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Flat-Plate
Solar Array Project

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The Aging Correlation (RH + t): Relative Humidity (%) + Temperature (°C)

E.F. Cuddihy

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ABSTRACT

An aging correlation between corrosion lifetime, and relative humidity RH(%) and temperature $t(^{\circ}\text{C})$ has been reported in the literature. This aging correlation is a semi-log plot of corrosion lifetime on the log scale versus the interesting summation term $\{\text{RH}(\%) + t(^{\circ}\text{C})\}$ on the linear scale. This empirical correlation was derived from observation of experimental data trends and has been referred to as an experimental law.

Using electrical resistivity data of polyvinyl butyral (PVB) measured as a function of relative humidity and temperature, it was found that the electrical resistivity could be expressed as a function of the term $\{\text{RH}(\%) + t(^{\circ}\text{C})\}$. Thus, if corrosion is related to leakage current through an organic insulator, which, in turn, is a function of RH and t , then some partial theoretical validity for the correlation is indicated. This article describes the derivation of the term $\{\text{RH}(\%) + t(^{\circ}\text{C})\}$ from PVB electrical resistivity data.

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CONTENTS

I.	INTRODUCTION	1-1
II.	DERIVATION	2-1
	A. THE {RH(%) + t(°C)} OBSERVATION	2-1
	B. HYGROSCOPIC PROPERTIES	2-2
	C. THE {RH(%) + t(°C)} DERIVATION	2-7
III.	ANALYSES	3-1
	A. DATA ANALYSIS	3-1
	B. LEAST-SQUARES ANALYSIS	3-2
IV.	SUMMARY	4-1
V.	REFERENCES	5-1

Figures

2-1.	Electrical Resistivity of PVB as a Function of Relative Humidity	2-3
2-2.	Electrical Resistivity of PVB as a Function of the Variable (RH + t)	2-4
2-3.	Generalized Hygroscopic Behavior of Polymeric Materials . .	2-5
2-4.	Electrical Conductivity Ratio for PVB as a Function of Atmospheric Water Vapor Pressure	2-8
2-5.	Electrical Resistivity of PVB Versus Atmospheric Water Vapor Pressure (Absolute Humidity)	2-9
3-1.	Electrical Resistivity of PVB Versus the Variable (1.414 t + RH)	3-3

Tables

2-1.	Electrical Resistivity of PVB at Various Temperatures and Relative Humidities	2-2
2-2.	Saturation Vapor Pressure, V_p , of Water at 30, 40, and 50°C	2-6

SECTION I

INTRODUCTION

The Jet Propulsion Laboratory (JPL) manages the Flat-Plate Solar Array (FSA) Project for the U.S. Department of Energy (DOE), having as a major goal the development of technologies related to achieving highly reliable and long-life photovoltaic (PV) modules for outdoor service. Accordingly, the project supports activities related to understanding fundamental mechanisms of degradation and aging, topics of which are reported on in References 1 and 2. An understanding of fundamental aging mechanisms should permit a rational basis for evolving aging models and, therefore, for generating relevant predictive mathematical expressions for assessing the outdoor service life of a photovoltaic module.

Occasionally, however, experimental aging studies chance on an empirically derived mathematical aging correlation, an experimental law, which seems to work, but which is apparently without any fundamental or theoretical support. Such a mathematical aging correlation has been reported by Desombre (Reference 3), who noted that the rate of corrosion is logarithmically related to the summation term, $RH + t$, where RH is relative humidity in percent, and "t" is temperature in degrees Centigrade. Thus, an accelerated aging experiment could be carried out at high levels of relative humidity and temperature, and from a semi-log plot of the experimentally measured corrosion lifetimes versus the variable term, $RH + t$, an estimate of corrosion lifetimes at lower levels of RH and t could be made by linear extrapolation.

The Reliability and Engineering Sciences Branch of the FSA Project is actively investigating electrochemical corrosion phenomena in encapsulated PV modules (References 4, 5, 6, 7), including accelerated aging from exposure to high levels of relative humidity and temperatures. The $(RH + t)$ aging correlation could be used for lifetime predictions related to electrochemical corrosion in photovoltaic modules. As part of the corrosion studies, the electrical resistivity of polyvinyl butyral (PVB) was measured as a function of relative humidity and temperature. An effort to estimate the electrical resistivity of PVB at 0% RH resulted in an observation which enabled a theoretical derivation of the variable term, $RH + t$. The derivation is described in this project report.

SECTION II

DERIVATION

A. THE {RH(%) + t(°C)} OBSERVATION

Electrical resistivity of PVB as a function of relative humidity and temperature is given in Table 2-1. These data were measured by Professor John Orehotsky of Wilkes-Barre College under FSA Contract 956766. The resistivity data are plotted in Figure 2-1 as log resistivity ρ versus relative humidity (RH) in percent, for the three temperature levels 30, 40, and 50°C. The intent was to estimate the resistivity of PVB at 0% RH by linear extrapolation, the estimated values of which are shown as black dots in Figure 2-1, and which are as follows:

t, °C	$\rho(t,0)$, ohm-cm
30	$5.8 * 10^{10}$
40	$3.3 * 10^{10}$
50	$1.8 * 10^{10}$

These values of resistivity at 0% RH obey an Arrhenius relationship

$$\rho(t,0) = \rho_0 \exp \left\{ \frac{\Delta H}{RT} \right\} \quad (1)$$

where by least-squares $\rho_0 = 453.05$ ohm-cm and $\Delta H = 11.243$ kcal/mole. In Equation (1), R is the gas constant having a value of 1.987 cal/mole-K, and $T = t + 273$ K.

However, it was observed for these semi-log plots that not only were the data traces basically straight lines, but that they were also essentially parallel, and separated horizontally on the RH axis by a RH difference in percent almost numerically equal to the difference in temperature in degrees Celcius. It was evident that the three data lines could be shifted horizontally to merge into a single, and common master line, using as a new variable on the abscissa, RH(%) + t(°C). Therefore, the resistivity data were again replotted as log ρ versus {RH(%) + t(°C)}, yielding essentially a common data line as shown in Figure 2-2. This interesting observation suggests that, perhaps, corrosion, as correlated with the variable term, RH(%) + t(°C), may be related to leakage currents through insulation materials whose resistivity (or conductivity), in turn, are related to the variable term. It then became of interest to determine if there was some fundamental basis for this observation, and the approach taken was to assume that this behavior derived, in part, from mathematical relationships associated with atmospheric water vapor absorption as a function of relative humidity and temperature.

Table 2-1. Electrical Resistivity of PVB at Various Temperatures and Relative Humidities*

RH, Relative Humidity, %	t, Temp °C	ρ , Resistivity, ohm-cm	Data Symbol
100	30	2.53×10^8	○
	40	9.86×10^7	○
	50	4.44×10^7	○
85	50	8.86×10^7	▽
80	30	6.24×10^8	△
	40	2.60×10^8	△
	50	1.35×10^8	△
54	30	3.02×10^9	□
	40	1.51×10^9	□
	50	7.07×10^8	□

*Experimental data measured by Professor John Orehtsky under JPL/DOE FSA Contract 956766.

B. HYGROSCOPIC PROPERTIES

From Figure 2-1, the electrical resistivity of PVB is clearly related to relative humidity, which alternately suggests that the electrical resistivity is related to the concentration of absorbed water vapor in the PVB. Absorption of atmospheric water vapor by polymers is a hygroscopic property which typically behaves as schematically illustrated in Figure 2-3. At any constant temperature, the absorbed water vapor content in a polymer increases with absolute water vapor concentration, V , in the atmosphere, here expressed as a pressure in units of mm Hg, and W is the absorbed water vapor content. The connective relationship between W and V , assuming linearity, is

$$W(t,V) = K(t)V \quad (2)$$

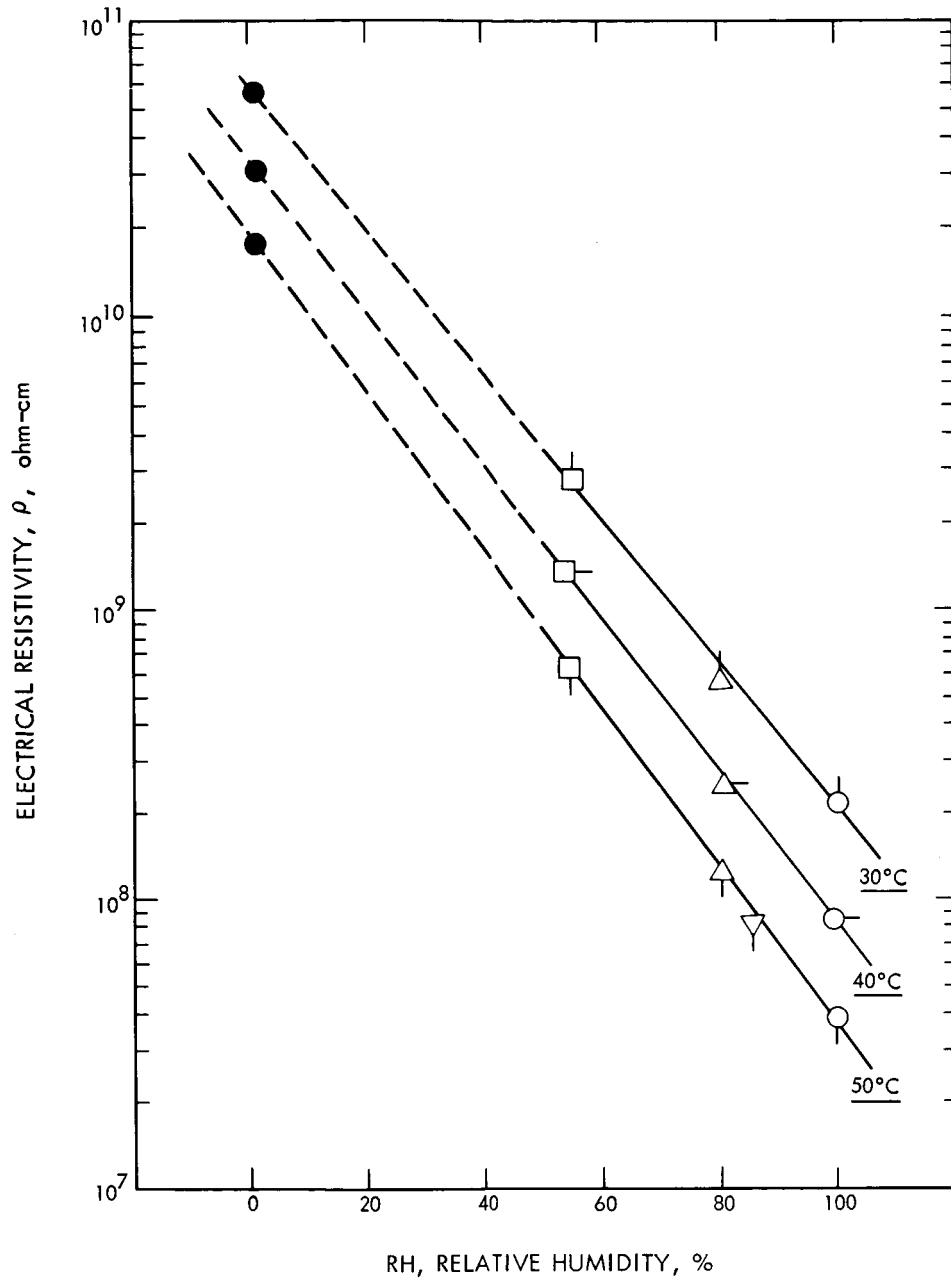


Figure 2-1. Electrical Resistivity of PVB as a Function of Relative Humidity

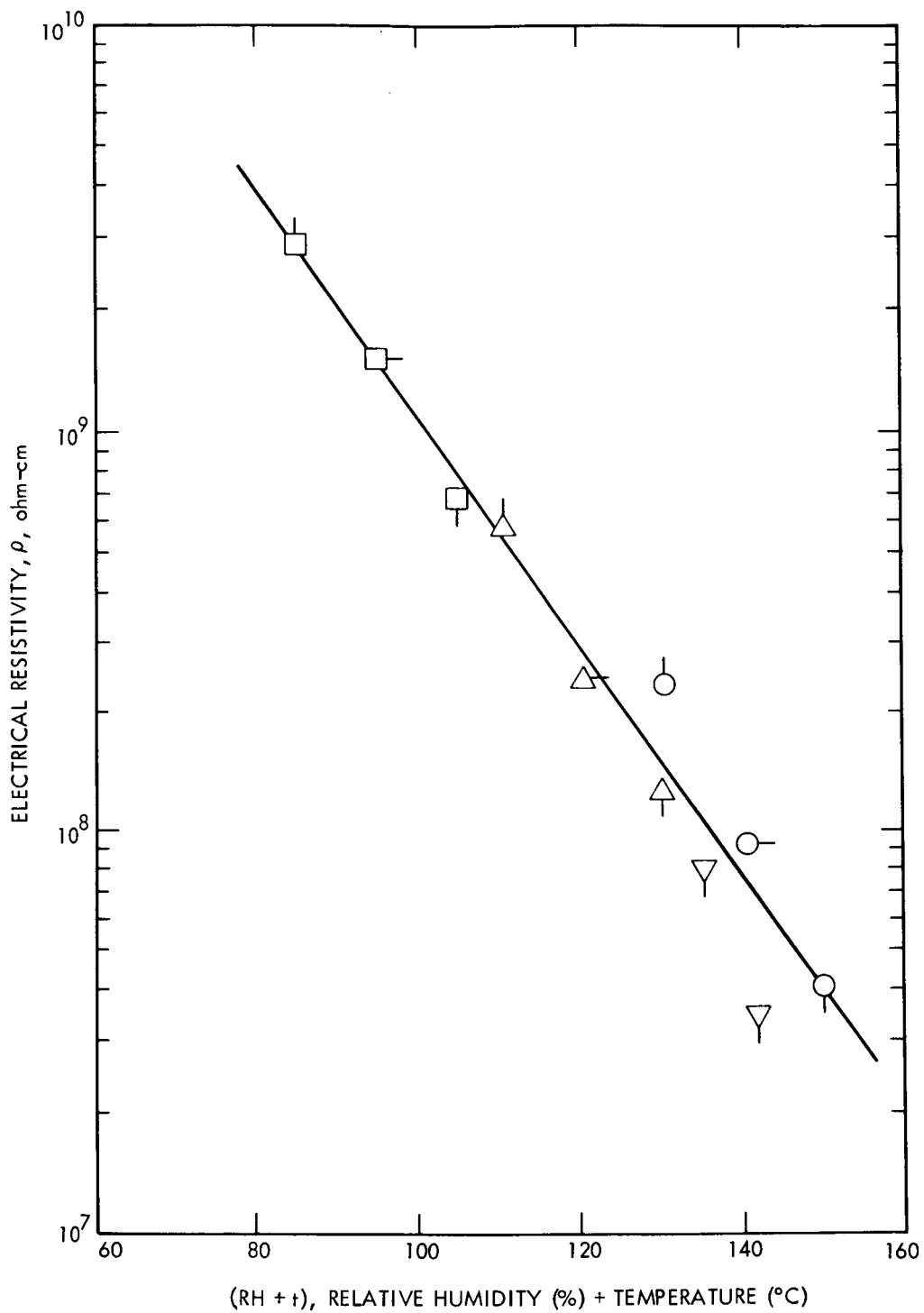


Figure 2-2. Electrical Resistivity of PVB as a Function of the Variable (RH + t)

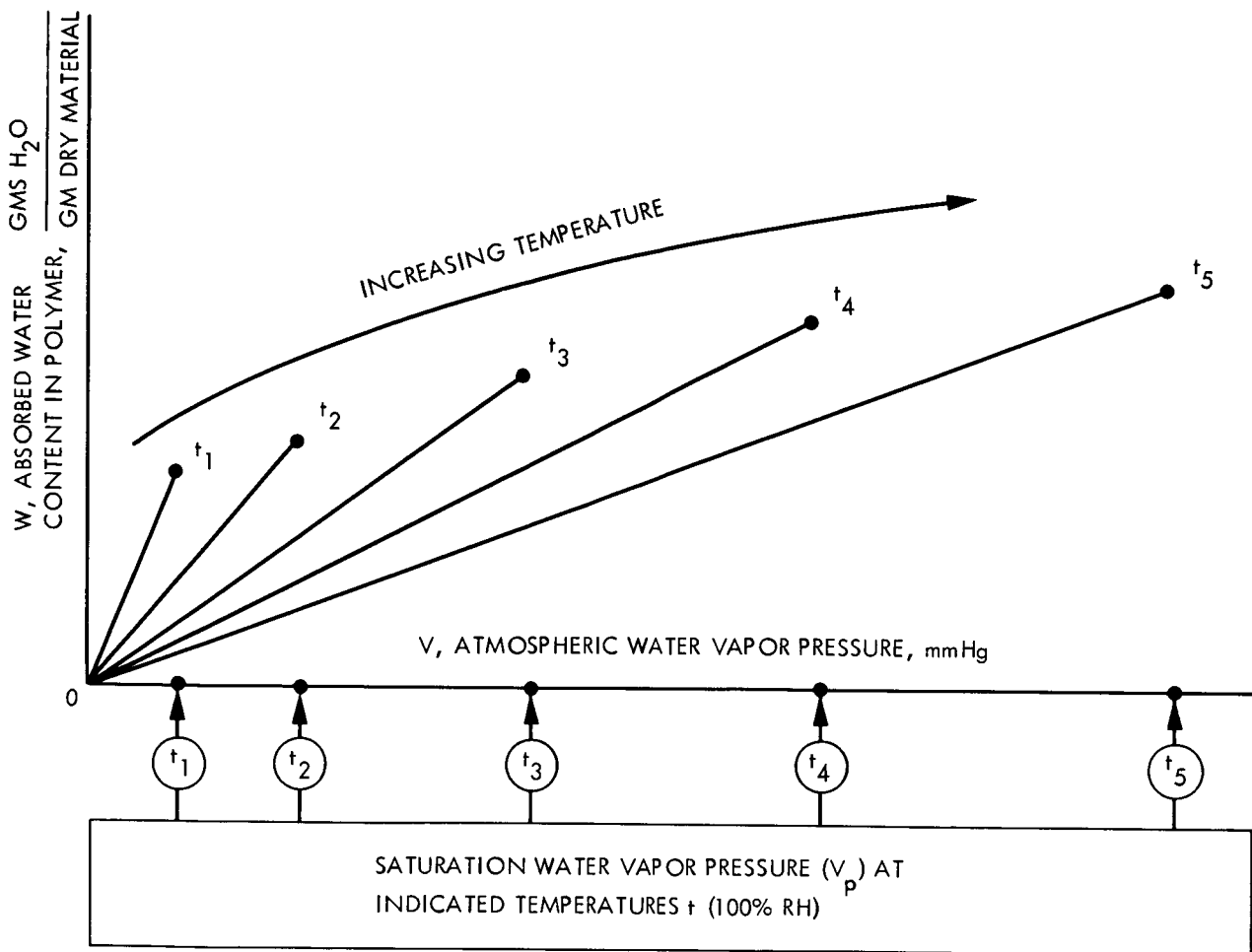


Figure 2-3. Generalized Hygroscopic Behavior of Polymeric Materials

where t is temperature $W(t,V)$ is the absorbed water vapor content at temperature t and atmospheric water vapor concentration V and $K(t)$ is the absorption isotherm, the slope of the line.

The temperature-dependence of $K(t)$ is generally Arrhenius,

$$K(t) = K_0 \exp \left\{ \frac{E_1}{RT} \right\} \quad (3)$$

where T is absolute temperature (K), E_1 is the activation energy for water vapor absorption, in units of cal/mole (or kcal/mole), and R is equal to 1.987 cal/mole-K. (Note in Figure 2-3 that for constant V, the absorbed water vapor content of hygroscopic materials decreases with increasing temperature t.)

At any given air temperature, the concentration of water vapor in the atmosphere cannot exceed a saturation limit, called the saturation vapor pressure, V_p . V_p is a function of temperature and obeys the exponential function

$$V_p(t) = V_o \exp \left\{ \frac{-E_2}{RT} \right\} \quad (4)$$

Values of V_p (in mm Hg) for the nominal temperatures 30, 40, and 50°C are given in Table 2-2, and by least squares, $V_o = 1.031 * 10^9$ mm Hg and $E_2 = 10.41$ kcal/mole.

Because, at constant air temperature t, V cannot exceed $V_p(t)$, the absorption lines for any constant temperature t shown in Figure 2-3 stop at the value of V equal to $V_p(t)$.

Relative humidity for any temperature t is the ratio of V to V_p , or more formally defined as

$$RH(t) = \frac{V}{V_p(t)} \times 100 \text{ (in percentage)} \quad (5)$$

Table 2-2. Saturation Vapor Pressure, V_p , of Water at 30, 40, and 50°C

Temperatures		Saturation Vapor Pressure
t, °C	T, K	V_p , mm Hg
30	303	31.824
40	313	55.324
50	323	92.51

C. THE {RH(%) + t(°C)} DERIVATION

The hygroscopic character of the PVB electrical resistivity data are illustrated in Figure 2-4. Here, electrical conductivity, σ , is used rather than electrical resistivity in order to generate a plotting format similar to that of Figure 2-3. In addition, the electrical conductivity data are normalized, using the values of conductivity, σ_0 (actually, resistivity), which were estimated in Figure 2-1 at 0% RH. V , the atmospheric water vapor pressure in units of mm Hg, were derived using Equation (5), and the values of RH in Table 2-1 and the values of V_p given in Table 2-2.

Note that the electrical conductivity increases with increasing V , presumably as a result of an increasing absorbed-water content in the PVB. But also note that, with increasing temperature, the conductivity increases more slowly with increasing V , similarly as shown in Figure 2-3.

If it can be assumed that the slopes of these data lines in Figure 2-4 are related to the absorption isotherm $K(t)$, then an estimate of E_1 , the activation energy for water vapor absorption in PVB can be made. So doing, a value of $E_1 = 9.23$ kcal/mole can be calculated.

To derive the variable term {RH(%) + t(°C)}, it is convenient to begin by plotting the resistivity data given in Table 2-1 versus V , the absolute water vapor concentration in units of mm Hg. These data plots are shown in Figure 2-5. Note that the slopes of the data lines in Figure 2-5 decrease with increasing temperature, reflecting the hygroscopic behavior that, at constant V , less water vapor is absorbed with increasing t .

The data lines of Figure 2-5 can be described by the following exponential expression

$$\rho(t,V) = \rho(t,0) \exp \{S(t)V\} \quad (6)$$

where $S(t)$ is the slope of each constant temperature line. Note that the exponential term $S(t)V$, is similar in form to Equation (2), $K(t)V$.

Values of $S(t)$ were generated from least-squares of the data lines in Figure 2-5, as follows:

$t, ^\circ\text{C}$	$S(t), (\text{mm Hg})^{-1}$
30	1.70×10^{-1}
40	1.08×10^{-1}
50	6.62×10^{-2}

and these values were found to obey an Arrhenius relationship

$$S(t) = S_0 \exp \left\{ \frac{E_1}{RT} \right\} \quad (7)$$

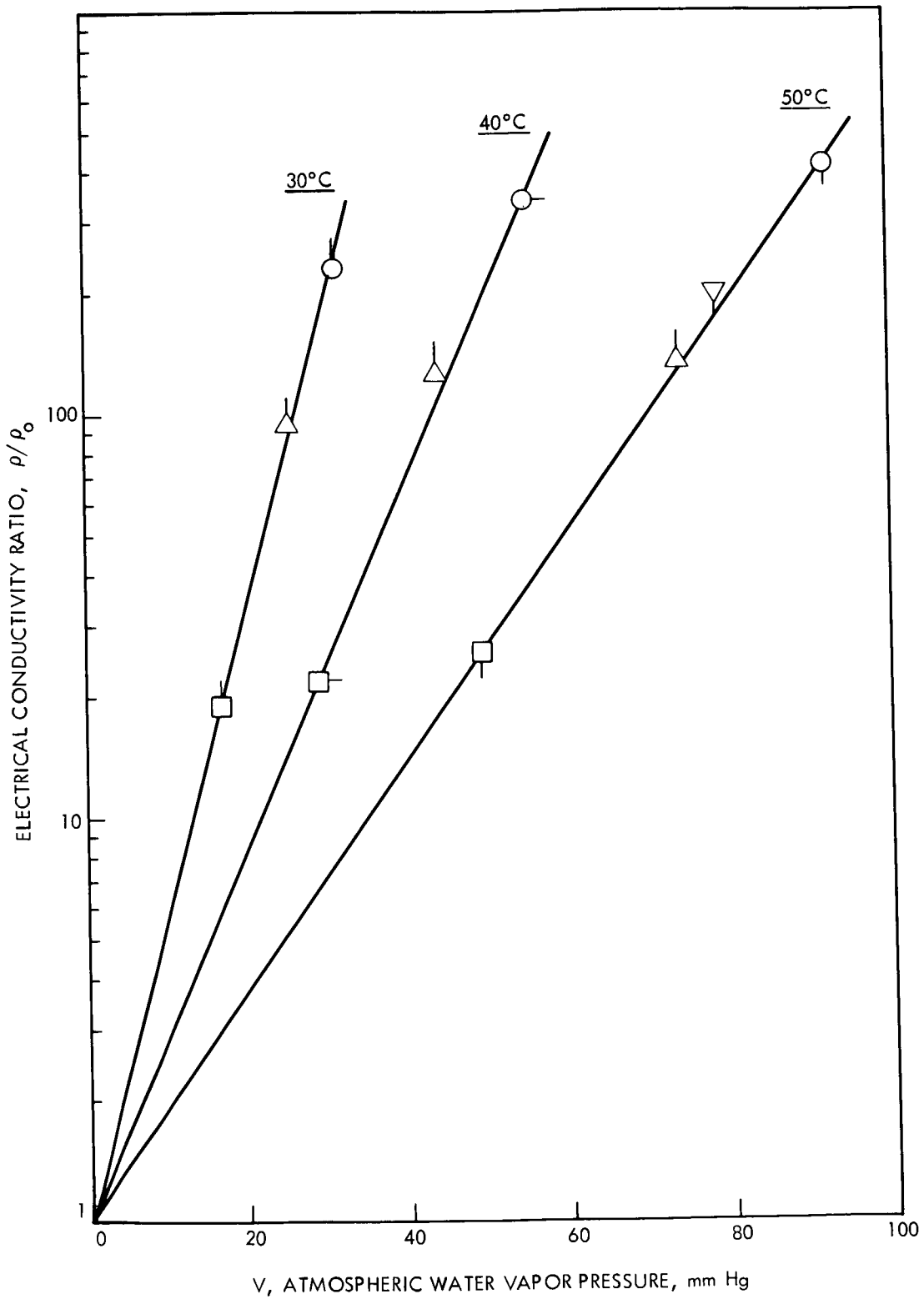


Figure 2-4. Electrical Conductivity Ratio for PVB as a Function of Atmospheric Water Vapor Pressure

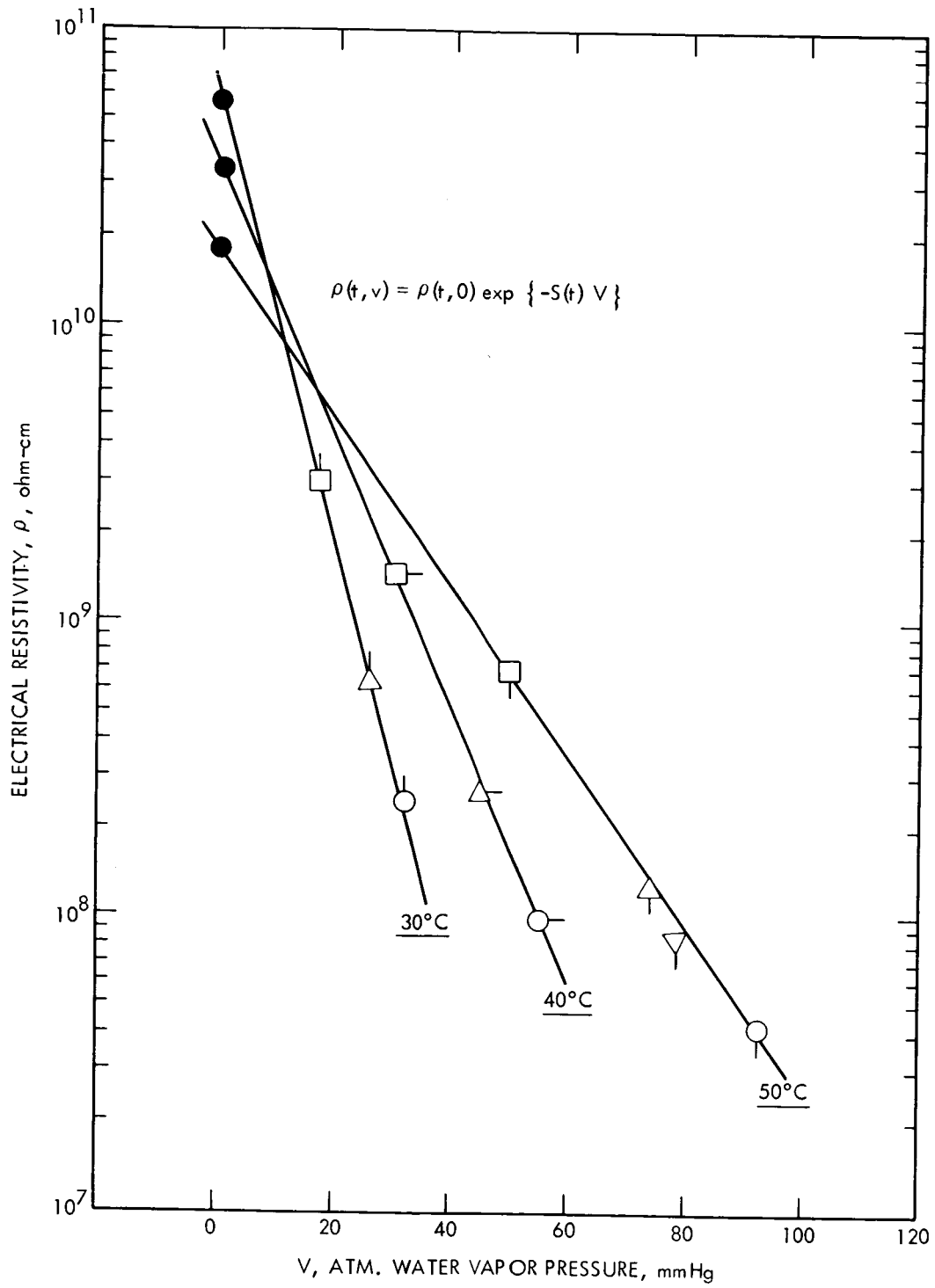


Figure 2-5. Electrical Resistivity of PVB versus Atmospheric Water Vapor Pressure (Absolute Humidity)

where, by least squares, $S_0 = 3.78 * 10^8$ (mm Hg) $^{-1}$ and $E_1 = 9.23$ kcal/mole. Because Figures 2-4 and 2-5 are the same data plotted in two different ways, the slopes of the data lines must yield the same value of E_1 . The purpose of Figure 2-4 was to more dramatically illustrate the hygroscopic character of the resistivity data, and to suggest that the activation energy value of 9.23 kcal/mole derived from these data may be the activation energy for water vapor absorption in PVB; hence, the use of E_1 as the symbol for this activation energy. Nevertheless, the derivation of the variable term, $RH(\%) + t(^{\circ}C)$, is independent of this assignment.

Equations (1) and (6) can now be combined to form the following expression

$$\rho(t,V) = \rho_0 \exp \left\{ \frac{\Delta H}{RT} \right\} \exp \{- S(t) V\} \quad (8)$$

which can be rewritten as

$$\ln \rho(t,V) = \ln \rho_0 + \frac{\Delta H}{RT} - S(t) V \quad (9)$$

Equations (4) and (5) can be combined to yield the following expression which connects V and $RH(\%)$,

$$V = \frac{V_0}{100} * \exp \left\{ \frac{-E_2}{RT} \right\} * (RH) \quad (10)$$

and, then, this Equation (10) and Equation (7) can be substituted into Equation (9) to yield an expression for ρ as a function of t and $RH(\%)$. In doing this, $\rho(t,V)$ becomes $\rho(t,RH)$, and it must be remembered that $T = t + 273$. The resultant expression is

$$\ln \rho(t,RH) = \ln \rho_0 + \frac{\Delta H}{RT} - \frac{S_0 V_0}{100} \exp \left\{ \frac{E_1 - E_2}{RT} \right\} (RH) \quad (11)$$

In Equation (11), it is noted that RH is present as a numerator term; therefore, the next step is to introduce t into this expression also as a numerator term. This can be done by a Taylor's expansion of the term, $\Delta H/RT$, where T is replaced by its definition, $t + 273$. Defining $T_0 = 273$, the following series can be generated

$$\frac{\Delta H}{RT} = \frac{\Delta H}{R} \left\{ \frac{1}{t + T_0} \right\} = \frac{\Delta H}{R} \left\{ \frac{1}{T_0} - \frac{t}{T_0^2} + \frac{t^2}{T_0^3} - \dots \right\} \quad (12)$$

For t in the order of 30 to 50 $^{\circ}C$, all terms t^2 and higher can be ignored with small error and, thus, $\Delta H/RT$ can be approximated as

$$\frac{\Delta H}{RT} = \frac{\Delta H}{R} \left\{ \frac{1}{T_0} - \frac{t}{T_0^2} \right\} = \frac{\Delta H}{RT_0} - \frac{\Delta H}{RT_0^2} t \quad (13)$$

Substituting Equation (13) into Equation (11) yields the expression

$$\ln \rho(t, RH) = \ln \rho_o + \frac{\Delta H}{RT_o} - \frac{\Delta H}{RT_o^2} t - \frac{S_o V_o}{100} \exp \left\{ \frac{E_1 - E_2}{RT} \right\} (RH) \quad (14)$$

having t and RH as numerator terms.

SECTION III

ANALYSES

A. DATA ANALYSIS

For convenience, Equation (14) can be simplified by defining the following:

$$A = \ln \rho_0 + \Delta H/RT_0, \text{ all constants}$$

$$k_1 = \frac{\Delta H}{RT_0^2}, \text{ a constant}$$

$$k_2 = \frac{S_0 V_0}{100} \exp \left\{ \frac{E_1 - E_2}{RT} \right\}, \text{ a function of } T$$

Therefore, Equation (14) becomes

$$\ln \rho(t, RH) = A - k_1 t - k_2(RH) \quad (15)$$

The term k_2 is a function of T , and all the constants, S_0 , V_0 , E_1 and E_2 , have been derived. Therefore, k_2 at 30, 40, and 50°C can be calculated, and are as follows:

t, °C	T, K	k ₂
30	303	0.0548
40	313	0.0584
50	323	0.0619

Over this temperature range, k_2 is practically a constant, having an average value of 0.0584.

The term k_1 can also be calculated, as ΔH has been derived (11.243 kcal/mole), and T_0 is equal to 273, hence

$$k_1 = \frac{11,243}{(1.987)(273)^2} = 0.0759$$

Thus, it is observed that k_1 and k_2 are numerically very close when t is in degrees Celcius, and RH is in percent; therefore, if treated as essentially equal, that is, $k_1 = k_2 = k$, Equation (15) becomes, simply,

$$\ln \rho(t, RH) = A - k(t + RH) \quad (16)$$

which corresponds to the empirical aging correlation reported by Desombre (Reference 3). This equation relates electrical resistivity, or equally electrical conductivity, to relative humidity and temperature. If corrosion is related to the leakage current through an organic insulator such as PVB, and if corrosion lifetime is monitored by some end-point which is related to a finite but fixed quantity of coulombs transferred, then Equation (16) would be experimentally associated with the correlation between corrosion lifetimes and relative humidity and temperature.

B. LEAST-SQUARES ANALYSIS

Earlier, ΔH was derived by a long, linear extrapolation of the data curves in Figure 2-1. Equation (15) permits a direct estimation of ΔH without any extrapolation. To do this, k_2 is considered to be a constant and given the data in Table 2-1, a least-squares analysis for Equation (15) can be carried out to generate A, k_1 , and k_2 . So doing, the following values are generated:

$$A = 25.9468$$

$$k_1 = 0.08033$$

$$k_2 = 0.0568$$

Therefore, ΔH can be calculated using the expression for k_1 ,

$$\Delta H = R k_1 T_o^2 = 11.896 \text{ kcal/mole}$$

which agrees well with the value of $\Delta H = 11.243$ kcal/mole derived from linear extrapolation.

Because direct least-squares analyses also show that k_1 and k_2 are not exact, Equation (15) can be rewritten as

$$\ln \rho(t, RH) = A - k_2 \left\{ \frac{k_1}{k_2} t + RH \right\} \quad (17)$$

where arbitrarily k_2 has been factored out. Equation (17) states that a better fit of data superposition will occur when $\ln \rho$ (or $\log \rho$) is plotted against the correlation variable, $(k_1/k_2)t + RH$, with t in degrees Celcius and RH in percentage. Using the above least-squared values for k_1 and k_2 , the ratio of k_1 and k_2 is equal to 1.414.

Figure 3-1 is a plot of $\log \rho$ versus $\{1.414 t + RH\}$ for the resistivity data given in Table 2-1. Data superposition is excellent.

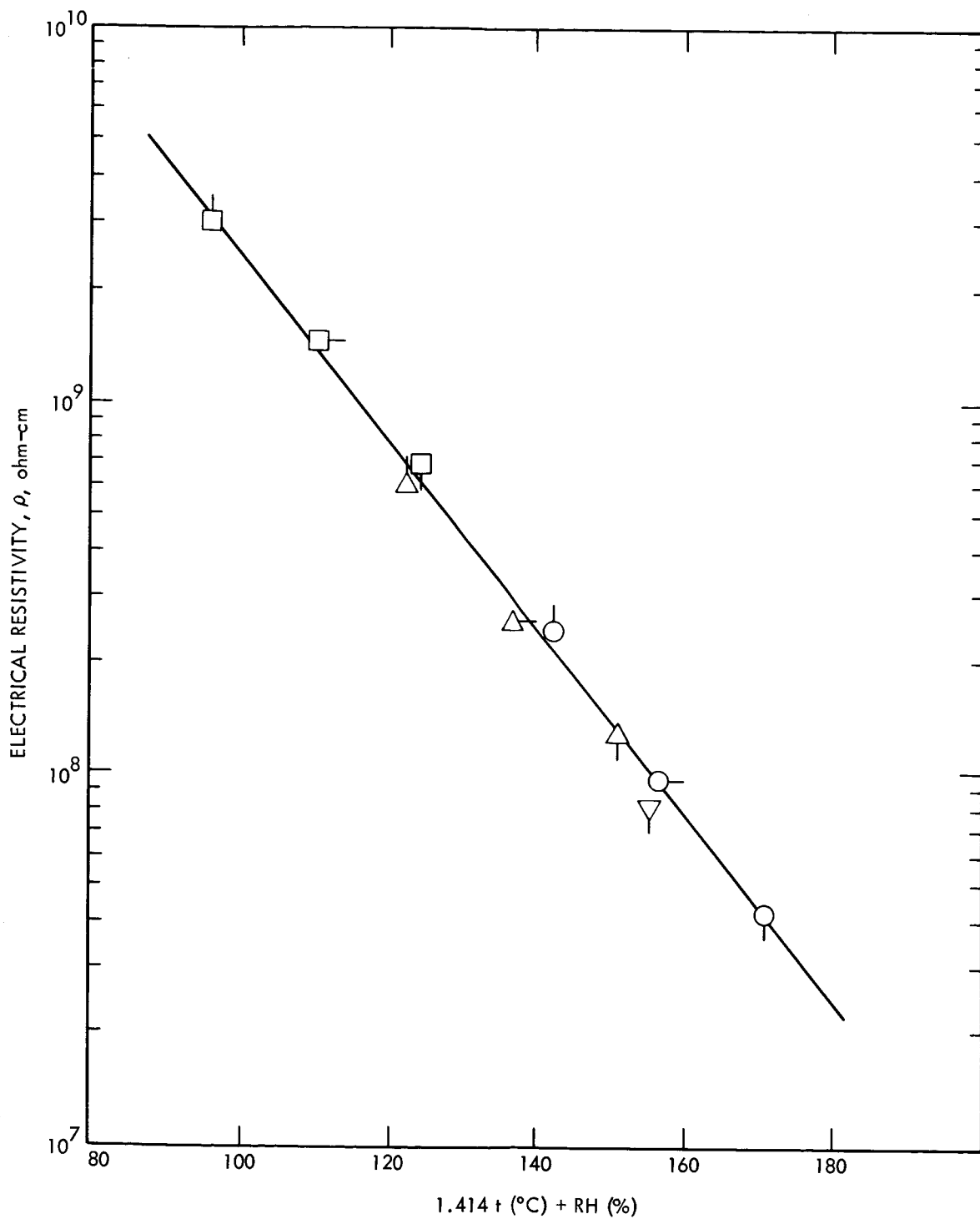


Figure 3-1. Electrical Resistivity of PVB versus the Variable ($1.414 t + RH$)

SECTION IV

SUMMARY

An aging correlation between corrosion lifetimes and both relative humidity RH (%) and temperature t (°C) has been reported in the literature. This correlation involves a semi-log plot of the corrosion lifetime plotted on the log scale versus the summation term {RH(%) + t(°C)} which is plotted on the linear scale. This correlation permits estimations of corrosion lifetimes at lower or ambient conditions of relative humidity and temperature, from accelerated corrosion aging studies carried out at higher levels of relative humidity and temperatures.

This article attempts to demonstrate that this empirical observation has some theoretical validity, deriving from the dependence of the electrical resistivity of organic insulators as a function of this summation term {RH(%) + t(°C)}. Thus, electrochemical corrosion related to leakage currents through electrical insulation materials could be expected to be also related to this summation term.

SECTION V

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