NATIONAL BUREAU OF STANDARDS REPORT

10 116

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OUTDOOR PERFORMANCE OF PLASTICS
III. STATISTICAL MODEL FOR PREDICTING WEATHERABILITY

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NATIONAL BUREAU OF STANDARDS

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NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT 4216370 – 421.04

30 October 1969

NBS REPORT 10 116

OUTDOOR PERFORMANCE OF PLASTICS
III. STATISTICAL MODEL FOR PREDICTING WEATHERABILITY

by

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ABSTRACT

This is the third in a series of reports on weatherability of 20 plastics in 3 climates. A general method is presented for correlation and prediction of performance. It is based on statistical characterization of weathering as a "wear-out" process, and quantitative description of the wear-out data by a mathematical model.

A Weibull-type model, analogous to that used for fatigue and failure analysis, is fitted to ultimate tensile elongation data. Parameters of the model are related to "characteristic life" and other meaningful measures of the physical deterioration.

A computer-based method of nonlinear regression is used for fitting data from 3 years exposure. Model parameters, their confidence intervals, and measures of goodness of fit are tabulated. The observed data and the calculated curves are illustrated graphically.

An approach is demonstrated for determining the relation between the model parameters and significant weather variables.

OUTDOOR PERFORMANCE OF PLASTICS

III. STATISTICAL MODEL FOR PREDICTING WEATHERABILITY

OUTDOOR PERFORMANCE OF PLASTICS
III. STATISTICAL METHOD FOR PREDICTING WEATHERABILITY

1. OBJECTIVE

This is the third in a series of reports on the outdoor performance of plastics. Two previous NBS Reports have given results and interpretation of measurements:

I. INTRODUCTION & COLOR-CHANGE (#9912) [1]
II. TENSILE & FLEXURAL PROPERTIES (#10014) [2]

The objective of this cooperative industry-government study is to develop rapid methods to accurately predict useful outdoor-life of plastics.

2. BACKGROUND

Appearance, physical and "early-detection" properties of 20 typical plastics were observed through 3 years exposure in Phoenix, Miami and Washington, D. C. Eight properties have been measured periodically: color, haze, gloss, surface roughness, tensile properties, flexural properties, electrical properties, and ultraviolet spectra. Computerized presentation and analysis of data have been, and will continue to be, emphasized in these reports.

Twenty plastics formulated from 6 base polymers were exposed to outdoor conditions and accelerated weathering in the laboratory to evaluate their performance and establish a relationship between the two types of exposures. The base polymers were polyethylene (PE), polymethyl methacrylate (PMMA), polyvinyl fluoride (PVF), polyethylene terephthalate (PETP), glass-reinforced polyester (RP), and polyvinyl chloride (PVC). Clear and white sheet and film are included.

The specimens were subjected to modified ASTM tensile and flexural tests. Parameters were then obtained from the resulting stress-strain curves. These included Young's modulus of elasticity, yield stress, yield strain, failure stress, ultimate elongation at break, and 5-percent stress (stress at 5% flexural strain).

2.1 Significance of Elongation Data

Of the physical properties, ultimate tensile elongation and 5-percent flexural stress showed the greatest change with time. Ultimate elongation decayed rapidly within one year for most of the plastics. Five percent stress increased substantially in a few months after which there was little or no change. An increase in 5 percent stress was usually accompanied by a decrease in ultimate elongation. These changes indicate a loss of elasticity and flexibility, resulting in increasing stiffness and probably brittleness.

The following investigation is based on ultimate elongation data as reported in [2]. An additional year's data have been obtained since publication of that report, and have been incorporated in this study.

The tensile test yielding these data is considered a low strain-rate test. In general, it can be said that low strain-rate tests are <u>less</u> sensitive measures of physical deterioration than high strain-rate tests (such as impact). Thus, it would be expected that not only ultimate tensile elongation but also impact strength of these plastics has decreased. This means that such a deteriorated plastic would show lower performance in an application involving impact.

Ultimate tensile elongation, therefore, is considered a sensitive and meaningful measure of physical deterioration. The exponential nature of this property change, proposed in NBS Report #10014, simplifies the formulation of a model. A relatively simple form was postulated to describe this weathering behavior quantitatively:

$$P = A \cdot e^{-Bt^n} + C$$

where A, B, C and n are constants to be determined for each plastic in a given exposure, t is time, and P is the property under study. Great similarity was noted between this form and those equations common in chemical kinetics, statistical reliability and several engineering applications. The especially significant work of Kamal and Saxon [3], as well as Daiger and Madson [4] was pointed out.

2.2 Usefulness of Mathematical Models

The weathering of a plastic can be characterized by definite behavior patterns of its properties over time. Oscillatory seasonal variation in color change and exponential loss of ultimate elongation have been described qualitatively in previous reports on color and physical properties. It is very desirable, however, to describe this behavior mathematically, and thus provide an accurate, compact, and precisely defined description of the property change as a function of exposure time and ultimately of the weather itself.

This effort was undertaken to:

a) construct a mathematical model of the change in a given property of a weathered plastic,

b) determine which weather factors caused this property change, and then,

c) mathematically relate these weather factors to the parameters of the model.

Having successfully accomplished this, it should then be possible to predict and describe the changes in material properties from knowledge of the environmental conditions under which a material has been or will be exposed. Thus, from knowledge of, for example, the total rainfall, average temperature, and cumulative ultraviolet radiation to which a sample has been exposed, the present and future loss of physical strength may be determined.

An immediate use of outdoor mathematical models would be in conjunction with indoor accelerated weathering devices. Much better simulators of outdoor weathering could be designed and constructed by comparing simulator results with mathematical models derived from outdoor exposures. Once the experimental results of accelerated weathering devices are correlated with mathematical models of property changes observed outdoors, models for new materials can be constructed directly from artificial weathering data collected indoors. Thus, in a very short time the outdoor behavior of a material could be predicted.

3. RELIABILITY AND FAILURE ANALYSIS

Many of the hypotheses in this study are based on analogies with problems related to fatigue life and reliability theory, and the behavior properties of various statistical models and distributions.

In choosing or rejecting a model, it is important to keep in mind the observed behavior of the property and the physical reality of the process. A plastic sample left outdoors undergoes many changes as a result of the weather conditions to which it is exposed. Weather factors that have been found to be the most significant in degrading plastics are ultraviolet radiation, humidity, temperature, rainfall, and to a lesser degree, air pollution and stress. As a result, some plastics discolor, surface texture changes, gloss decreases, and physical strength is lost. Weathered plastics tend to become brittler, stiffer, and less flexible. Degradation of these plastics is a cumulative effect of the time that samples have been exposed to weather conditions, and happens gradually.

An analogy can be drawn between stresses received by a sample in fatigue testing and those received in weathering. Fatigue testing usually implies subjecting a specimen to repeated stress by rotation, bending, etc., until, after N cycles, the specimen fractures or breaks. In this investigation of physical failure of plastics, the length of time exposed to the weather (e.g. the number of months until failure) is being associated with number of cycles. They are both measures of the duration of a given stress. In the case of weather, exposure time is a rough estimate of a complex of stresses to which a plastic is subjected. The number of months represents the cumulative effect of n diurnal cycles of weather stress. Whereas each cycle in fatigue testing often equals the next, each day of weather usually does not equal the next. Some days there is much ultraviolet stress and little rain stress while on other days a large amount of cloud cover greatly reduces the ultraviolet stress and increases the rain stress. These weather stresses have been measured and will be used in the final analysis to determine the total accumulated weather stress each plastic was subjected to. A plastic fails due to the net effect of n diurnal weather cycles just as a metal fails due to the net effect of N rotational cycles. In both cases the applied stress must be defined and its effects on the material analyzed.

W. R. Buckland in his monograph "Statistical Assessment of the Life Characteristic" [5] sets up three categories of physical failure: "(a) early failure, (b) random failure, and (c) wear-out failure... The <u>early failure</u> is generally reckoned to be due to catastrophic primary material failure or to industrial difficulties associated with reliability of fabrication and assembly: a quality problem. The <u>random failure</u> is one which occurs at a time which is independent of the life at failure. The <u>wear-out failure</u> is due to the gradual exhaustion of physical or other properties which in some way are directly related to the length of life."

Similarly, Kao [6] classifies electron tube failures into two types: catastrophic or sudden failures and wear-out or delayed failures. "A tube which is operating normally and then suddenly becomes completely inoperative is defined here as a <u>catastrophic failure</u>. A tube whose characteristics gradually fall outside some specifications is defined as a wear-out failure ." These classifications would seem to hold for life testing of plastics, too. Materials rarely "wear out" until a certain time period has elapsed. The probability of failure increases the longer the material has been in use. Since the failure is definitely time-dependent (and thus not random) and is a gradual process (i.e. not catastrophic), <u>degradation of weathered plastics may be characterized as a wear-out type of failure</u>.

4. CHOICE OF A MODEL

A search of the literature was made to see what mathematical models had previously been used in the field of life testing and what problems were described by those models. The Bibliography lists the major significant journal articles and texts consulted. From these a list of mathematical functions that could be associated with time-to-failure and wearing-out was compiled as follows:

(1) Simple Exponential

(2) Normal or Half Normal

(3) Log-normal

(4) Gamma (Pearson Type III)

(5) Extreme value (smallest)

(6) Weibull

4.1 General Form of the Model

Since the data appeared to vary exponentially with time and the curves seemed to approach the horizontal time axis asymptotically, a mathematical expression with these features was constructed as a starting model. It was also hoped that the data could be fitted by some family of curves and this too would be incorporated into the model. This first model was

$$Y = Ae^{-Bt^n} + C \qquad (1)$$

where A, B, C, and n are constants to be determined for each plastic for a given exposure, t is time, and Y is the property under study. For $n = 1$, equation (1) is a simple exponential of the form used to describe radioactive decay processes. For $n > 1$, it allows for an inflection point which is observed in many of the plots. The choice of this model was totally arbitrary in that no curve fits had been done (except by eye) and no extensive literature search had yet been done. This tentative model was mathematically flexible and did resemble several statistical distribution functions (for example, equation (1) is Gaussian for $n = 2$).

Another desirable feature of an exponential model is a mathematically defined "time-to-failure". This is the time at which the property has decreased to 36.8% (1/e) of its original value. Beyond this failure point the measured property can be considered no longer acceptable. This concept has been employed in analysis of ball-bearing fatigue and auto-parts failure, in defining skin depth of good electrical conductors, and in defining a critical time or time constant in R-C circuit theory. (See Bibliography)

Note the following similar uses of exponential equations:

a) Changes in concentration of reacting substances in chemical kinetics are described by equations such as $Y = A(1-e^{-Kt})$ where Y is concentration of the reaction-product at time t, A is initial concentration of reactant and K is the "rate constant". [7].

b) Kamal and Saxon in a study of accelerated weathering used $Y = Ae^{B(t-C)}$ where Y is the value of the property at time t, and A, B, and C are constants found to be dependent on exposure parameters. [3].

c) At du Pont, Daiger and Madson used the expression $Y = K-Ae^{-Bt^2}$ in paint evaluation studies. Y is red-reflectance of paint at time t, and A, B, and K are constants. [4].

The form of the equations in (a), (b), and (c) above and the assumption that a plastic's deterioration is a gradual process over time suggested that one or more of the six distribution functions listed earlier might represent the change in ultimate elongation as a function of exposure time as a first approximation. (Property change is actually a function of the weather which is different in Arizona and Washington, D. C., whereas exposure time is not different.)

4.2 Application of Statistical Distributions of Life Testing

In the following discussion, the properties of distribution functions will be presented but only the <u>functional</u> form of the distribution is of importance here [8]. There are too few data to say that property loss is described by an exponential, normal, or any other distribution. The <u>function</u> can be fitted to the data as would any other function such as $ax + b$ or x^2: <u>thus the distinction between an exponential function and an exponential distribution</u>. The behavior of the <u>function</u> and its properties are what is significant.

Although the ultimate elongation data are not sufficient to define their statistical distribution, the data are a measure of some underlying mechanism of failure. This unobserved failure process may actually be represented by a Weibull or Normal distribution. What is seen is only the gross change in the material. For example, in the case of physical strength, some kind of weakest-link theory may apply.

This says that the strength of a system is determined by the weakest component of that system. For example, if every link (assumed massless) on a chain is rated to support a 100 kilogram weight but one link can actually support only 97 kilograms, then the entire chain will only be able to lift 97 kilograms without breaking. At a weight greater than 97 kgm. the weakest link will break causing the whole chain to fail. Similarly, in a plastic certain bonds are weaker than others. Many times these weaker bonds reflect the presence of impurities such as polyenes in PVC. If one bond fails, a whole series of other bonds may fail. A process such as this could lead to total physical failure of the material. Perhaps the gradual weakening and gross physical failure of a plastic is indicative of an underlying weak link mechanism.

The exponential function is the least complex of the six listed. It is a special case of both the Weibull and Gamma distributions. (Note: In all the functions written below, Y defines the value of a property - e.g. ultimate elongation - measured after a sample had been exposed for t months.) The simple exponential function is

$$Y = \lambda e^{-\lambda t} \qquad t \geq 0, \ \lambda > 0 \qquad (2)$$

The t and λ must be greater than or equal to zero to insure that the function be decreasing. A plot of the function shows that there is no portion of the graph for $t \not\approx 0$ for which the rate of change of Y is small.

Physically, we usually expect and observe some initial period in which the property changes slowly with time. This "induction period" requires that the slope of the curve be near zero for some portion of the curve where t is small. Measurable property loss does not, it would seem, begin the instant the sample is placed outdoors but only after the plastic is slowly weakened by the weather. This initial period could be long or short depending on the composition of the material. For this reason a simple exponential function would not be a good model - its behavior does not allow for the physical behavior of a weathered plastic.

A frequently used function in failure analysis is the hazard function which gives the probability of failure during a very small time interval, assuming that no failure has previously occurred. This function is

$$h(t) = \frac{f(t)}{1 - F(t)}$$

where f(t) is the probability density function and F(t) is the distribution function for time-to-failure. h(t) dt represents the proportion of items that have not failed at time t that fail in an interval (t, t + dt). When applied to an exponential function, it can be seen that $h(t) = \text{constant} = \lambda$. λ is called the failure rate. This says that the probability that a sample which has survived 3 months outdoors will fail at some time $(3 + \Delta t)$ months is the same as the probability that a sample which has survived 12 months outdoors will fail at some time $(12 + \Delta t)$ months. This is suitable for random failures but unsuitable for wear-out failure. A weathered plastic would be more likely to fail after 12 months than after 3. Again, the nature of the simple exponential function does not fit the physical situation which it is meant to describe. Thus it was rejected.

A model based on a normal probability density function can be written as

$$Y = Ae^{-(x - \mu)^2/b^2} \tag{3}$$

This function approaches the time axis asymptotically as does the exponential function and thus satisfies that requirement. In addition the "normal" function has a failure rate that is an increasing function of time. This is more appropriate for wear-out failure. One problem still exists, though: the basic symmetry of equation (3). In discussing the use of "the normal distribution" for the representation of fatigue life and especially fatigue strength, Gumbel argues [9] that the "distribution cannot be used for a complete analysis because its basic feature, symmetry, simply does not exist. In addition, within this theory there is no place for a minimum life and an endurance limit i.e. the most important characteristics." On the basis of these objections, a "normal" model was not used. It didn't seem flexible enough to do the job. The model that was finally chosen, though, does incorporate equation (3) as will be demonstrated later.

By replacing X in (3) above with log X ($X>0$), a log-normal model can be constructed. The failure rate of a log-normal distribution is 0 at time 0, increases to a maximum, and then decreases back down to 0 with increasing time. The decrease of the failure rate back to 0 after some time does not represent the physical situation. Gumbel also notes that the log-normal distribution assumes certain symmetries as does the normal distribution. Consequently, a log-normal model seemed a poor model for wear-out failure and for the problem in general.

The gamma probability density function is

$$f(x) = \frac{\lambda^r}{\Gamma(r)} x^{r-1} e^{-\lambda x} \tag{4}$$

The functional form of this seemed too complex for a first attempt at a model. Also, the physical situations described by the gamma distribution were not as analagous to the situation being studied here as were several of the other distributions functions. Consequently, it was not used.

Extreme value functions are the most promising of all the functions considered. These 3 cases are of special interest [8]:

1. Type I Asymptotic distribution for maximum values
2. Type I " " " minimum "
3. Type III " " " minimum "

The third is also known as the Weibull distribution. These distributions are used to describe largest and smallest observations. Functions of this kind do not have constant failure rates which meet the requirements that the longer a plastic is exposed outdoors, the greater it would seem the probability of failure is in the near future. Thus the failure rate should be an ever-increasing function.

A look at the hazard functions for the two Type I extreme value distribution functions shows the failure rate for smallest values increases exponentially with time while the rate for largest values increases at a decreasing rate and asymptotically approaches a constant. A smallest extreme value function fits our physical requirements best. The tensile strength or ultimate elongation of a sample at any given exposure time should be a measure of the weakening of certain sub-elements of the plastic. What is sought is the time required for a minimum number of these components to fail, resulting in the gross physical failure of the material. Hereafter, when the extreme value function is referred to, the smallest value function is actually being discussed.

The Type I extreme value function (minimum) of the form

$$Y = \exp\left[-\exp(x)\right] \qquad (5)$$

satisfactorily meets the physical requirements of a model function--it is a decreasing exponential function which asymptotically approaches the x - axis; it has an increasing failure rate with time, and has successfully described many analagous problems. X in equation (5) may be replaced by $(x' - b)/a$ to add flexibility to the model. Besides this, b can be associated with a characteristic time to failure. Assigning physical meaning to the parameters of the model is one of the most sought-after phases of this study. Extreme value models have been used in the investigation of fatigue life of ball bearings, tensile testing of rubber, and metal fatigue analysis (see Bibliography).

4.3 Selection of Weibull-Type Model

The Weibull function [10] is the third of Gumbel's three types of extreme value functions. It has the following form:

$$Y = a \exp\left[-(t/b)^n\right] \qquad (6)$$

Like the Type I extreme value function above, the Weibull is taken from a distribution of minimum values. For n = 1, it reduces to the simple exponential function with a constant failure rate. For n = 2, it is similar to a Gaussian or "normal" function. Thus the Weibull incorporates features of two of the other models already considered. It is also more flexible than the extreme value function since it replaces exp (x) in equation (5) with $(t/b)^n$. The Weibull meets all of the criteria met by the extreme value function i.e. exponentially decreasing function, asymptotically approaches the x - axis, and an increasing failure rate with time. Furthermore, it has described many apparently unrelated problems including yield strength of steel, fiber strength of cotton, fatigue life of steel, electron tube failure, ball-bearing fatigue and automotive part failure, to mention a few. By adjusting the value of n in equation (6), the Weibull function can describe either an increasing or a decreasing failure rate. Thus, the major advantage of the Weibull over the extreme value function is the large family of curves it can describe. In addition, b in equation (6) can be associated with the time-to-failure or "characteristic life" of a material as was the case with the b in the extreme value function (5).

Of the six mathematical models proposed for this study, only two, the (smallest) extreme value and the Weibull, possess the desired behavioral properties and meet the physical requirements of the problem. The extreme value model is the simpler of the two but the Weibull is more flexible. Although somewhat more complex than the extreme value model, the Weibull was chosen as a first model for describing the physical strength loss of the weathered plastics. It was hoped that the greater complication of fitting this model to the data would be compensated by its wider applicability and that most of the data might be described by some family of Weibull curves. In addition, a Weibull model could be easily reduced to another form but the extreme value function could not be.

4.4 Methods of Model Fitting

Now that a tentative mathematical model had been chosen, the immediate problem was to find a method to determine the unknown parameters in the model. We were interested in finding the simplest but most efficient way of fitting the model to the data.

An analog computer was the first method investigated. It was hoped that an analog circuit could be designed to generate a function of the form of a Weibull as discussed above. By varying the potentiometers and viewing the results on an oscilloscope, parameter values could be obtained for each set of data. This approach was toyed with by the analog computer group at NBS but was eventually abandoned due to technical problems, the major one being outmoded equipment. The analog computer may still be a fruitful method. Not enough work was done here to either confirm it or rule it out.

Du Pont has developed a special purpose analog computer [11] which generates a series of component peaks and adds them to produce the original data. By generating the right function or functions, it was thought that the wave forms of the ultimate elongation data could be reproduced. The function(s) that fit the data could then be determined from the electronics and parameter values obtained similarly. Du Pont's "curve resolver" was, however, unable to generate skewed curves in all required forms to fit the data due to a lack of appropriate circuitry. Because of this, the technique could not be used in this study. New circuits that generate more complex functions may give the curve resolver the flexibility needed in analysis of data such as ours.

A method commonly used in fatigue testing and failure analysis is plotting on probability papers [12]. Depending on the distribution of the data, the points will plot as either a straight or curved line on a given probability paper. If a set of data is distributed linearly (i.e. $Y = a\ x + b$) then it will lie in a straight line on rectangular coordinate paper but not on log-normal paper. If a set of data is normally distributed, then only on normal probability paper will it lie on a straight line; on logarithmic or extreme-value paper, the data would curve. Similarly, data satisfying a Weibull distribution function will plot as a straight line only on Weibull probability paper [13]. Thus probability plots provide a simple way of testing a given functional relationship of the data and of obtaining the unknown parameters of a known distribution function.

Although we had no more than 7 points per case (at this stage of the investigation), cumulative % loss of ultimate elongation as a function of time was plotted for 16 cases on Weibull probability paper and 10 cases on extreme value paper. These plots were intended to give rough estimates of how well the model fit the data and approximate values for the parameters. Due to the scarcity of data, no conclusions could be drawn in the majority of cases. The points did seem to fall on a straighter line for the Weibull plots than for extreme value plots. With more data, this method would be a very simple and quick way of obtaining parameter values for a Weibull or extreme value model. The greater the number of points the more accurate the line drawn. In the few instances where data fell in nice straight lines, slopes were read off the plots. Only a few of these slopes came close to the values calculated by a Univac 1108 computer using a nonlinear regression program.

Hazard plotting was also considered as a method of analysis [14]. If the data on the number of specimens lost by embrittlement had been more detailed so as to establish exactly when embrittlement occurred, hazard plotting could provide the distribution of time-to-failure by embrittlement. Note that all the data considered here are multiply censored i.e. removed from testing periodically whether or not failure has occurred.

Since the above techniques proved inadequate, numerical methods had to be used to fit the model to the data. In most instances this means some form of linear least squares analysis performed with the aid of a digital computer. In this case, however, the model is intrinsically nonlinear, i.e. it is impossible to convert it into a form linear in the parameters. For example, consider a model $Y = \exp(a_1 + a_2 t^3)$. By taking the logarithm to the base e of both sides, the model can be transformed into the form $\ln Y = a_1 + a_2 t^3$ which is linear in the parameters. The model used in this study, however, is of a non-transformable form making it necessary to fit the data by nonlinear methods, in our case, by nonlinear least squares analysis [15].

In contrast to linear models, nonlinear models incorporate theoretical understanding of the mechanism of the process under investigation. While a linear model is used primarily to obtain predicted values of the dependent variable, the main interest in a nonlinear model is the values of the parameters, which many times have specific physical meaning. b, defined as characteristic life in the smallest extreme value function, is such a parameter. In addition, parameter estimates for a nonlinear model are often to be used later in other calculations. These considerations and the apparent exponential relationship between retention of elongation and exposure time made it preferable to fit a nonlinear model rather than an alternative, probably less realistic, linear model.

Now, for the linear least squares case, the equations used to determine the unknown parameters of the model are linear equations in the parameters. But when the model is nonlinear in the parameters so will be the equations that determine them. Solutions of these equations are very complicated making it necessary to employ iterative methods.

Several methods are commonly available for obtaining parameter estimates in nonlinear models. Algorithms for doing this are centered basically around two techniques: (1) Linearization - in which the model is expanded as a Taylor series and corrections to the parameters calculated at each iteration on the assumption of local linearity, and (2) Steepest descent - which uses an iterative process to minimize the sum of squares function Φ by correcting the trial parameter values in the direction of the negative gradient of Φ. Various modifications of these are currently in use.

Both methods have drawbacks for some situations. The Taylor series method many times diverges instead of converging, resulting in an increased sum of squares after each iteration. On the other hand, steepest descent methods converge agonizingly slowly after the first few iterations. Furthermore, the steepest descent method is not scale invariant.

D. W. Marquardt developed a method that represents a compromise between linearization and steepest descent techniques [16] and which seems to combine the good features of both while avoiding their major difficulties. A Fortran program [17] employing Marquardt's algorithm was chosen to fit the Weibull-type model in this study.

One thing should be noted in regard to all nonlinear least squares regression. This is the importance of good starting values for the parameters. Initial "guesses" estimating the parameter values are necessary for all iterative procedures but their choice can be critical in a nonlinear problem. Starting values should be estimated as accurately as possible. For nonlinear cases, convergence is dependent upon the model, the data, and the initial guesses for the parameters. The better the initial guesses, the greater the probability of convergence. Also, good initial values will result in faster convergence of an iterative procedure. If Φ has multiple minima or several local minima in addition to an absolute minimum, bad starting values may lead to convergence at unwanted minima. Final parameter values may then be physically unrealistic or not represent the true minimum of Φ .

5. REGRESSION ANALYSIS OF ELONGATION DATA

Four factors contributed to the formulation of the model fitted to the ultimate elongation data: (1) apparent exponential loss of elongation as a function of exposure time, (2) work done in related fields employing such functions, (3) statistical distributions of life testing and reliability, and (4) preferability of a nonlinear function as a more realistic mathematical description of the behavior. Thus, the following model was developed:

$$Y = b_1 \exp \left[-\left(\frac{t + b_2}{b_3} \right)^{b_4} \right] + b_5 \qquad (7)$$

Y is the percent retention of the property, t is the number of months of exposure time, and the b's are constant parameters to be determined for each curve fitted. When both b_2 and b_5 are zero, notice that the model is identical to the Weibull function (equation 6).

5.1 Mathematical Constraints

In fitting this model, certain mathematical constraints must be placed on the parameters to meet the physical requirements of the problem. Two things are essential from the outset. First, Y can only assume real values ≥ 0, i.e. percent retention of elongation can go no lower than 0%. Secondly, since t is defined as the number of months a sample has been exposed outdoors, t is a real time and must be ≥ 0. The restrictions on Y require the quantity to the right of the = sign in equation (7) to also be real and ≥ 0.

Two kinds of behavior are exhibited by the elongation data--either a monotonic decrease or an initial increase followed by a monotonic decrease (see Figure 1). It can be shown that for data that are strictly decreasing over the entire range, $b_4 > 0$. For the data which increase, then decrease, $b_4 = \frac{k}{m} > 1$ where k is an even integer and m an odd integer. See Appendix for derivation.

The term $[\,(t + b_2)/b_3\,]^{b_4}$ in equation (7) can be rewritten as $(b_3)^{-b_4}\,(t + b_2)^{b_4}$. If b_3 were permitted to be < 0, $(b_3)^{-b_4}$ would be real only for certain values of b_4. But this is an undesirable constraint, so from the start b_3 is restricted to be positive.

Now, if t becomes very large, the first term in equation (7) approaches 0 and Y approaches b_5. Thus b_5 represents the asymptotic value of Y below which Y will not go. b_5 must then be real and ≥ 0, and have the same dimensions as Y.

When $t = -b_2$ in equation (7), the property assumes its maximum value $Y = b_1 + b_5$. Thus, b_1 must be a real positive number and have the same dimensions as Y. If b_2 is negative, the maximum will occur at a positive value of t. This corresponds to the case in which Y initially increases to a maximum and then decreases. If b_2 is positive, the maximum will occur at a negative value of t not observable from the data. For $t \geq 0$, Y is, then, a strictly decreasing function. If $b_2 = 0$, Y is maximum at $t = 0$ and is monotone decreasing. The constraints are summarized below:

Parameter	Constraints		Units
b_1	> 0		%
b_2	none		Months
b_3	> 0		Months
b_4 $(b_2 < 0)$	$= \frac{k}{m} > 1$	(k even integer) (m odd integer)	-
$(b_2 = 0)$	> 0		-
$(b_2 > 0)$	> 0		-
b_5	≥ 0		%

Notice that b_1 and b_5 have dimensions in %, b_2 and b_3 have dimensions in time, and b_4 is dimensionless.

5.2 Estimation of Starting Values

Reasonably good guesses can be made for starting parameter values to be used in the Marquardt regression program by considering the mathematical behavior of the model, equation (7), and the physical significance of the parameters (see Figure 1). An estimate of b_5 can be obtained simply from the asymptotic value of the data.

If the percent retention increases and then decreases, b_2 must be negative and have a value equal to the time t corresponding to the maximum retention. When the data show no apparent increase for $t > 0$, b_2 may be zero or close to it.

Since $b_1 + b_5$ is the maximum value of Y, $b_1 = Y_{(max.)} - b_5$. Thus b_1 can be estimated from the guesses for $Y_{(max.)}$ and b_5. For a curve that appears to have a maximum at $t < 0$ (pre-aging), b_1 and b_2 are more difficult to estimate. Starting values can be used for a hypothetical maximum at $t = 0$.

Rate of loss of elongation is directly related to the values of b_3 and b_4. For a constant value of b_3, the larger the value of b_4 the more the function of equation (7) approaches a step function. An induction period followed by rapid loss of elongation down to some asymptotic value would be typical of a higher value of b_4. Little or no induction period may indicate a b_4 equal to or less than 1.

b_3 is associated with the characteristic life or time-to-failure of a material. When $t - b_2 = b_3$ in equation (7), $Y = \frac{b_1}{e} + b_5 = \frac{1}{e}(Y_{(max.)} - b_5) + b_5$. Thus, estimates of $Y_{(max.)}$ and b_5 can provide an estimate for b_3. If $b_5 = 0$, $b_3 + b_2$ corresponds to the time at which the percent retention of elongation is 37% $(\frac{1}{e})$ of its maximum value. If, in addition, b_2 is taken equal to zero, 37% of the initial measurement ($Y_{(max.)}$ for $b_2 = 0$) will be a very good estimate of b_3. A smaller value for b_3 represents a shorter lifetime than a larger value and in cases where $b_2 = b_5 = 0$, b_3 is the characteristic life of the material.

5.3 Normalization of Data

The regression was performed once on actual data to determine the best estimate of the initial value of ultimate elongation, i.e., the original elongation of a material before weathering. The predicted initial values were very close to the observed experimental values, within experimental error. Then the data for each material were normalized with respect to the material's observed initial value. Thus, the data were all expressed in terms of percent retention of original elongation before weathering. This is always 100% at the start and increases or decreases depending upon a gain or loss of strength. Performance of different materials is then comparable in terms of property retention, rate of loss of the property, etc.

6. RESULTS AND DISCUSSION

6.1 General

Using the model $Y = b_1 \exp\left[-\left(\frac{t + b_2}{b_3}\right)^{b_4}\right] + b_5$ and the constraints on the parameters described in Section 5.1, property decay curves were fitted to the normalized ultimate elongation data. Although there are theoretically 60 possible sets of data (20 plastics x 3 sites), all plastics were not exposed in all three locations leaving actually 54 sets of available data. Of these 54, 35 were fitted by the non-linear least squares method of Marquardt using the National Bureau of Standards' Univac 1108 computer. Fits were not attempted on cases where (1) the number of data points was less than the number of parameters in the model (7 cases: PE-1 (Ariz., Fla.), PVC-C4 (Ariz., Fla.), PVC-C60), (2) data were too scattered to be fitted meaningfully by any mathematical function (6 cases: RP, PVC-A4 (Fla.), PVC-A60 (Wash.), PVC-D10 (Fla.)), or (3) data showed a cyclic pattern not representable by the model chosen (6 cases: PMMA, PVF). A minimum of 6 points to a maximum of 9 points was fitted in the 35 cases for which results were obtained. Table 1 shows the actual number of points fitted in every case.

Constraints, in addition to the required mathematical ones, were placed on any of the 5 parameters when the physical situation seemed to warrant them. Unless there was significant evidence to the contrary, it was assumed there should be an induction period, no matter how small, during which the property value does not decrease. b_2 was thus constrained to be 0 in all cases but one where it was allowed to be any negative number. There was no evidence to substantiate any kind of pre-aging so positive values of b_2 were not allowed in the regression.

b_5 was constrained to be 0 in cases where the data approached 0 or the value of b_5 obtained from the regression was approximately 0.

The above constraints on b_2 and b_5 simplified the model in many cases in addition to improving the fit.

Since $b_1 + b_5 = Y_{max}$, b_1 and b_5 are dependent parameters so this relation was written into the computer program as a constraint. Because b_5 has physical significance, b_1 was defined as a function of b_5 although theoretically we could have just as well defined b_5 as a function of b_1. Thus we used $b_1 = Y_{max} - b_5$ rather than $b_5 = Y_{max} - b_1$ in the program.
In practice, it turns out that values of b_1 and b_5 obtained are slightly different depending on the way they are defined. Since b_5 has some meaning attached to it and it can be determined independently, it was more practical to choose b_5 as the independent parameter and use it to define b_1. b_1 will therefore be omitted from the discussion that follows due to its total dependence on b_5.

In 34 of 35 cases, $b_2 = 0$ gave the best fit. Thus, each of these curves has its maximum property value at $t = 0$ when the sample was originally placed outdoors. This means there is no pre-aging or post-curing evidenced by these data. For each of the 34 curves there is some finite induction period, perhaps small compared to 1 month, during which there is no property loss. In some cases (see, for example, plots of PVC-B60) this induction period is for all practical purposes negligible, while in other cases it is very significant (see plots of PVC-B4).

In only one case is b_2 non-zero. That is PVC-A4 in Washington, D. C. Here $b_2 = -7.85$ indicating an increase in elongation for $t > 0$. At 7.85 months the value is maximum and then the percent retention begins to decrease. Note that this case is distinguished from the others by the negative value of b_2 alone. From this one number, the general form of the decay curve can be predicted.

b_3 is probably the single most important parameter of the model since it can be associated with the time-to-failure for a given material. This concept is discussed in Section 6.4. In cases where b_2 and b_5 are close to zero, b_3 is a very good approximation of the time-to-failure. For $b_2 = b_5 = 0$, b_3 is exactly the time-to-failure. Thus b_3 in many instances is a very good, if not exact, measure of the lifetime and durability of a material in terms of its ultimate tensile elongation.

The values of b_3 obtained in the 35 cases range from 0.31 months for PVC-B60 in Arizona to 167.11 months for PE-60 in Washington, D. C. Consulting Table 1, we see that $b_2 = b_5 = 0$ for both these cases. Thus, for these two cases, b_3 is exactly the time-to-failure. Ignoring the error term for b_3, it takes 0.31 months in Arizona for PVC-B60 to lose 63.2% of its initial elongation and 167.11 months (or about 14 years) for PE-60 in Washington.

The vinyls and non-vinyls in this study can be distinguished quite well on the basis of their b_3 values. Non-vinyls, PETP and PE-60, have the highest values - substantially higher than the median (8.70) and the mean (16.58) of the 35 samples taken as a group. Generally, values of b_3 for the two climatic extremes, Arizona and Washington, D. C., separate themselves into two groups. Samples exposed in Washington have b_3's above the median (8 of 11) while Arizona samples have b_3's below the median (10 of 13). Florida samples show no preference. Since b_3 is a measure of a material's liftime, this would indicate that Washington samples last longer than Arizona samples with Florida samples falling into both categories. Clear vinyls are evenly distributed above and below the median but white vinyls show a definite tendency toward lower values - 9 of 14 are below the median. Thickness of the material has, in general, no effect on the value of b_3; however, for 60-mil vinyls, 8 of 11 have b_3's below the median. It is also interesting to note that 23 out of the 35 cases have b_3 values of less than 12 months. In other words, about two-thirds of the samples probably have lifetimes of less than one year.

b_4 is largely responsible for the shape of the decay curve. Values of b_4 for the 35 curves ranged from 0.24 to 9.95. Any $b_4 \leq 1$ represents a curve without an induction period. Although physically there should be an induction period for all of the 34 curves with $b_2 = 0$, there were no data with which to fit one in the crucial early portion of the curves. This plus a very low 6 month data point resulted in a curve fitted with a $b_4 \leq 1$. 13 cases were fitted in this way. They all decrease very rapidly during the first 6-12 months and reach 36.8% (the failure point) in a short time. For most, any induction period would have been insignificant.

Two-thirds of the cases have values of b_4 less than the mean of 2.35. Thus for the most part the values are low and in the same small range making it hard to differentiate between the cases.

Neither exposure site nor type of material seems to be directly associated with b_4. Thickness shows some relation in that all but one of the 10-mil samples fall above the median (1.38) and 9 of 14 60-mil samples fall below. Thinner samples split evenly about the median. b_4 seems therefore a poor measure of performance.

b_5 is the asymptotic value of the elongation - the minimum value retained by the material after its usefulness for the property of elongation has ceased. In 13 cases this is 0. The material is too brittle to elongate at all. In other cases, the sample continues to retain some small amount of the original property value, perhaps 1% or even 15%. PE-60 in Florida has a b_5 of 39.60%, the highest of the 35 cases. The average value of b_5 is 5.95% with 24 materials having values lower than this. Thus in the majority of cases b_5 is insignificant.

b_5 seems unaffected by exposure site but somewhat dependent on thickness. The thicker a material the more likely it will have a higher value of b_5. White vinyls PVC-D and PVC-M, both 60-mil materials, have b_5 values significantly higher than the average; this must be considered when determining the time-to-failure.

6.2 Goodness of Fit

Several combinations of constraints and starting parameter values were tried in each of the 35 cases to obtain the best possible fit to the data (Table 1). Four criteria were used to judge which of several fits for a given case was the most successful:

(1) Reality of the parameter values
(2) Statistical measures of the fit (Phi and S.E.)
(3) Standard error on each of the parameters
(4) Parameter correlations.

Parameter values were the object of the regression analysis and accordingly, they were the first numbers looked at. Since b_2, b_3, and b_5 represent physical reality, we had a good idea for each case in what range the parameter values would lie. Reasonable bounds can also be estimated for b_4 from the form of the data points. If the parameter values obtained from fit were not realistic, the fit was rejected. Occasionally the regression converged to a local minimum that gave a comparatively low sum of squares but had totally unrealistic values for the b's and was therefore rejected.

The statistical tests of "goodness of fit" which are applicable in the linear model case are, in general, not appropriate in the nonlinear case. Significance tests using the F-statistic cannot be used because the theory and tables are based on linear models. The unexplained variance, Phi, and Standard Error are the only statistical measures available with which to judge the general goodness of fit. $PHI = \sum_{i=1} [Y_i - \hat{Y}_i]^2$ where $Y_i - \hat{Y}_i$ is the difference between the observed Y and the Y predicted by the model, for a given time for each of the n data points. The Standard Error $S.E. = [PHI/(n-k)]^{\frac{1}{2}}$ for the n data points fitted and k parameters of the model. It is Phi that is minimized by the Marquardt program in optimizing the regression. The lower the value of Phi the better the fit. Phi, however, should not be considered in isolation since a low Phi may represent a local minimum with correspondingly poor parameter values. A relatively high value of Phi may actually give the best fit in terms of the confidence one can place on the parameters.

<u>Phi</u> values for the 35 cases of elongation data are as low as 0.14 for PVC-D4 in Arizona, and as high 957.53 for the same material in Washington. Fits with a Phi less than 100.0 are judged to be fairly good to very good. Except for PE-60 and PVC-B60, Phi is always lower in Arizona than in Florida or Washington for a particular plastic. This may be attributed to the smaller variation of the Arizona data compared to that of the other two sites. Washington, on the other hand, tends to have the highest values of Phi indicating greater fluctuation of the data points about the fitted curve.

<u>Standard error of the fit</u>, S.E., may be a better measure of fit than Phi. Differences in Phi can be due to different numbers of data points used in the fits--the more points the higher the Phi. Standard error takes the number of points into account, and in addition accounts for the number of unconstrained parameters in the model. For example, the value of Phi for PVC-A10 in Florida is 22.46, higher than the Phi for PVC-D60 in Washington. PVC-A10 would appear to have the worse fit but it also used one more point than PVC-D60. If this is allowed for by calculating the standard error in each case, the difference between the two fits becomes insignificant.

Standard error of the fit is also a good comparator for the effect of site on goodness of fit. S.E. of Arizona cases is usually lower than the corresponding value for the same plastic in Florida or Washington. Furthermore, Washington fits generally have the highest S.E. Thus, except for a few cases, S.E. (Ariz.) < S.E. (Fla.) < S.E. (Wash.).

Since the primary object of the regression analysis is to obtain values for the b's, it is important to know how good the values are. Thus, the standard error for each of the parameters was a major factor in accepting or rejecting a fit. Two sided 95% confidence intervals are given in Table 1 for each of the b's.

Correlations were done to check the relation between the magnitude of a parameter and the magnitude of its standard error. In general, b_1 and b_5 are virtually uncorrelated with their standard errors. The correlations between b_3 and its standard error and b_4 and its standard error are both about 0.65. These correlations were further broken down by exposure site. Only the following were statisfically significant at a 95% level of confidence: b_1 and its standard error in Florida, b_3 and its S.E. in Arizona and Washington, b_4 and its S.E. in Florida, and b_5 and its S.E. in Washington. Though statistically significant, none of these correlations were higher than 0.68, which may not be significant in reality.

Interactions among the parameters were eliminated whenever possible so that the parameters retained in the model would be independent of each other. High correlations between parameters can adversely affect a fit and prevent it from reaching an optimum result. Nine cases still show correlations greater than 0.9 between b_3 and b_4, and one case has a similar high correlation for b_1 and b_5. Further discussion of parameter correlations follows in Section 6.3.

In determining the best fit for a given case, convergence was not used as a criterion. Convergence turned out to be a poor measure of the quality of the fit and was considered only incidentally after the other four criteria had been examined. Seven cases listed in Table 1 never converged. Convergence may occur at any local minima of Phi. The resulting parameter values may then be totally unrealistic or have high standard errors.

Occasionally the minimization procedure will not converge but will oscillate about a value of Phi. After 50 iterations changes in the value of Phi become so small (less than 10^{-3} at each iteration) that the regression can be stopped. Here there is no convergence but Phi has reached a minimum and the parameter values have stabilized. This fit may be the best obtainable with the data.

Sometimes high correlations between parameters cause divergence rather than convergence. Eliminating or reducing these correlations many times helps convergence as well as generally improving the fit.

6.3 Parameter Correlations

Linear correlation coefficients were computed for all possible pairs of parameters, e.g. b_1 with b_3, b_1 with b_5, b_3 with b_5, etc. Linear correlations are not completely appropriate when a nonlinear model is involved but in conjunction with plots of one parameter vs the other they will be an index of the interaction of the parameters.

Since b_1 and b_5 are linearly dependent parameters, they should be highly correlated. The sum of the two is 100% in all cases but one, PVC-A4 in Washington. The latter case had a significant negative effect on the correlation resulting in a lower correlation than expected.

Besides b_1 and b_5, none of the other correlations or plots show any obvious relationships. Although some of the individual cases have highly correlated parameters, in general the parameters of the model seem to be independent (excepting, of course, b_1 and b_5). Any possible relation between b_2 and b_3 could not be determined from the data because in every case but one, b_2 equals 0.

The possibility of a relationship between parameter values in one exposure site and values of the same parameter in another site was also investigated. Since b_1 is a function of b_5 and the values for b_2 are trivial, only b_3, b_4, and b_5 were used in these correlations. None of these gave very high correlations - the highest were approximately 0.5 to 0.6. Arizona and Florida showed a slightly higher correlation than Arizona and Washington or Florida and Washington for all three parameters. Thus the values of b_3, b_4, and b_5 do not appear to be a simple function of the exposure sites.

6.4 Other Measures of Decay

Two extremely useful measures of a material's service life are the time it takes to decay to 37% of its original value and the rate at which this decay proceeds. Both of these can be calculated from the Weibull-type model describing the loss of elongation.

Unlike the exact Weibull or extreme value functions, the <u>characteristic life or time-to-failure</u> for ultimate elongation is not embodied in a single parameter of the elongation model except in special cases. The characteristic life is the time it takes for a material to lose 63.2% of its original elongation. At this time the plastic retains 36.8% (or 1/e) of the original value of the property. If we take the model equation

$$Y = b_1 \exp\left[-\left(\frac{t + b_2}{b_3}\right)^{b_4}\right] + b_5,$$

substitute 36.8% for Y and solve for t, we can define a time-to-failure

$$T = b_3 \left[\ln\left(\frac{b_1}{36.8 - b_5}\right)\right]^{1/b_4} - b_2.$$

For 34 of 35 cases, $b_2 = 0$ so that b_2 may be neglected. PVC-A4 in Washington has a b_2 equal to -7.85. This contributes substantially to the value of T. In the special case when $b_2 = b_5 = 0$, $T = b_3$. Thus b_3 is the characteristic life in this special case. For any case where $b_2 = 0$, b_3 is a very good approximation of T for small b_5. Compare the values for characteristic life in Table 2 with corresponding values of b_3 in Table 1. Notice that for high values of b_5 (for example, PVC-M60-W) b_3 and T are quite different but for low values of b_5 (for example, PVC-C4-W) b_3 and T are almost identical.

As with b_3, non-vinyls have the highest characteristic lives. 21 cases decay to 36.8% of their original property values within one year.

Linear correlations between b_3, b_4, b_5 and characteristic life were studied. In general, b_4 and b_5 show negligible correlations. Characteristic life increases and then decreases as b_4 increases indicating a possible quadratic relationship between the two but this has not been studied. b_3, however, is correlated 0.76 with characteristic life. Further correlations were done between parameter values for one site and the corresponding values of characteristic life for the same site. b_4 and b_5 again show no relation to time-to-failure, but b_3 is significantly correlated with it. The correlation between b_3 and T is 0.72 in Arizona, 0.99 in Florida, and 0.67 in Washington.

A <u>maximum decay rate</u> can be calculated for each fitted curve by differentiating the model equation and determining what value of t corresponds to the maximum slope of the curve. Decay rates are given in Table 2 for each of the 35 cases. For the 13 cases having $b_4 \leq 1$, the rate is infinite at the beginning of the curve and is not considered a meaningful measure.

Arizona samples tend to have higher decay rates than Florida or Washington samples, while Washington samples usually have comparatively lower rates of decay. This is supported by the shorter times-to-failure of Arizona samples and the longer lifetimes of Washington samples. Computed maximum rates are as high as 126% per month for PVC-M60 in Arizona and as low as 0.46% per month for PE-60 in Washington. Property loss occurs very rapidly in the former case and extremely slowly in the latter. Non-vinyls generally degrade at a slower rate than the PVC's.

One use of the degradation rate is in comparing the rate of decay of two samples with different induction periods. Although one sample remains stable longer than the other before degrading, the time it takes to reach a point of failure after decay has begun may be equal to that of the sample which decayed early. For example, PVC-B4 in Florida and PVC-A10 in Arizona have nearly equal maximum rates of decay, but PVC-B4 has a characteristic life twice as long as PVC-A10 probably indicating a longer induction period (see plots).

Linear correlations between the parameters b_3, b_4 and b_5 and maximum decay rate were insignificant. When the parameters and decay rate were correlated by site, b_4 and b_5 were moderately correlated (0.60 to 0.75) with the rate for Arizona and Florida cases but not at all for Washington cases. The correlation between b_3 and rate of decay was about 0.50 to 0.60 at all 3 sites.

Several of the plots of b_3 and b_4 vs. maximum rate of decay seemed to show an exponential relationship so all the correlations for these two parameters were repeated using the natural logarithms (ln) of b_3 and b_4. This did not improve the correlations in general but it did have a noticeable effect when the correlations were broken down by site. The correlation between ln b_3 and the decay rate increased to -0.73 in Arizona and -0.82 in Washington while the correlation between ln b_4 and decay rate increased to 0.82 in Florida. Other logarithmic correlations remained about the same.

7. RELATION OF PARAMETERS TO WEATHER

As Kamal has shown [3], exposure variables can be related mathematically to property changes. Our approach differs from Kamal's in that we have described deterioration as a function of time alone, whereas he described deterioration as a function of both time and ultraviolet radiation. The functional form of Kamal's simplified equation (and Daiger and Madson's [4]) is quite similar to ours. However, they did not seem to recognize the relation between their empirical equations and the statistical reliability functions described in this report.

7.1 Linear Approximation Using Exposure Variables

The second stage of Kamal's analysis is quite similar to ours: establish a mathematical relationship between the fitted parameters (b's) and the weather variables (W's). He had sufficient data to use a complete quadratic form; our experiments were not designed to give extensive data of the type necessary for weather analysis. We have made preliminary attempts to associate each of the b's with a simpler linear combination of weather variables:

$$b_i = \sum_j C_{ij} \; W_j$$

where the C's are coefficients of the fit. For example,

$b_3 = C_{31} W_1 + C_{32} W_2 + C_{33} W_3 + C_{34} W_4 + C_{35} W_5$ where W_1 is is ultraviolet radiation, W_2 is langleys, W_3 is air temperature, W_4 is relative humidity and W_5 is inches of rainfall. In addition, two other exposure variables are being examined: thickness of the plastic and "sol-air-temperature" [18]. Sol-air temperature (SAT) is analogous to the "wind-chill index" used by the Weather Bureau to describe the cooling effect of wind blowing over the surface of the skin.

Effective temperature of an exposed material depends on the material's thermal conductivity, absorptivity and emissivity and the weather variables total incident sunlight, ambient temperature and wind. The three weather variables may be combined into one:

$$SAT = T + \frac{a\ L}{w}$$

where T is air temperature, L is langleys, a is a constant for the material (called solar absorptivity [19]), and w is a constant for the material and local environment (called surface conductance [20]). Solar absorptivity (a) is closely related to the color of the material; for example, its value for white PVF film is about 0.2 and its value for black asphalt is about 0.9 [21]. Surface conductance (w) is related to heat losses by conduction, convection and radiation and increases approximately linearly with air velocity. Surface conductance varies from about 2 for windless conditions to about 8-16 (depending on material) for 30 m.p.h. air velocity.

Standardizing these weather variables presents a further refinement, rendering them dimensionless, and significantly simplifying calculations with them [8, 22]. Thus,

$$W' = \frac{W - \overline{W}}{s}$$

where W' is the standardized weather variable, W is the observed weather variable, $\overline{W}$ is the mean of the weather variable for the time under study, and s is the standard deviation from the mean. By using <u>dimensionless weather variables</u>, the solution is unaffected by whether one uses, for example, temperature in °C, °F or °K.

7.2 Multiple Regression Method

The problem of optimizing the model can be broken down into 2 categories:

1) selection of the exposure factors to be included in the model, and

2) determination of the C's for best fit.

There are 5 basic methods [15] for selecting the exposure factors and determining the C's: 1) all possible regressions, 2) backward elimination, 3) forward selection, 4) stagewise regression, and 5) stepwise regression.

Stepwise regression was selected as best for our case, because it consists of "forward selection with a backward glance". It uses forward selection as the basis for variables to enter the model, that is, the exposure variables accounting for the most explained variance of the parameter (b) is selected to enter the model first. The second exposure variable is similarly selected from the remaining exposure variables, then backward elimination is used to eliminate statistically insignificant variables. The F-test is used to calculate significance for entering or leaving the model. This procedure continues until the model contains all the exposure variables considered statistically significant.

A computer program was available at NBS for carrying out this stepwise regression: BMD-02R from the UCLA Biomedical Computer Programs [23]. This program computes a sequence of multiple linear regression equations in a stepwise manner. At each step one variable is added to the regression equation. The variable added is the one which makes the greatest reduction in the error sum of squares, Φ. Variables are automatically removed when their F-values become too low. The algorithm [24] for the program is analogous to the stepwise regression procedures of Draper and Smith [15].

7.3 Preliminary Results

Although this stage of the data analysis is in its infancy, limited sucess has been achieved with stepwise regression procedures. Thickness was included as a variable in addition to the weather variables in this first attempt with stepwise regression. This was done to increase the limited number of data points available for each plastic, because only 2 years of elongation data were available at the time the runs were done. The general model used in these trials was:

$$b_i = C_{iu}\ U + C_{iL}\ L + C_{iT}\ T + C_{iR}\ R + C_{iD}\ D$$

where U, L, T and R are weather variables of ultraviolet radiation, langleys, air temperature and inches of rainfall, respectively. Monthly values averaged over the 3 years of exposure were used for each site. D is thickness of the specimens. Note that sol-air temperature and humidity were not included in these preliminary runs.

It may be expected that b_2, b_3, b_4 and/or b_5 are related to the weather variables. A complicating factor is that b_3 and b_4 were occasionally found to be correlated with each other. Preliminary stepwise regression procedures considered the significance to b_3, b_4 and b_5 (from Marquardt analysis of 24-month data) of thickness, total radiation, UV radiation, temperature and rainfall. Relative humidity was not included because it was found to be highly correlated (non-linearly) with rainfall. Early results indicate that thickness, total and UV radiation, and temperature appear to be the most significant of these variables in the physical degradation of clear PVC's. Thickness, total radiation and rainfall were found significant for white PVC's. Results for polyethylene and polyethylene terephthalate were inconclusive. There appears to be no logical pattern, as yet, for the dependence of b_3, b_4 or b_5 on any set of variables. Much investigation remains to be done on this second stage of the analysis.

Having successfully expressed a set of b's in terms of weather variables, one could then predict the values of the b's from a knowledge of the weather at a given location and from the previously determined coefficients C_{ij}. An estimated lifetime of a plastic in terms of some property may then be calculated from the appropriate model.

8. SUMMARY & CONCLUSIONS

A general method for accurately predicting weatherability of plastics has been outlined. The method is based on statistical characterization of outdoor deterioration as a "wear-out" failure process. The proposed procedure consists of:

a) Measuring significant properties of plastics exposed outdoors and in accelerated-testing devices,
b) Fitting the exposure data with a mathematical model,
c) For a given class of plastics, relating the accelerated and outdoor exposure results, then
d) Calculating outdoor life for a new plastic of the same class from accelerated-testing data.

An additional use of such mathematical models lies in their use to confidently predict future outdoor performance on the basis of behavior measured to the present. As with all prediction procedures, the longer-range the prediction the less certain it is.

Outdoor performance in different climates can be compared by fitting the model to exposure data from different sites and/or relating the parameters of the model to weather variables characteristic of the sites.

The applicability of statistical reliability and failure analysis techniques to weatherability was demonstrated. Use of these techniques was illustrated by fitting a mathematical model (Weibull-type) to physical deterioration data (ultimate tensile elongation) for diverse types of plastics in 3 climates. Criteria for selecting this type of model were: a) exponentially decreasing function, b) asymptotically approaching the time axis, c) describes increasing failure rate with time, d) flexibility, and e) successful application to fatigue problems. In addition, one of its parameters can be associated with "characteristic life" of a material.

Various methods of fitting the model to the data were described, nonlinear least squares analysis being chosen for our purposes. Mathematical aspects of the nonlinear regression were detailed, with emphasis on the parameter constraints and initial estimates of the parameters. Results of the fits were tabulated and shown graphically. Interpretation of the results confirms the less quantitative conclusions of NBS Report #10 014:

a) Arizona deterioration is generally fastest, and Washington generally slowest (confirmed by the calculated maximum degradation rate) -
b) Non-vinyls usually retained elongation longer than PVC (confirmed by the "characteristic life" estimates).

Criteria for determining "goodness of fit" were standard error of the fit, standard errors on the parameters and unexplained variance. In general, fits were best for Arizona data because of their lower scatter.

Because of the statistical nature of the data treatment, it was possible to calculate 95% confidence intervals on the parameters of the model. This is very useful in the practical problem of forecasting performance.

The relation between the parameters of the model and weather variables was discussed. Preliminary results of a multiple linear regression study confirmed that significant weather variables for decrease in elongation may be selected from: ultraviolet and total radiation, temperature, rainfall and humidity.

9. RECOMMENDATIONS

Statistical reliability and failure analysis should be applied to weatherability. Other performance data should be fitted to similar models; our color-difference data will next be tried.

The models should be used to establish correlations between geographic sites, between accelerated testing devices, and between outdoor and accelerated tests. The latter correlation provides the means for quickly and accurately predicting outdoor life.

Significance of the parameters, especially b_2, b_3 and b_4, should be investigated further. Establishing industry-wide "characteristic life" benchmarks for plastics would be invaluable.

Relations should be defined between the model parameters (b's) and weather variables.

Improved fits, and better predictive ability should be obtained by more frequent measurements, especially early in the weathering process.

Relations between these models and those of polymer degradation theory should be calculated.

10. ACKNOWLEDGEMENTS

These are the results of a team effort. Significant suggestions and contributions have been made to the statistical approach by Drs. Brian Joiner and Julius Lieblein of NBS, Mr. Robert Bowles of B. F. Goodrich Chemical Co., Mr. Edwin Harrington of Monsanto Co. and Dr. Wayne Nelson of General Electric Company.

Dr. Alex Craw of NBS has guided us carefully through the statistics, the mathematical model-building and the weather analysis. He was assisted in carrying through the weather analysis by our MCA summer student, Mr. J. A. R. Gould.

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TABLE 1

RESULTS OF NON-LINEAR REGRESSION

$$Y = b_1 \exp\left[-\left(\frac{t + b_2}{b_3}\right)^{b_4}\right] + b_5$$

Plastic	Initial* Value %	b_1 (%)	b_2 (Mos.)	b_3 (Mos.)	b_4	b_5 (%)
(1)PE-1-W	504.0	100.00 ±5.05	0.00	3.24 ±2.34	0.66 ±0.26	0.00
(2)PE-60-A	814.0	94.66 ±19.12	0.00	25.01 ±2.68	5.57 ±3.45	5[illegible].34 ±16.01
-F	814.0	60.40 ±3.76	0.00	16.64 ±0.63	9.95 ±7.61	39.60 ±2.54
-W	814.0	100.00 ±8.55	0.00	167.11 ±867.97	1.62 ±5.50	0.00
(5)PETP-5-A	173.0	100.00 ±5.74	0.00	50.87 ±8.65	1.22 ±0.36	0.00
-F	173.0	100.00 ±12.29	0.00	39.17 ±8.33	1.63 ±0.95	0.00
-W	173.0	100.00 ±9.01	0.00	64.74 ±27.08	1.11 ±0.63	0.00
(7)PVC-B4-A	198.0	97.60 ±7.03	0.00	8.24 ±0.34	6.23 ±1.80	2.40 ±2.88
-F	198.0	95.79 ±7.17	0.00	13.19 ±0.66	4.60 ±1.26	4.21 ±3.77
-W	198.0	97.66 ±16.09	0.00	19.02 ±2.54	2.32 ±0.80	2.34 ±11.53
(8)PVC-B10-A	203.0	99.21 ±1.94	0.00	9.29 ±0.17	2.24 ±0.13	0.79 ±0.85
-F	203.0	100.00 ±15.11	0.00	17.66 ±2.94	1.73 ±0.69	0.00
(9)PVC-B60-A	155.0	100.00 ±10.69	0.00	0.31 ±1.60	0.24 ±0.32	0.00
-F	155.0	100.00 ±13.42	0.00	8.70 ±4.35	0.48 ±0.25	0.00
-W	155.0	100.00 ±11.23	0.00	13.22 ±2.55	0.97 ±0.29	0.00
(10)PVC-C4-W	91.0	97.01 ±1.82	0.00	2.59 ±1.39	1.15 ±0.72	2.99 ±0.74
(11)PVC-C10-A	21.7	100.00 ±4.38	0.00	1.32 ±1.14	0.29 ±0.10	0.00
-F	21.7	86.30 ±8.80	0.00	7.75 ±0.78	2.29 ±0.80	13.70 ±3.64
(13)PVC-N60-A	85.5	93.46 ±1.90	0.00	0.72 ±1.69	0.56 ±0.62	6.54 ±1.01
-F	85.5	97.29 ±18.11	0.00	4.65 ±2.04	0.65 ±0.58	2.71 ±15.71
-W	85.5	100.00 ±15.99	0.00	11.06 ±3.99	0.81 ±0.39	0.00
(14)PVC-A4-A	113.0	97.67 ±1.49	0.00	0.77 ±1.26	0.57 ±0.46	2.33 ±0.78
-W	113.0	105.28 ±9.87	-7.85 ±0.72	12.30 ±1.08	3.33 ±0.94	15.84 ±6.21
(15)PVC-A10-A	155.0	95.59 ±7.21	0.00	6.34 ±0.61	1.96 ±0.70	4.41 ±2.95
-F	155.0	82.20 ±9.26	0.00	11.34 ±0.70	5.51 ±2.60	17.80 ±4.43
(17)PVC-D4-A	191.0	98.57 ±0.33	0.00	0.97 ±0.26	1.00	1.43 ±0.12
-F	191.0	100.00 ±8.63	0.00	10.98 ±1.33	1.31 ±0.33	0.00
-W	191.0	100.00 ±15.84	0.00	14.23 ±1.72	8.01 ±6.67	0.00
(18)PVC-D10-A	14.20	97.38 ±0.65	0.00	4.53 ±0.12	1.74 ±0.14	2.62 ±0.26
(19)PVC-D60-A	50.7	89.88 ±1.72	0.00	2.77 ±0.51	0.75 ±0.16	10.12 ±1.01
-F	50.7	85.20 ±10.66	0.00	4.23 ±2.23	0.99 ±0.92	15.80 ±5.45
-W	50.7	89.08 ±24.84	0.00	6.90 ±4.22	0.71 ±0.64	10.92 ±22.46
(20)PVC-M60-A**	178.0	92.41	0.00	1.90	6.98	7.59
-F	178.0	79.13 ±12.30	0.00	7.78 ±1.74	1.38 ±0.74	20.87 ±6.36
-W	178.0	82.13 ±15.20	0.00	10.59 ±2.44	1.55 ±0.74	17.87 ±8.69

Note: Two sided 95% confidence intervals are given for each of the parameter values.

* These are the unnormalized measured values of ultimate elongation for the original unweathered materials.

** Variance-covariance matrix is singular and no statistical evaluation of the b's was obtained.

ON NORMALIZED ELONGATION DATA (36 MONTHS) TABLE 1

Plastic	No. of Pts. Fitted	PHI*	Std.** Error	Constrained*** Parameters	Convergence	Correlated**** Parameters
(1)PE-1-W	6	19.09	2.52	b2,b5	x	b_3,b_4
(2)PE-60-A	9	350.17	8.37	b2		
-F	8	18.60	2.16	b2	x	
-W	9	175.34	5.41	b2,b5		b_3,b_4
(5)PETP-5-A	9	57.91	3.11	b2,b5		
-F	9	321.95	7.33	b2,b5		
-W	8	113.50	4.76	b2,b5		
(7)PVC-B4-A	8	41.20	3.21	b2	x	
-F	9	70.53	3.76	b2	x	
-W	9	127.71	5.05	b2		
(8)PVC-B10-A	9	3.68	0.86	b2	x	
-F	9	393.46	8.10	b2,b5	x	
(9)PVC-B60-A	9	171.47	5.35	b2,b5	x	b_3,b_4
-F	9	270.51	6.71	b2,b5	x	
-W	8	159.50	5.65	b2,b5		
(10)PVC-C4-W	9	3.47	0.83	b2	x	b_3,b_4
(11)PVC-C10-A	9	28.72	2.19	b2,b5	x	b_3,b_4
-F	9	79.36	3.98	b2	x	
(13)PVC-N60-A	9	3.25	0.81	b2	x	b_3,b_4
-F	9	95.43	4.37	b2	x	
-W	8	320.99	8.01	b2,b5	x	
(14)PVC-A4-A	9	2.00	0.63	b2	x	b_3,b_4
-W	8	58.89	4.43			
(15)PVC-A-10-A	9	53.88	3.28	b2	x	
-F	9	121.36	4.93	b2	x	
(17)PVC-D4-A	9	0.14	0.16	b2,b4	x	
-F	8	94.29	4.34	b2,b5	x	
-W	9	957.53	12.63	b2,b5	x	
(18)PVC-D10-A	8	0.35	0.29	b2	x	b_3,b_4
(19)PVC-D60-A	9	2.37	0.69	b2	x	b_3,b_4
-F	9	104.15	4.56	b2	x	
-W	8	98.90	4.97	b2	x	b_1,b_5
(20)PVC-M60-A	9	12.51	1.58	b2	x	
-F	9	134.51	5.19	b2	x	
-W	9	180.38	6.01	b2	x	

*PHI = $\Phi = \sum_{i=1}^{n} [Y_i - Y_i']^2$ where $Y_i - Y_i'$ is the difference between the observed Y and the Y predicted by the model, for a given value of x for each of the n data points fitted.

**Std. Error = $[\Phi/(n-k)]^{\frac{1}{2}}$ for the n data points fitted and k parameters of the model.

***Parameters set equal to the indicated values and not allowed to vary during the regression.

****Parameters with correlation coefficients equal to or greater than 0.9.

TABLE 2

CHARACTERISTIC-LIFE & MAXIMUM-DEGRADATION-RATE

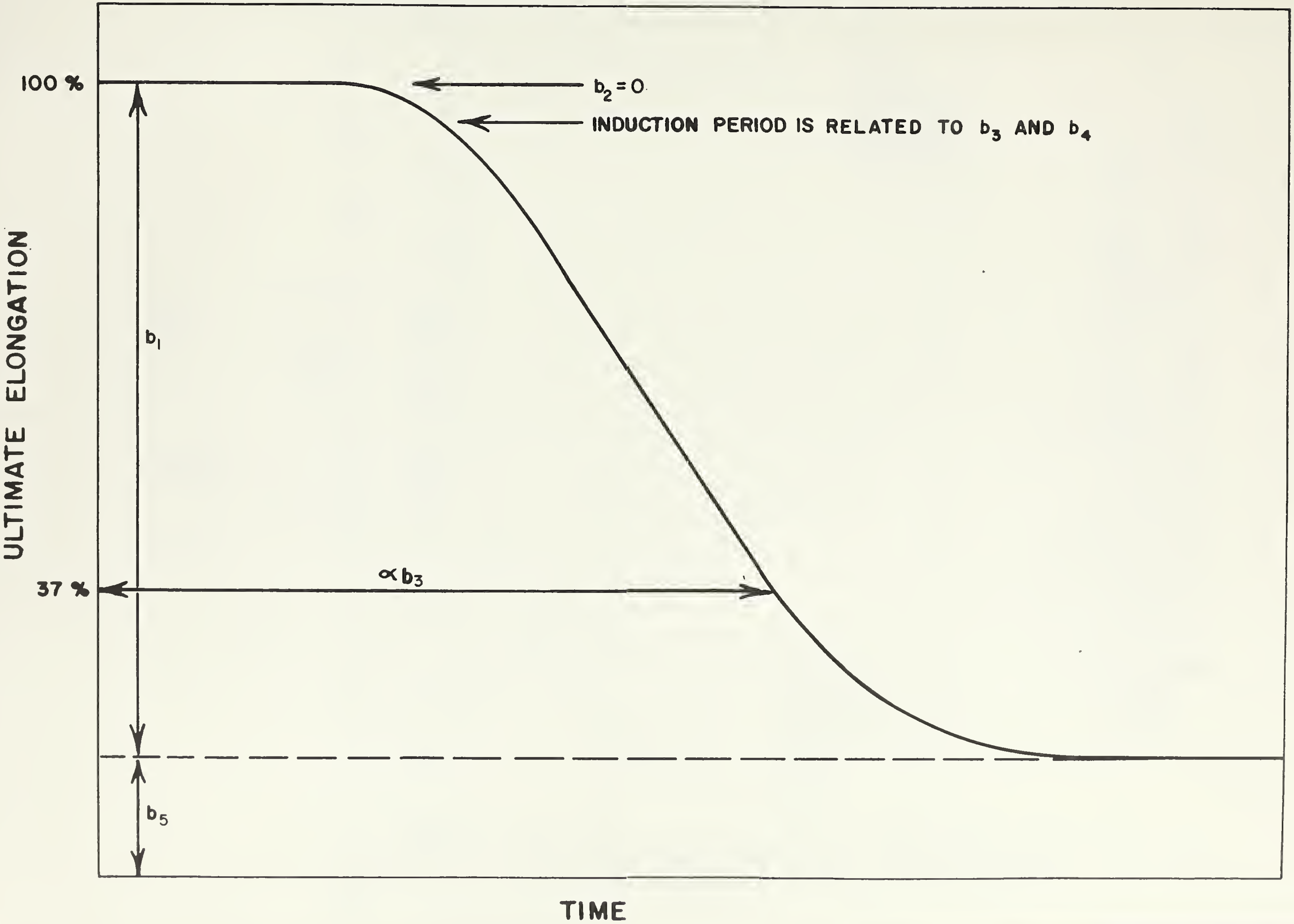
Plastic	Site	Characteristic Life*	Maximum Rate**
(1) PE-1	W	3.24 months	** %/month
(2) PE-60	A	25.45	7.89
	F	***	13.36
	W	167.10	0.46
(5) PETP-5	A	50.87	1.47
	F	39.17	1.96
	W	64.74	1.23
(7) PVC-B 4	A	8.30	27.52
	F	13.41	12.61
	W	19.36	4.89
(8) PVC-B 10	A	9.35	9.91
	F	17.66	4.46
(9) PVC-B 60	A	0.31	**
	F	8.70	**
	W	13.22	**
(10) PVC-C 4	W	2.71	28.99
(11) PVC-C 10	A	1.32	**
	F	8.74	10.51
(13) PVC-N 60	A	0.89	**
	F	5.01	**
	W	11.06	**
(14) PVC-A 4	A	0.83	**
	W	22.05	11.03
(15) PVC-A 10	A	6.60	12.77
	F	12.15	14.95
(17) PVC-D 4	A	0.99	**
	F	10.98	6.70
	W	14.23	20.88
(18) PVC-D 10	A	4.65	16.99
(19) PVC-D 60	A	3.59	**
	F	5.90	**
	W	9.30	**
(20) PVC-M 60	A	1.94	126.24
	F	10.95	7.47
	W	13.57	5.84

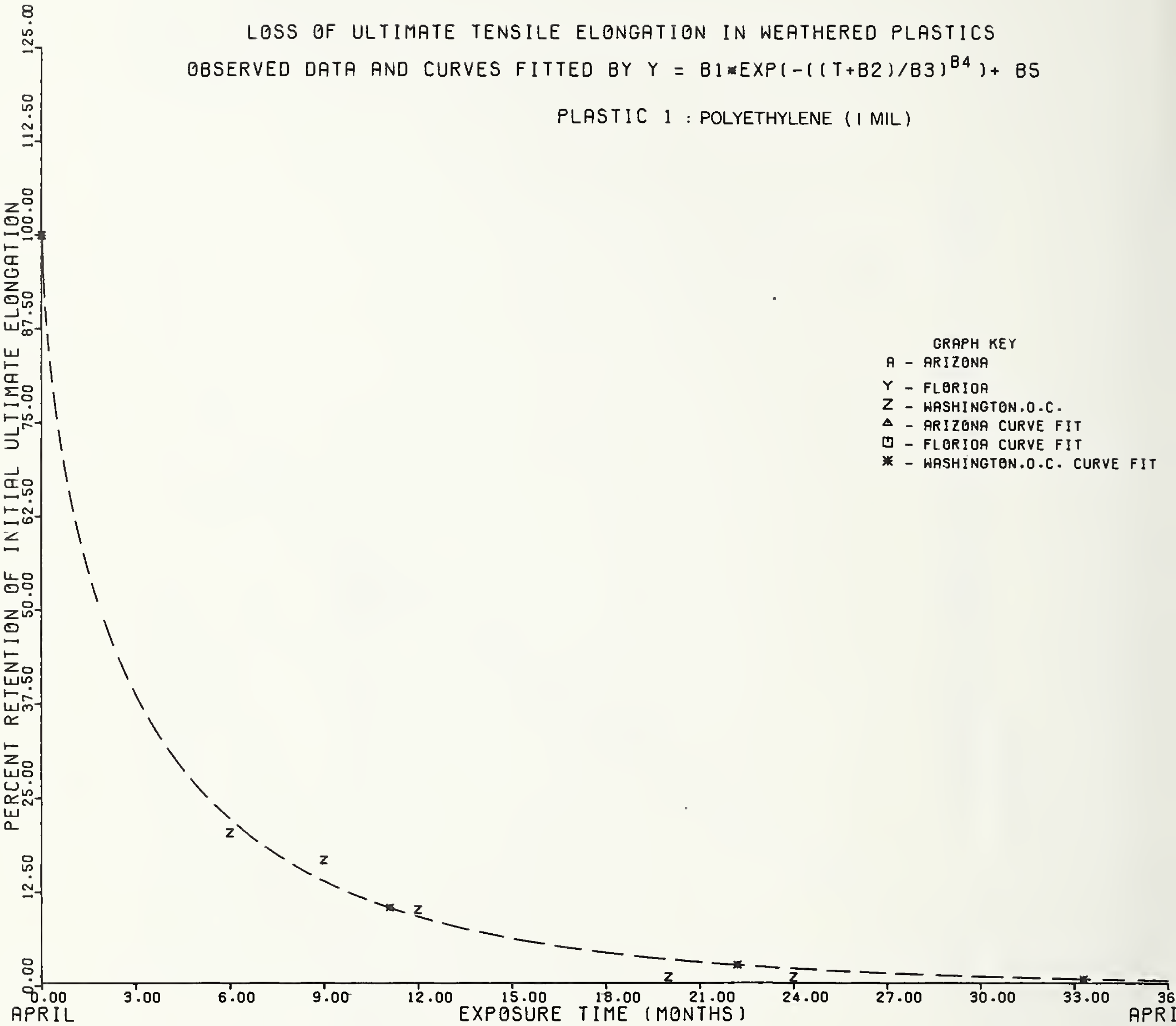
* Time for property to reach 36.8% of original value. See Section 6 of text for method of calculation.

** Maximum slope of fitted curve. For $b_4 \leq 1$, rate is infinite at time = 0, and therefore not considered a meaningful measure.

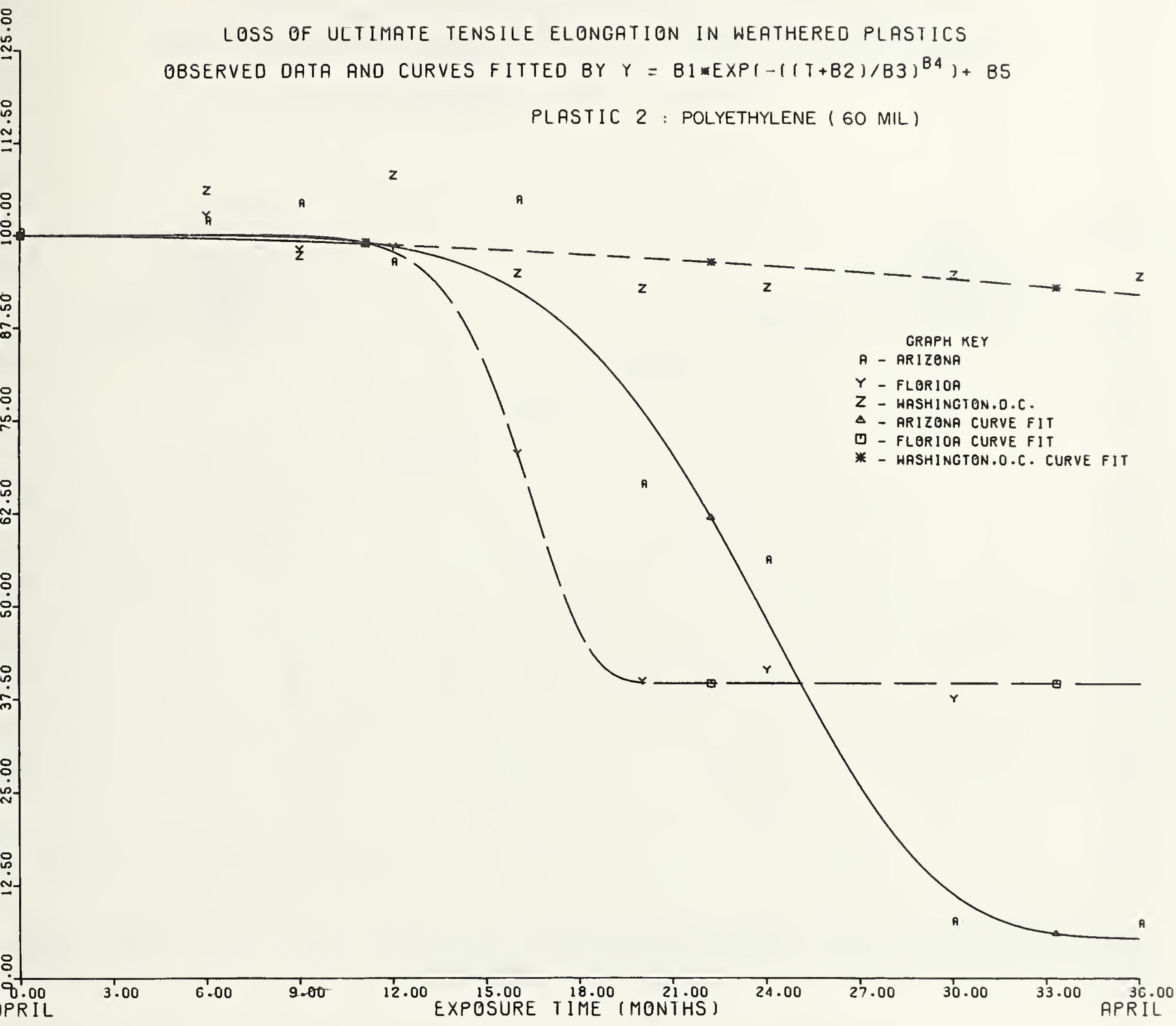
*** Asymptote, b_5, is 39.6% which is greater than 36.8%.

TYPICAL DECREASE OF ELONGATION WITH WEATHERING

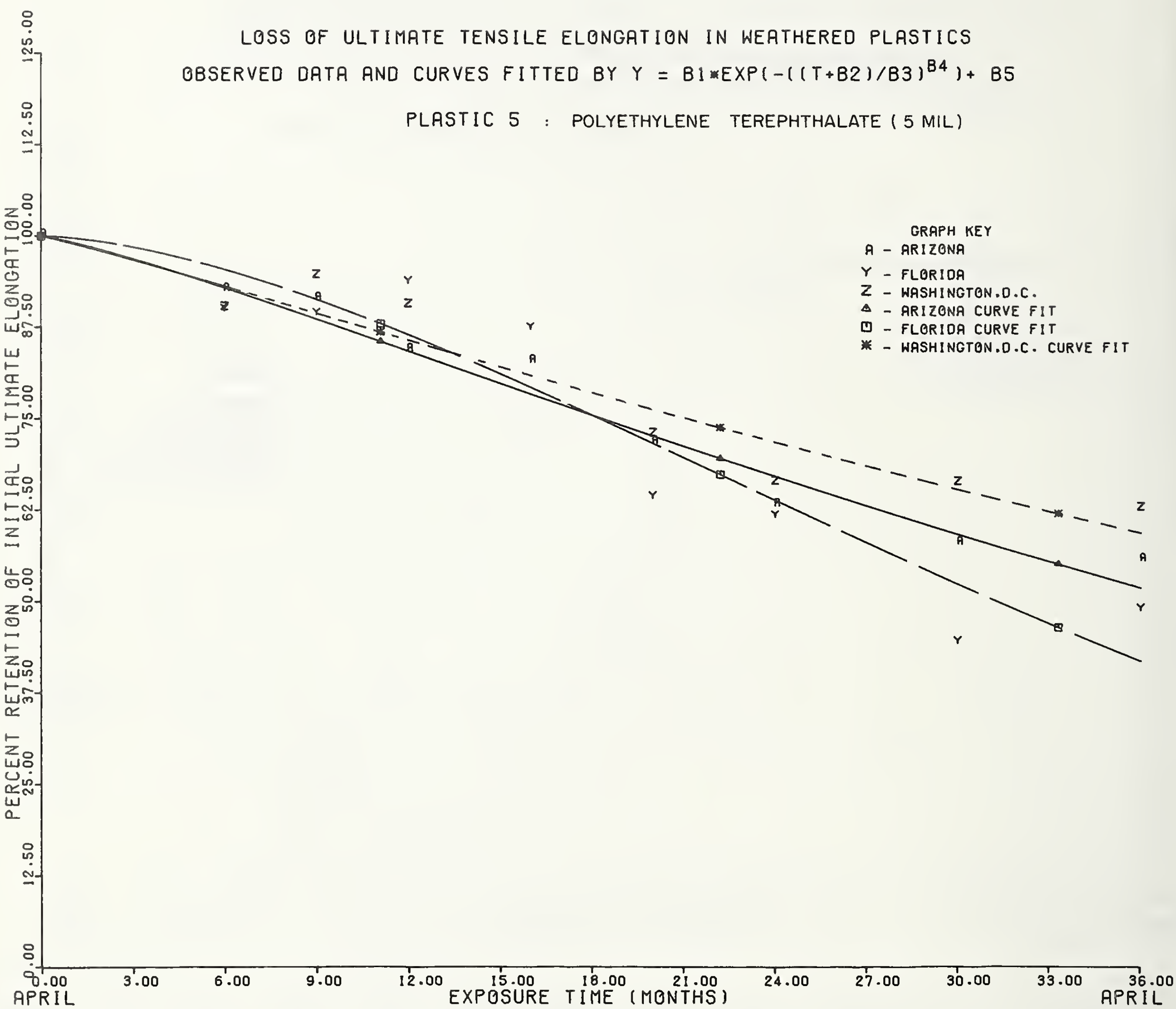




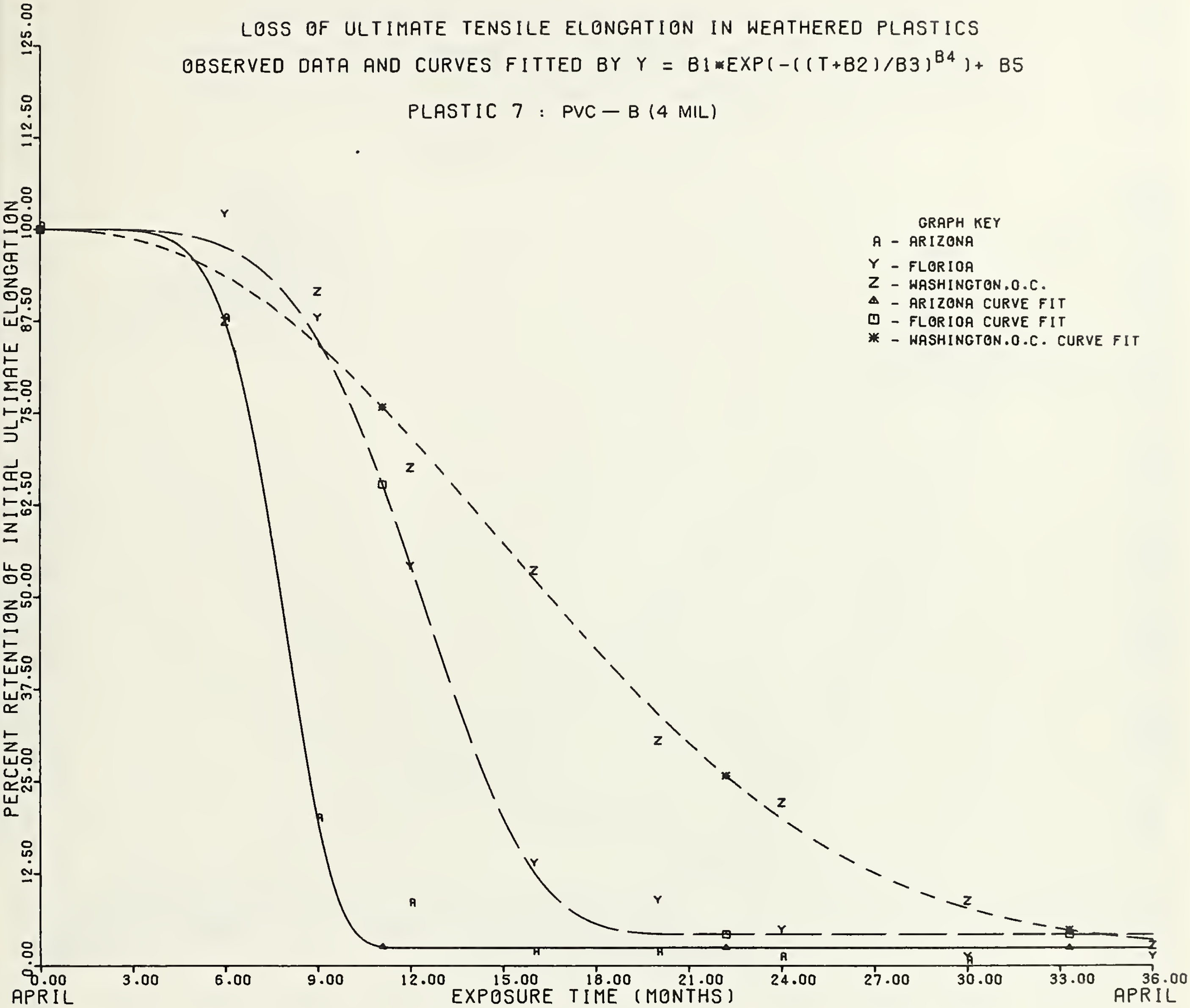
	b_3 (months)	b_4
Washington, D.C.	3.24	0.66



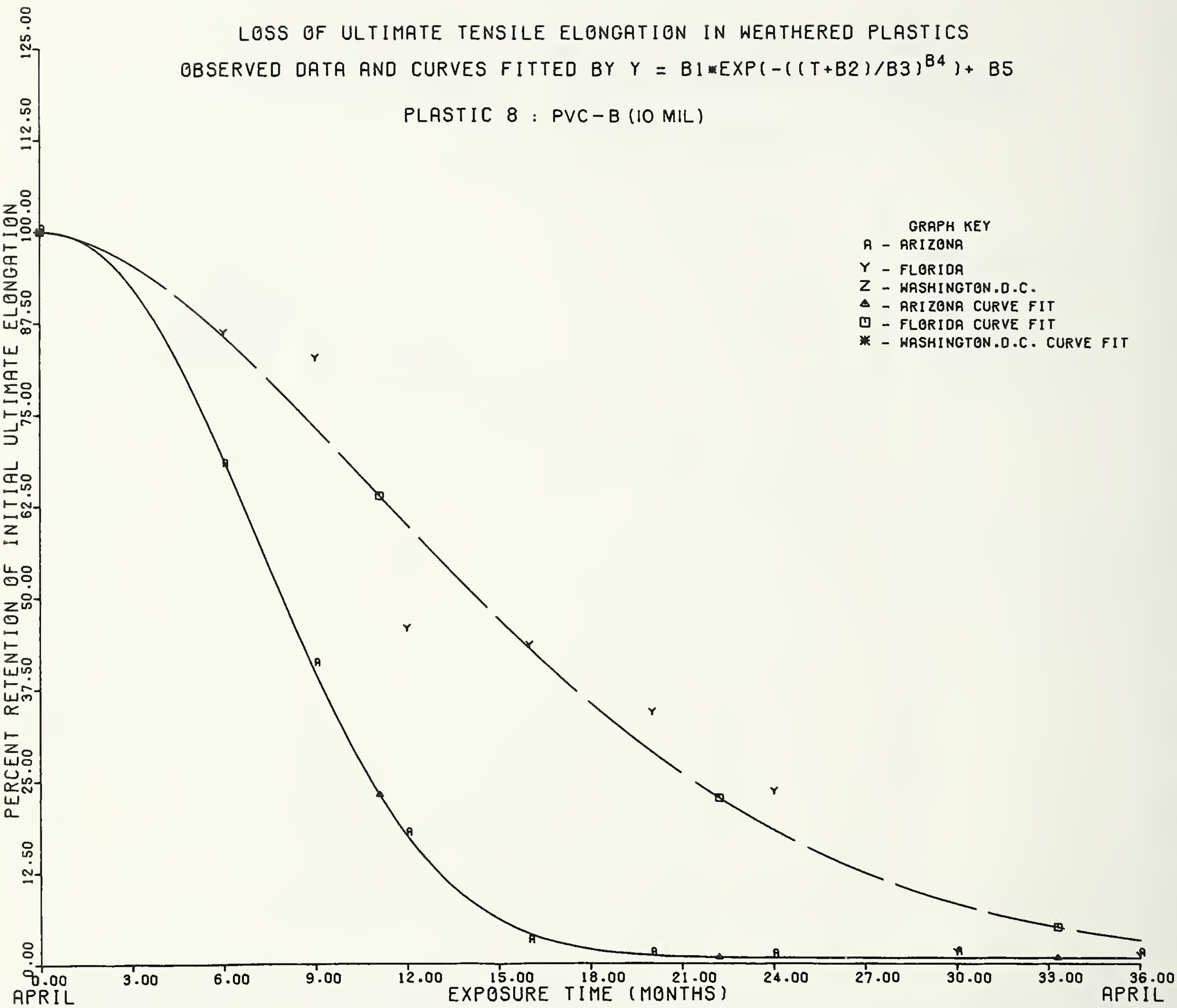
	b_3 (months)	b_4
Arizona	25.0.	5.57
Florida	16.64	9.95
Washington, D.C.	167.11	1.62



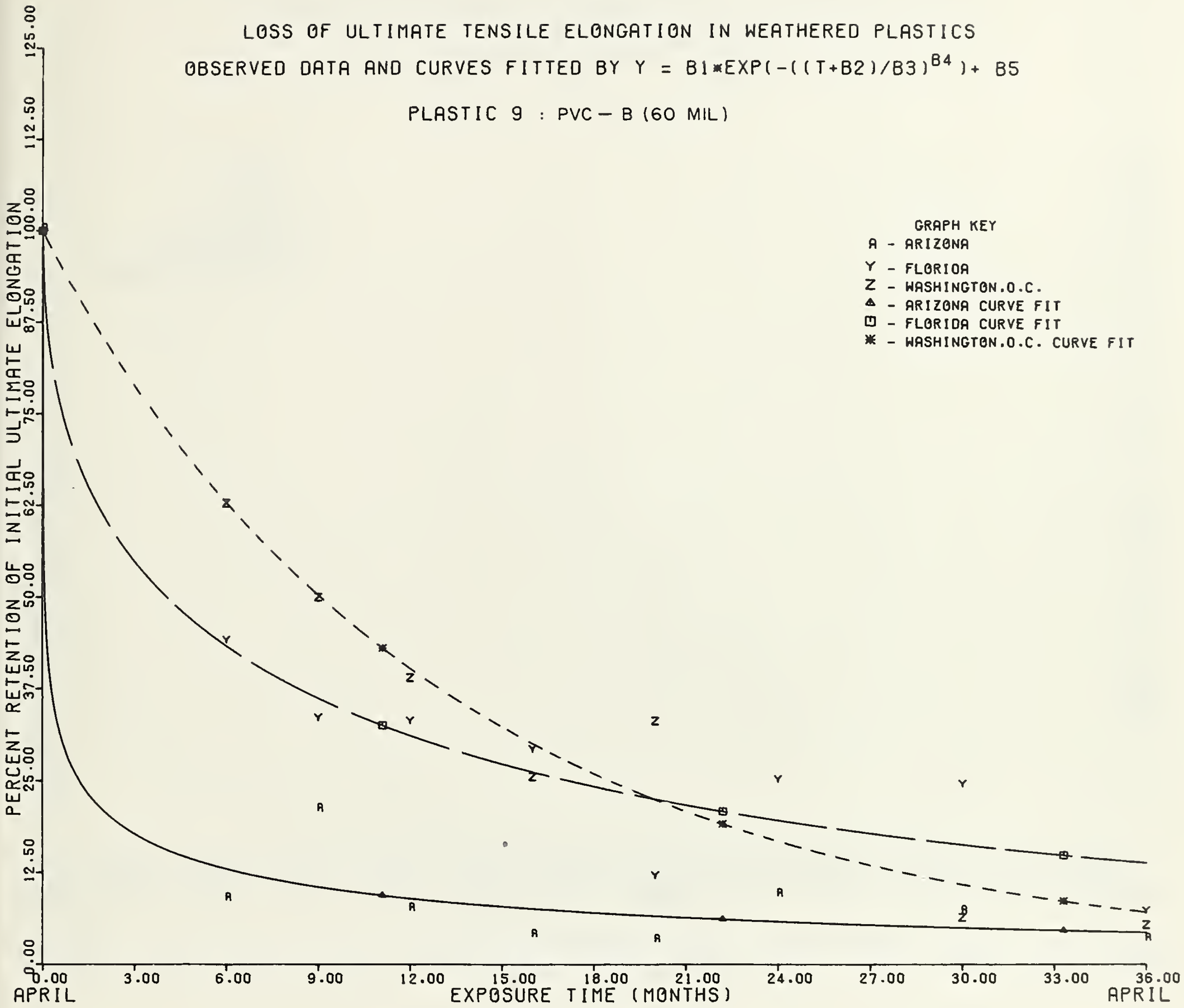
	b_3 (months)	b_4
Arizona	50.87	1.22
Florida	39.17	1.63
Washington, D.C.	64.74	1.11



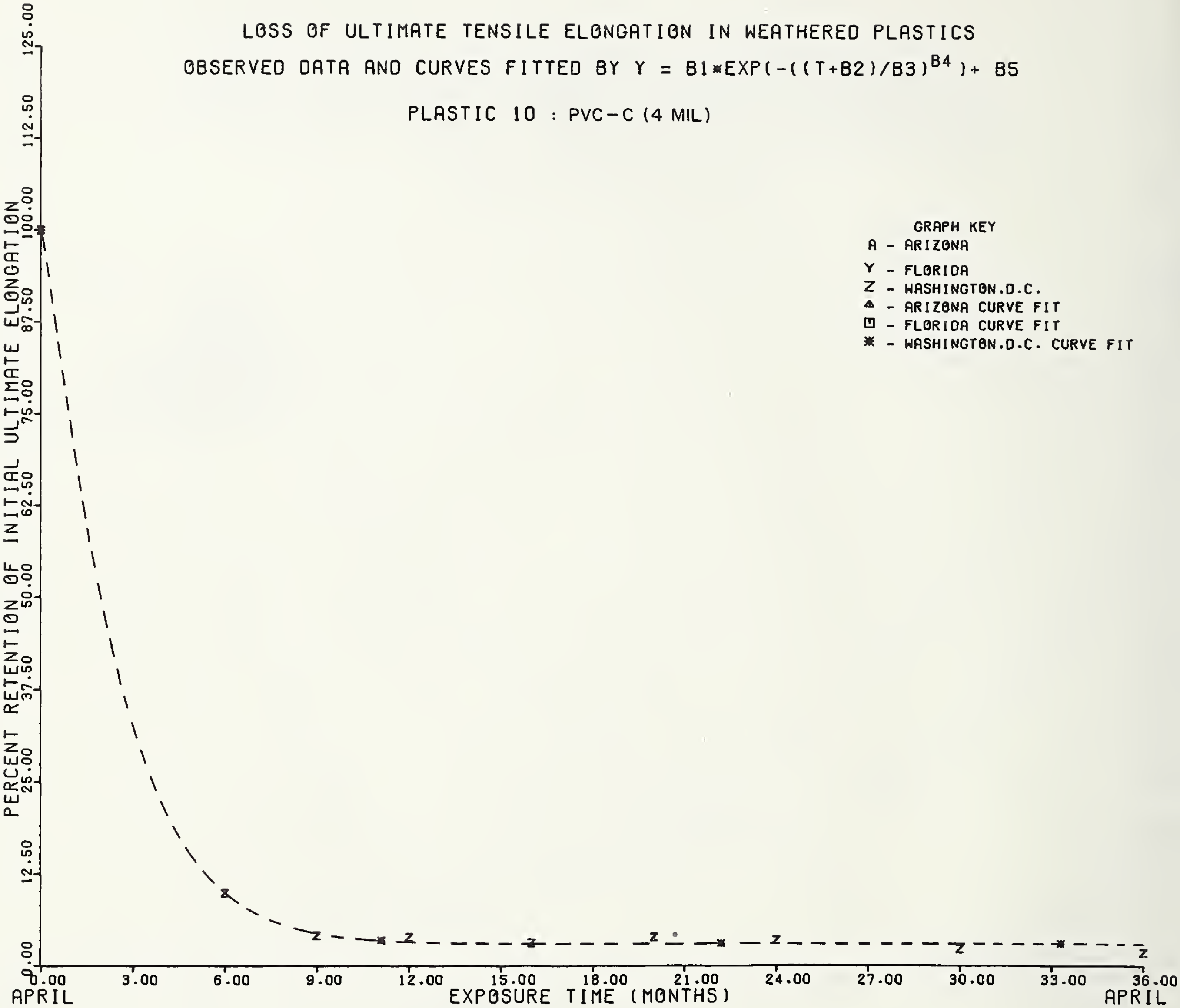
	b_3 (months)	b_4
Arizona	8.24	6.23
Florida	13.19	4.60
Washington, D.C.	19.02	2.32



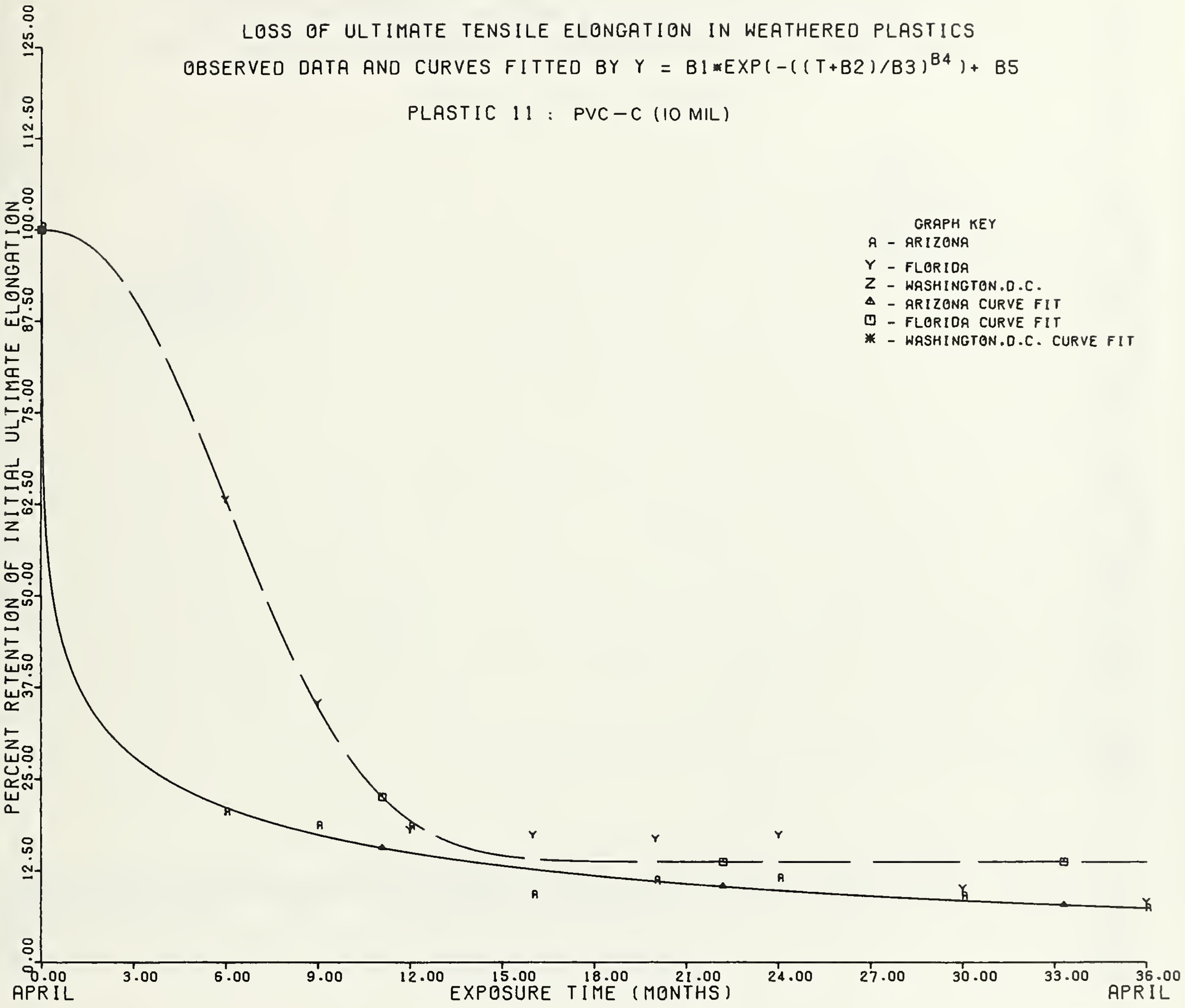
	b_3 (months)	b_4
Arizona	9.29	2.24
Florida	17.66	1.73



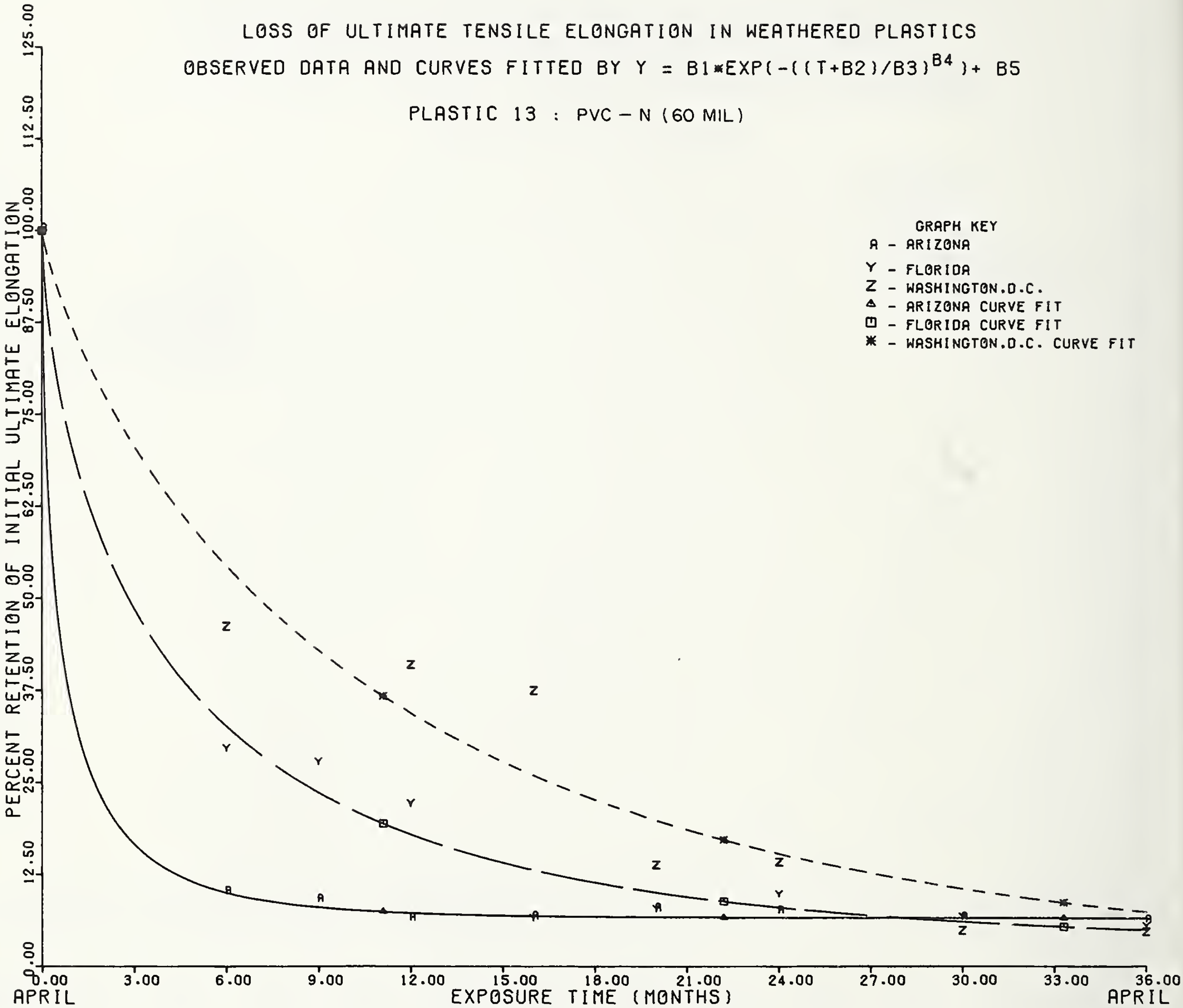
	b_3 (months)	b_4
Arizona	0.31	0.24
Florida	8.70	0.48
Washington, D.C.	13.22	0.97



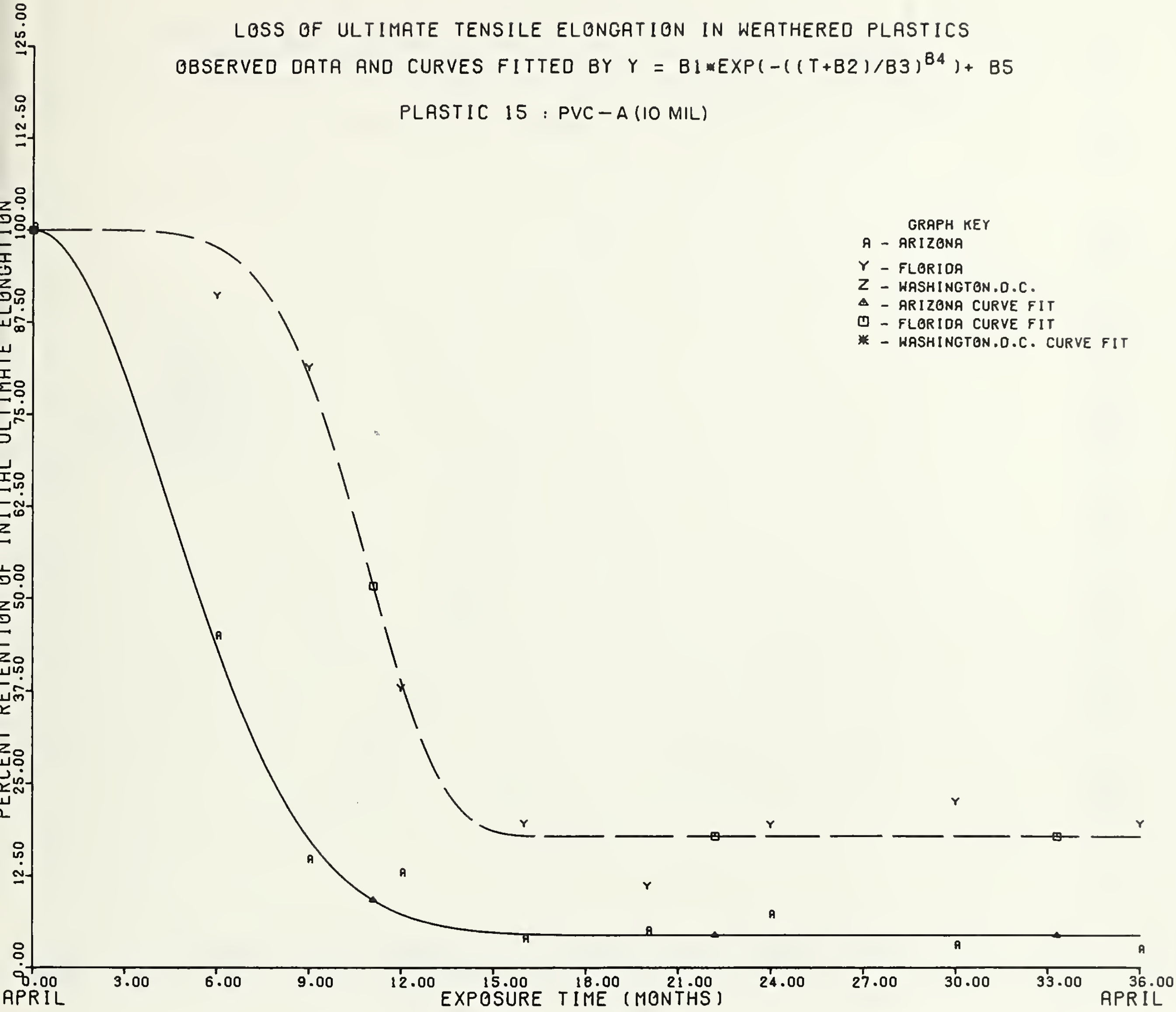
	b_3 (months)	b_4
Washington, D.C.	2.59	1.15



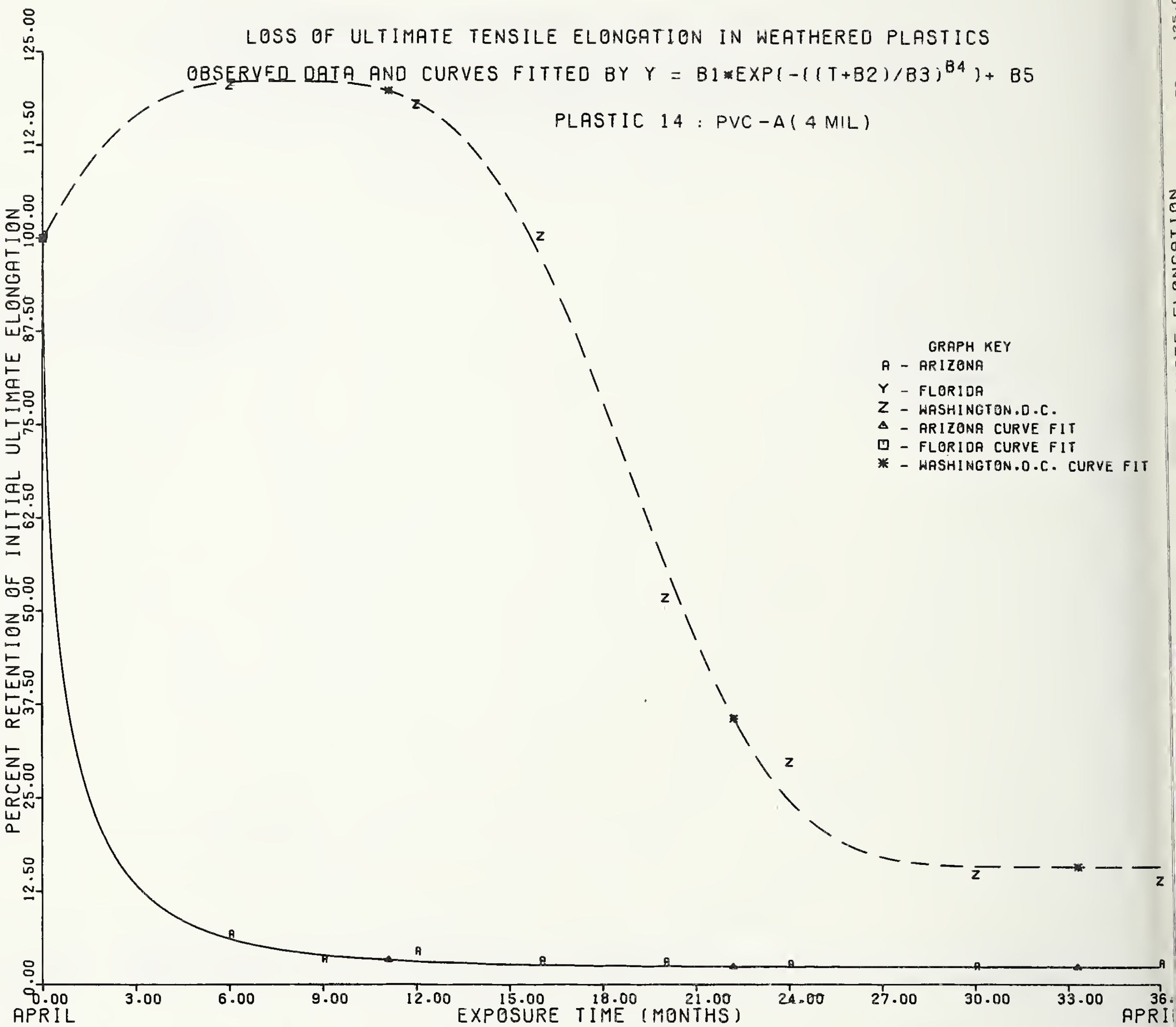
	b_3 (months)	b_4
Arizona	1.32	0.29
Florida	7.75	2.29



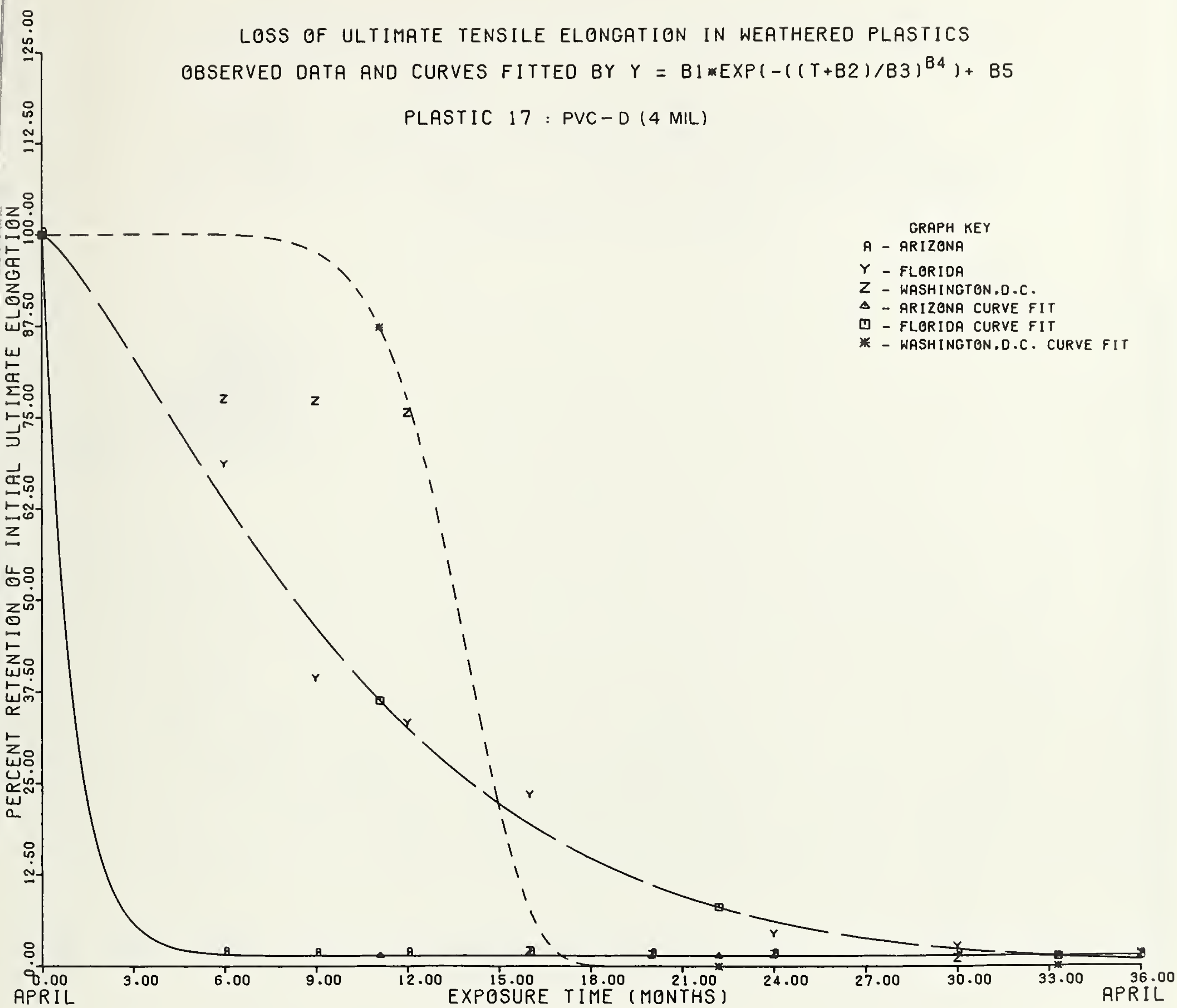
	b_3 (months)	b_4
Arizona	0.72	0.56
Florida	4.65	0.65
Washington, D.C.	11.06	0.81



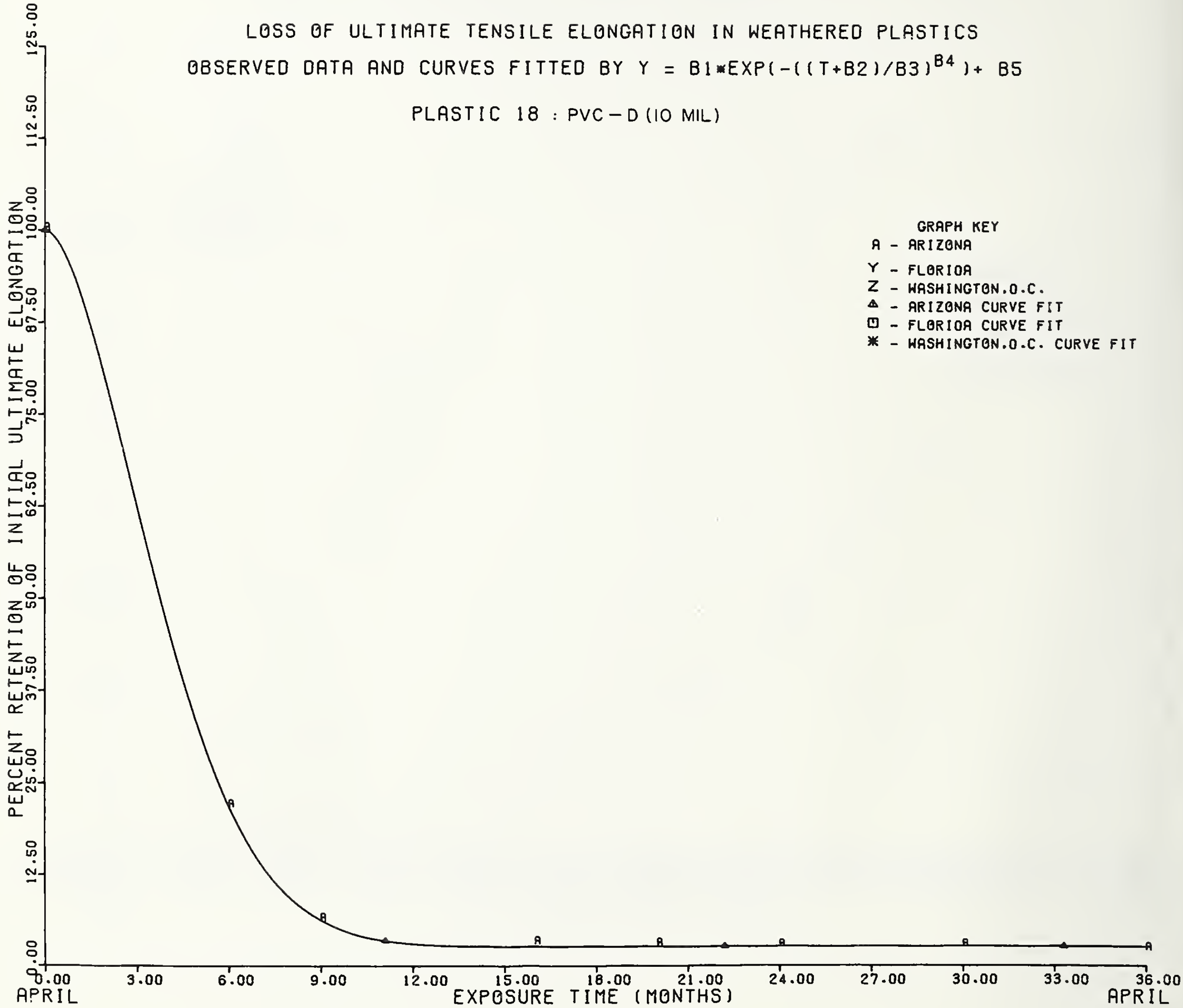
	b_3 (months)	b_4
Arizona	6.34	1.96
Florida	11.34	5.51



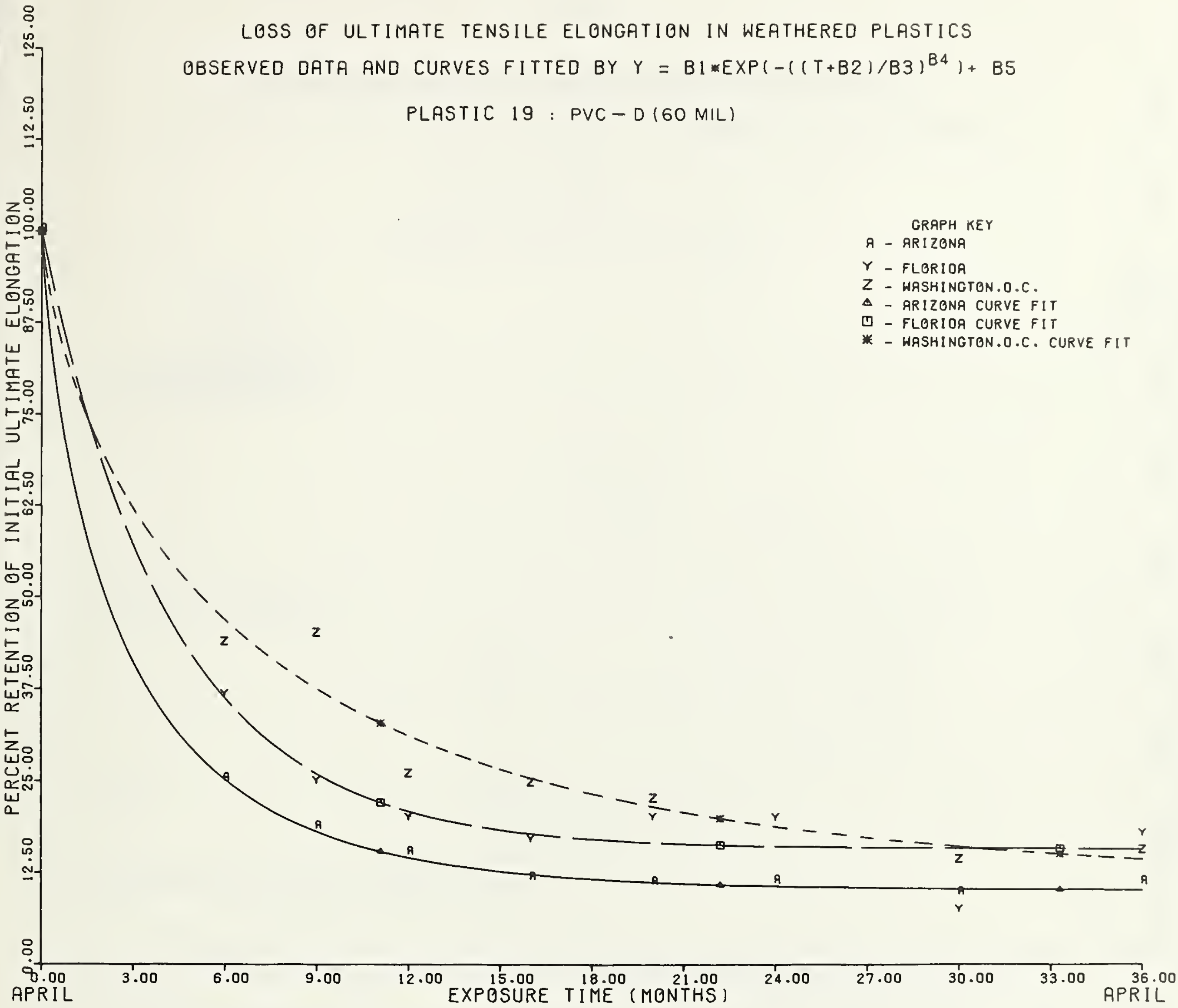
	b_2	b_3	b_4
Arizona	0.00	0.77	0.57
Washington, D.C.	-7.85	12.30	3.33



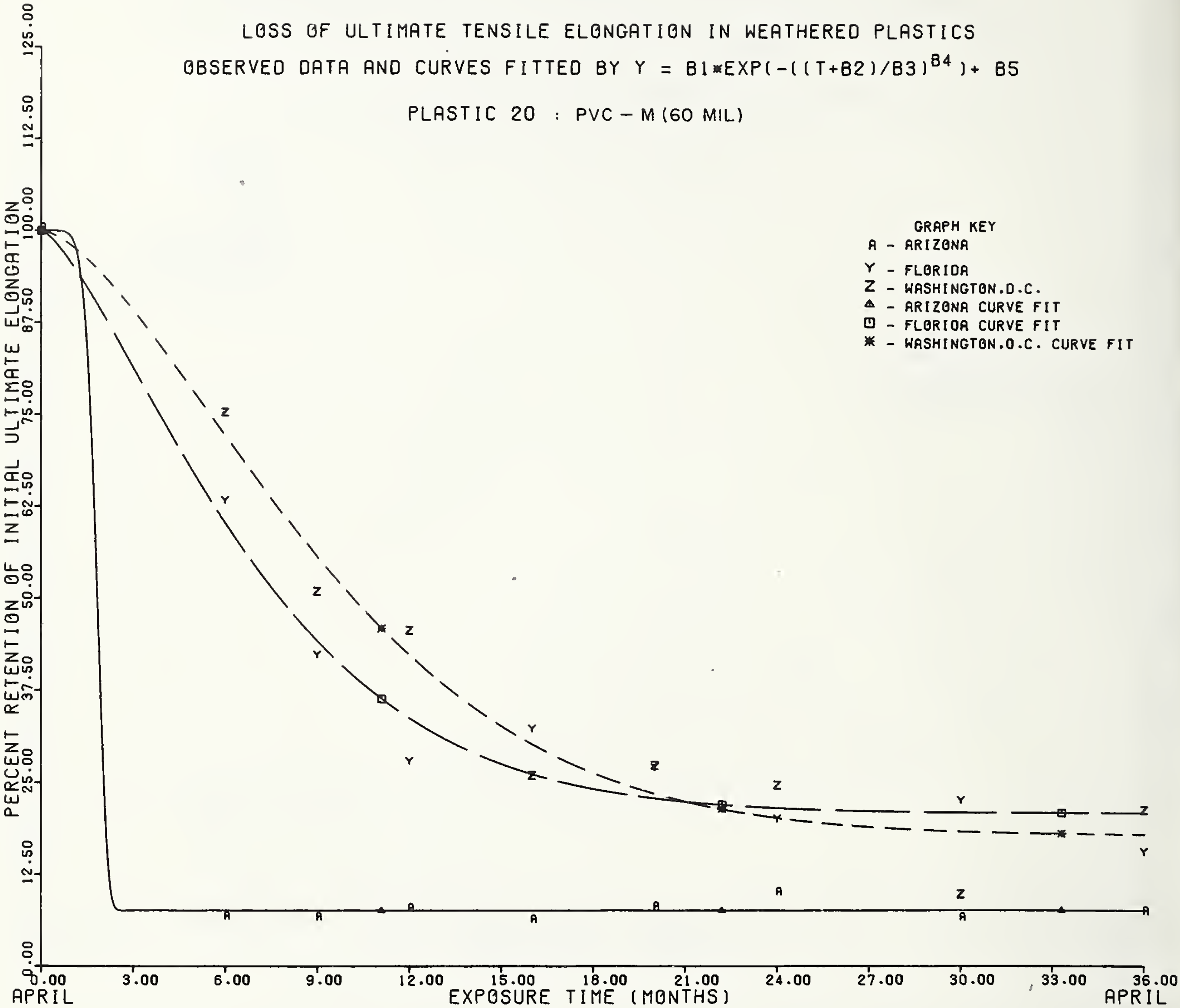
	b_3 (months)	b_4
Arizona	0.97	1.00
Florida	10.98	1.31
Washington, D.C.	14.23	8.01



	b_3 (months)	b_4
Arizona	4.53	1.74



	b_3 (months)	b_4
Arizona	2.77	0.75
Florida	4.23	0.99
Washington, D.C.	6.90	0.71



	b_3 (months)	b_4
Arizona	1.90	6.98
Florida	7.78	1.38
Washington, D.C.	10.59	1.55

APPENDIX

MATHEMATICAL PROPERTIES OF THE SELECTED FUNCTION

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We shall summarize the types of curves possible from the five (5) parameter family

$$R = b_1 \exp\left[-\left(\frac{t+b_2}{b_3}\right)\right]^{b_4} + b_5 \qquad (1)$$

by exhibiting a series of graphs. To make life a little easier we consider a simpler function

$$P\ (T) = \frac{R-b_5}{b_1} = \exp\ (-T^{\beta}) \qquad (2)$$

where $$T = \frac{t+b_2}{b_3}, \quad \beta = b_4$$

This function has all the geometric properties of (1).

The function P(T) is defined and real for all $T>0$ and all real positive β, and over the range $0<T<\infty$ P(T) is a monotone decreasing function.

For T fixed

$$\lim_{\beta\to\infty} P(T) = \begin{cases} 1 & \text{for } 0<T<1 \\ e^{-1} & \text{for } T=1 \\ 0 & \text{for } 1<T<\infty. \end{cases}$$

All curves of the family pass through $(1, e^{-1})$ and $P(T) \to e^{-1}$ as $\beta\to 0^+$.

For $T>0$, P(T) assumes the constant value e^{-1} when $\beta=0$.

These facts are summarized in the Figures 1, 2, and 3.

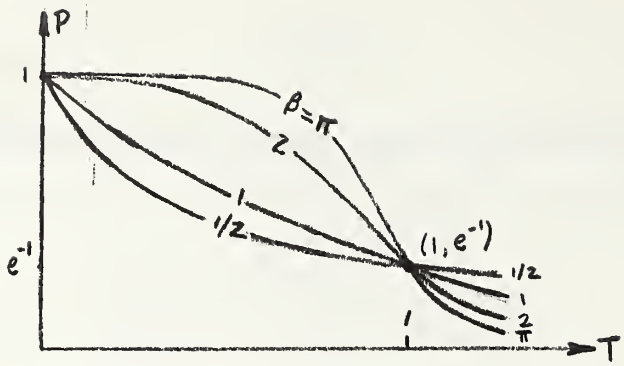

Figure 1: P(T) for T$\geq$0, β>0

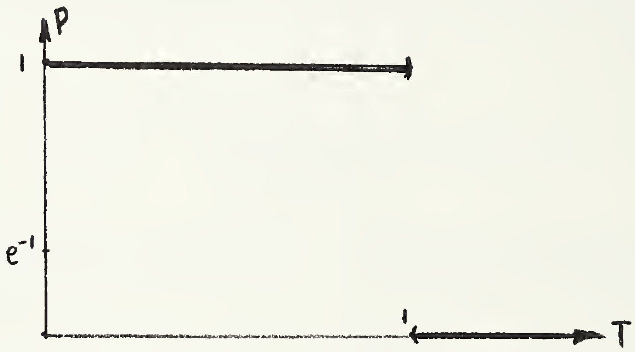

Figure 2: Limiting values of P(T) as β→∞, T>0

Figure 3: P(T) for β=0, T>0

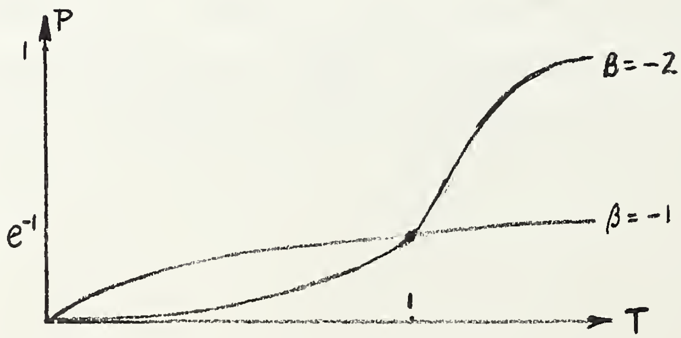

Figure 4: P(T) for β<0, T>0

For $T>0$ and all real $\beta<0$, $P(T)$ is an increasing function of T and $P(T)\to 1$ as $T\to\infty$, $\beta<0$ (see Figure 4).

The function $P(T) = \exp(-T^\beta)$ is real only for special values of the parameter β when T is negative. To see this, let z be a complex variable. The function e^{-z} can be written

$$e^{-z} = e^{-x}(\cos y - i \sin y) = u + i\, v, \quad z = x + i\, y$$

$$= e^{-x}\cos y - i\, e^{-x}\sin y$$

or $$u = e^{-x}\cos y, \quad v = -e^{-x}\sin y.$$

e^{-z} is real only for $v = -e^{-x}\sin y = 0$, i.e., only for $\sin y = 0$

i.e., $y = 0 \pm m\pi$, m an integer. Thus, for $z = T^\beta$,

e^{-T^β} is real for $T<0$ only if T^β is real or is a complex number of the form $x + m\pi i$, where m is an integer.

For $T<0$ we can write

$$T = |T|\,[\cos(1+2n)\pi + i\sin(1+2n)\pi] \quad n \text{ an integer}$$

and $T^\beta = |T|^\beta\,[\cos\beta(1+2n)\pi + i\sin\beta(1+2n)\pi] = U + i\,V$

$V = 0 = |T|^\beta \sin\beta(1+2n)\pi$, which holds for all $T<0$

only for $\beta = \frac{k}{1+2n}$, k, n integers.

The case V a complex number of the form $x + m\pi i$ leads nowhere, for this would require for all $T<0$ that

$$|T|^\beta = \frac{m\pi}{\sin\ \beta(1+2m)\pi}$$, an impossibility, except for $m=0$.

Thus $P(T) = e^{-T^\beta}$ is real only for special values of the parameter β when T is negative. The only allowable values for β are those for which β belongs to the set of rational numbers with odd integer denominators. Thus, $\beta = 1/2$ or $(1/2)^k$ is not permissible for $T<0$; by the same token, β cannot be an irrational number and have $P(T) = e^{-T^\beta}$ real for $T<0$. To repeat, no graph of the function $P(T) = e^{-T^\beta}$ appears for $t<0$ except for special values of β.

We will examine the value T = -1 for various allowable β.

$$(-1)^{\beta} = 1^{\beta}\,[\cos \beta(1+2n)\pi + i \sin \beta(1+2n)\pi] = \begin{cases} +1, & \beta \text{ even integer} \\ -1, & \beta \text{ an odd integer} \end{cases}$$

For β = 1/3

$$(-1)^{1/3} = \cos\left(\frac{1+2n}{3}\right)\pi + i \sin\left(\frac{1+2n}{3}\right)\pi$$

$$= \begin{cases} \cos \frac{\pi}{3} + i \sin \frac{\pi}{3}\,, & n = 0 \qquad \text{(non-real)} \\ -1\,, & n = 1 \qquad \text{(real)} \\ \cos \frac{5\pi}{3} + i \sin \frac{5\pi}{3}\,, & n = 2 \qquad \text{(non-real)} \end{cases}$$

For β = 2/3

$$(-1)^{2/3} = \left((-1)^{1/3}\right)^{2} = \begin{cases} \cos \frac{2\pi}{3} + i \sin \frac{2\pi}{3} & \text{(non-real)} \\ +1 & \text{(real)} \\ \cos \frac{10\pi}{3} + i \sin \frac{10\pi}{3} & \text{(non-real)} \end{cases}$$

In general, for β = k/m, m odd integer $(-1)^{k/m} = \begin{cases} -1 & k \text{ odd} \\ +1 & k \text{ even} \end{cases}$

The graphs of $P(T) = e^{-T^{\beta}}$ are illustrated for some select β.

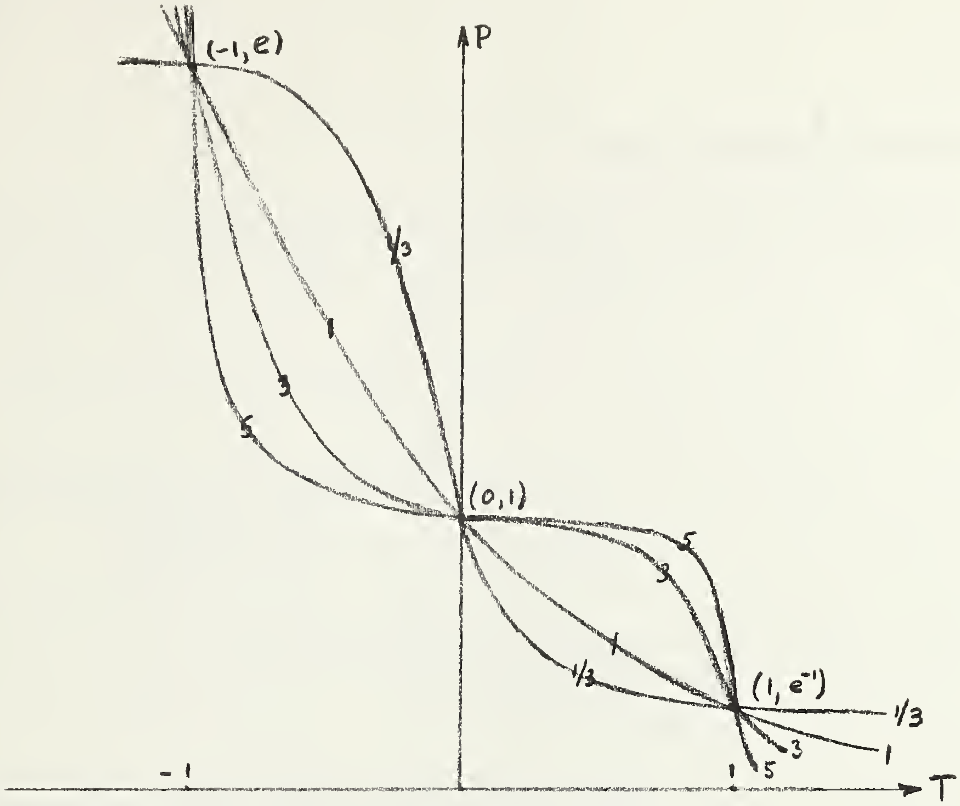

Figure 5: P(T) for β = k/m > 0, k, m odd integers

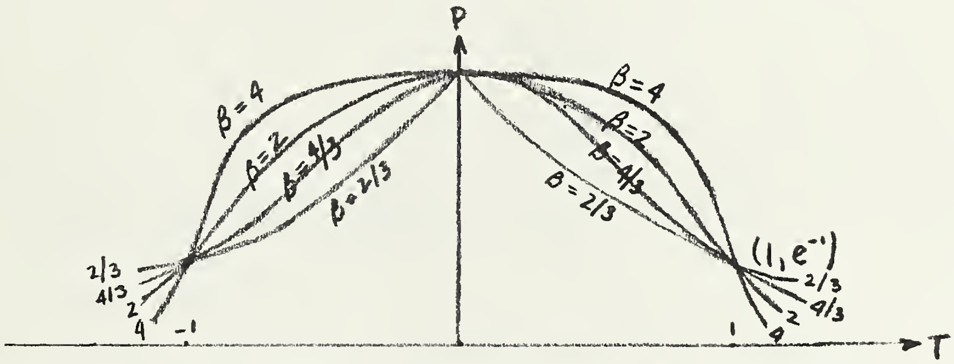

Figure 6: P(T) for β = k/m > 0, k even integer, m odd integer

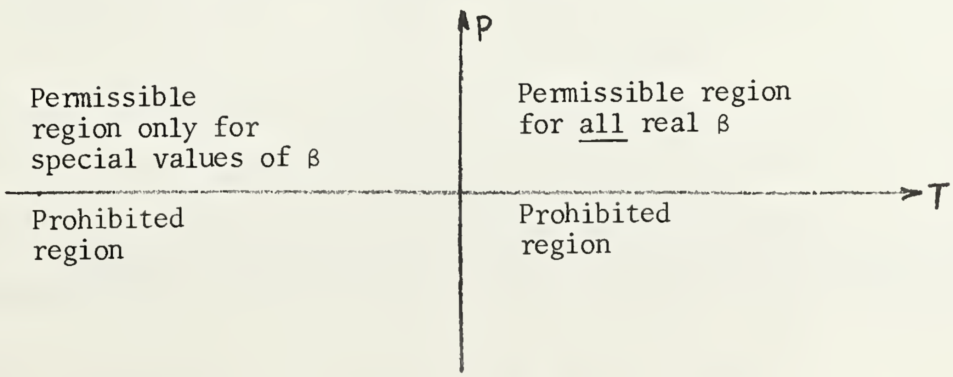

Figure 7: Permissible and prohibited regions for graphs of P(T)

Application to Empirical Data

For data which show the function P to be decreasing over the entire range we want $\beta>0$. For data which show P to increase for a while and then decrease, we will have to choose $\beta = (k/m)>1$ where k is an even and m an odd integer, or resort to another functional form $P^* = e^{-|T|^{\beta}}$, which is defined and real for all real β; to avoid cusps at T = 0, select $\beta>1$.

Returning to the function (1) we thus want $b_4 = \beta$ to be positive or, in the case of increasing P followed by decreasing P, b_4 should be greater than 1 and have the special form $b_4 = \beta = k/m$ mentioned above.

Since $T = (t+b_2)/b_3$, we will want $b_3>0$ to keep the directions of t and T the same. Alternatively, equation (1) can be written

$$R = b_1 \exp\left[-B_3(t+b_2)^{b_4}\right] + b_5 \tag{1'}$$

where $B_3 = \left(\frac{1}{b_3}\right)^{b_4} = b_3^{-b_4}$ and where we want B_3 to be real. If one were to permit $b_3<0$, then, as before, $b_3 = |b_3|\, e^{\pi i}\, e^{2n\pi i}$ and

$$b_3^{-b_4} = |b_3|^{-b_4}\, e^{-b_4(1+2m\pi)i}$$

which is in general a complex number that is a real number only if b_4 belongs to a special set of numbers. However, we would like to assume any value in the continuum. Thus from the outset we restrict b_3 to be positive.

b_1 and b_5 are fitting constants that have the physical dimensions of the property R. b_2 and b_3 have the physical dimensions of the variable t (here time), while b_4 is dimensionless. Since $R>0$, $b_4>0$, $b_3>0$, $\lim_{t\to\infty} R = b_5$, we will want $b_5>0$. Also $\lim_{t\to -b_2} R = b_1+b_5$. Obviously we want $b_1>0$. b_5 is the asymptotic value of P for large $t>0$. b_1+b_5 is the maximum value of the property and occurs at $t = -b_2$. If b_2 is positive, this maximum value will occur at a negative value of t and one will not be able to get an estimate of b_1+b_5 from the observed data. But for the case of decreasing R, a good guess for the starting value of b_1+b_5 can be obtained from the observation at t = 0.

If $b_2 > 0$, say $b_2 = 2$ and $b_3 = 1$ for convenience, then graphically

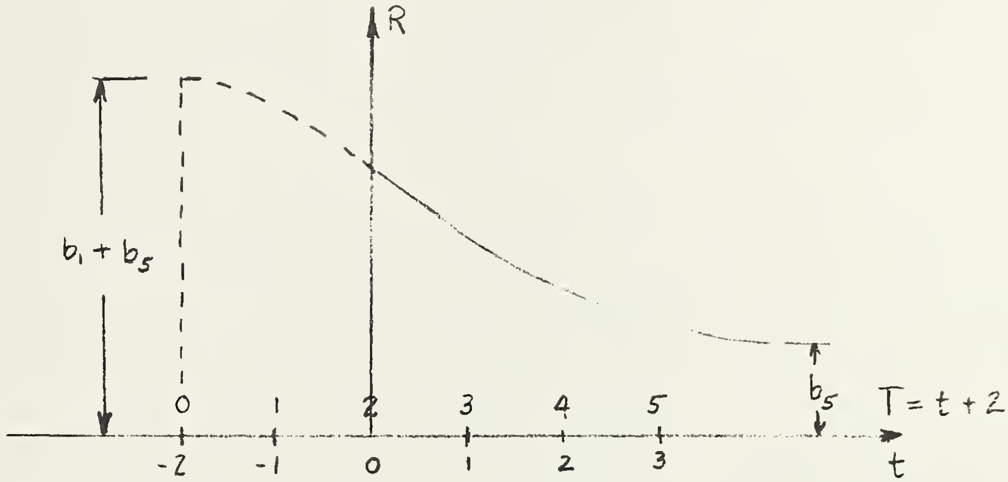

Figure 8: R(t) for $b_2 = 2$, $b_3 = 1$, $b_4 > 0$

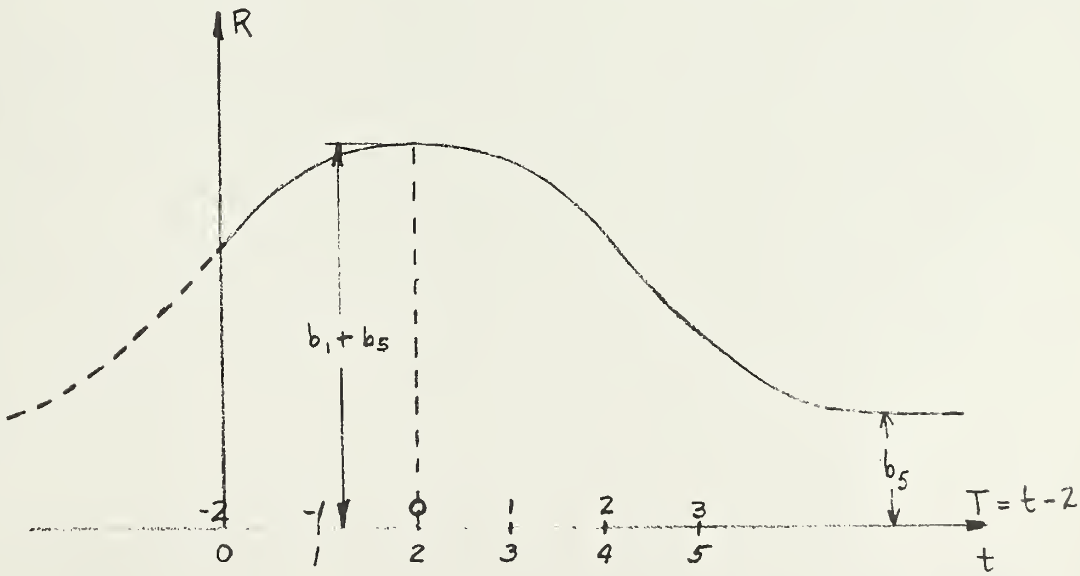

Figure 9: R(t) for $b_2 = -2$, $b_3 = 1$, $b_4 > 0$ with $\left\{ \begin{array}{l} \text{even numerator} \\ \text{odd denominator} \end{array} \right.$

If the curve of R against t first increases and then decreases (as in Figure 9) then we would want to take initially $b_2<0$, and b_4 of special form.

If we have a nearly constant R for some time followed by a decline of R then one would probably want $b_2 = 0$, b_4 large and positive (Figure 10).

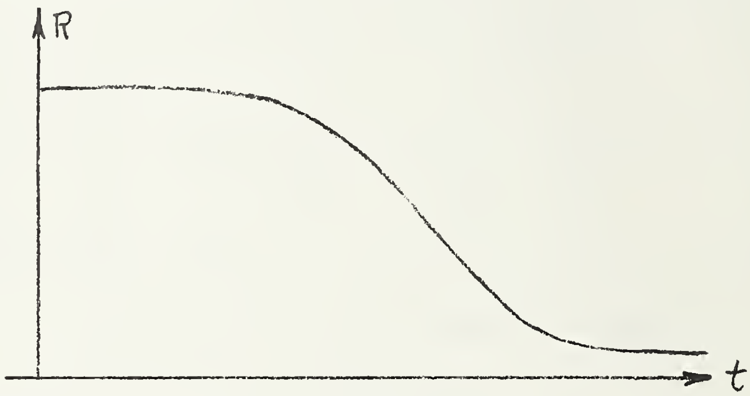

Figure 10: R(t) for $b_2 = 0$ b_4 large and positive