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Methodologies for Predicting the Service Lives of Coating Systems

Jonathan W. Martin, Sam C. Saunders, F. Louis Floyd, and John P. Wineburg

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Methodologies for Predicting the Service Lives of Coating Systems

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EXECUTIVE SUMMARY

Over the last two decades, the organic coatings industry has undergone rapid technological and structural changes. These changes have been induced by legislative actions such as restrictions pertaining to hazardous chemicals, toxic effluents, and volatile organic compounds. The consequence of these changes has been the displacement of almost all commercially-important, well-established coatings (largely high-solvent coatings) by newer systems, the formulation and application of which are based on different chemistries and technologies. Unlike the displaced coatings, however, the new coatings do not have performance histories and the only accepted method for generating performance data is through an extensive outdoor exposure program. Since outdoor exposure results typically take five years to obtain, a desperate need exists for a methodology which is capable of generating timely, accurate, and reliable service life estimates of a coating system.

This report reviews the attributes of the service life prediction problem which are common to all materials, components, and systems in an effort to establish a set of criteria for assessing the adequacy of existing or proposed service life prediction methodology for coating systems. The current durability methodology and the reliability-based methodology are then evaluated against these criteria.

The proposed criteria include the ability to 1) handle high variability in the time-to-failure data for nominally identical coated panels exposed in the same service environment, 2) analyze multivariate and censored time-to-failure data, 3) establish a connection between laboratory and field exposure results, and 4) quantitatively predict the service life of a coating system exposed in its intended service environment.

The current durability methodology was developed prior to the recognition of the proposed criteria and, as such, was not designed to satisfy these criteria. Efforts to correct its deficiencies have been made over the last 80 years, but success has been elusive. The failure of the current methodology has generally been ascribed to inadequacies in laboratory-based aging tests, specifically, the inability to simulate weathering conditions in the laboratory. However, we suggest that the failure of the current methodology can be attributed to its being based on faulty premises, inadequacies in experimental design, and the lack of reproducibility of the weather over any time scale.

An alternative, reliability-based methodology is reviewed and assessed. This methodology has a strong theoretical basis plus a history of successful applications in the electronics, medical, aeronautical, and nuclear industries. A number of experiments with coatings has already been conducted using this methodology. The results indicate that this methodology can be applied in predicting the service life of coating systems and that it satisfies the proposed service life prediction criteria.

Implementation of a reliability-based methodology will require substantial changes in the current experimental procedures. These changes result from the quantitative nature of the service life data and will include 1) more systematic characterization of the initial properties of a coating system, 2) quantitative characterization of each of the weathering variables comprising the in-service environment, 3) quantification of macroscopic degradation and relating submacroscopic to macroscopic measures of degradation, 4) utilization of experimental design techniques in planning and executing short-term laboratory-based experiments, and 5) development of computerized techniques for storing, retrieving, and analyzing collected data. These changes will be justified in view of the greater reliability of the results.

KEYWORDS: Computerized materials databases, fault tree, fundamental mechanistic experiments, in-service exposures, performance characteristic, reliability theory, reliability-based methodology, service life, time series, UV-radiation

CONTENTS

1. INTRODUCTION

Over the last two decades, the organic coatings industry has undergone rapid technological and structural changes. These changes have been induced by legislative actions such as restrictions pertaining to hazardous chemicals, toxic effluents, and volatile organic compounds. Further changes have been induced by competitive and consumer pressures to produce environmentally and user friendly coatings without sacrificing ease of application, initial appearance, or, most importantly, without significantly reducing the expected **service life** of the coating systems. The consequence of these changes has been the displacement of almost all previously commercially-important, well-established coatings (largely high-solvent coatings) by newer systems, the formulation and application of which are based on different chemistries and technologies.

Unlike the coatings which are being displaced, the new coatings do not have well-established performance histories. At present, generating a reliable performance history for a new coating requires an extensive in-service or outdoor exposure program. Attempts at avoiding this task, by employing various forms of short-term laboratory-based aging tests, have had limited success, largely because of confounded causal effects in the current durability protocols. Alternatively, creating a performance history from results of in-service exposures requires long exposure times and yields results which have limited reproducibility since the weather never exactly repeats itself.

Therefore, the coatings industry is faced with a dilemma. On one hand, the coatings industry needs a method for generating performance data rapidly with assured reliability. On the other hand, the results from laboratory-based experiments, the most promising method for acquiring service life data in the shortest time, have historically been viewed with suspicion by the coatings industry.

However, a lack of confidence in results from short-term laboratory tests is not found in all industries. The electronics, medical, aeronautical, and nuclear industries have long since made the transition from an overwhelming dependence on long-term in-service tests to reliance on short-term laboratory tests. This change has greatly reduced the time required to introduce new products and helped improve the competitive status of these industries. The service life prediction methodology used by these industries, however, is quite different from the one used in the coatings and other building industries. It is based on reliability theory and life testing analysis (see sec. 4.0); henceforth, this will be termed the **reliability-based methodology**. Because of the success of the reliability-based methodology, it seems worth comparing it with the current durability methodology used in the coatings industry to determine if it is indeed superior.

The goals of this paper, therefore, are to:

1) Compare the current durability methodology used in the coatings industry with the reliability-based methodology used in other industries;
2) Identify the elements of each methodology and their underlying assumptions;
3) Identify the interrelationships between these elements; and
4) Identify technical barriers, including deficiencies in standards, and critical research areas which need to be addressed to improve the ability to predict the service lives of coatings.

Although the scope of this paper is broad, it is not a definitive treatise on the service life prediction problem. Instead, it is a review of important issues and difficulties in predicting the service life of a coating system with suggestions as to how to proceed. It is hoped that this presentation will foster discussion within the coatings community and serve to alleviate doubts about the feasibility of implementing a successful quantitative service life prediction methodology.

2. GENERAL ATTRIBUTES OF THE SERVICE LIFE PREDICTION PROBLEM

Before comparing the current durability methodology with the proposed reliability-based methodology, attributes of the service life prediction problem which are common to all materials, components, and systems are reviewed. The presentation in this section is largely descriptive; in section 4.1, it is given a more mathematical structure. The purpose of this section is to derive a set of criteria for judging the efficacy of any existing or proposed service life prediction methodology.

2.1 Sources of Service Life Data

Data for use in service life prediction can be generated from three sources[1] (see fig. 1): 1) **short-term laboratory-based exposures**, 2) **long-term in-service or outdoor exposures**, and 3) **fundamental mechanistic studies** [Dickie, 1992]. Each source is capable of providing useful data for predicting the service life of the system under investigation. For example, in short-term laboratory-based aging and fundamental mechanistic experiments, it is possible to control the intensities of individual weathering factors, generate reproducible experimental results, and derive fundamental information about the failure modes and failure mechanisms causing a coating system to degrade. Long-term in-service exposure studies assure that a coating system degradation will not fail by "unnatural chemistry" [Bauer, 1993] and also provide valuable insight into the dominant failure modes and the distribution of times-to-failure. However, long-term in-service exposure results seldom provide useful information about the cause of failure or the events leading up to failure, which are the strengths of both fundamental mechanistic and laboratory-based experiments [Amster et al., 1982; Lawless, 1983; Dickie, 1992].

The success of any service life prediction methodology, therefore, hinges on its ability to utilize the strengths, establish information linkages, and integrate the knowledge gained from each of these data sources. To facilitate the establishment of these linkages, the mission and experimental protocol for each of

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[1]Experience, expert knowledge, and published results also play an important role in establishing a coating system's performance history [ASTM E 632, 1992; Masters and Brandt, 1987, 1989]. The information obtained from these sources, however, is often non-quantitative or fuzzy [Zimmermann, 1991] and, thus, difficult to assimilate in deriving a quantitative estimate of the service life of a coating system. For this reason, the emphasis in this review is on quantitative data of known precision and accuracy.

the three sources of service life data must be coordinated. That is, each data source must complete a well-defined mission which provides unique, complementary, and comparable data useful in modeling the degradation response, identifying weaknesses, and predicting the service life of a coating system. In generating the necessary data, several key issues must be addressed including:

1) Sufficiently detailed identification of the initial properties measurements of a coating system which will be sufficient to completely describe a coating system (see sec. 4.2.1 and 4.2.5).
2) Characterization of weathering factors in a manner which is equivalent to the way these factors are characterized in laboratory-based experiments (see sec. 4.2.2).
3) Quantification of coating system degradation in a way that the data collected from each source can be compared and used with data collected from the other sources (see sec. 4.2.3).
4) Establishment of acceptable limits of precision and accuracy for initial property, coating degradation, and weathering factor measurements (see sec. 4.2).
5) Identification of a method for analyzing collected data, the outcome of which is a quantitative estimate of the service life of a coating system exposed in its intended service environment (see sec. 4.1 and 4.2.4).
6) Creation of a means for efficiently storing, processing, and retrieving initial property, environmental exposure, and degradation data to facilitate the organization and integration of this knowledge in making service life prediction estimates (see sec. 4.2.5).

2.2 Fault Trees

The service life of all commercial products is affected by many variables including weathering variables and variables associated with the materials, manufacturing, and design of the product. The relationship among these variables and the service life of the product is seldom well understood. It would be helpful, therefore, if a graphical tool was available for displaying the current state of knowledge as to how each of these variables interact and affect a product's service life. One such tool is **fault tree analysis** and its possible application in predicting the service life of coating systems is discussed here. Fault tree analysis is a deductive, systems analysis technique which provides a formal structure for graphically and logically relating a top event, the failure of a coating system, to its underlying faults [Haasl, 1965; Vesely et al., 1981]. Fault tree analysis is an important tool for diagnosing weaknesses in complicated systems [Bergman, 1985] and is heavily used in the electronics [Fussell et al., 1979; Bro and Levy, 1990], nuclear [Vesely et al., 1981], and aerospace [Haasl, 1965] industries.

Coating systems function to protect or improve the appearance of a substrate or both. Whenever the coating system no longer performs its intended function, it has failed. Failure of a coating system occurs by any number of **failure modes**. However, before exposure in its intended service environment, it is seldom possible to anticipate which failure mode will predominate. For architectural coatings, common failure modes include chalking, gloss loss, cracking, peeling, and fading (see fig. 2). For antifouling, appliance, automotive, aerosol can and maintenance coatings, the dominant failure modes are often quite different from those for architectural coatings. For example, maintenance coatings usually fail from a loss-of-protection failure (e.g., corrosion, blistering, undercutting, or cracking) and seldom from a loss-of-appearance failure.

Failure of a coating system (see fig. 3) can normally be attributed to a number of **root faults** which are associated with the 1) coating application technique, 2) design of the structure to be coated, 3) manufacturing and processing of the coating system components, 4) properties of the materials comprising the coating system, and 5) exposure environment. Moreover, each root fault can be partitioned into sub-faults. For example, faults related to the materials used in a coating system can be subdivided into those related to the coating and those related to the substrate[2]; substrate faults can be further subdivided into those associated with surface morphology, surface chemistry, and surface contamination. Faults can continue to be subdivided until a **basic fault** is reached which is not further developed for the purpose of analysis. Thus, a basic fault defines the **limit of resolution** of the causes of a failure, and this limit often differs from one failure mode to another. For example, the limit of resolution for loss-of-appearance may be at the molecular level, whereas, for loss of protection it is often at the macroscopic level. Guidelines for establishing limits of resolution for complex systems have been discussed in Vesely et al. [1981], Amster et al. [1982], and Bro and Levy [1990].

Root faults are linked to a failure mode by a sequence of degradation steps. The specificity with which these steps can be described depends on our knowledge of the degradation mechanisms. When the degradation mechanisms are known at a fundamental mechanistic level, the linkage may be made through the **degradation kinetics** governing the chemical or physical (fatigue and crack growth) deterioration of the coating system. Our knowledge of the underlying degradation mechanisms, however, is seldom so complete. Consequently, the linkage must often be made empirically through **cause-and-effect**[3] or **dose-response relationships**. Sometimes a plausible relationship cannot be identified, in which case the linkage is indicated by a **black box** (see fig. 4).

For most commercially important materials [Bogdanoff and Kozin, 1985], including organic coatings, the linkage between the observed failure modes and root faults falls somewhere between a cause-and-effect relationship and a black box. Possible exceptions include the cracking of latex paints [Floyd, 1983], appearance failure modes like chalking [Völz et al., 1976; Braun, 1987, 1990; Braun et al., 1992], and the photodegradation of clear films [Mielewski et al., 1991, Bauer, 1993 and Bauer et al., 1984, 1987 a,b, 1991, 1993] where the degradation chemistry appears to be much better understood. This increased knowledge is reflected in the smaller size of the fault trees (see fig. 5).

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[2]The properties of the coating/substrate interface are also important; however, interfacial property measurements are difficult and time consuming to make. For this reason, they are not included in the fault tree.

[3]An operational definition of causality is as follows [Blum, 1982]: A is said to cause B if over repeated observations 1) A is generally followed by B; 2) the intensity of A is correlated with the intensity of B; 3) there is no known third, confounding, variable responsible for the correlation; or 4) there is a plausible failure mechanism linking A and B.

Graphically, a fault diagram looks like an inverted tree. It is not surprising, therefore, that this procedure is commonly referred to as **fault tree analysis** [Lambert, 1975; Vesely et al., 1981; Fussell et al., 1979]. In establishing a fault tree, several key issues need to be addressed including:

1) Identification and inclusion of the factors responsible for each failure mode.
2) Establishment of the limits of resolution for each fault.
3) Identification of analysis techniques which are capable of eliminating unimportant faults from the trees or, conversely, emphasizing faults which are major contributors to the incidence of a failure. Faults having negligible effect will, of course, be removed from the tree.
4) Determination of the relative frequency and importance of different failure modes for a given exposure environment and establishment of a firmer connection between the incidence of a failure mode and the underlying causes of the failure (see Vesely et al. [1981]).

2.3 Service Life Data Attributes

The degradation of a coating system over time, and thus its performance, is usually monitored through changes in its appearance or protection **performance characteristics** or both. Associated with each performance characteristic is a maximum or minimum **critical value,** η_{crit}, above or below which the coating system is said to have failed (see fig. 6) [Gertsbakh and Kordonskiy, 1966; Martin and McKnight, 1985]. The assigned critical performance value may differ from one failure mode to another and from one application to another.

An **induction time** (denoted by t_o in fig. 6) often exists before which the performance characteristics of a coating system do not change, but after which at least one characteristic changes irreversibly. Failure occurs when one of the coating's critical performance characteristics first exceeds (falls below) its critical value, η_{crit}. Such failures, which are called **out-of-tolerance** or **drift-type failures** [Shooman, 1968], are common for automobile tires, batteries, electronic packages, and medical dysfunctions like cataracts. A less common type of failure for coating systems is a **catastrophic** or **instantaneous failure** in which a coating system undergoes a rapid change from an unfailed to a failed state. Examples include the spalling of a coating resulting from the impact of a projectile [Zehnder et al., 1992; Ramamurthy et al., 1993], the etching of a clear coating resulting from acid deposition [Wolff et al., 1990], and the thermal degradation of chlorinated polymers [Davis and Sims, 1983]. The **time-to-failure**, τ, of a coating system is the minimum time after application of the coating until a critical performance characteristic of the coating system reaches its critical value (fig. 6).

Sometimes a performance characteristic of a coated panel changes so slowly that it never exceeds its critical value before the experiment is terminated. That is, neither the failure nor the failure time of the panel is observed; the times-to-failure for these specimens are said to be **censored.** Censoring can also be caused by damage during handling, loss in shipment, or removal of a panel from an experiment in order to destructively analyze the degradation products (see discussion in Nelson [1990]). Due to the omnipresence of censoring in service life prediction experiments, it is necessary that any proposed service life prediction methodology be capable of handling censored data.

When a number of nominally identical coated panels are placed on exposure at the same time and in the same environment, it is not uncommon to observe a large variability in their temporal degradation response. This is true for coating systems that undergo loss-of-protection failures [Rothwell, 1969: Haspardaruk et al., 1978; Becka, 1983; Poole, 1986, 1990; Martin and McKnight, 1985; Galván, Feliu, and Morcillo, 1989; Tait et al., 1993 a,b]. The variability in the loss-of-appearance response of nominally identical coated panels can also be considerable[4] [Papenroth, 1978; Schutyser and Perera, 1992, 1993; Crewdson, 1993; and Grossman, 1993].

As an example of the high temporal variability in loss-of-protection response of nominally identical coated panels [Martin et al., 1990], 24 replicate specimens were immersed in a 5% salt solution for 6000 h (see fig. 7). In this experiment, the first panel started to degrade through cathodic delamination after approximately 1000 h of immersion, while 6 of the 30 panels displayed no signs of degradation after 6000 h of immersion. Thus, the performance of these nominally identical specimens ranged from a poorly performing (time-to-failure less than 1000 h) to a well-performing coating system (time-to-failure greater than 6000 h). Such large temporal variability in the performance of nominally identical coated specimens has been observed by others (Schutyser and Perera [1992, 1993], Tait [1993a, 1993b], and Crewdson [1993]).

When a coating system is placed on exposure, it is common that a number of performance characteristics may change simultaneously; thus, for example, performance characteristics related to loss of protection and appearance may change simultaneously (Walker, 1974). Each performance characteristic, therefore, effectively competes with the others in causing a coating system to fail (often termed **competing risks** [David and Moeschberger, 1978]). The failure mode which usually "wins out" is called the **dominant failure mode** for a given exposure environment. The dominant failure mode may change with a slight change in the initial properties of a coating or in the intensity of some of the weathering factors [Rychtera, 1970; Degussa, 1985]. For example, the dominant failure mode for a coating system exposed in a semi-desert environment like Arizona is often associated with a loss of appearance due to the high intensity of the spectral ultraviolet radiation, whereas, for the same coating system exposed in Florida, the dominant failure mechanism may be associated with a loss of protection, which is attributable to the long time of wetness associated with a semi-tropical environment.

The high variability in service life data, the presence of censored times-to-failure, and the effects of competing risks on the failure of a coating system are common to many materials, components, and systems (see, for example, the citations in Nelson [1990]). These factors dictate the way data can and must

[4]Large variations in the appearance of nominally identical panels exposed to the same service environment have been reported by Papenroth [1978] and Fischer et al. [1991b]. The sources of this variation were later ascribed to measurement errors [Braun, 1987] and variations in the exposure conditions [Fischer et al., 1991b], while the contribution to the total variability from the degradation process was considered to be small. Schutyser and Perera [1992, 1993] and Crewdson [1993], however, also observed considerable variability in their loss-of-appearance time-to-failure data which they did not associate with experimental error.

be analyzed. Specifically, for a set of nominally identical specimens exposed to the same environment over the same period, the high variability in degradation response poses several important questions including:

1) What level of degradation should be designated as failure? This failure designation essentially defines the service life of a coating system. (See sec. 4.1.1).
2) How does the accuracy of the estimated service life of a coating system depend on the number of replicates placed on test? The number of observed failures? (See sec. 4.1.2).
3) Does the interval between successive failures of nominally identical specimens provide any indication of the cause of failure or the remaining service life of the coating system? (See sec. 4.1.1).

In addition to these issues, the method used in analyzing data should be capable of

1) Determining the expected change in the service life of a coating system resulting from a change in the surface treatment of the substrate, reformulation of the coating, or a change in intensity of one or more weathering factors.
2) Relating the times-to-failure to the initial properties of the coating system, the age of the coating, or the exposure conditions in a verifiable manner.
3) Reformulating the parameters of the service life prediction model in terms of the fundamental mechanistic equations governing degradation.

2.4 Characterization of Weathering Environments

Field environments are difficult to monitor and impossible to control. Moreover, the intensity of the weathering factors (e.g., spectral ultraviolet radiation, relative humidity, temperature, SO_x, NO_x, O_3, and NaCl) display high spatial and temporal (diurnal, seasonal, and annual) variabilities. Extensive analysis of the published weather data and weathering data has been performed to determine if individual weather factors cycle over predictable time scales. It was concluded from this analysis that none of the factors comprising the weather exhibit a predictable cyclic behavior over any time scale [Kincer, 1933, 1946; Burroughs, 1992]. Thus, one of the main difficulties in relating laboratory and field results will be in characterizing the field exposure history in such a manner that this history can be compared to laboratory-based exposure histories [Scott, 1983].

At present, conventionally collected meteorological data have little relevance in predicting the service life of a coating system exposed outdoors and can not be compared to the data used in characterizing laboratory exposures. For example, the temperature governing the rate of degradation of a polymeric material is the temperature of the test specimen and not ambient temperature. Although it is relatively simple to monitor specimen temperature in the laboratory, such direct measurements are seldom practical in the field (an exception to this is the work of Fischer et al. [1991a]). As shown by eq (33) in section 4.2.2, the temperature of a coated specimen is not directly related to ambient temperature [Saunders et al., 1990], the most common variable used in characterizing temperature in outdoor environments.

The quantitative characterization of in-service environments raises some critical questions including:

1) Can the weathering factors causing the predominant degradation of a coating system in a specified in-service environment be isolated from the factors which have only a secondary effect?
2) Is the average intensity of each weathering factor sufficient for characterizing the severity of an in-service environment, or will a more precise knowledge of each of these factors be necessary? (See sec. 4.2.2).
3) Can the value of a weathering factor be converted into some common metric of degradation (e.g., total dosage (see eq (34)) which is the same for both laboratory and field studies? (See sec. 4.2.2).

2.5 Storage, Retrieval, and Analysis of Data

During manufacturing and pretesting, coating manufacturers routinely collect and store large amounts of information about a coating. Similarly, many coating end-users require that candidate coatings be independently assessed under conditions approximating in-service conditions. As discussed in section 2.2, formulation, processing, and application variables often affect the service life of a coating system and, therefore, this information should be available for refining the service life estimates for a coating system. This data would be most accessible if it were stored in an electronic format [Rumble and Carpenter, 1990].

Computerized databases have enjoyed widespread acceptance in the chemical [Buchanan and Mitchell, 1978; Langley et al., 1987], medical [Wiederhold, 1981; Blum, 1982; Kissman and Wexler, 1985] and aerospace [Whittaker and Besumer, 1969] industries. Also, the development of computerized databases has been identified by Ambler [1985] and others as a national economic priority. Computerized databases quickly become the repository for the collective institutional knowledge about complex systems. This knowledge can be queried to discover interrelationships among variables [Glymour et al., 1987; Piatetsky-Shapiro and Frawley, 1991] and, thus, databases eventually become inexpensive adjuncts to physical experimentation.

If the full potential of computerized coating databases is to be achieved, however, several key issues must be addressed including:

1) Standardization of the terminology used in describing coatings, substrates, and defects.
2) Selection and standardization of variables for describing a coating system.
3) Identification of reliable methods for quantifying the degradation of a coating system which will facilitate comparisons between results from different methods.
4) Development of a strategy for ensuring the accuracy of stored data [Herring, 1992].
5) Storage of data in a format which is easily transportable -- that is, a format which is not inextricably linked to anyone computer software/ hardware system [Rumble and Smith, 1990].

2.6 Criteria for Judging the Adequacy of any Proposed Service Life Prediction Methodology

Based on the discussion about the attributes of the service life prediction problem common to most materials, components, and systems, a set of criteria is proposed for assessing the attributes of any proposed or existing service life prediction methodology. These criteria include the ability to:

1) Handle large variability in the times-to-failure for nominally identical specimens (sec. 2.3).
2) Analyze multivariate data (sec. 2.2).
3) Discriminate among these variables. That is, the service life prediction methodology should be able to separate the few significant variables from the many insignificant variables (secs. 2.2 and 2.5).
4) Fit both empirical and mechanistic failure models to short-term laboratory-based exposure results (sec. 2.3).
5) Establish a connection between short-term laboratory-based and long-term in-service results (secs. 2.3 and 2.4).
6) Provide mathematical techniques to predict the service life of a coating system exposed in its intended in-service environment (secs. 2.3 and 2.4).

3. CURRENT DURABILITY METHODOLOGY

The current durability methodology started up in the early 1900's with the construction of several outdoor exposure sites [Gardner, 1911] and the development of crude (by today's standards) weathering devices based on mercury-arc and carbon-arc light sources [Muckenfuss, 1913; Capp, 1914; Nelson, 1922; Nelson and Schmutz, 1926]. Since that time, many technical advances have occurred in monitoring and controlling laboratory-based aging experiments and in monitoring outdoor environments. These improvements, however, have not removed the industry's distrust of laboratory-based aging tests or lessened its dependence on outdoor exposure tests. The question arises, therefore, whether it would be possible to change the situation by improving the predictive capabilities of the current durability methodology or replacing it with a different methodology, such as for example, one based on reliability theory.

3.1 Description of Methodology

The current durability methodology was designed to **compare** the performance of duplicate sets of coating systems, one being exposed in a laboratory and the other in its intended in-service environment, by designing a laboratory-based exposure experiment which simulates in-service environments [Nelson, 1922]. Thus, this methodology mainly utilizes data obtained from short-term laboratory and long-term in-service experiments and **neglects fundamental mechanistic studies**.

The experimental protocol for this methodology is as follows. Two panels from each of **m** different coating systems are prepared. One panel is randomly assigned to the laboratory-based aging experiment, while the other is assigned to the outdoor exposure experiment. The two sets of panels are then exposed in their respective service environments; after a specified period of time, the panels in both environments are ranked by performance. The two rankings are then correlated through a non-parametric statistic like the Spearman Rank correlation coefficient [Epple, 1968; Mitton and Richards, 1971; Grossman, 1977; Fischer, 1984]. If the correlation coefficient is high (e.g., greater than 0.90), it is concluded that the proposed laboratory-based aging experiment successfully simulates field environments; otherwise, the laboratory-based experiment is judged to be deficient. In addition to a correlation coefficient, an attempt is often made to provide a quasi-quantitative estimate of the service life for new coating systems through the incorporation of one or more **control coatings** into the laboratory and outdoor exposure panel sets [Appleman, 1989b]. The service lives of these control coatings are then used as reference points through which the service life of a coating system can be approximated.

Over the years, a number of promising laboratory-based experimental procedures have been developed in which, at least initially, a high correlation has been claimed for relating laboratory and field results. **None of these procedures, however, has consistently produced a high correlation with long-term outdoor exposure results** [Reinhart, 1958; Nowacki, 1962; Kamal, 1966; Quackenbos and Samuels, 1967; Hoffmann and Saracz, 1971; Alumbaugh and Hearst, 1975; Ellinger, 1977; Campbell et al., 1981; Lindberg, 1982; Leidheiser, 1982; Yaseen and Raju, 1984; Chandler and Bayliss, 1985; Funke et al., 1986; Cutrone and Moulton, 1987; Simms, 1987; Masters, 1987; Wicks, 1988; Skerry et al., 1988; Himics and Pineiro, 1992]. Failure to produce a high correlation has usually been assigned to deficiencies in laboratory-based aging experiments and, in particular, the inability to design a laboratory-based experiment containing a "balance of exposure conditions" [Stieg, 1966; Ellinger, 1977; Skerry et al., 1988]. However, in light of continued failures, the question must be asked whether the current durability methodology has inherent limitations.

3.2 Underlying Premises

The validity of a methodology may hinge on the validity of the underlying premises. The premises of the current methodology appear to be as follows:

PREMISE 1. The performance of a coating system can be assessed using one, or at most three, replicates;

PREMISE 2. The results from an outdoor exposure experiment are the **de facto standard of performance** with which the results from any laboratory-based experiment must correlate; and

PREMISE 3. The **results from one laboratory-based experiment** should correlate with the **results from any outdoor exposure experiment**.

Now let us examine these premises. Premise 1 fails to take into account the high variability in protection provided by nominally identical specimens exposed at the same time to the same environment (see sec. 2.3 and fig. 7). The current practice could, of course, be modified to include more replicates. But, the late recognition of this need places into doubt the validity and usefulness of any existing databases for making inferences about the performance of a coating system (see sec. 4.2.5). The high variability in the degradation response of nominally identical coated panels also challenges the notion that "control coatings" exist. Control coatings should provide "consistent and reproducible properties in standardized tests"[5] [Appleman, 1989b]. However, the coating is only one component of a coating system and may or may not be the most important component controlling its service life. Of equal, and sometimes greater, importance are the presence of defects in the coating [Gowers and Scantlebury, 1987; Martin et al., 1990],

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[5]Although the use of a control coating has been proposed by many researchers, the authors could not find any published results supporting the existence of a coating which is capable of providing reproducible results.

the physical and chemical properties of the substrate [Coduti, 1980; Maeda, 1983; Groseclose et al., 1984; Drisko et al., 1985; Reinhard, 1987; Perfetti, 1991], the properties of the coating/substrate interface, and variables associated with the manufacturing, processing, and application of the coating. Most of these variables are neither controlled nor controllable. Thus, it seems presumptuous to believe that "control coatings" exist.

Premises 2 and 3 are highly interdependent and, thus, will be considered together. Both premises are fundamental to the validity of the current methodology. If either premise can be challenged, then the technical soundness of the current practice is placed in doubt. Their validity can be tested by examining the reproducibility of outdoor exposure results and the reproducibility of the weather and individual components of the weather.

A few papers have been published in which the reproducibility of outdoor exposure results has been investigated. From these studies, it is known that the observed failure mode for nominally identical specimens often changes from one environment to another [Scott, 1983] and that the rankings of outdoor exposure results do not agree for coated specimens exposed 1) at the same site and at the same time of year, but in different years [Rosendahl, 1976], 2) at the same site, but at different times of the same year [Greathouse and Wessel, 1954; Morse, 1964; Singleton et al., 1965; Stieg, 1966; Grinsfelder, 1967; Rosado, 1968; Mitton and Richards, 1971; Stieg, 1975; Rosendahl, 1976; Gaines et al., 1977; Scott, 1977; Ellinger, 1977; Lindberg, 1982], 3) at the same site, same year, and the same time of year, but for different durations [Hoffmann and Saracz, 1969b], and 4) at different sites, but at the same time of the same year [Block, 1957; Morse, 1964; Singleton et al., 1965; Epple, 1968; Kamal, 1966; Stieg, 1966; Hoffmann and Saracz, 1969a, 1969b, 1971, 1972; Oakley, 1971; Gaines et al., 1977; Scott, 1983; Fischer, 1984]. **In fact, no study was found claiming that outdoor exposure results are reproducible**.

Based on laboratory studies [Martin and McKnight, 1985; Schutyser and Perera, 1992, 1993], the rate of degradation of a coating system clearly depends on the intensity of each of the weathering factors comprising an exposure environment. The reproducibility of outdoor exposure results, therefore, depends on the reproducibility of the weather.

Time series for three weathering factors -- total UV radiation dosage[6] [Goldberg, 1986; Berger, 1987; Correll et al., 1992; Kerr and McElroy, 1993], temperature [Labrijn, 1945; Mitchell, 1963; Oliver, 1976; Wallén, 1984; Gibbs and Martin, 1989; Hileman, 1992], and precipitation [Kincer, 1946] -- are displayed in figures 8, 9, and 10, respectively. Time series for other weathering factors (e.g., time-of-wetness [Grossman, 1978; Sereda et al., 1982; and Mannsfeld, 1982, 1988], atmospheric halocarbons [Hileman, 1992], and acid deposition species (e.g., NO_x, SO_x, NH_4^+, Ca^{++}, and H^+) [Bilonick, and Nichols, 1983; Correll et al., 1984; Likens et al., 1984; Correll, et al., 1987; Studt, 1991; Jordan et al., 1992] have been published but, the lengths of these time series are too short to establish if there are any trends in the data.

Spectral ultraviolet radiation is the dominant weathering factor in loss-of-appearance failure modes and may contribute to the loss of protection of some coating systems. Since 1975, spectral solar UV-radiation has been monitored by the Smithsonian Institution [Klein and Goldberg, 1978] at four locations

[6]Total UV radiation dosage is the product of spectral irradiance, spectral absorption, and spectral quantum yield integrated over the range of photolytically effective wavelengths and the duration of the exposure. Mathematically, it is defined by eq (34).

(Rockville, Maryland; Mauna Loa, Hawaii; Barrow, Alaska; and Panama City, Panama). Correll et al. [1992] recently published the data from the Rockville, MD site (fig. 8) in which they observed that total UV-B radiation dosage (see Footnote 6) increased 35 percent from 1978 to 1985 and that in 1990, it dropped precipitously by 30 percent, perhaps as a result of increased sunspot and volcanic activity. Similar behavior has been observed by Berger [1987] and McKenzie et al. [1991].

Wallén [1984] tracked changes in the consecutive 5-year smoothed average of the July temperatures from 1880 to 1980 at seven weathering stations in the northern hemisphere[7] (see fig. 9). Note that in the North Platte (the Great Plains of the United States), the smoothed average July temperature was at a maximum during the 1930's, the "dust bowl" years. Figure 10 depicts deviations from global average for consecutive five-year average temperature and precipitation data for the Great Plains of the United States. From figure 10, an increase in the mean temperature relative to the global average temperature was accompanied by a decrease in the mean precipitation relative to the global average precipitation and this, in turn, could correspond to an increase in the total UV-B radiation dosage, since there were probably fewer cloudy days. Thus, at least in the Great Plains, it is possible that the degradation mode for coatings could have shifted from loss of protection during the high precipitation years of 1910 to a loss of appearance during the 1930's.

It is obvious from figures 8, 9 and 10 that the principal weathering factors are not reproducible from year to year. Moreover, Burroughs [1992] analyzed many data sets on all sorts of weather related phenomena which have been collected over the last couple of centuries and concluded that the weather is an enormously complicated physical system which does not display any cyclic patterns over any time scale. That is, **there is no such thing as an "average Florida year."**

3.3 Assessment of Current Durability Methodology

Attempts at refining the current durability methodology have been made over the last 80 years without any significant improvement in its predictive capability. This lack of improvement has usually been blamed on deficiencies in laboratory-based aging tests. The blame seems to be more appropriately assigned to the neglect of the inherent high variability in the times-to-failure of nominally identical coated panels exposed to the same service environment, the inability to design a laboratory-based experiment which can simulate all service environments, and the lack of reproducibility of the weather over any time scale. This leads to Grinsfelder's [1967] lament that, "How can one ever expect a laboratory method to duplicate the weather when the weather can never duplicate itself?"

Assessing the current durability methodology against the proposed criteria (see sec. 2.6) is not entirely fair, since this methodology was not designed to satisfy these criteria. Instead, it was designed to make comparisons between the results of laboratory and field exposures. Actually, the current methodology does not satisfy any of the proposed criteria.

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[7]For material degradation purposes, the consecutive 5-year smoothed average temperature is a relatively insensitive measure of temperature change at an exposure site. Time series of the daily maximum temperatures or hourly temperatures would be more useful. Figure 10 supports the premise, however, that the temperature at an exposure site does not display random behavior about a constant mean and that the temperature from year to year is unpredictable.

4. RELIABILITY-BASED METHODOLOGY

The reliability-based methodology is of relatively recent origin[8], dating back to the early 1950's. The need for such a methodology was driven by the high incidence of equipment failures experienced by the military during World War II [Shooman, 1968; Lawless, 1983]. Its rapid growth and acceptance had to wait until the 1960's, after its successful application in the Minuteman Missile Program [Nalos and Schultz, 1965] and in programs to improve the airworthiness of military and commercial aircraft [Whittaker and Besumer, 1969; Birnbaum, 1983]. Since that time, reliability theory has been successfully applied to many materials, components, and systems including metals, plastics, adhesives, lubricants, electronics, batteries, and bearings (see Nelson [1990]). Presently, advances in reliability theory are published in at least 14 monthly journals, hundreds of books, and numerous conference proceedings.

4.1 Reliability Theory and Life Testing Analyses

In this section, the mathematical basis of a reliability-based service life prediction methodology is presented. Specifically, in section 4.1.1, some basic reliability concepts are introduced. In section 4.1.2, the simplest reliability testing program is discussed, the case in which coated panels are exposed to a single environment and, after any exposure time t, the coated panels are classified as either having failed or survived. In sections 4.1.3 through 4.1.6, increasingly complex cases are considered. In section 4.1.3, the analysis is generalized to include multiple failure modes. In section 4.1.4, the life distribution models are extended to include the effects of explanatory variables. In section 4.1.5, life-stress analyses are introduced in which the intensity of one or more weathering factors is systematically changed over its expected range and, in section 4.1.6, models for connecting laboratory and field results are discussed. Finally, in section 4.2, changes in the experimental protocols required to implement a successful reliability-based methodology are presented.

4.1.1 Basic Concepts

4.1.1.1 Time-to-failure for a Single Coated Panel

When a coated panel is exposed in an adverse environment (e.g., in Miami, Florida, or in a salt fog cabinet), one or more of its performance characteristics will eventually begin to degrade toward a less desirable state. Changes in a performance characteristic over time can be represented by some function, $\eta(t)$, which has been termed a **sample function** [Doob, 1953; Gertsbakh and Kordonskiy, 1966; Bogdanoff and Kozin, 1985].

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[8]In medical and actuarial communities, reliability theory is often called **survival analysis**. For all practical purposes, the two techniques are identical. Survival analysis publications, however, date back to the early 1800's. The popularization and increased use of survival analysis have often been attributed to the successful application of reliability theory in improving the service lives of military equipment following World War II [Miller, 1981].

In the simplest case, the sample function, $\eta(t)$, changes linearly with time

$$\eta(t) = a + bt \tag{1}$$

where

$\eta(t)$ is the value of the performance characteristic at time t;
a is the initial state of degradation;
b is the rate of degradation;
t is time of exposure;

and, if there are multiple, supposedly identical, specimens the values of **a** and **b** often vary stochastically from specimen to specimen. That is, a and b are random variables across the population of specimens. Thus, if a specimen were to be randomly selected from the specimen population, we would express its degradation function, X(t), as

$$X(t) = A + Bt \qquad \textit{for } t > 0, \tag{2}$$

where A, the initial state, is a random variable, the distribution of which must be estimated from the values of the initial states of the specimens placed on test. B, the degradation rate, is also a random variable, the distribution of which must be estimated from the corresponding measurements made on the random sample. Thus, given a failure criterion η_{crit}, the distribution of times-to-failure, say T_f, can be determined mathematically by using probability theory and the empirical knowledge of the distributions of A and B as

$$T_f = \frac{\eta_{crit} - A}{B} \tag{3}$$

Linear sample functions (see fig. 11) appear to be reasonable for modeling temporal changes in a wide range of performance characteristics including changes in the percent area blistered [Martin et al., 1990], chalking [Daiger and Madson, 1967], corrosion protection loss [Galván et al., 1989; Martin et al., 1989], UV-stability [Gerlock et al., 1985; Bauer et al., 1987], color retention [Johnston-Feller, 1977, 1986], loss of coating mass [Lindberg, 1975], and gloss loss [Ellinger, 1977; Lindberg, 1982; Braun, 1990]. Non-linear sample functions appear to provide a better fit to changes in a coating's polarization resistance [Skerry et al., 1988], gloss loss [Tahan et al., 1975; Simms, 1987], and changes in wet-adhesion strength [Leidheiser and Funke, 1987].

4.1.1.2 Life Distributions

Due to the high variability in the observed times-to-failure of nominally identical coated panels exposed to the same service environment, it is common to simultaneously expose **n** nominally identical panels in the same service environment. For each panel, changes are observed in a performance characteristic, a sample function is fitted to the temporal data, and the time-to-failure for the panel computed given a failure criterion. This is demonstrated in figure 12a for a set of 23 scribed panels; all were simultaneously exposed to the same service environment. The panels degraded through cathodic delamination in which the coating became disbonded from the substrate. The failure criterion was set at 20 percent and all 23 panels exceeded this failure criterion by the time at which the experiment was terminated [Martin et al., 1989].

It is seldom practical or beneficial to wait for all the coated panels to fail. Instead, it is common to terminate the life test at a prespecified time or after the r-th failure[9], where r < n. Since all the specimens were placed on test at the same time, it follows that the observed times-to-failure are ordered: the smallest of the **n** times-to-failure is observed first; the next-smallest time-to-failure is observed next; etc. If the test is terminated after the r-th failure but before the (r + 1) failure, the remaining (n - r) failure times are only known to be greater than the termination time; they are said to be **censored**. That is,

$$t_1 \leq t_2 \leq \ldots \leq t_i \leq \ldots \leq t_r \tag{4}$$

where t_i is the i-th observed time-to-failure and the times-to-failure for the remaining panels, being larger than the time the test is terminated, are not observed; these failure times are said to be **censored**.

From these ordered times-to-failure and an appropriate assumption about the family of life distributions, a sample life distribution of the times-to-failure, $F_s(t)$, can be created and fitted with a theoretical **life distribution**, F(t), such that

$$F(t) = P(T \leq t) \tag{5}$$

where

T is the failure time for a randomly chosen panel;
P(•) is the probability of the event within the parentheses; and
F(t) is the fitted theoretical life distribution (also called a cumulative distribution function).

The sample and theoretical life distributions for the previously discussed 23 scribed and continuously immersed panels are shown in figure 12b.

The complement of the probability of failure of a coated product by time **t** (eq (5)) is the probability of survival beyond time **t**. This probability is the **reliability**, R(t), of a coating system and is mathematically defined as

$$R(t) = P(T > t) = 1 - F(t). \tag{6}$$

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[9]Censoring and the existence of censored data are inherent in life testing. Censoring can significantly reduce the duration of a life test (and, hence, save money and time). Censoring also provides important information about the early failure characteristics of a life distribution [Schafft et al., 1988; Lechner, 1991]. There are many types of censoring besides stopping a life test after a prespecified exposure time or after a prespecified number of failures. For a more complete discussion, the reader is referred to Nelson [1990].

The derivative of the life distribution with respect to time is called the **probability density function, f(t)**; that is

$$f(t) = \frac{dF(t)}{dt} \tag{7}$$

where f(t) satisfies the following conditions

$$f(t) \geq 0 \quad for\ all\ t, \tag{8}$$

$$\int_o^{\infty} f(t)\ dt = 1 \tag{9}$$

and for any a, b, with $0 < a < b < \infty$,

$$P(a \leq T \leq b) = \int_a^b f(t)\, dt. \tag{10}$$

Akin to the concept of a life distribution is the concept of a **hazard rate, h(t).** Mathematically, the hazard rate is defined as the limiting value of the probability that a device will fail in the next small time interval given that it has survived up to the start of the interval, divided by the interval length, and mathematically it is defined by

$$h(t) = \lim_{h \to 0} \frac{P(T \leq t+h \mid T > t)}{h} = \frac{f(t)}{(1 - F(t))} \tag{11}$$

and it is related to reliability, R(t), through

$$R(t) = \exp\left(-\int_o^t h(s)\, ds\right). \tag{12}$$

Practically, the hazard rate provides important information on the way a product ages, its proneness to failure [Bergman, 1985], its remaining service life, and possible causes of a coating system's failure. Examples of different hazard rates [Bergman, 1985] include:

1) A **decreasing hazard rate** (DHR), which occurs whenever the product appears to improve with age (that is, "old is better than new"). A decreasing hazard rate is often associated with the presence of flaws or defects in an applied coating causing its premature failure (let's say within the first two years). In the reliability literature, such failures are often termed **infant mortality**, **crib deaths**, or **freak failures**. Strategies for eliminating, or at least reducing, the effect of premature failures have been extensively studied by Jensen and Petersen [1982] and Saunders [1983]. Examples of failure modes which may exhibit a

decreasing hazard rate include alkyd leaching, surfactant leaching, edge swell, acid etching, and some forms of blistering.

2) A **constant hazard rate**, which occurs whenever the probability of failure of a product in the immediate future, given survival to the present, remains constant (that is, "old is as good as new" or equivalently, "the product does not age"). Examples of failure modes which may exhibit a constant hazard rate include spalling, blistering, and frosting.

3) An **increasing hazard rate** (IHR), which occurs whenever the probability of failure of a product in the immediate future, given survival to the present, increases (that is, "new is better than old"). Thus, an increasing hazard rate is indicative of a product which is aging, or wearing out, in which the chances of failure increase with age. Examples of failure modes which may exhibit an increasing hazard rate include corrosion, chalking, color retention, cracking, and mildew.

4) A **"bathtub shaped" hazard rate** curve results from a mixture of the previously discussed failure modes (see fig. 13). The classical example of a bathtub-shaped hazard rate curve is exemplified by human mortality in which the hazard rate decreases early in life, stays constant during the middle of life, and increases late in life.

The theoretical life distributions which have been most studied for analyzing service life data include the exponential, Weibull, lognormal, Gumbel, gamma, and generalized gamma distributions. Less studied distributions include the inverse Gaussian and Birnbaum-Saunders distributions, both of which have strong foundations in the fundamental mechanisms of materials degradation. The statistical properties of these distributions have been reviewed in a number of textbooks including those by Mann et al. [1975], Lawless [1982], and Nelson [1990].

Of these distributions, the **Weibull distribution** has clearly emerged as the most widely studied and applied life distribution in the reliability literature [Mann et al., 1975; Lawless, 1982; Abernethy et al., 1983], and it has found some application in coatings research [Hill, 1975; Martin et al., 1985; Martin et al., 1989; Schutyser and Perera, 1992; Crewdson, 1993]. For this reason, the Weibull distribution was selected to demonstrate the previously discussed concepts.

The Weibull life distribution has the form

$$F(t) = 1 - \exp\left[- \left(\frac{t}{\beta}\right)^{\alpha} \right] \quad \text{for } t \geq 0 \qquad (13)$$

where $\alpha, \beta > 0$ are respectively, shape and scale parameters. The Weibull reliability function is given as

$$R(t) = 1 - F(t) \qquad (14)$$

while its probability density function is given by

$$f(t) = \frac{\alpha}{\beta}\left(\frac{t}{\beta}\right)^{(\alpha - 1)} exp\left[-\left(\frac{t}{\beta}\right)^{\alpha}\right] \tag{15}$$

The hazard rate for the Weibull distribution is found by dividing eq (15) by eq (14) and is given by

$$h(t) = \left(\frac{\alpha}{\beta}\right)\left(\frac{t}{\beta}\right)^{(\alpha - 1)}. \tag{16}$$

Note that the Weibull hazard rate function is capable of modeling all three kinds of hazard rate functions. That is, when the shape parameter has a value less than one (that is, $\alpha < 1$), the hazard rate function for the Weibull distribution is decreasing. When the shape parameter value equals one, $\alpha = 1$, the hazard rate function for the Weibull distribution is constant. And, finally, when the shape parameter value greater than one, $\alpha > 1$, the hazard rate function for the Weibull distribution is increasing.

4.1.1.3 Service Life Estimates for a Coating System

The median time-to-failure of a coating system has very little practical significance in most coating application other than to inform the manufacturer that approximately 50 percent of the coated products will fail before this time. This parameter has little practical significance, because few coating manufacturers or original equipment manufacturers could possibly sustain the high costs, both monetary and loss of goodwill, associated with the failure of 50 percent of their coated products, particularly if the first failures occur decades in time before the median time-to-failure. Instead, the time of more practical significance to a manufacturer is the time at which some small percentage (often much less than 1 percent) of the coated products fail. Reliability analysis was specifically designed to provide estimates of these early times, called quantiles, and to make inferences about the estimates.

Assume that sample data available from testing already completed under a prescribed set of conditions. The recorded times of observed failure are $t_1, \ldots, t_r$ while the **run-outs or right censored times** (the times recorded when observation ceases even though failure has not yet occurred) are $t_{r+1}, \ldots, t_n$. Using established statistical tools, like **maximum likelihood estimators** [Mann et al., 1975; Saunders, 1982; Saunders and Myhre, 1983; Nelson, 1990], estimates of the Weibull parameters, α and β, labelled $\hat{\alpha}$ and $\hat{\beta}$, can be readily computed from the observed time-to-failure and censored data. (Maximum likelihood estimates are the values of the parameters which make the data most likely.) These estimated values are **statistics** since they are computed from the data. (Hence, they are subject to error and possible bias, and they can be no better than the data itself; unreliable data will always yield unreliable estimates.)

Once the estimates of the Weibull distribution parameters are known, one can compute an estimate of the reliability, R(t), namely,

$$\hat{R}(t) = exp[-(t/\hat{\beta})^{\hat{\alpha}}] \qquad for\ t > 0. \tag{17}$$

If the largest allowable fraction of failures in service, because of warranty costs, is δ then the associated **reliable life** at level δ, say t_{rl}, would be defined, if the true parameter values were known, as $t_{rl} = R^{-1}(1 - \delta)$. Accordingly, we can calculate the best statistical estimate of the reliable life at level δ, as

$$\hat{t}_{rl}^{\,1} = \hat{R}^{-1}(1 - \delta) = \hat{\beta}\, ln(1 - \delta)^{1/\hat{\alpha}} \tag{18}$$

It, too, is a statistic and subject to sampling error since it is a function of the estimates of and which are themselves functions of the sample.

When the allowable fraction of failures is extremely low, and inspection to detect failures in service is difficult, it is often the practice to provide an extra level of assurance and to set a **safe life**, t_s, of confidence (1 - γ), where γ « 1. (This is a statistical tolerance bound.) One wishes to find t_s such that

$$P[R(t_s) > 1-\delta] = P\{\beta[-ln(1-\delta)]^{1/\alpha} > t_s\} = 1-\gamma \tag{19}$$

Because no simple way has been found to calculate such a t_s, simulation (Monte Carlo) methods must be used in conjunction with pseudo-random samples to compute the percentiles of the distribution. But this is not always possible since required information about the cause of censoring is sometimes lacking.

A schematic representation of these two concepts is shown in figure 14. Assuming that the life distribution is a two-parameter Weibull distribution, then the procedure for finding the reliable and safe lives for a coating system is as follows:

1) Estimate the Weibull shape, α, and scale, β, parameters from either laboratory or field experimental data (methods for estimating parameters are discussed in Mann et al. [1975] and Nelson [1990]).

2) Using these estimates, construct a point estimate of the Weibull distribution and compute, for a specified value of δ, the reliable life, t_{rl}, for the coating system.

3) Construct a lower γ confidence bound (often called a tolerance bound) for t_{rl} (also called a tolerance bound for the Weibull distribution) , which gives an estimate of the safe life for the coating system population.

Despite the mathematical complexity of these procedures, such a reliability plan has found widespread acceptance in many industries (see for example Whittaker and Besumer, 1969; Murray, 1993) and has direct application in predicting the service life of coating systems.

4.1.2 Estimation of the Parameters of a Life Distribution for a Coating System Failing by a Single Failure Mode

The simplest reliability-based experiment is one in which a sample of **n** panels is randomly selected from a coating system population, exposed in a well-characterized service environment, and the first **r** out of **n** times-to-failure ($t_1 \leq t_2 \leq \ldots \leq t_r$, where $r \leq n$) observed. In this experiment, no attempt is made to differentiate among failure modes, establish the cause of failure, or quantify the exposure environment. Such an experiment is capable of determining the variability in the times-to-failure and in determining if the performance of one coating system is significantly better than the performance of any of the other coating systems on test. This kind of experiment, however, is not capable (unless the sample is inordinately large) of determining the relative frequency of different failure modes, establishing cause-and-effect relationships between the properties of the coating system and the incidence of failure, or establishing a connection between laboratory and field exposure results. Thus, with the exception of specimen replication, this experimental design is very close to the one used in the current durability methodology. Our interest, therefore, is to gain a better appreciation of the value of replication. Specifically, how does one estimate the parameters of the life distribution, place confidence bounds on these estimates, perform hypothesis tests, and determine the effects of different sample sizes on these estimates?

Parametric estimators, θ, for a life distribution can be computed from the observed times-to-failure in a variety of ways. These estimators can be computed from either censored or uncensored data using maximum likelihood estimation procedures which are versatile and have many desirable asymptotic statistical properties [Mann et al., 1975; Saunders, 1982; Saunders and Myhre, 1983; Nelson, 1990].

Since the parametric estimators for a life distribution are random variables, it is important to provide confidence bounds around these estimators. Confidence bounds are often derived through the use of pivotal quantities. A pivotal quantity, Q, is a function of the sample observations and the parameters of the life distribution to be estimated, and it has a distribution which is independent of the true parameters of the life distribution. As an example, pivotal quantities for the normal distribution are the chi-square, $[(n-1)s^2/\sigma^2]$, and the t-variate, $(x-\mu)/(s/\sqrt{n})$. Confidence intervals for a pivotal quantity are given by

$$P(q_1 < Q < q_2) = \xi \quad \textbf{(20)}$$

where q_1 and q_2 are the lower and upper confidence bounds and ξ is the confidence coefficient.

The pivotal quantities for the Weibull distribution [Bain, 1978] are

$$\frac{\hat{\alpha}}{\alpha} \quad when\ \beta\ is\ known \tag{21}$$

$$\left(\frac{\hat{\beta}}{\beta}\right)^{\alpha} \quad when\ \alpha\ is\ known \tag{22}$$

$$\left(\frac{\hat{\beta}}{\beta}\right)^{\hat{\alpha}} \quad when\ neither\ \alpha\ nor\ \beta\ are\ known \tag{23}$$

and these pivotal quantities are valid for both censored and uncensored samples [Saunders, 1976]. For certain sample sizes and at specified quantiles, confidence bounds can be found for small sample sizes by referring to the appropriate tables [Thoman et al., 1970; Mann et al., 1975] or through Monte-Carlo techniques [Lawless, 1982].

Tests of hypothesis are used in determining if the life distributions for two or more coating systems are significantly different. Such comparisons are of interest, for example, in determining whether the service life of a re-formulated coating system is significantly greater than the original formulation, whether one exposure environment is more severe than another, or whether the cleanness of a substrate has a significant effect on a coating system's service life. Assume, for example, that the first r ordered times-to-failure for a sample of **n** specimens of coating system X, where $r \leq n$, are given by $X_1, \ldots, X_r$ and the first s ordered times-to-failure from a sample of **m** specimen of coating system Y, where $s \leq m$, are given by $Y_1, \ldots, Y_s$ and assume further that the times-to-failure from both coating systems have the same distributional form, e.g., the Weibull distribution, but have different parametric values. Thus, the life distribution for coating system X is given by $F_X(t; \theta_X)$, while the life distribution for coating system Y is given by $F_Y(t; \theta_Y)$. One key question which may be asked is whether the two coating systems have significantly different life distributions (or life distributional parameters) given the sample sizes, the number of observed failures, and the associated risks of making incorrect decisions. That is, can the null hypothesis, H_o, be rejected in favor of the alternative hypothesis, H_1, where

$$\begin{aligned} H_o&: F_X(t;\theta_X) = F_Y(t;\theta_Y) \ or\ \theta_x = \theta_y \\ H_1&: F_X(t;\theta_X) \neq F_Y(t;\theta_Y) \ or\ \theta_x \neq \theta_y. \end{aligned} \tag{24}$$

Methods for performing hypothesis tests are discussed in Mann et al. [1975], Lawless [1982], and Nelson [1990].

Our confidence in the accuracy of the parametric estimators, the size of our confidence bounds on the computed reliable life, and our ability to discriminate among the service lives of different coating systems clearly depends on the size of our samples and the number of observed failures. Thus, it is important to assess the effects of different sample sizes on these statistics. The effects of different sample sizes and degrees of censoring can be determined through the pivotal quantities, eqs (21-23). In the limit, the expected value of eqs (21-23) is one. The expected loss, a criterion for evaluating the goodness of an estimator [Mann et al., 1975], for complete or censored samples, is the square of the expected value of (the pivotal quantity minus its sample value). For example, in the case of eq (22), the expected loss is given by

$$EXPECTED\ LOSS = E(1 - \frac{\alpha}{\hat{\alpha}})^2 \quad (25)$$

which has been computed for uncensored samples by Whittaker and Besumer [1969]. This expected loss function is plotted in figure 15. Whittaker and Besumer also determined the effect of different sample sizes for the other two Weibull pivotal quantities. From figure 15, it can be concluded that even for sample sizes as small as ten, maximum likelihood estimates provide good approximations to the true parameters. Ideally, a sample size of between 20 and 30 uncensored times-to-failure would be obtained, but, in practice such experiments are rare. The researcher is often constrained to smaller sample sizes and censored data. *Nonetheless, it must be emphasized that reliability analysis is essential for assessing whether two coating systems have significantly different service lives.*

4.1.3 Estimation of the Parameters of a Life Distribution in the Presence of Competing Failure Modes

A coating system seldom fails through only one failure mode. Instead, several independent (sometimes dependent) failure modes and mechanisms act simultaneously. For example, it is common for changes to occur simultaneously in both loss of appearance and loss of protection for coating systems exposed outdoors. A coating system is said to fail whenever the first critical performance value is exceeded. The competing failure modes and mechanisms are called **competing risks** or **competing causes of failure**.

Mathematically, the competing failure modes problem is stated as follows [David and Moeschberger, 1978]. Let C_i (i = 1,2, . . ., k) be the i-th cause of failure or failure mode and let $\mathbf{Y_i}$ be the random time-to-failure for a coated panel if only the i-th failure mode was operating. Then, in the presence of all **k** competing causes of failure, the observed time to failure will be associated with that cause having the smallest time-to-failure, **T**; that is, the observed time-to-failure is given by

$$T = \min(Y_1, Y_2, \ldots, Y_k) \quad (26)$$

where

Y_i is the time-to-failure from the i-th cause of failure and
T is the time-to-failure of the coated panel for any cause.

Clearly, differentiating among failure modes is an advance over grouping all failures under one category (see sec. 4.1.2), and it should be obvious that it is not valid to extrapolate from the results of one exposure environment to another if there is a change in the dominant failure modes.

As in the case of a single failure mode (sec. 4.1.2), the parameters of the life distribution, the reliable life, and the safe life can be estimated and inferences can be made on these estimators. The maximum likelihood estimators for the Weibull competing risk model, as well as a number of other parametric models, are presented in David and Moeschberger [1978].

4.1.4 Estimation of the Parameters of a Life Distribution Containing Concomitant Variables

Throughout the coating process, many variables are monitored, controlled, and recorded. Some of these variables are continuous in nature and are precisely monitored; examples include the concentration of the coating constituents and the viscosity of the coating. Other variables are discrete in nature including the batch number for a lot of paint and the method using in applying a coating (e.g., 1 = spray applied, 0 = roller applied).

An important mission of any service life prediction methodology is to identify the variables, often called **concomitant** ("occurring together") or **explanatory variables** [Elandt-Johnson, 1980; Nelson, 1990], which directly affect the service life of a coating system. Particular importance is assigned to variables which are linked to the early times-to-failure, since improvement in these variables often leads to an improvement in the service life of a product. This is demonstrated by the following example. Four sets of panels were immersed in a synthetic seawater solution at 82 °C and the time at which each panel exceeded a critical performance level was recorded. Each set of panels differed from the other sets in either its solvent (Solvent I or II) or colorant (Colorant A or B, or both); the formulations of the coatings were otherwise identical. The failure times of the four sets of panels are presented in figure 16. Note that a change in colorant had no appreciable effect on the performance of either coating system, while a change in the solvent had a large effect, especially in the early times-to-failure [Poole, 1986, 1990]. Thus, the type of solvent is an important concomitant variable for this coating system since it affects the early times-to-failure.

Techniques for identifying concomitant variables and establishing a mathematical relationship between these variables and the life distribution parameters have been discussed by Cox [1972], Elandt-Johnson and Johnson [1980], David and Moeschberger [1978], and Nelson [1990].

4.1.5 Estimation for Short-term Laboratory-based Aging Experiments

Laboratory-based aging experiments in a reliability-based methodology are tasked with a broader assignment than are such experiments in the current durability methodology. *Instead of being designed to simulate an in-service exposure environment, laboratory-based aging experiments are systematically designed to determine the relative effects of the different weathering factors which, acting alone or in concert, cause the degradation of a coating system.* Once the dominant weathering factors have been identified, the relationship between changes in the intensity of each weathering factor and the life distribution parameters of the coating system can be derived. This can only be accomplished with confidence through the use of experimental designs in which the intensities of the weathering factors are systematically varied.

As discussed in ASTM E632-92, the number of weathering factors which should be considered is often large. Fortunately, experiences show that three weathering factors (spectral ultraviolet radiation, time-of-wetness, and temperature) are responsible for most coating system degradation. Other factors, such as pollutants and abrasives, play a role in more specialized environments (e.g., industrial environments). Thus, the assumption is made that, if the degradation response of a coating system is known for these three factors, then results from properly-designed experiments can be used in making service life estimates for a coating system. If this assumption is not valid, as is the case for coatings exposed in industrial environments, then the experimental design will have to be enlarged to include other weathering factors.

Mathematically, let **S** denote a vector of weathering factors to which a coating system may be exposed in service. If only the three primary weathering factors need be included in this vector, select **p** combinations of these weathering factors (S_i, i = 1,. . ., p) covering the range of weathering combinations. For example, $\mathbf{S_o}$ may be a combination which is considered to be relatively benign; whereas, weathering combination $\mathbf{S_p}$ may contain at least one weathering factor which is set at a level which would be normally considered to be severe in service. That is, the more adverse weathering combinations are typically considered as accelerated aging tests. Now let there be an ordering of these weathering combinations (the severity of each weathering combination is not less than its predecessor) such that $S_j \le S_{j+1}$ for all j = 0,. . . ,(p-1), or equivalently,

$$S_0 \le S_1 \le . . . \le S_{j+1} \le . . . \le S_{p-1}. \qquad (27)$$

Since the severity of the life tests increases with an increase in the severity of the weathering combination (i.e., $S_{j+1} > S_j$ for j = 1, 2, . . . , p-1), it follows that the probability of failure at any time **t** for a coated panel exposed to the weathering combination $\{S_{j+1}\}$ should always be greater than the probability of failure for a panel exposed to any lower weathering combination $\{S_k$ for k = 0, ..., j$\}$; that is, $P_{j+1}(T \le t) > P_j(T \le t)$). In terms of cumulative distribution functions, this is stated equivalently as follows:

$$F(\theta_{j+1}) \ge F(t;\ \theta_j) \qquad (28)$$

for all t > 0 and for all j = 0,. . ., p-1 and where θ_j is vector of parameters of the theoretical life distribution F(t) for j-th weathering combination.

Assuming that eq (28) holds for all weathering combinations and that the time-to-failure distributions for all weathering combinations come from the same family, then a function, $p(t;\Theta_j)$, may exist relating the distributional parameters to the intensity of the weathering combinations as follows:

$$F_j(t) = F_o(p(t;\theta_j)) \qquad (29)$$

where

$F_o(t)$ is the life distribution under normal weathering conditions, and
$p(t;\theta)$ is called a time transformation function.

The time transformation function can often be assumed to be a linear function. That is $p(t;\theta) = \Psi(S,\theta)\cdot t$ over a range of weathering levels [Barlow and Scheuer, 1971; Viertl, 1983] where the most frequently used models for $\Psi(S,\theta)$ include the Arrhenius, the Eyring, and the inverse power law models and the Williams, Landel and Ferry superposition model [Mann et al., 1975; Nelson, 1990; Martin, 1982]. The use of eq (29) is supported by the results of Martin et al. [1985] and Schutyser and Perera [1992].

In the case of the Weibull life distribution (eq (13)), Halpin and Polley [1967] assumed that the shape parameter, α, was the same for all weathering combinations, whereas the scale parameter, β, varied with the intensity of the weathering factors[10] according to

$$\beta = \frac{G}{a_T \; a_d \; a_{UV}} \tag{30}$$

where G is a constant; a_T, is the acceleration factor for temperature; a_d, is the acceleration factor for dilutions; and, a_{UV}, is the acceleration factor for spectral ultraviolet radiation. Empirically, this multiplicative model appears to have some validity for predicting the service lives of polymeric materials [Brunt, 1962; Kwei, 1966; Halpin and Polley, 1967; Martin et al., 1985] and, more recently, for predicting the service lives of optical disks [Murray, 1993]. Other models are discussed by Viertl [1980, 1983], Nelson [1990] and Crowder et al. [1991].

From eq (29), a probability-of-failure/stress/time-to-failure (P-S-T) diagram can be constructed (see fig. 17) which plots iso-probability lines as a function of weathering level and exposure time. It gives the time at which a given fraction of panels can be expected to have failed (or to have survived). As is apparent from figure 17, for a given probability of survival, the time-to-failure increases as the severity of the weather decreases.

4.1.6 Cumulative Damage Models

One of the remaining problems in reliability theory is to establish a mathematical connection between laboratory and field exposure results. Under certain circumstances, it is possible to predict the service life of a coating system exposed anywhere outdoors from laboratory exposure results using cumulative damage models [Saunders, 1983]. These circumstances occur whenever the incremental damage sustained by the coating during each exposure interval is a random variable having a distribution of incremental damage which remains stationary (that is, the distribution of damage does not change during the lifetime of the coating) and the coating system fails whenever the accumulated damage exceeds a critical level.

The first cumulative damage model was proposed by Palmgren [1924] to calculate the service life of ball bearings. He used a deterministic formula giving the life of metallic components sustaining repetitions of combinations of stresses. If, under repetitions of the i-th load, the component will last μ_i cycles for i = 1,...,k, then under repetitions of a spectrum of service loads each of which eontains n_i applications of the i-th load, the number N of such load spectra before failure is given by

$$N = [\sum_{i=1}^{k} (\frac{n_i}{\mu_i})]^{-1} \tag{31}$$

[10]The assumption that the shape parameter remains constant does not always hold. In some cases, both the shape and scale parameters depend on stress level. A method for analyzing accelerated aging data in which the failure distribution is assumed to be Weibull, and both the shape and scale parameters depend on applied stress, is discussed by Viertl [1983].

This result gives the average damage rate per spectrum as the harmonic mean of the rates of accumulated damage. This result, rederived by Miner [1945], is often called Miner's cumulative damage rule. Assuming incremental damage was a random variable, Birnbaum and Saunders [1968] gave Miner's rule a stochastic interpretation. Later, Birnbaum and Saunders [1969] proposed a cumulative damage model based on renewal theory. Bogdanoff and Kozin [1985] advanced a model based on Markov chain theory, which is history-dependent and attempted to relate parameters of the distribution of fatigue life to the physical constants governing the failure mechanism. More recently, Doksum and Hóyland [1992] proposed a cumulative damage model in which accumulated decay was governed by a continuous Gaussian process whose distribution changed with the magnitude of applied stress.

Even though cumulative damage models seem to be intuitively applicable, to date, no cumulative damage model has been proposed to connect laboratory and field exposure results for polymeric materials. So none has been verified. One of the few cumulative damage models which has been developed which may have application to polymeric materials is one which is commonly used in the medical and biological fields for predicting the degradative effects of spectral UV radiation. Specifically, this model has been used to predict the incidence of melanoma and non-melanoma cancers in humans from laboratory exposure results; it is discussed in section 4.2.2.

4.2 Proposed Changes in the Current Data Collection Procedures

In section 4.1, the mathematical underpinnings of the proposed reliability-based methodology were briefly discussed. In this section, changes in the experimental procedures needed to implement a reliability-based methodology are discussed and recommendations made.

4.2.1 Quantification of Initial Property Measurements

Very few databases containing useful data on the service life of coating systems exist in the current durability methodology even though laboratory-based and outdoor exposure tests have been conducted for over seventy years [Appleman, 1990]. In the proposed reliability-based methodology, however, computerized databases will play a pivotal role due to the quantity and quantitative nature of the collected data and to the high costs associated with collecting data.

Computerized databases are receiving increasing attention because of their widespread use in other disciplines [Ambler, 1985; Rumble and Carpenter, 1990; Glazman and Rumble, 1990; Long et al., 1991; Frawley et al., 1992; Gibbons, 1992; Desmond et al., 1992; Barry and Reynard, 1992; Newton, 1993; White, 1993]. For computerized databases to be successful, the data must be stored in a standardized format and each data set must be uniquely described by a set of identifiers. These identifiers are needed not only to describe the data stored within a data set, but also to act as benchmarks for determining the extent of degradation of a coating system and to serve as an index for navigating among databases in search of concomitant information which may be useful in explaining or predicting the performance of a coating system.

The most obvious identifiers for a data set are a coating system's composition and initial properties. However, the choice of which compositional and initial property values to measure is complicated by the large number of variables which can be selected. Using too few variables or the wrong variables may hinder the establishment of causal relationships between a coating system's initial properties and its performance, as well as hindering the intercomparison, interchange, and regrouping of data from different databases or from different coating systems. On the other hand, using too many descriptors may make the database too cumbersome and too expensive to develop and maintain (since all measurements are expensive to make); it may also describe a nominal population which has so few members that no statistically significant relationships can be established [Amster et al., 1982].

Guidance in developing database formats for materials is provided by Glazman and Rumble [1988], Barry and Reynard [1992], and Newton [1993]. Help for selecting identifiers, standardizing data storage formats, and standardizing terminology is provided by ASTM E 1313-90, Standard Guide for Development of Standard Data Records for Computerization of Material Property Data, and ASTM E 1314-89, Standard Practice for Structuring Terminological Records Relating to Computerized Test Reporting and Materials Designation Formats. ASTM E1338-90, Standard Guide for the Identification of Metals and Alloys in Computerized Material Property Databases, provides guidelines for identifying metals and metal alloys. Finally, and most important for our purposes, a draft standard guideline for identifying coatings is under development by the Committee E-49.

4.2.2 Quantification of In-Service Exposure Environments

From section 3.2, it is evident that in-service exposure and outdoor results are not reproducible at any location over any time scale. Outdoor results, however, provide valuable information about the dominant failure modes and times-to-failure for a coating system exposed at a given site over a specified period of time. These benefits can only be realized if the severity of each weathering factor is quantified in such a way as to facilitate comparisons with laboratory-based exposure data and with data collected from other outdoor exposure sites or at the same outdoor site but over a different time period.

Initially, it is proposed that only the three most common weathering factors (ultraviolet radiation, temperature, and time-of-wetness) be used in characterizing the exposure at an outdoor site. These factors are known to cause the degradation of most coating systems and are the ones which are most often monitored and controlled in the laboratory. If in-service environments cannot be adequately characterized by these factors, then other weathering factors must be included in characterizing an exposure environment.

In the current practice, it is common to assume that weathering factors act independently from each other and that the weather repeats itself after a sufficiently long period of time. Statistically, these factors are usually characterized by their daily and monthly total accumulated values for ultraviolet radiation and precipitation or by their averages and their high and low values for temperature, relative humidity, and dew point. Physically, solar UV-irradiance is characterized by total UV-irradiance (total irradiance between 295 and 385 nm) incident on flat panels sloped at one or more angles relative to the horizon. Temperature is characterized by ambient, black panel, and under-glass temperatures, while measures of the moisture level include time-of-wetness [ASTM G84-92], dew point, relative humidity, and precipitation measurements.

Although weather statistics have been reported monthly for a long time by most commercial exposure sites, the National Oceanic and Atmospheric Administration (NOAA), and others [Hennig, 1990], this data is seldom used since no known functional relationship has been established between reported values and coating system degradation [Douglas, 1993]. Reasons for this may be that these factors are not being properly characterized.

With respect to statistical characterization, it is known from laboratory-based studies that weathering factors act synergistically in causing a coating system to degrade and that often, for values below some threshold, the rate of degradation related to a weathering factor is so low that the degradation at levels below this threshold can be neglected for all practical considerations. For example, wet-dry cycles (and perhaps freeze-thaw cycles) have been implicated in the cracking of paint and are viewed by some as a major cause of coating system failure in the field [Timmins, 1979; Smith, 1988; Appleman, 1989a,b; Skerry et al., 1990; Oosterbroek et al., 1991]. Temperature and moisture are known to have threshold values below which the rate of degradation is so low that it can be neglected; but above which, the rate of degradation increases exponentially with any increase in temperature, moisture, or both [Vernon, 1931; Martin and McKnight, 1985; Schutyser and Perera, 1992].

The existence of synergistic effects, the effects of wet-dry cycles, and the possible presence of threshold values raise serious questions as to whether characterizing weathering factors by their mean value and viewing the degradation effects of these factors as acting independently is meaningful in the context of service life prediction. As an alternative, it is recommended that until more is known about the effect of the individual weathering factors on the degradation process, time series for each of the primary three weathering factors be simultaneously monitored and characterized.

The time series for a weathering factor can be generated by sampling its intensity at set constant time intervals and it can be quantitatively characterized as an infinite series of sine and cosine functions (a **Fourier Series**) in which the amplitudes are estimated using **Fourier analysis** [Barry and Perry, 1973; Körner, 1989; Burroughs, 1992].

The Fourier series for a weathering variable, X(t), is expressed as a sum of harmonics as follows:

$$X(t) = \overline{X} + A_1\sin\left(\frac{2\pi t}{P}\right) + B_1\cos\left(\frac{2\pi t}{P}\right) + A_2\sin\left(\frac{4\pi t}{P}\right) + B_2\cos\left(\frac{4\pi t}{P}\right) + \ldots + A_n\sin\left(\frac{2n\pi t}{P}\right) + B_n\cos\left(\frac{2n\pi t}{P}\right) \quad (32)$$

where

$\overline{X}$ is the average of X(t) over the entire series
n is the number of the harmonic and is an integer, and
P is the time span of the entire series.

Through Fourier analysis it is possible to compress volumes of data into a small set of Fourier coefficients with little or no loss of information. Then, the estimated Fourier coefficients can, at any time, be substituted back into the Fourier series (eq (32)) and the time series can be regenerated with virtually no loss in information. This has been demonstrated for the temperature of painted panels exposed on outdoor racks by Saunders et al. [1990] and for solar spectral UV-radiation by Martin et al. [1993] using the data generated by the Smithsonian Institution at their Rockville, MD site [Correll et al., 1992].

In addition to changing the way weathering factors are statistically characterized, it is recommended that changes be made in the way they are physically characterized. For the purposes of the service life prediction of coatings, outdoor weathering factors should be characterized using metrics which are relevant to the way that coating systems degrade and the way these factors are characterized in the laboratory. Metrics for expressing the severity of temperature and UV-degradation are proposed in the following paragraphs. A satisfactory metric for expressing the degradation effects of moisture has not yet been identified, although extensive efforts have been made in making wetness measurements [Grossman, 1978; Sereda et al., 1982; Haagenrud et al., 1984; and Mannsfeld, 1982, 1988; Rosen and Martin, 1991].

One of the temperatures controlling the rate of degradation of a coated panel is the temperature of the panel. In laboratory experiments, the temperature of the coated panels can be monitored directly by outfitting each panel with a thermocouple or indirectly by controlling the exposure conditions. Obviously, such methods would be expensive if the number of specimens was large, as at many commercial outdoor exposure sites. A more economical and practical approach to monitoring panel temperature, but one that is dependent on the availability of adequate models, would be to determine the thermal properties of a coating system before its exposure in its expected in-service environment. Additionally, common meteorological variables like ambient temperature, sky temperature, background temperature, wind speed, and total solar radiation during its exposure need to be monitored. Then the panel temperature for all the coated panels at an exposure site can be computed by solving for T_p for each panel using the following energy balance equation [Duffie and Beckman, 1991]

$$A H_t \alpha = 2hA(T_p - T_a) - \varepsilon A \sigma (T_s^4 - T_p^4) - \varepsilon A \sigma (T_b^4 - T_p^4) \quad (33)$$

where

- A is the surface area of a panel (m^2);
- H_t is the total solar radiation ($W\ m^{-2}$);
- α is the absorptivity of the coating;
- h is the convection coefficient ($W\ m^{-2}\ K^{-1}$), which is a function of wind speed;
- σ is the Stefan-Boltzmann constant which is $5.67 \times 10^{-8}\ W\ m^{-2}\ K^{-4}$;
- T_a is the ambient temperature (°K);
- T_b is the background temperature (°K);
- T_p is the panel temperature (°K);
- T_s is the sky temperature (°K); and
- ε is the panel emissivity.

The feasibility of this approach has been demonstrated by Saunders et al. [1990].

Ultraviolet radiation is deleterious to most organic materials. The medical, biological, and agricultural communities characterize the degradative effects of ultraviolet radiation using a different approach from the one used in the coatings community [Zerlaut, 1993]. They relate the degradative effects [Cutchis, 1978; Fears and Scotto, 1983; Scotto et al., 1975, 1987] directly to **total effective UV dosage**, D_{tot}, whereas the coatings' community tends to use total UV irradiance. The total effective UV dosage is defined by

$$D_{tot}(t) = \int_{0}^{t} \int_{\lambda min}^{\lambda max} Eo(\lambda, t)(1 - e^{-A(\lambda)})\phi(\lambda) d\lambda\, dt \quad (34)$$

where

λ_{min} and λ_{max}	are the minimum and maximum photolytically effective wavelengths, respectively;
$E_o(\lambda,t)$	is the UV spectral irradiance to which the material is exposed at time t ($W\ m^{-2}\ nm^{-1}$);
$(1 - e^{-A(\lambda)})$	is the spectral absorption of a material (dimensionless); and
$\phi(\lambda)$	is the spectral quantum yield of the material (dimensionless).

Thus, the total effective UV-dosage is computed by integrating the product of the spectral irradiance, $E_o(\lambda,t)$, the spectral absorption coefficient, $(1 - e^{-A(\lambda)})$, and the UV solar spectral efficiency of the absorbed radiation, $\phi(\lambda)$, over both the range of photolytically effective wavelengths and the duration of the exposure. Experimentally, the spectral absorption and the spectral quantum yield coefficients are determined from laboratory-based experiments. The spectral irradiance measurements are monitored in both the laboratory and field. The total effective dosage, D_{tot}, can then be related to biological damage using a damage function. The possible application of this approach to coatings has been discussed by Martin [1993] and some preliminary analyses of spectral UV irradiance measurements have been performed by Martin et al. [1993] and Lechner and Martin [1993].

4.2.3 Quantification of Coating System Degradation

Over the last two decades, significant advances have been made in the quantification of appearance and protective properties of coating systems.

Examples of advances in appearance measurements at the microscopic or molecular level include infrared spectroscopy [Bauer et al., 1984; Hartshorn, 1992; Bauer, 1993; van der Ven, 1993], x-ray photoelectron spectroscopy [Wilson, 1993], electron spin resonance [Gerlock et al., 1985], and ATR spectroscopy [Wernstahl, 1993]. Improvements in macroscopic appearance measurements have largely revolved around the computerization of existing optical appearance measurements [Schläpfer, 1989].

Examples of advances in corrosion protection measurements at the microscopic level include chemical property measurements of coating system degradation using Fourier transform infrared spectroscopy [Nguyen and Byrd, 1987; Nguyen et al., 1991], changes in the electrochemical properties using AC impedance spectroscopy [Leidheiser, 1992; Tait, 1993], and changes in the internal mechanical stress properties in a coating system as it ages [Croll, 1979; Perera and van den Eynde, 1981, 1987; Perera, 1990]. Improvement in macroscopic corrosion protection measurements include imaging corrosion products or blistered areas using visible or thermographic cameras linked to a computer image processor [McKnight and Martin, 1984, 1989; Bentz and Martin, 1987; Duncan and Whetton, 1993] and along with a wide variety of other techniques [Beissner and Birring, 1988].

Although significant measurement advances have occurred in both the microscopic and macroscopic properties of a coating system, few of these measurements have been linked with one another making it difficult to establish a connection among degradation measurements and, hence, making it difficult to compare data generated in the same or different laboratories. It is recommended that an effort be made to establish linkages between degradation measurements to facilitate the intercomparison of collected data.

4.2.4 Experimental Designs

Design of experiments provides a systematic plan or strategy for conducting experimental investigations so as to collect data in the most efficient manner [Hahn, 1977; Box et al., 1978; Box and Bisgaard, 1987]. In our case, the goals are to design experiments which are cost effective and yet capable of 1) distinguishing among important and unimportant factors in regard to their effect on the service life of a coating system, 2) obtaining information about possible interactions among the experimental factors affecting a coating system's service life, and 3) generating reliable data which advance understanding of coating degradation processes and which provide coating system performance data which can be stored in a database for future retrieval and analysis.

The experimental design which is selected often depends on the number of factors which have to be considered and the existing state of knowledge about the interactions among these factors. When the number of factors is large and our knowledge of the interactions among the factors is rudimentary, fractional factorial designs at two levels are often used to screen out unimportant factors and, correspondingly, identify important factors. Once the number of factors has been reduced to a manageable size (e.g., five or less), then full factorial experiments can be used to gain a better understanding of how these remaining variables interact. Finally, once the functional relationships between the few significant variables is understood, experiments can be designed to optimize a product or to predict its service life. Often, during this last stage of the process, the experiments are designed to validate a mechanistic model containing all the important independent variables.

Design of experiments is not new to the coatings industry in that experimental designs are commonly used in formulating new coatings to ensure good application and initial appearance properties [Cox, 1984; Rooney, 1991; Vaidya and Natu, 1992; Neag et al., 1994]. However, the techniques have seldom been extended to the design of laboratory-based aging tests, even though the logic is clear. In a reliability-based service life prediction methodology, design of experiments is essential in planning cost-effective laboratory-based experiments.

Design of experiments for laboratory-based aging tests is complicated by the need to handle censored and non-normally distributed time-to-failure data. Fortunately, Nelson [1990] has shown that standard maximum likelihood and regression techniques are capable of handling such complications when the list of factors has been reduced to a manageable size. Problems arise, however, in analyzing highly censored data generated from highly fractionated experimental designs. In this case, maximum likelihood estimators may no longer exist. Current methods for-analyzing such data have been reviewed by Hamanda and Wu [1991].

4.2.5 Databases

The quantity of data to be collected in a reliability-based methodology far exceeds that collected in the current durability methodology. It is the ability to handle, store, retrieve, and discover knowledge from the collected data which will justify the costs of the reliability-based methodology. The only realistic way of handling large data sets is through the use of **computerized materials databases** [Barry and Reynard, 1992; Newton, 1993].

Progress in the development of computerized databases, including intelligent databases, can be attributed to the combination of faster computers, powerful workstations, massive storage capability (e.g., optical storage), expert systems, neural nets, and advances in sensor technology. The importance of computerized databases lies in the ability they give to the researcher to instantly access massive amounts of data from a variety of sources and to use it to discover relationships and to confirm hypotheses. The sources of the data can be diverse and are not limited to service life data. For example, historical data and data collected during the pre-qualification of a coating system may provide concomitant information useful in explaining the service life performance of a coating system. Obviously, the database grows by incorporating new data gained through the execution of new laboratory and field experiments.

According to Rumble [1992], the success of any computerized material database depends on:

1) Complete, unique, and unambiguous identification of the initial properties of the subject material.
2) Quantitative characterization of material degradation in terms which are relatable to its performance.
3) Storage of the collected data in an electronic format which makes its retrieval transparent to other software and hardware systems.
4) Identification of efficient algorithms for making data inquiries and for establishing causal relationships among the data.

The importance of unique identification of a coating system for which data is to be entered into the database was briefly discussed in section 4.2.1. The issue of determining which material and performance properties should be selected and measured was discussed in section 4.2.1 and 4.2.4. The difficulty exemplified by cases in which there are different measures of the same failure mode (e.g., electrochemical and visual evaluation of corrosion) was discussed in section 4.2.3. It is expected that agreement on the preferred data will require extensive interactions and discussion among representatives of the coatings community. Finally, issues 3 and 4 must involve end users and experts in computerized materials databases.

4.3 Assessment of Reliability-based Service Life Prediction Methodology

A reliability-based methodology has been discussed as a possible alternative to the current durability methodology. It differs from the current durability methodology in both its goals and its underlying assumptions. Its goal is to predict the service life of a coating system exposed in its intended exposure environment, as opposed to comparing the performance rankings of nominally identical sets of coated panels exposed in the laboratory and field. In making these predictions, data from all three sources of service life data -- short-term laboratory-based experiments, long-term, in-service experiments, and fundamental mechanistic studies -- are used.

Implementation of a reliability-based methodology will require changes in all aspects of the current durability methodology. These changes result from the quantitative nature of the service life estimates and include 1) more systematic characterization of the initial properties of a coating system, 2) quantitative characterization of each of the weathering variables comprising the in-service environment, 3) quantification of macroscopic degradation and relating these measurements to microscopic degradation measurements, 4) utilization of experimental design techniques in planning and executing short-term laboratory experiments, and 5) development of computerized techniques for storing, retrieving, and analyzing collected data. These changes will be justified in view of the greater reliability of the results.

The greatest changes will occur in the objectives of short-term laboratory based and long-term in-service experiments; the objective of fundamental mechanistic studies will remain essentially unchanged. In a reliability-based methodology, long-term in-service experiments are viewed just like a laboratory-based experiment, albeit one in which individual weathering factors cannot be controlled. This is accomplished by characterizing in-service environments in the same manner that exposure environments are characterized in the laboratory and relating in-service exposure results to laboratory-based exposure results through **cumulative damage models**. In order to compare laboratory-based and in-service exposure results, individual weathering factors need to be quantitatively characterized in the same manner that these factors are characterized in the laboratory (see sec. 4.2.1). Cumulative damage models are discussed in section 4.1.6. Laboratory-based experiments are systematically designed to identify and isolate variables affecting the service life of the coating system. This is accomplished through well-recognized experimental design procedures. Finally, since reliability-based experiments generate quantitative results, of known precision and accuracy, it would be a waste not to build upon these data. This is accomplished by storing the data from each experiment in a database (see sec. 4.2.5) and, once the database has reached sufficient size, querying the data in an effort to establish relationships among the pooled data which were not previously recognized.

The successful application of the reliability-based methodology to coating systems has been demonstrated by a number of researchers, including Martin et al. [1985, 1989], Schutyser and Perera [1992, 1993], Tait [1993a, 1993b], and Crewdson [1993].

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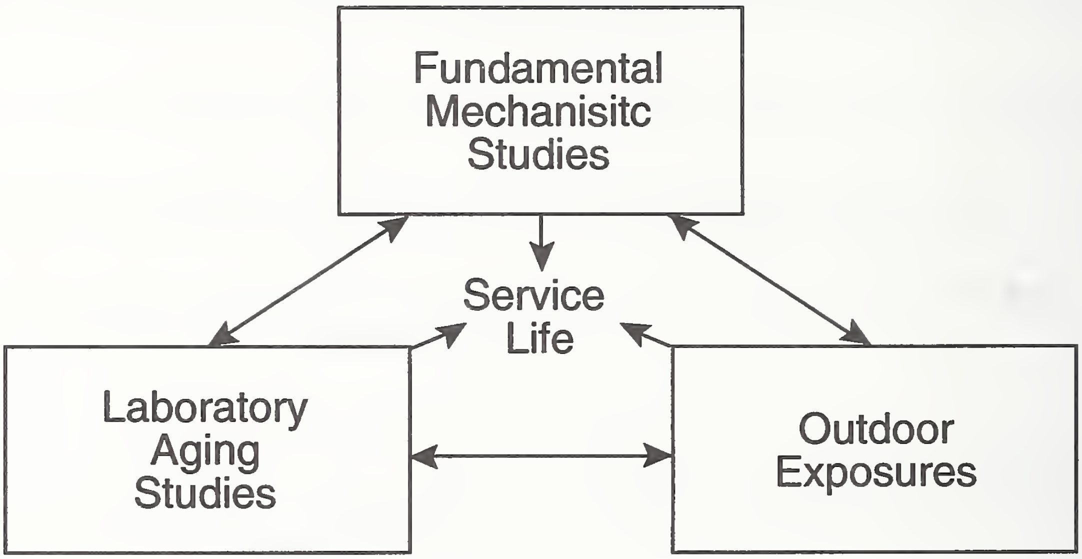

Figure 1. Three Primary Sources of Quantitative Service Life Data.

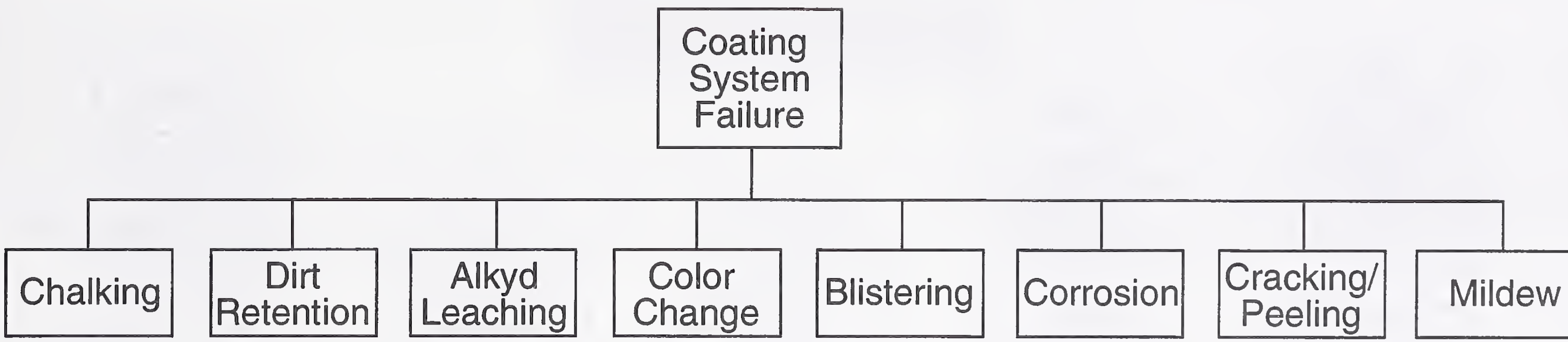

Figure 2. Common Failure Modes for Architectural Coatings

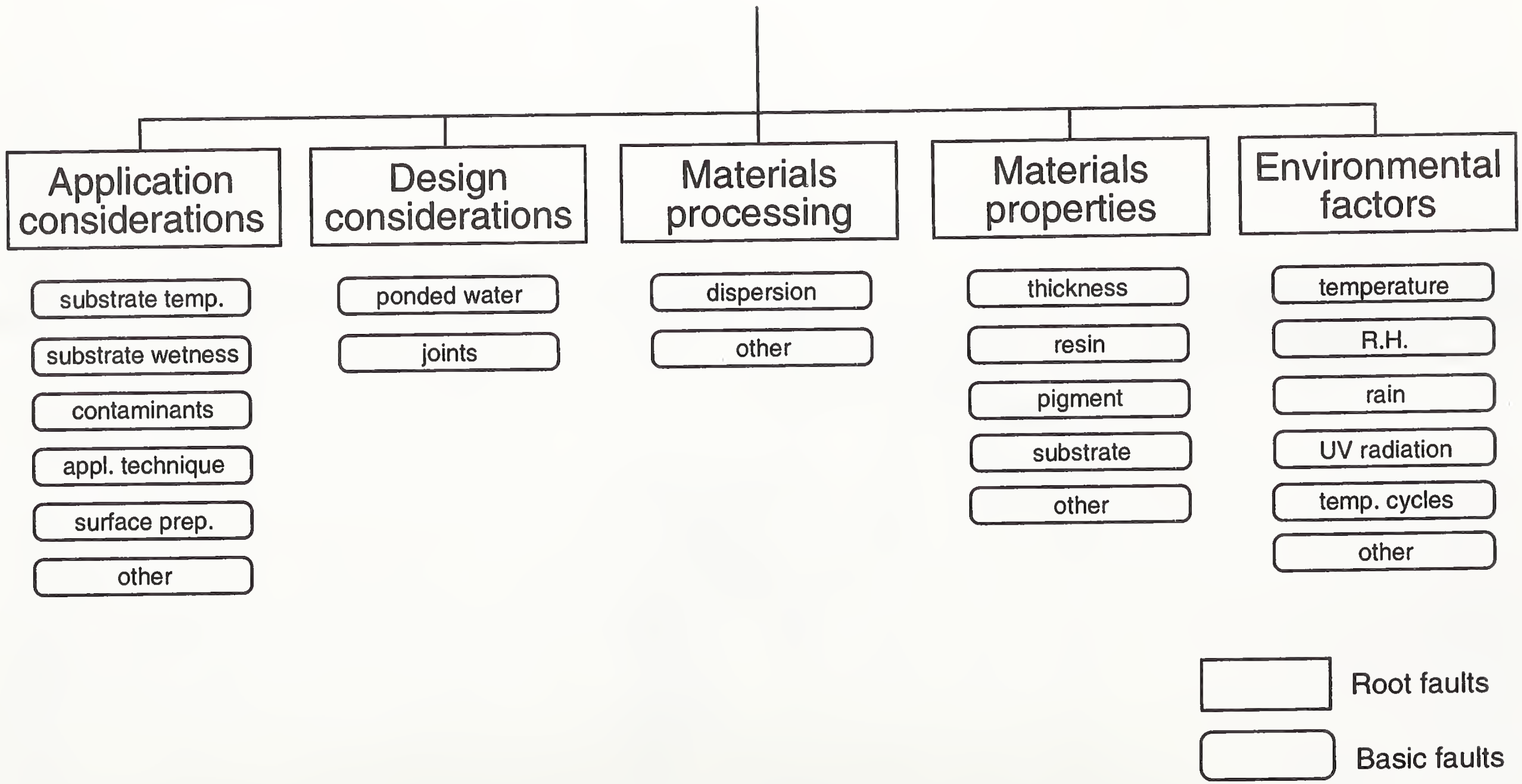

Figure 3. Common Root and Basic Faults Associated With the Failure of Architectural and Non-Architectural Coating Systems.

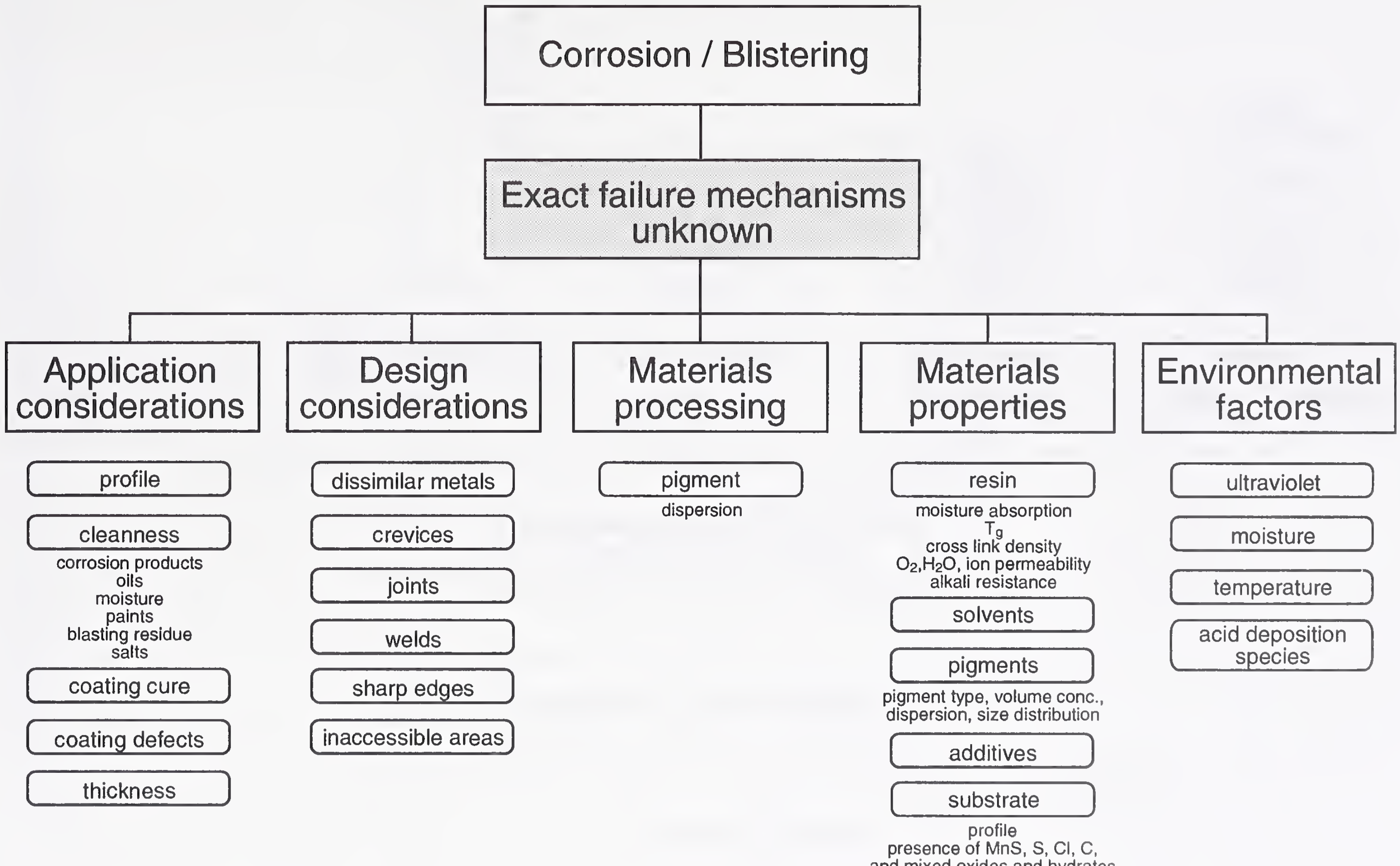

Figure 4. Fault Tree for Loss of Protection Due to Corrosion where the Underlying Failure Mechanisms Are Poorly Understood. This Lack of Understanding is Graphically Portrayed by the Black Box Between the Observed Failure Mode and the Root Faults

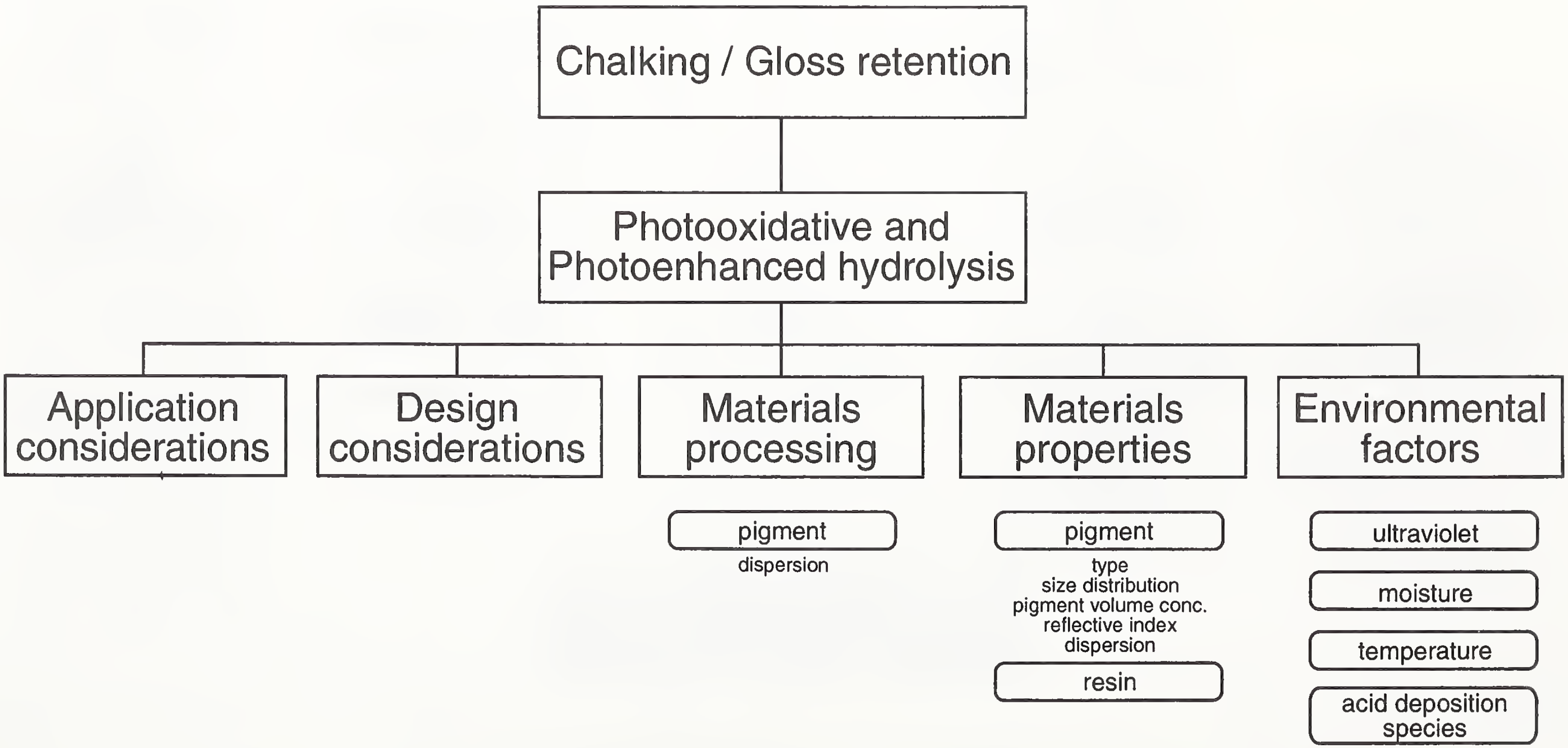

Figure 5. Fault Tree for Loss of Appearance Due to Color and Gloss Loss Where the Underlying Failure Mechanisms are Reasonably Well-Understood.

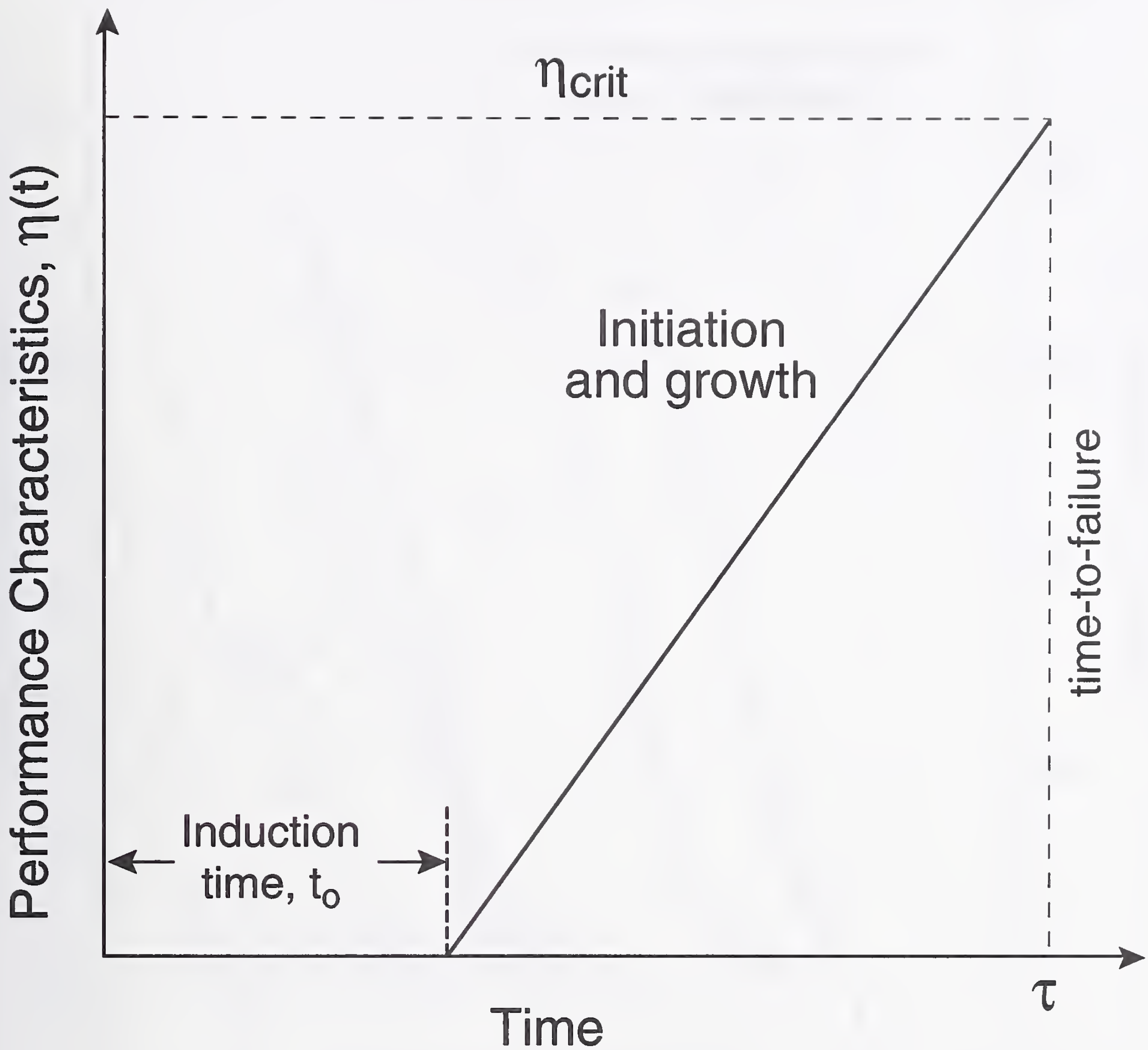

Figure 6. Schematic Representation of Changes in a Coating System's Performance Characteristic (e.g., Blistering) Over Time.

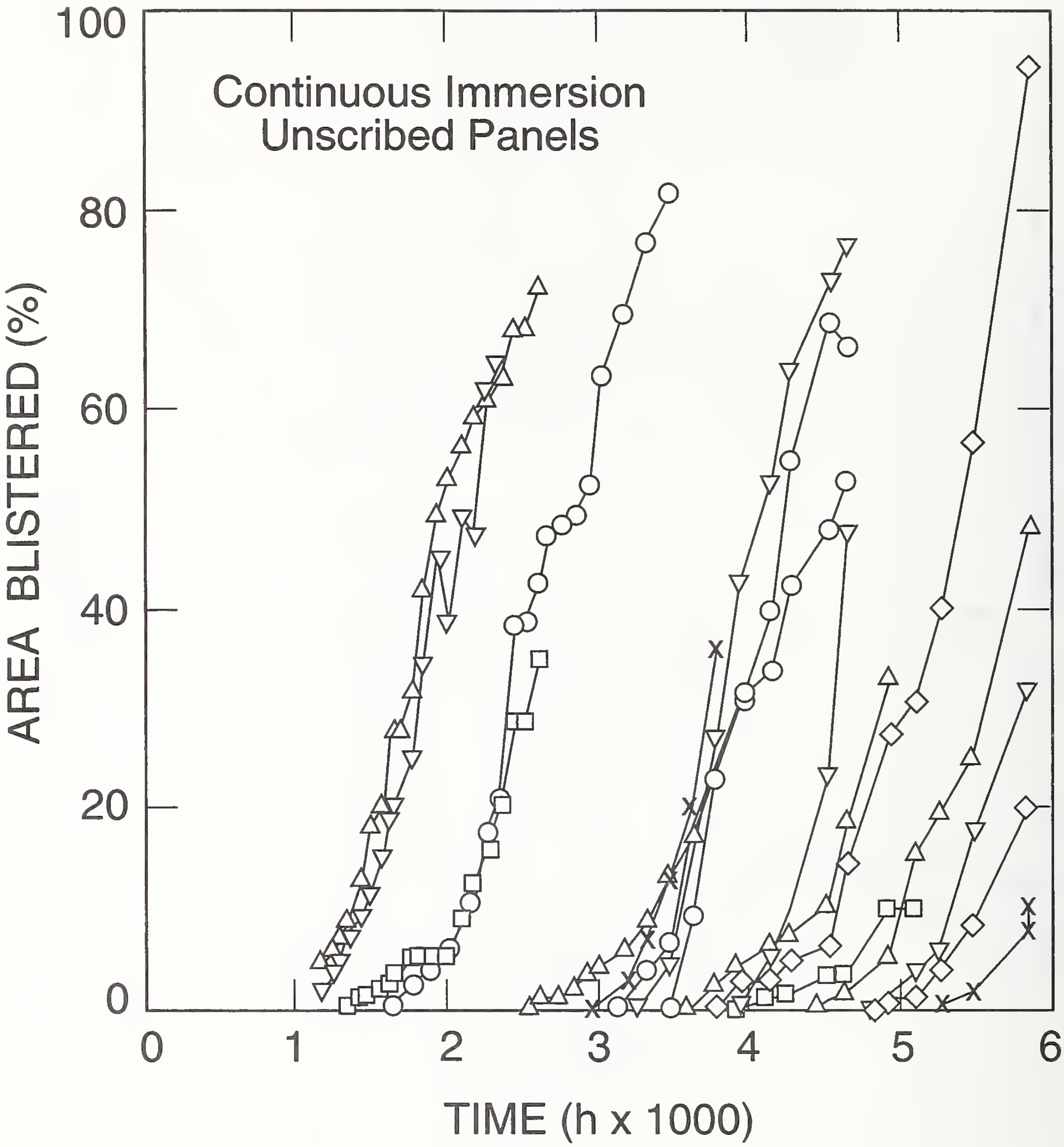

Figure 7. Percent Area Blisters Versus Immersion Time for Twenty-Four Coated Steel Panels With No Intentionally Induced Defects. The Panels Were Continuously Immersed in a 5% NaCl Solution. Six of the Twenty-Four Panels Displayed No Degradation After 6000 h of Immersion; Data for These Panels are not Displayed [Taken from Martin et al., 1990].

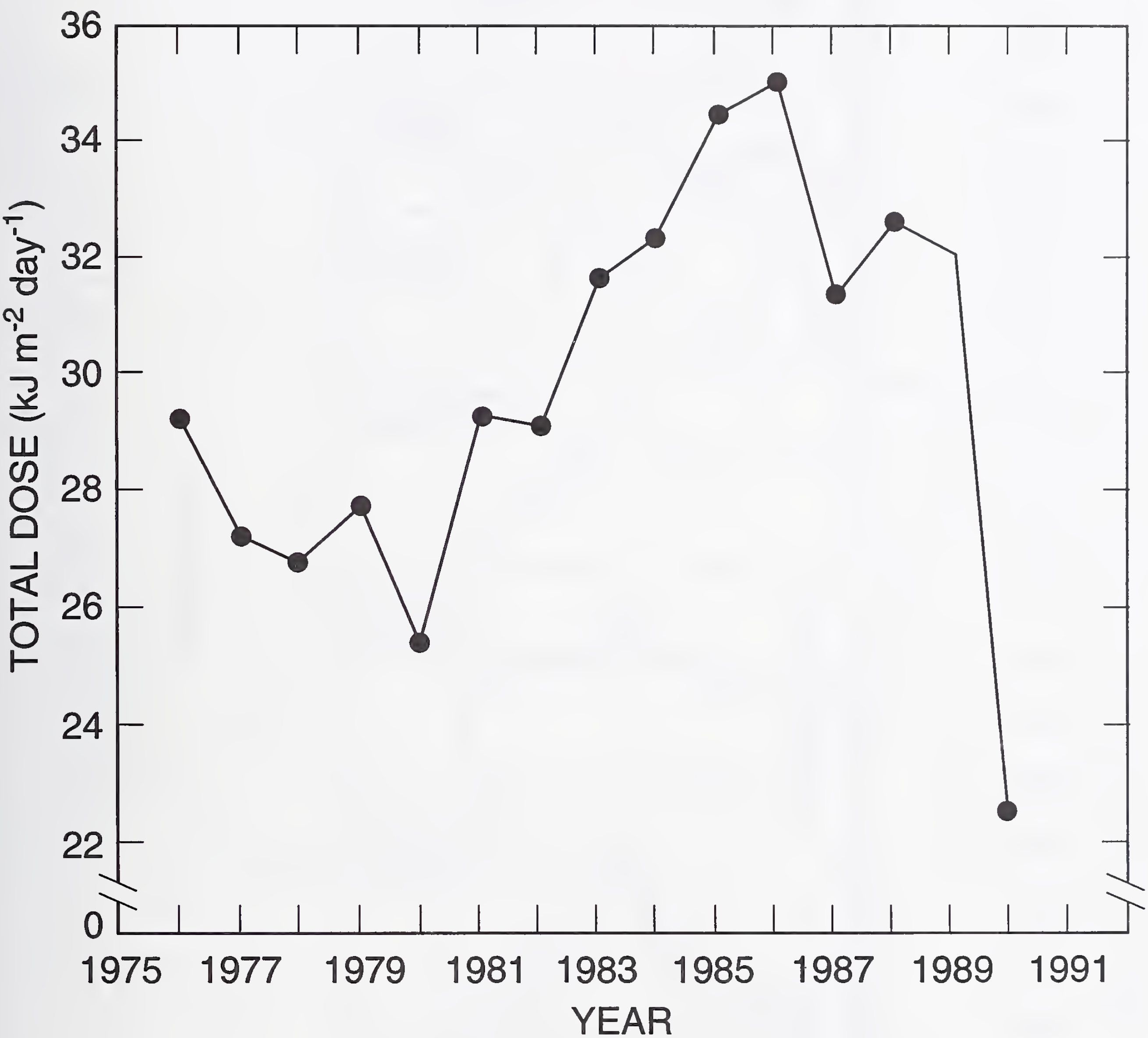

Figure 8. Time Series of the Calendar-Year Average of Total Average Daily UV-B Radiation Dosage From 1975 to 1990 in Rockville, MD [taken from Correll et al., 1992].

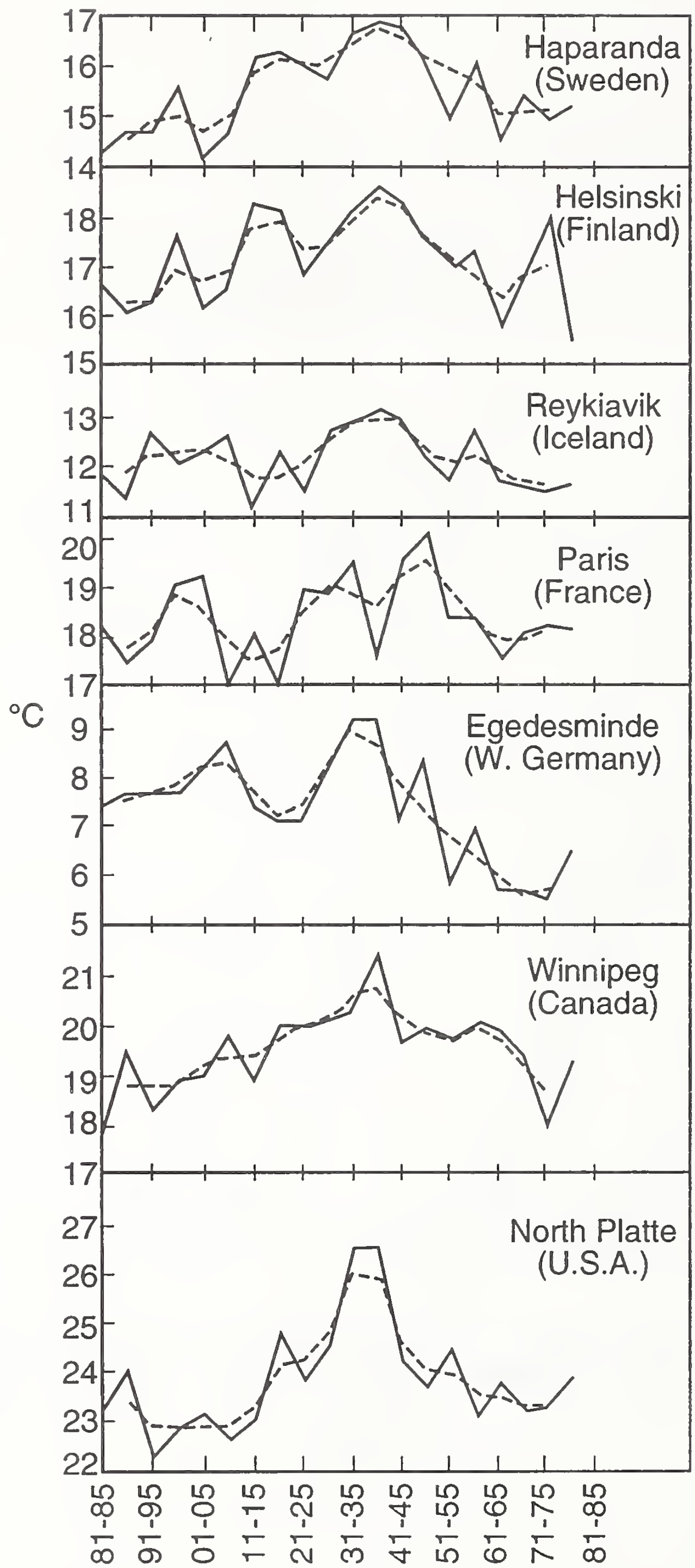

Figure 9. Time Series of 5-Consecutive-Year Mean July Temperatures at Seven Northern Hemisphere Weathering Stations From 1880 to 1980 (taken from Wallen [1984]).

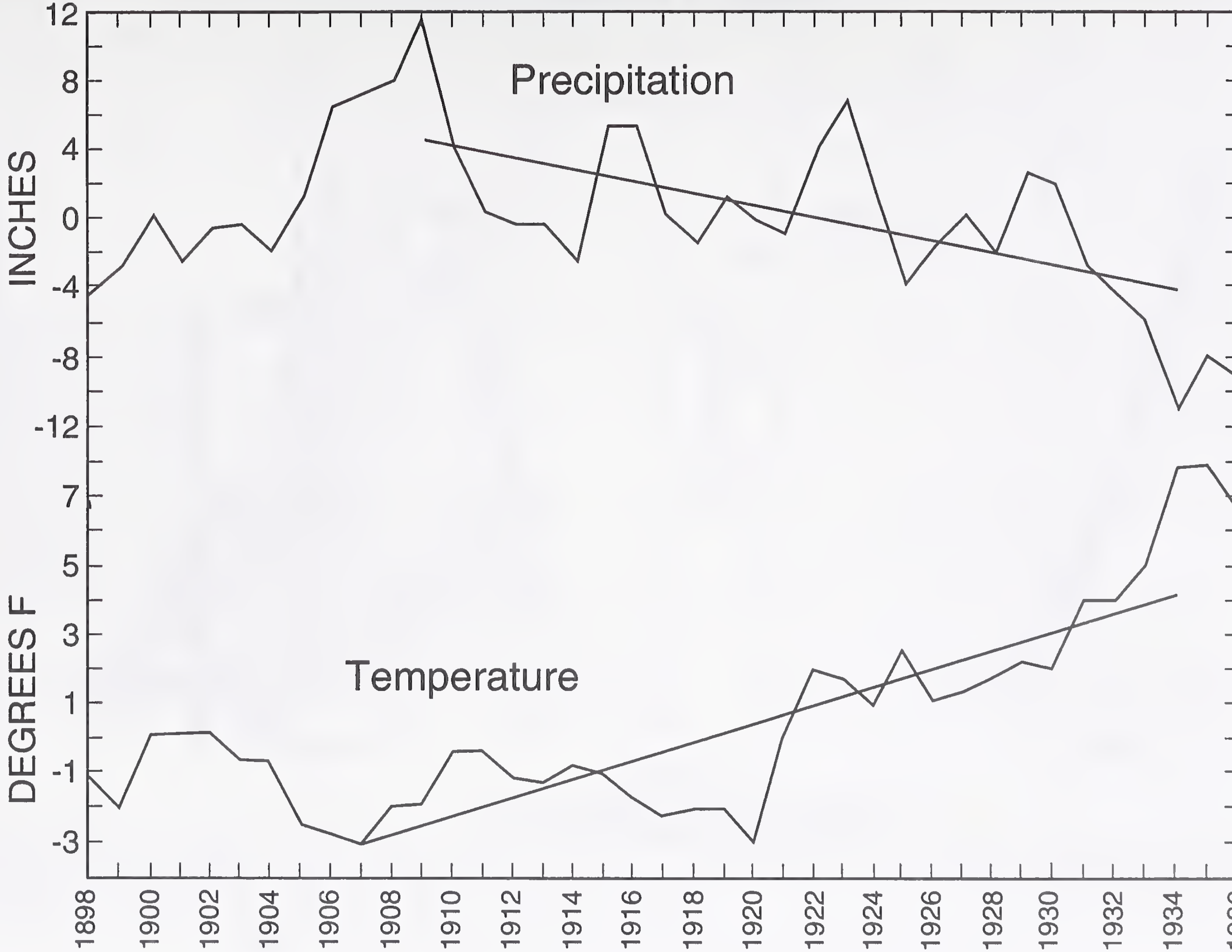

Figure 10. 5-Consecutive-Year Mean Precipitation and Temperature Departures From Normal for the Great Plains of the United States From 1898 to 1936 (Taken from Wallen [1984]).

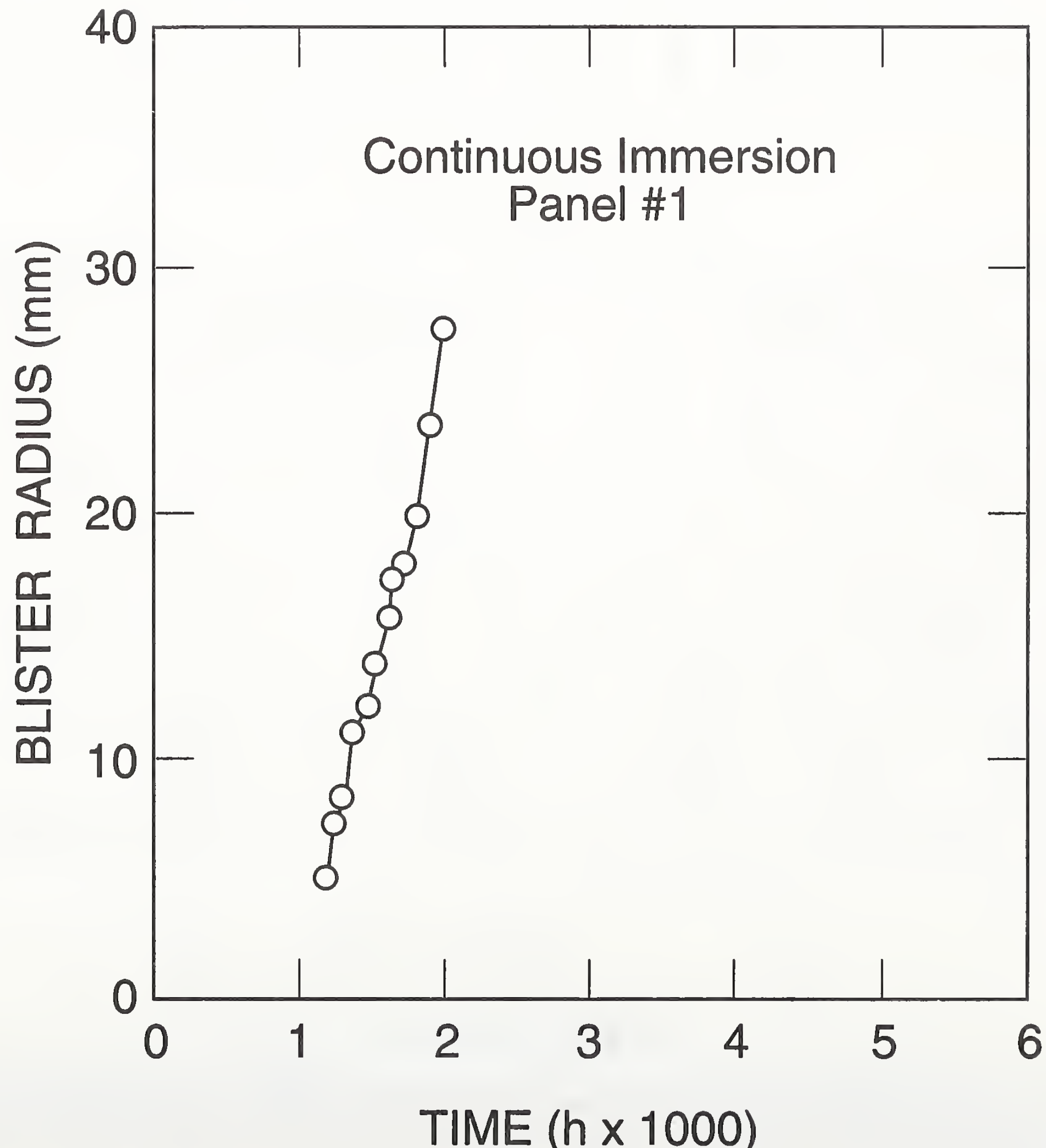

Figure 11. Sample Function for the Radial Growth of a Cathodic Blister for an Unscribed, Alkyd-Coated Steel Panel Continuously Immersed in a 3.5% NaCl Solution [Martin et al., 1990].

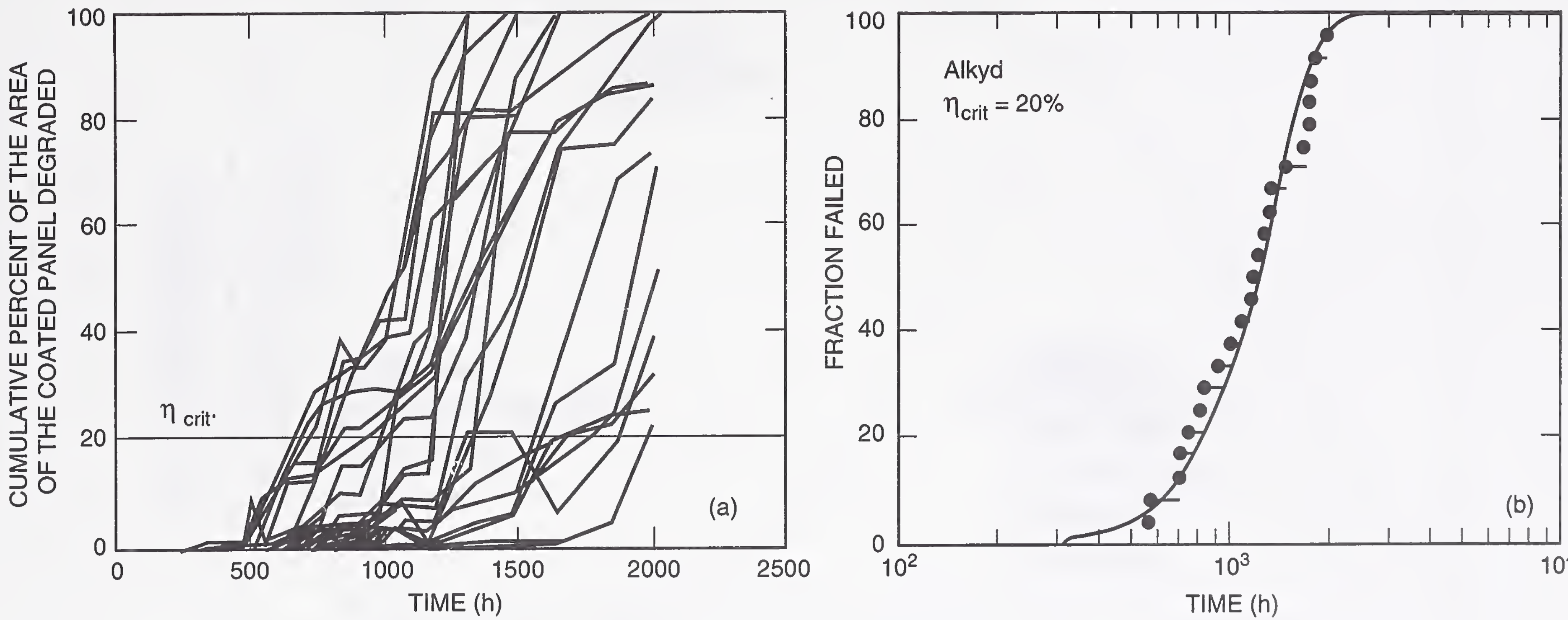

Figure 12. A) Sample Functions for 23 Scribed alkyd-Coated Panels, Continuously Immersed in a 3.5% NaCl Solution. Each Line is the Sample Function for the Degradation of One Panel. B) Sample and Theoretical Time-to-Failure Distributions Fitted to the 23 Sample Functions Using 20% Delaminated Area as the Failure Criterion. The Dots Show the Sample Life Distribution.

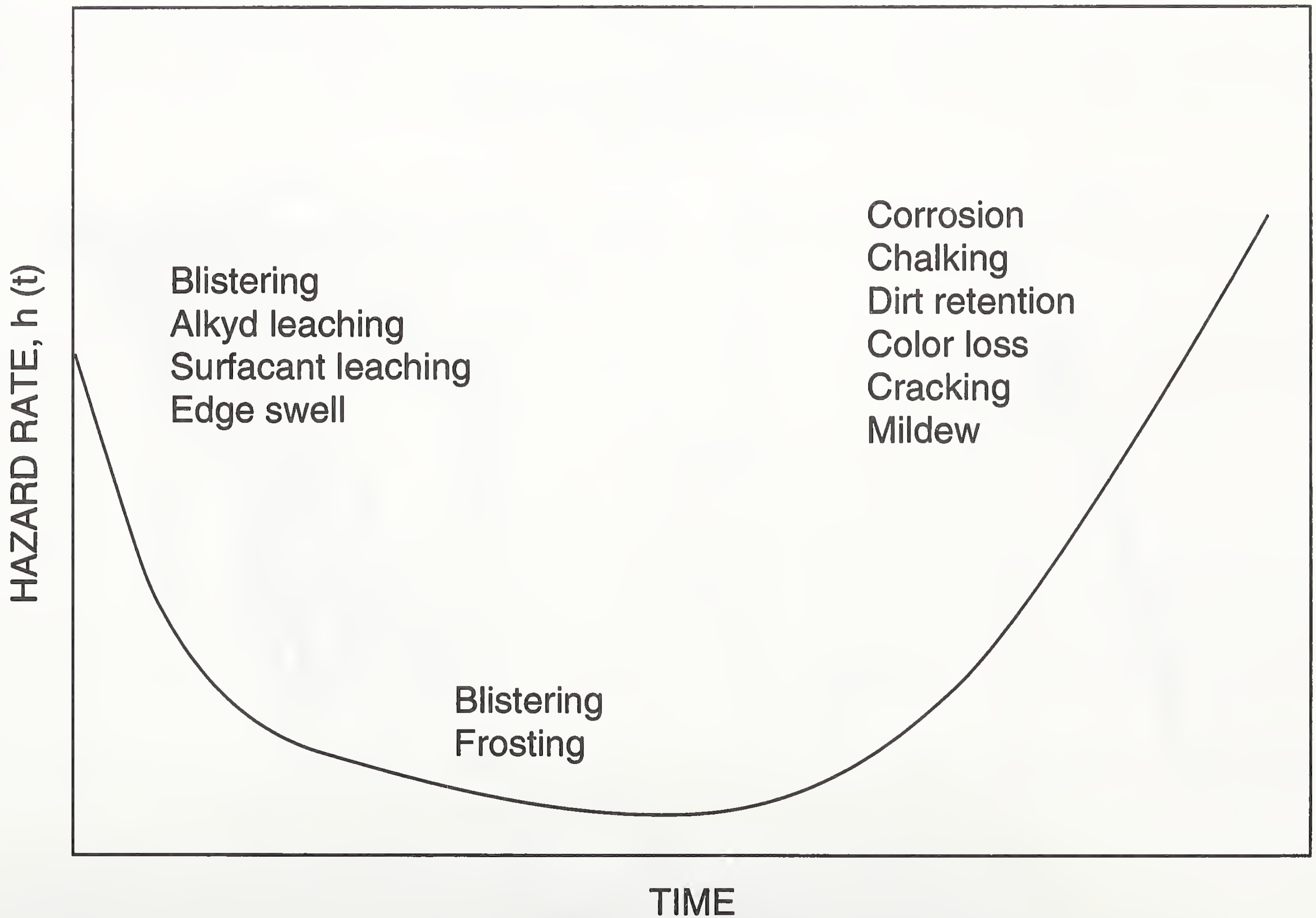

Figure 13. Bathtub-Shaped Hazard Rate Curve Such as is Common for Architectural Coatings. The Common Failure Modes Which Contribute to the Slope of the Curve are Identified.

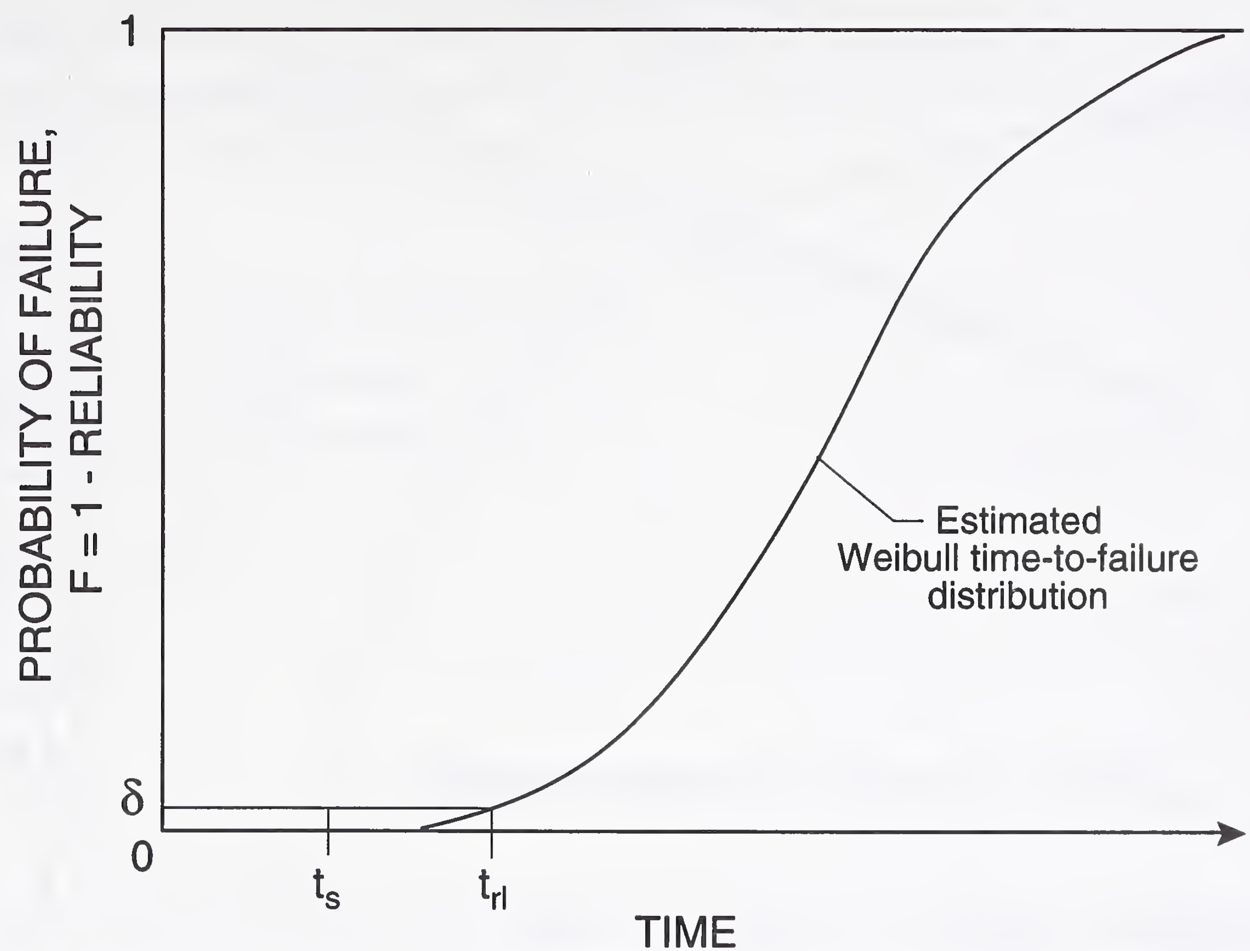

Figure 14. Schematic Representation of Proposed Reliability Plan Depicting the Weibull Life Distribution and a Lower Tolerance Bound for this Distribution. t_{rl} and t_s are the Reliable Life and the Safe Life, Respectively and δ is the Fraction of Specimens that are Permitted to Fail.

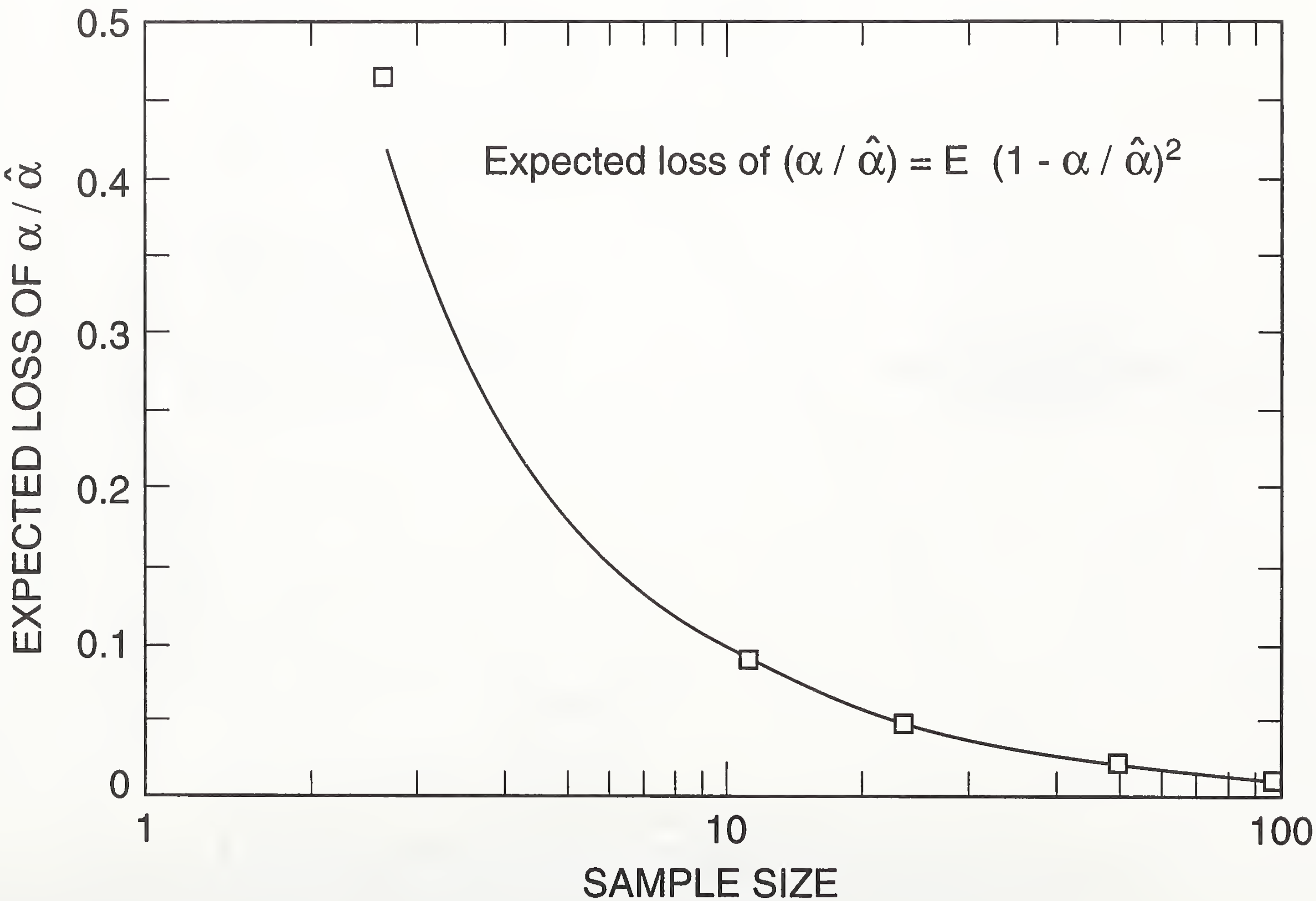

Figure 15. A Measure of the Sampling Error for Complete Samples for the Weibull Shape Parameter as a Function of Sample Size (Adapted from Whittaker and Besumer [1969]).

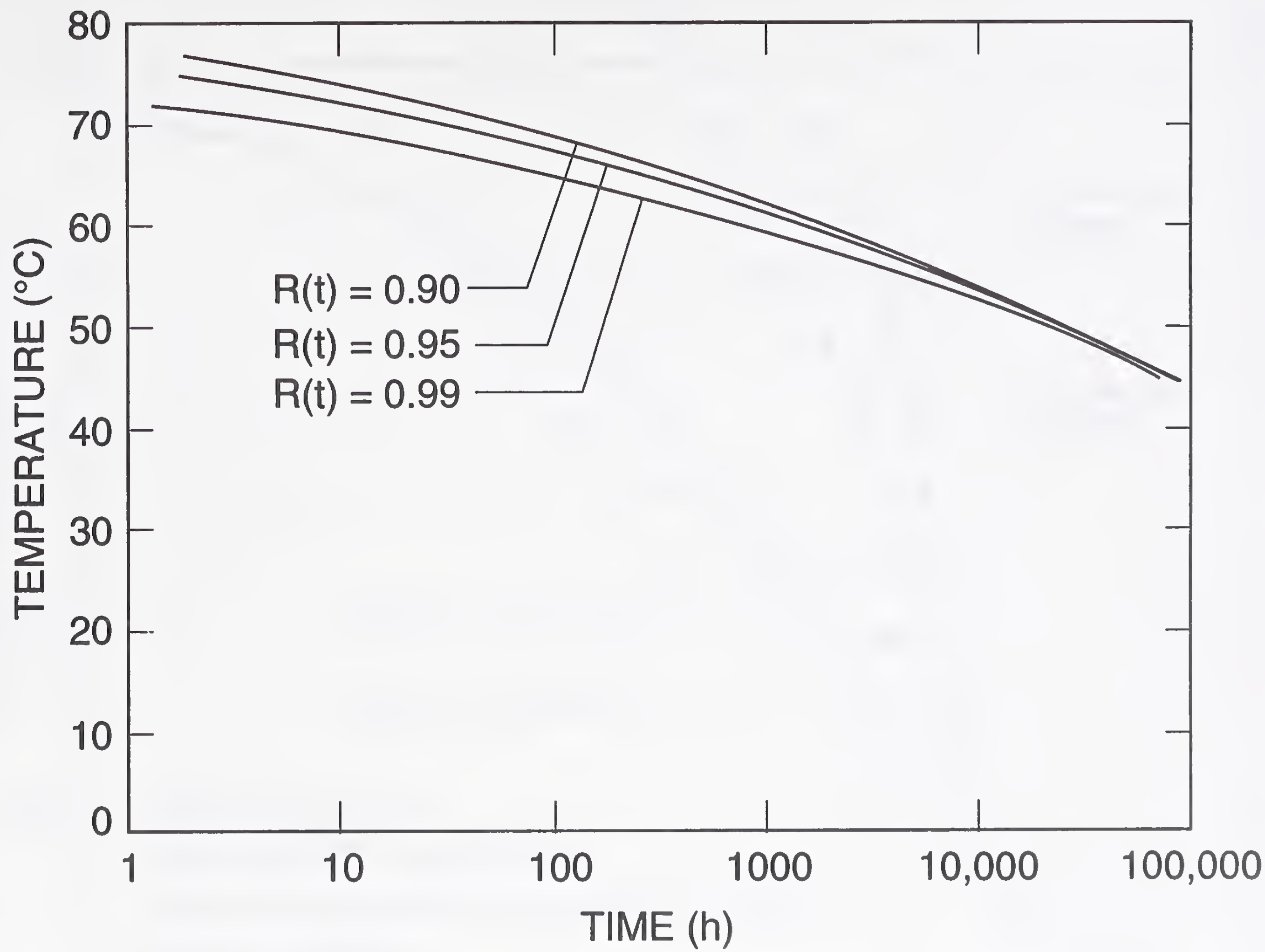

Figure 17. Probability-of-Failure/Temperature/Time-to-Failure Diagram for an Alkyd Coating on Steel Exposed at 95% r.h. and 40°C [Martin and McKnight, 1985].

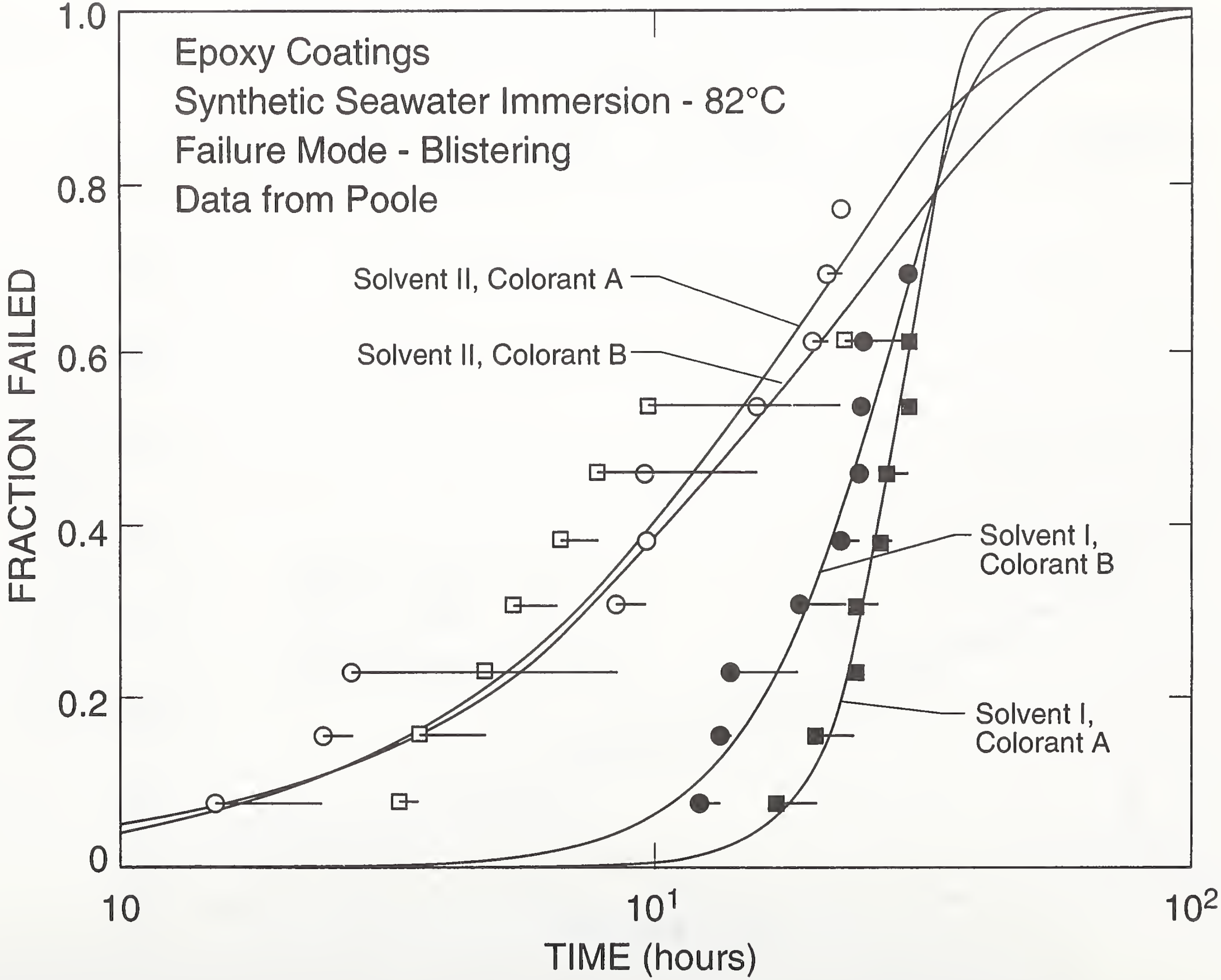

Figure 17. Probability-of-failure/Temperature/Time-to-failure diagram for an alkyd coating on steel exposed at 95% r.h. and 40°C [Martin and McKnight, 1985].

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