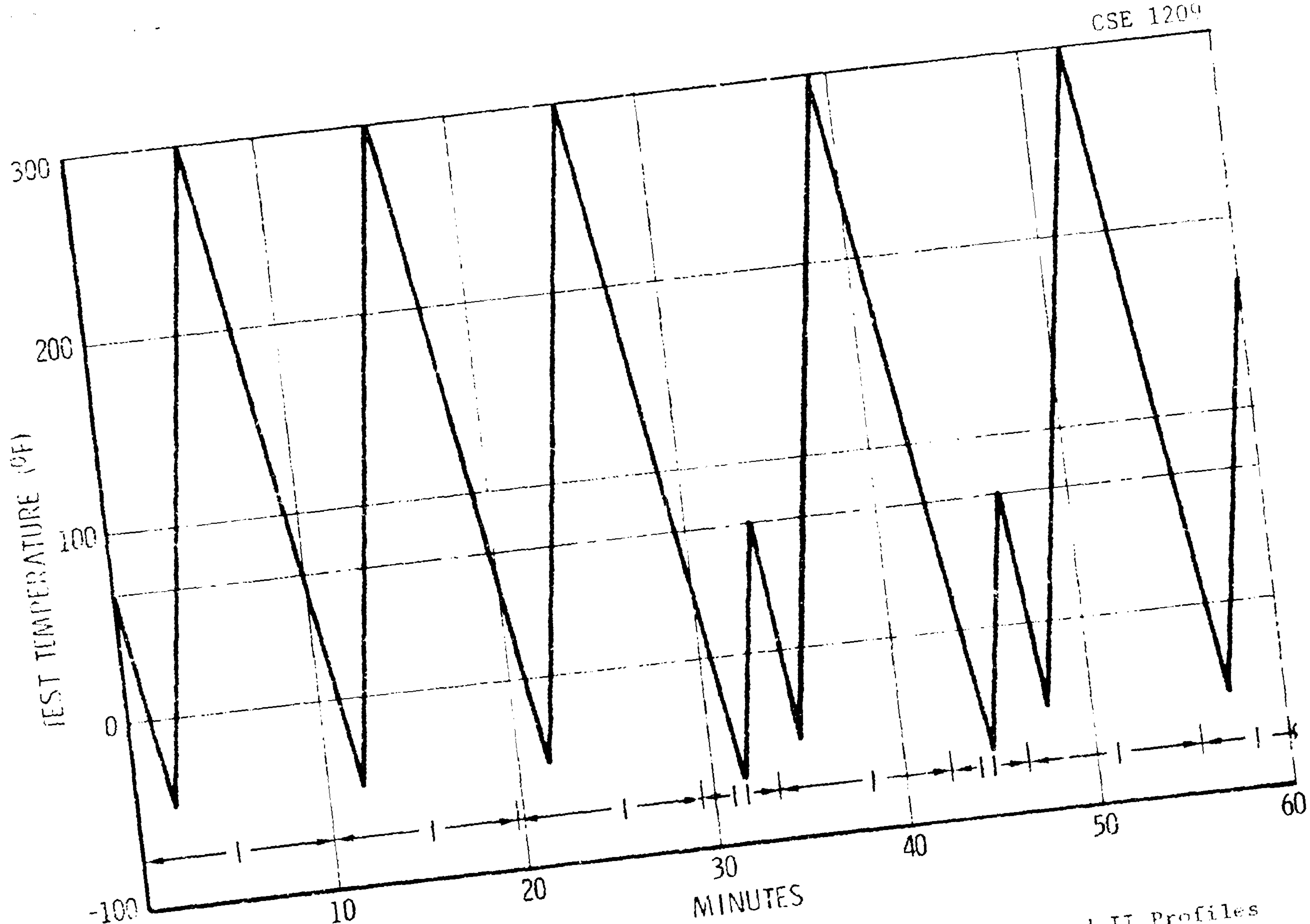

Figure 79 Typical One-Hour Temperature Cycle Involving Mission I and II Profiles

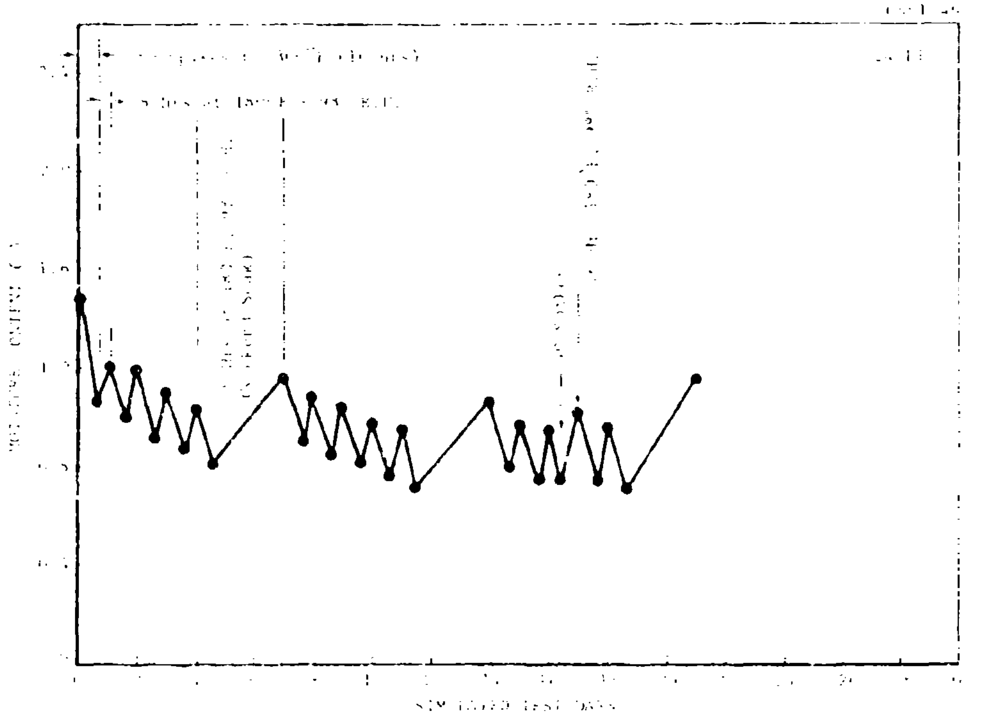

Figure 80 Simulated Box Beam Test, Initial Hygrothermal Equilibrium

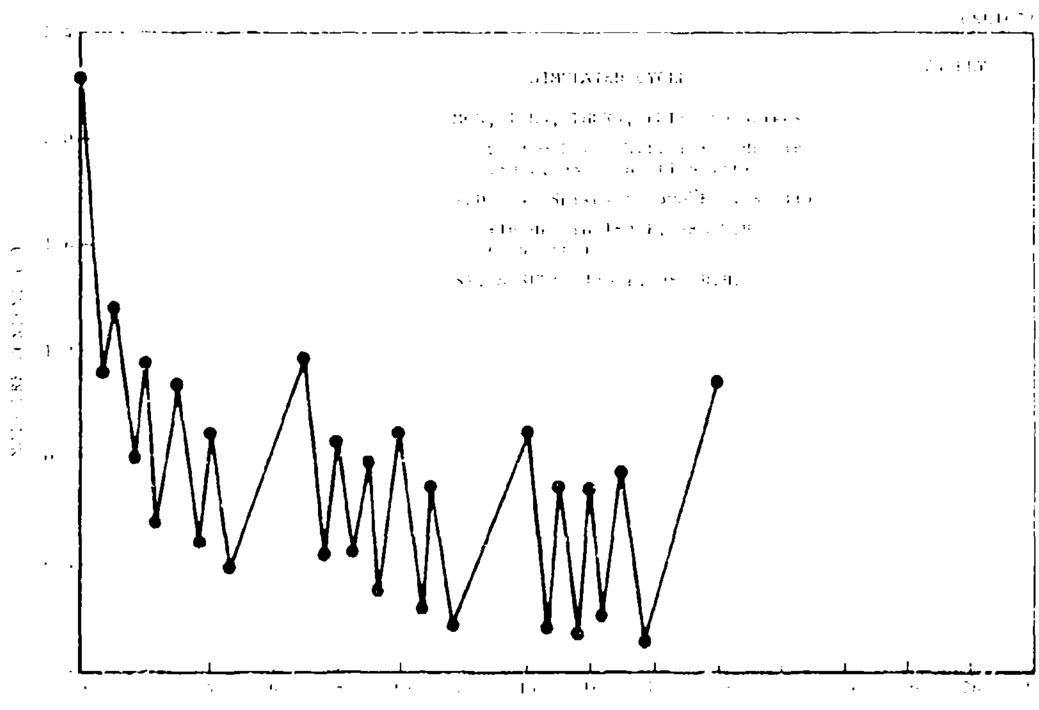

Figure 81 Simulated Box Beam Test, Initial Spiked Equilibrium

The 24-ply specimens were preconditioned until the average moisture content was 2.2%. Then, they were subjected to the same sequence of 80 spikes and 8 hours at 180°F and 98% relative humidity. The moisture loss during the first two simulated test days was severe; therefore, the third (or Wednesday) test cycle was reduced to 40 spikes so that the laminate could be soaked for two consecutive shifts. The use of 80 spikes was resumed for the fourth and fifth cycles. This sequence was continued for the equivalent of three test weeks. The moisture content history through the total test period is shown in Figure 81.

The results of these tests showed that it was not practical to maintain high saturation levels in the box beams during testing. However, it was practical to precondition the specimens so that the absorptivity and diffusion coefficients were altered as they would be in actual service. It was also practical to provide a fluctuating moisture level representing a background humidity level of as much as 50%.

SECTION VII

CONCLUSIONS

Graphite-epoxy composites absorb moisture from the atmosphere. Three material properties determine the rate and extent of moisture absorption at a given temperature and humidity. One of these is an absorptivity coefficient that determines the amount of moisture that can be absorbed in a given humidity. The other two determine the rate of absorption at a given temperature. These are the permeability index and the activation energy for diffusion.

Values of these three properties were determined for laminates made of Narmco's 5208 epoxy resin reinforced with Union Carbide's Thornel 300 graphite fibers. For laminates with a resin content of 30% by weight, the absorptivity coefficient is 0.0146. The permeability index is 0.001415 cm^2/sec, and the activation energy for diffusion is 8600 cal/gm.

It has been demonstrated that moisture diffusion in this fiber-reinforced plastic is described by a nonlinear model containing these property values. The model is based upon Fick's second law of diffusion, and it is applicable to both absorption and desorption.

Some desorption occurs when a laminate is exposed to the elevated temperatures of supersonic service. However, moisture content eventually climbs to an equilibrium value despite supersonic service. In fact, exposure to supersonic service temperatures causes permanent changes in the subsequent moisture diffusion behavior of T300/5208. Periodic exposure to a thermal spike typical of a supersonic dash increases moisture absorptivity. The absorptivity coefficient was doubled by such exposures. All of the absorbed moisture was removed by drying at $180^{\circ}F$; however, the diffusion behavior was permanently changed. Exposure to sub-zero temperatures, on the other hand, caused no changes in diffusion behavior.

In general, exposure to either a hygrothermal cycle or to a realistic cycle involving supersonic heating effects appears to cause insignificant reductions in fiber-controlled mechanical properties. However, at elevated temperature, resin-controlled properties diminish with increasing moisture contents.

Preparation of specimens for testing should involve exposure to moisture so that service environment effects can be simulated. This preparation can be accelerated by exposure to 180°F steam. If the service requirements include supersonic flights, the specimens should be heated periodically. This heating should conform to the heating profile typical of the supersonic mission. Daily exposure to the supersonic heating profile has been shown to be adequate.

SECTION VIII

RECOMMENDATIONS

Mechanical and physical properties of resin matrix composites should be determined for moisture contents that represent equilibrium service conditions. This is particularly important for resin-controlled properties.

Further investigations should be conducted on effects of intermittent supersonic service combined with humidity exposure. This effort should center in mechanical property characterizations.

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