Dr. 319

ERDA/JPL/954328-76/2

**STUDIES OF ENCAPSULATION MATERIALS FOR
TERRESTRIAL PHOTOVOLTAIC ARRAYS**

Third Quarterly Progress Report, March 16, 1976—June 15, 1976

June 28, 1976

Work Performed Under JPL Contract No. 954328

**Battelle Columbus Laboratories
Columbus, Ohio**

**ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Division of Solar Energy**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161

Price: Paper Copy \$4.50 (domestic)
\$7.00 (foreign)
Microfiche \$2.25 (domestic)
\$3.75 (foreign)

THIRD QUARTERLY PROGRESS REPORT
Covering the Period March 16, 1976, to June 15, 1976

on

**STUDIES OF ENCAPSULATION MATERIALS
FOR TERRESTRIAL PHOTOVOLTAIC ARRAYS**

JPL Contract No. 954328

Encapsulation Task
Low-Cost Silicon Solar Array Project

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the U.S. Energy Research and Development Administration, Division of Solar Energy.

The JPL Low-Cost Silicon Solar Array Project is funded by ERDA and forms part of the ERDA Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays.

June 28, 1976

D. C. Carmichael
Program Manager

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Ray

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
STUDY 1. EVALUATION OF WORLD EXPERIENCE AND PROPERTIES OF MATERIALS FOR ENCAPSULATION OF TERRESTRIAL PHOTOVOLTAIC ARRAYS	3
INTRODUCTION	3
STATUS OF STUDY 1	3
STUDY 2. DEFINITION OF ENCAPSULANT SERVICE ENVIRONMENTS AND TEST CONDITIONS	4
INTRODUCTION	4
STATUS OF STUDY 2	4
STUDY 3. INVESTIGATION OF TEST METHODS AND PROPERTIES OF CANDIDATE ENCAPSULATION MATERIALS	5
INTRODUCTION	5
STATUS OF STUDY 3	5
STUDY 4. DEVELOPMENT OF ACCELERATED AND ABBREVIATED TESTING METHODS FOR PREDICTING PERFORMANCE OF ENCAPSULATION MATERIALS OVER 20-YEAR LIFETIME	7
INTRODUCTION	7
TECHNICAL DISCUSSION OF RESULTS THIS QUARTER	8
Factors Affecting Weathering Tests and Data Analysis for Polymeric Materials	8
Sample Preparation	9
Sample Mounting	10
Abbreviated-Test Sites	10
Accelerated-Testing Environment	15
Sample Testing	15
Degradation Effects and Tests for Glasses	20
Acidic Attack	20
Alkali Attack	21
Solarization and Dirt Effects	22
Natural Weathering Tests	23
Artificial Weathering Tests	23
Conclusions	24

TABLE OF CONTENTS
(Continued)

	<u>Page</u>
Analysis of Available Aging Data and Models	25
Aging Studies and Models	26
Critique of Literature Aging Studies	32
Conclusions	34
Background and Initial Development of the	
Methodology for Aging Tests	34
Experimental Objectives	34
Stress Levels	35
Relating Degradation Rates to Stress Levels	36
On Predictions	36
Description of a Prototype Aging Experiment	37
Critique of Property-Versus-Time Models	42
Some Preliminary Calculations	43
Sources of Data	46
Experiment Designs for Aging Tests	46
PLANS FOR THE NEXT QUARTER	47
NEW TECHNOLOGY	48
REFERENCES	49

LIST OF TABLES

	<u>Page</u>
Table 1. Materials and Properties Evaluated in NBS-MCA Study on Weathering of Plants	27
Table 2. Rubber and Plastics Research Association (RAPRA) 5-Year Prediction Results for Modulus	31
Table 3. Critique of Aging Studies of Polymeric Materials Reported in the Literature for Specific Applicability to the Evaluations to be Conducted in Study 4	42
Table 4. Values of Degradation Constant for Several Values of Fractional Property Degradation at the End of 20 Years for Simple Model	45
Table 5. Fractional Degradation for Various Elapsed Times Based on K-Values in Table 4	45

LIST OF FIGURES

Figure 1. Relative Intensity of Diffuse Solar Radiation Impinging on Various Surfaces During a Year's Time Span in Australia	11
Figure 2. Relative Intensity of Direct Solar Radiation Impinging on Various Surfaces During a Year's Time Span in Australia	12
Figure 3. Relative Rate of Degradation of Unstabilized Polyethylene Function of Mounting Angle in an Outdoor Exposure Test . . .	13
Figure 4. Correlation Between Percent Strength Loss of PET Fibers and Cumulative UV Exposure in Florida and Arizona	14
Figure 5. Correlation Between UV Exposure and Hours of Exposure to a Xenon Arc to Produce 25 Percent Loss in Tensile Strength in Various Fibers	16
Figure 6. Carbonyl Formation as Measured by ATR-IT and Transmission IR (From Both Sides of Film) as a Function of Polymer Film Thickness	17
Figure 7. Correlation Between Percent Elongation to Break for Polypropylene and Carbonyl Formation as Measured by ATR-IR Absorbance as Functions of UV Irradiation Time . . .	18

LIST OF FIGURES
(Continued)

	<u>Page</u>
Figure 8. Correlation of Percent Elongation at Break for Polypropylene With Increase in Carbonyl Formation as Measured by ATR-IR Absorbance	19
Figure 9. Outdoor Exposure Performance of Polystyrene Versus Values Predicted From Xenon-Arc Weatherometer	30
Figure 10. Schematic of a Prototype Aging Experiment as Described in the Text	39
Figure 11. Average Resistance as a Function of Operating Time for 120 Carbon-Composition, 1/2-Watt Resistors Operated at Full-Rated Power at a Nominal Temperature of 70 C	40
Figure 12. Average Resistance as a Function of Operating Time for 120 Carbon-Composition, 1/2-Watt Resistors Operated at Full-Rated Power at a Nominal Temperature of 100 C.	40
Figure 13. Average Resistance as a Function of Operating Time for 120 Carbon-Composition, 1/2-Watt Resistors Operated at Full-Rated Power at a Nominal Temperature of 125 C.	41
Figure 14. Slope-Temperature Relation for Resistance Degradation	41
Figure 15. Acceleration Factor as a Function of Operating Temperature	44
Figure 16. Overall Regression Line for Transformed Data	44

THIRD QUARTERLY PROGRESS REPORT

on

**STUDIES OF ENCAPSULATION MATERIALS
FOR TERRESTRIAL PHOTOVOLTAIC ARRAYS**

JPL Contract No. 954328

Encapsulation Task
Low-Cost Silicon Solar Array Project

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

from

BATTELLE
Columbus Laboratories

June 28, 1976

ABSTRACT

This Third Quarterly Progress Report on JPL Contract No. 954328 covers work conducted in the period from March 16, 1976, through June 15, 1976. The research is part of a five-task development project, the Low-Cost Silicon Solar Array Project (LSSA Project), being managed by the Jet Propulsion Laboratory for the Energy Research and Development Administration, Division of Solar Energy. The Encapsulation Task (Task III) of this project includes four studies assigned to Battelle-Columbus. The status of the studies active during this quarter is summarized in this report.

Study 1 of this contract is entitled "Evaluation of World Experience and Properties of Materials for Encapsulation of Terrestrial Photovoltaic Arrays". The objectives of this study are to provide a summary of world experience related to polymeric and glass protective systems for terrestrial arrays and to recommend candidate encapsulation materials and processes which can be expected to provide a service life of 20 years. This study is in its final stages. Essentially, the review and analyses are complete; the draft of the final report is now being written. The provisions of the contract, therefore, are that no quarterly report is to be prepared on Study 1 at this time; a brief objective and status statement is included to identify the scope of the total investigation.

The objective of Study 2, "Definition of Encapsulant Service Environments and Test Conditions", is to determine the frequency and duration of climatic and other environmental conditions for a 20-year array lifetime and identify conditions that can be used in testing candidate encapsulant materials for a service life of 20 years in terrestrial environments. Study 2 also is in its final stages. The draft of the final report is now being prepared. While no technical discussion of Study 2 is to be included in this report; a brief statement of scope is included.

Study 3 is in the planning phase, and is concerned with evaluation of the properties of candidate encapsulation materials to be identified in the final report on Study 1. The initial portion of the effort of Study 3 is concerned with identifying and evaluating measurement methods and techniques for determining properties of materials as described in test standards and other similar sources. The major portion of the study is concerned with determining important properties of potential encapsulation materials under selected conditions. This effort is now planned to include determining degradation-rate data on properties of selected materials and material interfaces for use in the development of aging tests in Study 4. This point is discussed under the sections of this report covering Study 3 and Study 4.

Most of this report is concerned with Study 4, "Development of Accelerated and Abbreviated Testing Methods for Predicting Performance of Encapsulation Materials Over a 20-Year Lifetime". The outputs of the study are to be (1) the specification of a methodology for developing the experimental designs for aging tests, and (2) the development of the experimental designs for aging tests for selected materials and material interfaces. Pursuant to these goals, the aging behavior of polymeric materials has been reviewed to lead to identifying possible failure mechanisms and thus to appropriate choices of characteristics to be measured and stresses to be used in accelerated/abbreviated tests. Some of the results of this review were presented in the Second Quarterly Progress Report, and the presentation is completed in this report. A similar review has been made for glasses. The results are discussed in this report. Aging data and data analysis methods (models) which have been used in other investigations have been identified and critiqued; these results are presented. Initial results of efforts on developing the methodology are also presented in the discussion of Study 4.

STUDY 1. EVALUATION OF WORLD EXPERIENCE AND PROPERTIES OF MATERIALS FOR ENCAPSULATION OF TERRESTRIAL PHOTOVOLTAIC ARRAYS

F. A. Sliemers, C. W. Kistler, Jr., R. E. Sharpe,
G. B. Gaines, R. D. Igou, and D. C. Carmichael

INTRODUCTION

Achievement of acceptable low-cost, silicon photovoltaic arrays with a life of 20 years requires the selection and/or development of encapsulation materials and processes that are compatible with the photovoltaic array and that afford the required encapsulant life under terrestrial climatic conditions. The final process for producing the active silicon arrays and the engineering design of the array are yet to be evolved. The output of Study 1 is formulated to contribute to design evolution and materials and process selections through a review and analysis of world experience in the area of materials for encapsulation/protection systems for solar cells and related devices. Out of the analysis will come a list of the most promising candidate materials and processes for encapsulating terrestrial photovoltaic arrays and their properties. Such criteria as cost, known and potentially achievable properties, availability, and ease of automation will govern the selection of candidate materials and processes. Data on world experience and materials properties have been drawn from published and unpublished literature, personal contacts, and site visits.

STATUS OF STUDY 1

The analysis phase of Study 1 is scheduled to be completed this quarter. In accordance with the terms of the contract, no quarterly report is to be prepared at this time; this brief section is included to indicate the scope of the total investigation. The effort remaining is directed to preparing the draft of the final report, which is anticipated to be completed on schedule in July.

STUDY 2. DEFINITION OF ENCAPSULANT SERVICE ENVIRONMENTS AND TEST CONDITIONS

R. E. Thomas, R. M. Cote, J. B. Miller, J. L. Gemma,
R. C. Behn, P. R. Sticksel, S. G. Talbert,
R. B. Bennett, G. B. Gaines, and D. C. Carmichael

INTRODUCTION

The objectives of Study 2 are to develop the statistical methodology, determine the frequency and duration of climatic and other environmental conditions for a 20-year array lifetime, and identify corresponding conditions that can be used in testing candidate encapsulation materials for a service life of 20 years in terrestrial environments.

The methodology for accomplishing these objectives involves several stages. Climatic data (temperature, relative humidity, wind speed, etc.), insulation data, air-pollution data, and data related to miscellaneous hazards are being gathered for the following geographic locations: Albuquerque, New Mexico; Bismarck, North Dakota; Boston, Massachusetts; Brownsville, Texas; Cleveland, Ohio; Fairbanks, Alaska; Los Angeles, California; Miami, Florida; and Phoenix, Arizona. These data are being statistically analyzed to quantify past environmental conditions and to make 20-year forecasts. Special attention is being focused on the frequency and duration of combinations of environmental conditions that are likely to initiate and/or promote material degradation. These projected conditions furnish the basis for selecting environmental factors and levels that can be used in testing candidate encapsulation materials.

STATUS OF STUDY 2

The major analyses on this study are completed and preparation of the final report is under way. In accordance with the provisions of the contract, no input to this Third Quarterly Technical Progress Report was prepared. This brief section has been included, however, to state the scope and status of Study 2.

STUDY 3. INVESTIGATION OF TEST METHODS AND PROPERTIES OF CANDIDATE ENCAPSULATION MATERIALS

F. A. Sliemers, C. W. Kistler, Jr., R. B. Bennett,
G. B. Gaines, and D. C. Carmichael

INTRODUCTION

To date, the experience with encapsulation of photovoltaic solar arrays for terrestrial applications has been rather limited. Moreover, the encapsulant materials used so far have been employed based on criteria not entirely appropriate for the goals of the LSSA project, especially cost and ease of processing using automated methods. There is a considerable need, therefore, for important information on the properties and aging behavior of materials which are candidates for encapsulating low-cost photovoltaic arrays and are prepared by methods suitable for automated processing. Also, because of the newness and some unique requirements of the terrestrial photovoltaic arrays, standard methods of measuring the properties of candidate encapsulation may not be useable.

The objectives of this study, therefore, are to

- (1) review test standards for appropriateness to the requirements of the candidate materials and processes, and
- (2) measure properties of selected materials under conditions which will make feasible a choice among candidate materials processes for use in future encapsulation systems.

As part of the second area, materials and measurement techniques will also be experimentally evaluated to obtain information for use in development of aging tests in Study 4.

STATUS OF STUDY 3

Study 3 is in the planning phase. Initial effort has been directed toward identification and examination of potentially applicable test standards and other specifications. Property measurements on candidate materials which require property data either not available or not determined under appropriate conditions will be initiated as soon as the results of Study 1 have been compiled. Also, Study 3 will include investigations of the degradation rates of selected materials and material interfaces considered to be critical in the further development of an acceptable encapsulation system. A portion of this effort is to be devoted to an analysis of service degradation mechanisms of photovoltaic arrays. These investigations

will particularly contribute to the development of accelerated/abbreviated tests in Study 4 as described in the next section, but should provide information also useful in other parts of the project.

STUDY 4. DEVELOPMENT OF ACCELERATED AND ABBREVIATED TESTING METHODS FOR PREDICTING PERFORMANCE OF ENCAPSULATION MATERIALS OVER 20-YEAR LIFETIME

G. Derringer, C. W. Kistler, Jr., R. E. Thomas,
D. M. Bigg, R. D. Igou, G. B. Gaines,
and D. C. Carmichael

INTRODUCTION

To be economically feasible, photovoltaic solar arrays should have a service life of at least 20 years. Silicon solar cells, if properly protected from the atmosphere, are expected with reasonable confidence to have such a lifetime. The success of the Low-Cost Silicon Solar Array Project depends substantially on identifying a low-cost encapsulation material system that will protect the solar cell for that period of time with little loss in electrical output. The success of an encapsulation material, therefore, depends on its ability to withstand 20 years of outdoor service in various environments. Since 20 years of service testing is obviously impractical, methods for short-term (abbreviated/accelerated) aging tests must be developed from which service life can be predicted with acceptable confidence.

Although a specific accelerated/abbreviated test for the ultimate encapsulant system cannot be verified until the system is defined, the objectives of this study are to accomplish the following significant steps in establishing such a test.

- (1) developing a suitable methodology for designing the statistical and experimental techniques for such a test, and
- (2) using this methodology to specify detailed test designs for aging tests on specific materials and material interfaces which are representative of candidate encapsulation systems.

Subsequent work would involve conducting the tests and analyzing the data in accordance with the test design ("test plan") to verify the methodology and techniques and to obtain high-confidence predictions of service life.

The methodology to be developed will describe all important factors that must be considered in the detailed test design and describe suitable statistical and experimental techniques for treating the important factors including statistical data analysis and prediction methods.

The test designs will specifically describe the total elements of a test plan, including material selection, specimen design and number, environmental parameters and operating conditions, properties to be measured, instrumentation to be utilized, and data analysis methods. Inputs regarding the selection of materials and interfaces to be considered will come from Study 1. Study 2 will furnish environmental descriptions of various geographical sites of interest.

Also, as indicated previously, Study 3 will be directed, in part, to furnishing experimental data on selected materials, materials interfaces, and measurement techniques to aid in formulating the methodology and test designs and in validating the methodology in Study 4. This information is necessary because the initial efforts in Study 4 indicated a lack of data obtained under acceptable conditions and on relevant materials for use in this study.

TECHNICAL DISCUSSION OF RESULTS THIS QUARTER

The effort thus far on Study 4 has been directed primarily to developing the required methodology by analyzing the experience to date on accelerated testing, on the methodologies used for such testing, on aging mechanisms, and on aging data for materials which are expected to be relevant to the final encapsulation system. This effort was divided into two material classes: polymeric materials and glasses. Also included in these reviews were property-measurement methods and techniques. The results of the initial review for polymeric materials were included in the Second Quarterly Progress Report on this contract (ERDA/JPL-954328-76/1). Further considerations were given to this effort this quarter, particularly to those test-design factors which affect aging tests. The results of this part of the review are presented in the first subsection of this report on Study 4.

Also in this quarter, the same type of review was directed toward glasses. The second subsection presents these results.

An additional input needed to develop the outputs of Study 4 is information on the methodology of accelerated testing in general and on the availability of specific aging data relevant to the encapsulation system. This effort was continued this quarter with special attention devoted to aging models used with success in the past and to analyzing the available aging data. The third subsection presents the results to date.

Based on these results and on our experience with accelerated and abbreviated testing, the development of the required methodology has been initiated this quarter. The background and basic approaches being pursued for important factors in the development of the methodology are presented in the fourth subsection of this Study 4 report.

Factors Affecting Weathering Tests and Data Analysis for Polymeric Materials

In previous efforts, current experience was reviewed to uncover available weathering data for various polymers, to identify the most successful accelerated/abbreviated test procedures, and to establish the most precise method of correlating accelerated/abbreviated test data with outdoor weathering data. The results were

presented in the Second Quarterly Progress Report referenced above. The general conclusion drawn from the review was that current abbreviated and accelerated test methods generally are inadequate for generating data that can be used in a predictive manner. Principal deterrents to accurate life prediction have been the inability to quantify outdoor exposure environments and to reasonably simulate any natural environment in artificial weathering devices. These shortcomings are primarily a result of the lack, until very recently, of sufficiently precise measuring instruments, and the high cost of conducting a well-disciplined weathering study. As an extension of this review, some factors that significantly affect weathering tests and data evaluation for polymers are discussed below. These factors are concerned primarily with the design of the accelerated/abbreviated test methods.

Sample Preparation

Because polymers are composed of large molecules, the manner in which the bulk material is formed affects the molecular and macromolecular arrangement of the molecules. In turn, the arrangements affect the properties, including weatherability, of the bulk material. For suitable aging tests to be performed on a material, the test sample must be prepared in a manner that closely approximates the end-use processing method. Ideally, the final system (encapsulant plus active devices) should be tested. However, full-system testing will not be feasible initially since part of the current program is to "screen out" unacceptable encapsulant materials and since the final system design has not yet been established and may depend on the choice of encapsulant.

The following examples demonstrate the importance of sample preparation. NASA researchers have shown that the water vapor permeability of fluorinated ethylene propylene (FEP) copolymer films applied to silicon solar cells increased by an order of magnitude as a result of morphological changes incurred during the lamination procedure.^{(1)*} The increased water permeability led to delamination of the FEP-solar-array bond in a high-humidity environment. Laminating temperature was found to be the most significant factor affecting water permeability. Laminating the FEP to the solar array at temperatures above the optimum bonding temperature increased the crystallinity of the FEP and decreased its water permeability.

The major cause of photodegradation of polyethylene and polypropylene is UV absorbance and subsequent radicalization of carbonyl bonds present within the polymer.⁽²⁾ A significant source of carbonyl in polyolefins is surface oxidation during melt processing.^(3,4) Stresses imparted during injection molding also increase the susceptibility of polymers to photoinduced oxidation.⁽⁵⁾ Residual monomer present in polymethyl methacrylate (PMMA) polymerized in situ increases its rate of photodegradation.⁽⁶⁾ PMMA does not absorb UV radiation in the 280 to 400-mm region, but methyl methacrylate does.

*References are listed at the end of the report.

The above examples offer strong evidence that processing techniques must be accounted for in designing an experimental weathering program. Two of the above discussed polymers are candidates for the solar encapsulation system (FEP and PMMA).

Sample Mounting

Sample mounting is extremely important in outdoor-weathering experiments. If the material is stressed in use, it should be stressed during the weathering tests since stress reduces the life of polymers.

The mounting angle of the test sample is critical to outdoor testing. While the often-used procedure is to mount the samples at an angle of 45 degrees, facing south, this is not the optimum angle from the viewpoints of (1) exposing the sample to the most severe solar environment and (2) obtaining good correlations with solar radiation. A thorough investigation has shown that dispersed skylight directs as much UV energy on the earth's surface as does direct sunlight.⁽⁷⁾ Since skylight radiates normally to the earth's surface, the optimum angle of exposure is the average between the angle normal to the sun's position and horizontal.⁽⁸⁾ This is clearly shown in Figures 1 and 2. Figure 1 shows the relative intensity of skylight impinging on samples mounted in three ways -- horizontal, at 45 deg, and in a follow-the-sun mode -- during a year's time span. Since the study was conducted in Australia, March 21 represents the autumn equinox. The horizontally mounted specimen receives the most indirect radiation, the 45-deg-mounted sample, the least. The amount of diffuse radiation received by the sample tracking the sun varies seasonally.

Figure 2 shows the relative intensity of direct solar radiation on samples mounted in the same way as those in Figure 1 over a year's time span. As expected, the follow-the-sun mode receives the most direct radiation, while the amount received by the samples mounted at 0 deg (i. e., horizontally) and 45 deg varies seasonally. On Figure 3 is plotted the relative rate of degradation in 1 year for an unstabilized polyethylene as a function of mounting angle. Maximum degradation occurs at an angle of 15 deg, which is approximately the average of 0 deg (horizontal) and the angle of the latitude of the test site (28 deg in this case). The maximum rate of degradation is 44 percent higher than the sample mounted at 45 deg.

Abbreviated-Test Sites

Abbreviated tests which are run under normal stress levels can be conducted as field-exposure tests. Because the climate varies from region to region, it will be necessary to account for the local variability of weathering factors in the experimental design. Singleton, et al., has shown that differences between test sites are important.⁽⁹⁾ Excellent correlations between total UV exposure in Arizona and Florida and the loss of tensile strength of polyethylene-terephthalate (PET), nylon, and triacetate fibers were obtained. As shown in Figure 4, the Florida and Arizona

FIGURE 1. RELATIVE INTENSITY OF DIFFUSE SOLAR RADIATION IMPINGING ON VARIOUS SURFACES DURING A YEAR'S TIME SPAN IN AUSTRALIA⁽⁸⁾

FIGURE 2. RELATIVE INTENSITY OF DIRECT SOLAR RADIATION IMPINGING ON VARIOUS SURFACES DURING A YEAR'S TIME SPAN IN AUSTRALIA⁽⁸⁾

FIGURE 3. RELATIVE RATE OF DEGRADATION OF UNSTABILIZED POLY-ETHYLENE FUNCTION OF MOUNTING ANGLE IN AN OUTDOOR EXPOSURE TEST⁽⁸⁾

FIGURE 4. CORRELATION BETWEEN PERCENT STRENGTH LOSS OF PET FIBERS AND CUMULATIVE UV EXPOSURE IN FLORIDA AND ARIZONA⁽⁹⁾

correlations for PET are not the same. At the same UV exposure, the samples weathered in Florida degraded faster. Climatological analysis revealed that the main difference between Florida weather and Arizona weather is the higher humidity in Florida.

Environmental characterizations of nine U.S. sites are currently being made in Study 2. It would be logical to use these sites as locations for abbreviated tests. Cost will dictate just how many sites can be used. To properly conduct the tests, testing equipment must be available at each site. This will permit some samples to be removed from the exposure rack, tested, and remounted without a significant loss of exposure continuity.

Accelerated-Testing Environment

The major limitation of accelerated testing is the inability to simulate a real environment in an enclosed chamber. Kamal has shown that, if this can be done, correlations between accelerated tests and natural weathering are possible.^(10,11) The curve presented in Figure 5 was developed by Singleton, et al.,⁽⁹⁾ to show that outdoor exposure can be correlated with accelerated aging. The points on the curve represent polymer fiber specimens which have lost 25 percent of their original tensile strength. Hours in a xenon-arc weatherometer are plotted against outdoor UV exposure to reach the same degree of strength loss. From this, one can conclude that a 100-hr exposure to a xenon arc is roughly equivalent to 500 mw-min/cm² of exposure of UV energy outdoors.

From Study 2, environmental conditions can be drawn so as to set the parameters in the test chamber. Since UV intensity, humidity, condensation, sample temperature, pollutant type and concentration, and exposure time can be controlled independently, a reasonable approximation to a given environment is possible.

Sample Testing

Inadequate sample-testing techniques have been one of the most severe limitations to obtaining precise abbreviated-test data. Recently, however, equipment and techniques have become available which permit precise measurements of properties which can be correlated with weathering degradation. Figure 6 shows that attenuated total-reflectance infrared measurements (ATR-IR) can follow changes in carbonyl formation at the surface of a polymer film.⁽⁴⁾ Polymer degradation occurs initially and primarily at the exposed surface.^(4,7) Changes in the amount of carbonyl formed are indicated by growth of the IR absorption band at the 1715 cm⁻¹ wave number. IR transmission spectroscopy does not show the sensitivity to surface degradation that ATR does. Figure 7 shows relationships of both elongation to break (a bulk property) and carbonyl formation as measured by ATR-IR to UV irradiation. From this, Figure 8 can be constructed which shows loss of a bulk property as measured by an analytical chemical technique.

FIGURE 5. CORRELATION BETWEEN UV EXPOSURE AND HOURS OF EXPOSURE TO A XENON ARC TO PRODUCE 25 PERCENT LOSS IN TENSILE STRENGTH IN VARIOUS FIBERS⁽⁹⁾

FIGURE 6. CARBONYL FORMATION AS MEASURED BY ATR-IR AND TRANSMISSION IR (FROM BOTH SIDES OF FILM) AS A FUNCTION OF POLYMER FILM THICKNESS⁽¹¹⁾

FIGURE 7. CORRELATION BETWEEN PERCENT ELONGATION TO BREAK FOR POLYPROPYLENE AND CARBONYL FORMATION AS MEASURED BY ATR-IR ABSORBANCE AS FUNCTIONS OF UV IRRADIATION TIME⁽¹¹⁾

FIGURE 8. CORRELATION OF PERCENT ELONGATION AT BREAK FOR POLYPROPYLENE WITH INCREASE IN CARBONYL FORMATION AS MEASURED BY ATR-IR ABSORBENCE⁽¹¹⁾

Other extremely precise measurement techniques are also available to follow degradation reactions. These include chemiluminescence, ATR, and sonic modulus measurements.

Degradation Effects and Tests for Glasses

A review of the aging effects in various environments and test methods and procedures to determine these effects was carried out for glasses, the second class of materials expected to be important in solar-array encapsulation. Although glasses are known to exhibit long lifetimes, they are susceptible to some weathering by chemical attack, especially by moisture. Moisture not only lowers the strength of glass (as evident by its susceptibility to static fatigue), but also, on prolonged exposure, can chemically leach and/or etch the surface. In those glasses with poor durability, this results in a permanent haze or translucency. In some glasses, solarization (UV-enhanced darkening) has been known to occur, but this is normally not a problem with glasses as it can be avoided by compositional modifications.

Acidic Attack

Glass is susceptible to moisture attack by a leaching mechanism (selective attack or exchange of sodium ions by hydrogen ions). The more acidic the solution, the higher the rate of attack. Because the leaching process results in a depleted surface layer, subsequent attack is controlled by diffusion through this layer, so that the rate of attack may vary with the square root of time, assuming no change in the physical properties of the skin. (12,13) Weatherability of glass is sometimes judged initially on the basis of resistance to attack by water, as measured by one or more alkali-extraction tests. But visual changes can occur in some glasses in which alkali extraction is not significant. (14) Weatherability is also dependent on relative humidity, although alkali-extraction data may not correlate with visual changes occurring on surfaces in different humidities. (14)

The chemical nature and thermal history of the glass surface also have pronounced effects on the chemical durability, as evidenced by surface treatments used to de-alkalize the interior of soda-lime glass containers (such as treatment with hot SO₂ or fluorine compounds). (15) The SO₂ treatment can increase the chemical durability to leaching by a factor of 25, but has little effect on chemical attack by alkali, where etching is the predominant attack mechanism. (12) The tin-rich surface of float glass is also more weather resistant than the silica-rich top surface, although specific data have not been reported. (16)

Alkali Attack

Glass can also be attacked by alkaline solutions which essentially dissolve the silica structure of the glass. If no residue buildup occurs, the reaction rate proceeds linearly with time, and, unlike acid attack, will increase by a factor of 2 or 3 with each change in pH unit.⁽¹²⁾ In accordance with the difference in corrosion mechanism, the rate of attack for most glasses is several orders of magnitude higher in alkalis than in acids. Alkali attack is not normally encountered in weathering situations unless strong detergents are used for cleaning purposes.

Property Changes Resulting from Surface Degradation

Loss of transmittance and strength are two factors of major concern for terrestrial encapsulants. These properties are known to be affected by environmental conditions, such as whether or not the glass surface is washed, or the weathering products are allowed to accumulate under static exposure conditions⁽¹⁴⁾, and whether the environment abrades the surface. Although abrasion can reduce the normal transmittance, solar cells can utilize diffuse light, and surface abrasion may not be seriously detrimental to total light transmission.

Although loss in transmittance by weathering can be observed visually by the formation of a hazy surface, it is not commonly used to follow the process of corrosion, probably because of a lack of an instrument with a sensitivity comparable to that of the eye. Even the "haze test"⁽¹⁷⁾, which measures only the amount of diffused or scattered light transmitted by a sample, has been found to be less sensitive than the eye and results are not reproducible⁽¹⁴⁾. Ellipsometry, a technique for measuring the refractive index and thickness of coatings on glass⁽¹⁸⁾, has been used to follow weathering of high-lead glasses in laboratory experiments.⁽¹⁹⁾ A variety of analytical techniques are available for characterizing chemical changes occurring at surfaces⁽¹⁹⁾, and have been used to show that "as-fabricated" glass containers are weathered to some extent.⁽²⁰⁾ Attenuated total-reflectance (ATR) spectroscopy has also been applied to the study of glass surfaces.⁽²¹⁾ Usually, however, chemical leach tests are used to predict the performance of materials in corrosive environments; appearance evaluations of exposed samples are used to confirm laboratory predictions.

The time dependence of glass strength in a moist environment is a well-known mechanical characteristic called static fatigue which is attributable to chemical attack of the surface. Depending on the environment, the long-term strength of glass for any one surface condition may be reduced to a value approximately 20 percent that of the "dry" strength⁽²²⁾, beyond which the fatigue curve becomes horizontal and failure does not occur regardless of the period of stress duration. This "endurance limit" is attributed to the healing of flaws by chemical etching at a rate higher than a "crack" can propagate.⁽²²⁾ Depending on the type of glass, aging or storage of stress-free glass in various moist environments can either increase or decrease the strength.⁽²³⁾ Unlike chemical attack, static fatigue is caused by the formation of a hydrated layer on the surface (rather than solution or ion exchange).

Strength is relatively independent of pH, except at very high values, where it is increased (presumably by chemical etching of flaws at a higher rate than growth can occur), or at a very low value of pH, where it is decreased. ⁽²²⁾

The physical nature of the surface also affects the strength of glass. For this reason, glass which may be subjected to an abrasive environment is often abraded by one of several techniques ^(22, 24, 25) before testing. Because surface and environmental factors affect the strength of glass, strength data are usually reported only in the technical literature. Manufacturers usually report conservative "working" values reflecting the strength of abraded samples subjected to long-term loads, unless a particular application warrants otherwise.

Because static fatigue is caused by slow crack growth, fracture mechanics techniques, using proof testing, have been used to study and predict the failure time (life) of glass for any stress condition. ⁽²⁶⁾ Crack-velocity measurements (made in solutions of varying pH), used in calculating glass strength, have shown that at low crack velocities (long-duration loads) the pH of the solution can affect crack-propagation rates. At high-crack velocities (short-duration loads), the crack propagation rate, independent of pH, is governed by the environment (acidic in water) at the crack tip. ⁽²⁷⁾ Fracture-mechanics principles may, therefore, prove useful in the selection or evaluation of materials, and in prediction of the life of ultimate system components.

Solarization and Dirt Effects

Loss of transmittance can occur by solarization and dirt accumulation, as well as by weathering. Solarization is defined as the phenomenon whereby the transmission and, possibly, color of a glass changes on exposure to natural sunlight. The transmission decrease in the visible range is attributed to a change in oxidation state of multivalent cations in the glass by the following type of reactions:

Reaction (1) imparts a purple discoloration; Reaction (2) accounts for aging of UF-transmitting glasses, ⁽²⁸⁾ Sb_2O_5 functions in the same manner as As_2O_5 . Obviously, the best method of avoiding solarization is to minimize iron and other multivalent ions in the glass. In addition, as arsenic and antimony oxides usually are not used as firing agents in soda-lime glasses, solarization is not common.

Dirt accumulation is perhaps a more serious problem, depending on the inclination angle of the surface. ⁽²⁹⁾ This effect is, however, related to a specific environment and is relatively independent of material type unless the surface is etched or abraded either prior to or during exposure.

Natural Weathering Tests

Because of the long natural life of glasses and the conventional use of chemical durability tests to predict the weatherability of various glass compositions before use, relatively little information has been published on the weatherability of modern-day glasses. Attempts have been made to protect these glasses with polymeric coatings, but the results of accelerated humidity-cabinet exposures⁽³⁰⁾ suggest that little success has been achieved.

With respect to strength, the stress-free aging of both annealed and toughened (method unspecified) soda-lime plate glass has been studied for times up to 5 years.⁽³¹⁾ The effect of outdoor exposure on the strength of chemically strengthened glass panels has been reported as insignificant at the conclusion of 1 year of a 5-year test program.⁽³²⁾ As might be expected, lot-to-lot variability, surface-abrasion conditions, edge-initiated failures, and testing techniques were factors which also affected strength results.⁽³²⁾ U. S. Navy researchers have exposed chemically strengthened and thermally tempered glass to seawater in both the laboratory and ocean for periods up to 3 years. They found no fatigue effects at the 50 percent stress level; exposure actually made the glass stronger.⁽²⁵⁾ U. S. Army researchers have compiled static fatigue data on some glasses.⁽³³⁾

Generally, a real or simulated system has been tested, rather than testing just a glass material, to evaluate materials-compatibility, design, and assembly factors -- the areas in which most problems occur.

Artificial Weathering Tests

The glass industry has found that results of ASTM alkali-extraction tests conducted on either containers or powdered samples correlate quite well with outdoor weatherability.⁽³⁴⁾ For glasses with extremely long-term durability requirements, dynamic-corrosion-test techniques are also available.⁽³⁵⁾ The thermal history of a glass must also be considered, since heat treatments can result in phase separation and a drastic decrease in chemical durability.⁽³⁶⁾ In Morey's book, The Properties of Glass, the chapter on chemical durability of glass includes a dated but good discussion of test methods and compositional factors for bulk glass; it does not include any information on coatings or surface treatments developed in recent years.⁽³⁷⁾ In Tooley's book, The Handbook of Glass Manufacture, the section on chemical durability emphasizes liquid-media test techniques which yield quantitative data for predicting durability at any service condition on the basis of accelerated test data plotted in Arrhenius form⁽³⁸⁾, but this technique is of questionable usefulness for glasses exposed to natural weather environments.

For coatings on architectural glass, acidic attack⁽³⁹⁾, as well as salt-spray, relative-humidity, or weatherometer "cabinet" tests may be employed to evaluate the durability of a product. Because coated architectural glass is relatively new, test procedures which simulate failure mechanisms in actual environments are evolving as manufacturers accumulate field data. Information of this type is

generally proprietary and not published. Ellipsometry^(18,19) and ATR⁽²¹⁾ (discussed above) appear to be techniques by which surface property changes could be quantified for measuring the rate with which surfaces weather in nonliquid environments.

The high-temperature, high-humidity, cyclic-temperature tests of actual components by the microelectronics industry represent typical procedures used to develop and evaluate improved systems before placing them in actual service.^(40,41) The types of failures encountered in these accelerated tests have been found to occur in service, so the tests are useful in predicting whether or not a unit design will fail, assuming that it will not fail by another mechanism. Weibull plots are used by this industry in the analysis of the data.^(42,43) The significance of this technology is that the electrical characteristics of the system are similar to those of silicon solar cells (semiconductor material, interconnect corrosion and fatigue, encapsulation purposes, etc.). Glass applied by fusion of powders is a prime silicon-device encapsulant when thermal-fatigue, electrical-stability, and moisture-resistance characteristics are critical.⁽⁴⁴⁾

Information relevant to the weatherability of solar-array encapsulant systems can also be found in the experience of manufacturers of insulating glass.⁽⁴⁸⁾ In Canada, a set of tests described in Canadian Government Specification Board Specification 12-GP-8 has been used to qualify manufacturers and compare systems, but there has been no direct correlation between any one type of test and field-failure experiences. However, the use of the tests has resulted in improved product quality and a decreased field-failure rate.⁽⁴⁵⁾ One U. S. manufacturer has reported that conclusive correlations between accelerated and field performances were not possible⁽⁴⁶⁾, whereas another (which used organic sealants) reported that field performances correlated with combined UV exposure (500 hr) and temperature cycling (20 to 120 F) test results⁽⁴⁷⁾. The expression:

$$F(x) = 1 - \exp(-x/\theta),$$

where $F(x)$ = cumulative failure probability, x = failure time, and θ = mean failure time, was found to describe the failure probability of field units after 17 years of experience.⁽⁴⁷⁾ The development of test methods used by insulating-glass manufacturers has been reviewed⁽⁴⁵⁾ with conclusions that none of the methods can be used to predict durability in actual service, but, combined with field experience, they can be helpful in predicting poor field performance⁽⁴⁸⁾. Currently, ASTM Committee E-6 is preparing a draft of proposed practices for accelerated testing of insulating glass, but the report is not yet available.

Conclusions

This review of the experience on aging characteristics and/or weatherability data for glasses has revealed no quantitative information on degradation rates of glass under normal ambient conditions. The review indicates, in part, the proven durability of the material. Although weathering is not usually a problem with

modern-day glasses, it can occur in specialty glasses which have not been developed with this consideration in mind. Moisture and temperature are usually the two most important factors affecting weatherability. Although they may not visibly affect the transmission or appearance of glass, the long-term strength of glass under stress can be reduced drastically by a phenomenon known as static fatigue (or stress corrosion). If the glass is not exposed to a high mechanical stress, aging in a moist environment may increase or decrease the strength slightly. Solar-array encapsulant systems will probably be designed so that residual stresses in the system are minor, but environmental stresses such as wind and snow loads may require that static fatigue characteristics be considered in the design.

In most encapsulation systems using glass today, the glass is used in conjunction with some organic sealant material (e. g., pottant, film, adhesive). Consequently, durability of the glass and sealant interface would be a more likely cause of failure than degradation of either bulk material. This type of degradation phenomenon is known to be enhanced by moisture.⁽⁴⁹⁾ Accelerated-test procedures which can quantitatively measure degradation rates at interfaces and/or surface nondestructively would be highly useful in this respect.

Although accelerated tests on powdered or bulk glass are commonly used in the laboratory to evaluate durability, quantitative measurements are usually made only on materials tested in liquid media, where the media can be analyzed. Experience has shown a general correlation between weatherability and resistance to water, but that weatherability must be verified by exposure of bulk specimens to high humidities. Unfortunately, techniques for quantitatively measuring surface-degradation characteristics are not well-developed, and visual observations are usually employed. For predicting the life of a system, degradation rates must be known, and procedures by which surface (and/or interface) degradation can be quantitatively measured must be developed. Attractive analytical techniques that are emerging may make this possible.

Analysis of Available Aging Data and Models

One requirement of Study 4 is to identify and analyze the available long-term aging data on materials expected to be relevant to the encapsulant system. Additionally, the aging models being used and their applicability are to be assessed. This subsection deals with these aspects.

Literature data on aging of polymeric materials are quite extensive. The types of aging studies found can be divided into two almost mutually exclusive classes according to the goals of the study. One class, representing the great bulk of literature on aging of polymeric materials, deals mainly with descriptive data and simply describes, for example, material properties before and after aging for a given time under a given set of conditions. The other class deals with studies which attempt to describe aging behavior by mathematical modeling. The latter type of information is most consistent

with the goals of Study 4; the most pertinent findings are summarized in this section, both with respect to the data illustrated and to the methodology brought to bear on their mathematical representation.

Aging Studies and Models

NBS-MCA Study^(50, 51). One of the most ambitious studies of natural and accelerated weathering to date was the joint industry-government program undertaken by the National Bureau of Standards and Manufacturing Chemists Association. In this program, 20 plastic materials, including 6 generic plastic species, were exposed beginning in 1966 in Miami, Florida; Phoenix, Arizona; and Washington, D. C. They were exposed as both clear films and white films of various thicknesses. A description of the materials exposed and a listing of the properties measured are given in Table 1. The program was designed to last for 10 years but was almost aborted after only 6 years as a result of a lack of funding. Property measurements were made initially at 3-month intervals and, later in the program, at 1-year intervals. Since the stated goal of the study was to correlate accelerated and natural aging data, weatherometer testing was also done on the same materials.

In the NBS data-analysis approach, the property-versus-time data were fitted to the following equation derived from the Weibull probability density function:

$$P = b_1 \exp \left\{ - \left[\frac{t + b_2}{b_3} b_4 \right] \right\} + b_5 , \quad (3)$$

where P is the property level at time, t , and b_1 through b_5 are fitted parameters. The five fitted parameters were claimed to have physical significance as follows:

- b_1 - is related to maximum property level
- b_2 - is related to pre- or postaging
- b_3 - is related to characteristic life defined as the time required for 63 percent property degradation
- b_4 - is related to the presence or absence of an initial induction period
- b_5 - is the asymptotic property level at infinite time.

Because of these relationships, the b_i 's were called exposure parameters.

TABLE 1. MATERIALS AND PROPERTIES EVALUATED
IN NBS-MCA STUDY ON WEATHERING OF
PLANTS

Number of Compositions	Materials Evaluated		Thickness, mils
	Generic Class	Color	
Two	Polyethylene	Translucent	1 and 60
One	Polymethylmethacrylate	Clear	60
One	Polyvinylfluoride	Clear	1
One	Polyethylene terephthalate	Clear	5
One	Crosslinked polyester	Clear	60
Fourteen	Various PVC materials	Clear and white	9, 10, and 60
Properties Evaluated			
Color		Tensile properties	
Haze		Flexural properties	
Gloss		Electrical properties	
Surface roughness		UV spectra	

The next step in the data analysis consisted of fitting the important exposure parameters, or meaningful functions of them (such as characteristic life) to a linear equation in meteorological variables as follows:

$$b_i = C_i + C_{iL}(L) + C_{iU}(U) + C_{iH}(H) + C_{iR}(R) + C_{iT}(T) , \quad (4)$$

where L is total radiation in langleys, U is UV radiation (Coblentz langleys), H is relative humidity, R is inches of rainfall, T is air temperature, and the C_i 's were parameters fitted by stepwise regression. Thus, from the basic meteorological variables L, U, H, R, and T, it should be possible to predict the values of b_i , which in turn could be used to predict property levels or rate of property change at time, t.

The complete data analysis was made only for elongation at break and only for 3 years of data. Therefore, a judgement as to the success or failure of this approach is rather difficult. From the limited data analysis, however, successful results appear to have been obtained for some of the material-site combinations, whereas gross deficiencies were apparent for other combinations.

Leikina and Tatevos'yan Study⁽⁵²⁾. In this accelerated-aging study, a central-composite, response-surface experimental design⁽⁵³⁾ was employed to study the effects of temperature, X_1 (30 to 65 C), and radiation intensity, X_2 (150 to 300 w/m²), on tensile strength, elongation to break, and IR

absorption (1720-1780 cm^{-1}) of 0.1-mm polyethylene film. This type of design allowed each response to be fitted to a second-degree polynomial equation in X_1 and X_2 as follows:

$$P = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2, \quad (5)$$

where P is the fitted property and the b_i 's are parameters fitted via multiple-linear-regression analysis. Statistical-significance testing indicated that the equations fitted within experimental error. From the fitted equations, interpolations, possible within the limits of the design, enabled property predictions for conditions not actually evaluated. Since such fitted equations are purely empirical, however, extrapolation outside of the design limits results in predictions with a high level of uncertainty.

Leikina, Tatevos'yan, Kuznetsova, and Melkumov Study⁽⁵⁴⁾. In this study the effects on polyethylene and polyvinyl chloride of four variables - irradiation intensity (350-700 w/m^2), specimen surface temperature (20 to 75 C), fraction of time exposed to water during test cycle (1/6 to 1/2), and total test time (170 to 340 hr) - were investigated. The investigators employed a Soviet DKSTV-6000 weatherometer with a xenon lamp. The experimental design employed was a full 2^4 factorial in which all combinations of the two levels of the four variables were examined. This design permitted the fitting of the following empirical equation to the same properties as in the previous study:

$$P = b_0 + \sum_{i=1}^4 b_iX_i + \sum_{j=1}^4 \sum_{i=1}^4 b_{ij}X_iX_j, \quad (6)$$

where, again, P is the property level and the b_i 's are fitted parameters. Again, the fitted equations were useful for interpolation, but not for extrapolation.

This study and the previous one are significant because the experimental designs employed enabled interactions between different independent variables to be elucidated. Interaction (i. e., synergistic) effects go undetected in classical one-variable-at-a-time experimentation, but may be the most important information obtained from an experimental investigation. For example, for polyethylene tensile strength, the interaction between exposure time and temperature turned out to be the most significant effect.

Kamal Study⁽¹⁰⁾. Dr. Kamal's study is similar to the two Russian studies just cited, but is somewhat more rigorous even though it predates them. Using a xenon-arc weatherometer, he set up a program consisting of 16 sets of fixed weatherometer conditions (e. g., fixed temperature, fixed length of wet time, and fixed fraction of total time sample was wet). For each set of conditions, polystyrene, polyvinyl chloride, and crosslinked-

polyester samples were exposed for 400 hr and properties of interest, including tensile strength, color change, and UV absorption, were measured at 100-hr intervals. Property-versus-time data were fitted to the equation

$$\text{Log } P = b_0 + b_1(t-250) , \quad (7)$$

where P is the property level at time, t , and b_0 and b_1 are fitted parameters. Clearly, b_0 is the log of the property level after 250 hr, and b_1 is the logarithmic rate of change of the property with time. Kamal referred to b_0 and b_1 as exposure parameters and fitted each of them to a quadratic equation in the weatherometer variables as follows:

$$\begin{aligned} b_0 \text{ or } b_1 = & C_0 + C_1X_1 + C_2X_2 + C_3X_3 + C_{11}X_1^2 + C_{22}X_2^2 \\ & + C_{33}X_3^2 + C_{12}X_1X_2 + C_{13}X_1X_3 + C_{23}X_2X_3 , \end{aligned} \quad (8)$$

where X_1 = temperature, X_2 = length of wet cycle, and X_3 = percent of time in each cycle during which the sample was wet.

As part of this study, samples of the same materials were exposed outdoors with concurrent estimates of temperature, wetness, and UV energy conditions. From information in Equation (6), outdoor property values were predicted as a function of time and compared with the actual exposure data. Some of the results obtained in this manner were surprisingly good. Figure 9 shows the results for tensile and color change of polystyrene for up to 52 weeks. With the exception of the 52-week color-change value, the predictions shown by the solid line matched the actual data points extremely well. These results are, therefore, being further investigated.

Natural Rubber Producers Research Association (NRPRA) Study⁽⁵⁵⁾. In this study D. K. Thomas and R. Sinnott predicted room-temperature modulus changes in both polyacrylonitrile and polychloroprene elastomer systems for up to 5 years from accelerated-heat-aging data at 100 to 150 C. Assuming first-order degradation kinetics, they fitted the equation:

$$\log \left(\frac{P_t}{P_0} \right) = kt , \quad (9)$$

where P_t and P_0 are property levels at time t and time zero, respectively, k is the first-order rate constant, and t is time. They then related k to temperature, T , using the Arrhenius equation:

$$k = A \exp (-B/RT) , \quad (10)$$

where A and B are fitted constants (B , the activation energy for the process causing failure). These equations were then used to predict P_t at room temperature for several properties for up to 5 years. The results are shown in Table 2 for 100 percent modulus along with actual property levels from concurrent outdoor testing.

FIGURE 9. OUTDOOR EXPOSURE PERFORMANCE OF POLYSTYRENE VERSUS VALUES PREDICTED FROM XENON-ARC WEATHEROMETER⁽¹⁰⁾

As can be seen the results are quite good, especially in view of the fact that extrapolations were made over wide temperature and time intervals.

TABLE 2. RUBBER AND PLASTICS RESEARCH ASSOCIATION (RAPRA) 5-YEAR PREDICTION RESULTS FOR MODULUS⁽⁵⁵⁾

Time at Room Temperature, years	Change in Modulus, percent			
	Nitrile Rubber		Neoprene Rubber	
	Predicted	Observed (RAPRA)	Predicted	Observed (RAPRA)
1	6	5	4	16
2	12	11	8	19
3	19	17	12	20
4	26	22	16.3	22
5	34	27	21	23

Lockheed Study⁽⁵⁶⁾. The purpose of this study was to predict service life of a propellant. In the accelerated-testing plan, cartons of the propellant were aged under nitrogen at 30, 70, 86, 115, and 145 F and at 0 and 5 percent strain for periods up to 120 weeks. Gel content, degree of swell, creep compliance, dilation, and crack propagation were measured at intervals during the testing period. The property-versus-time data were fitted to one of the following equations:

$$P = P_0 + k \log t, \text{ or} \quad (11)$$

$$P = P_0 + k_1 \log t + k_2 \log^2 t, \quad (12)$$

where P and P_0 are property levels at time t and 1 week, respectively, and k , k_1 , and k_2 are fitted rate constants. The linear equation usually was adequate. Where it was not, the quadratic equation was employed. The rate constants k , k_1 , and k_2 were related to temperature by the Arrhenius Equation (10). The compliance equations were extrapolated over time and temperature to arrive at a predicted 1 sigma (σ) service life interval of 4.6 to 11 years. Good agreement was claimed with 7 to 8-year modulus data.

Hill Air Force Base Study⁽⁵⁷⁾. In this study several properties of various components are being monitored at storage conditions to "detect changes which could reduce service life estimates". The components include various potting compounds, adhesives, spiralloy, and pressure seals. Properties include tensile strength, elongation, hardness, and lap shear strength. Breakaway torque and leak rate are measured on the seals. Data are presently available for up to 8 years for the adhesives and potting compounds and 13 years for the seals.

Measurement intervals for all but the seals are approximately 1 year except for the first year where 1 and 6-month measurements were made for some properties. The number of replications at each data point vary from three to ten. Pressure seals are tested every other month with no replication.

Reported data treatment consisted simply of fitting a linear relationship to the data as follows:

$$P = P_0 + b_1 t , \quad (13)$$

where P is property level at time t , P_0 is initial property level, and b_1 is the fitted slope. The slope was then tested for statistical significance. No attempts were made to predict service life or to evaluate alternative models.

Since the information in the report is rather sparse, the Hill Air Force Base was contacted for some of the details relayed above and to determine the availability of raw data not included in the report. The data are stored on computer tapes, and will be requested formally when it is determined that they be useful in this study.

Critique of Literature Aging Studies

In critiquing literature aging studies relative to the goals of Study 4*, it is helpful to list the most important characteristics of such a study. Those characteristics applicable to both accelerated- and abbreviated-test plans are:

- (1) Replication
- (2) Sufficient data points for model building
- (3) Sufficient number of properties measured
- (4) Characterization and/or randomization over materials studied.

Replication is necessary if the signal and noise content of the data are to be separated. Without replication, it is impossible to determine to what extent the model is being fitted to noise rather than signal.

Without a sufficient number of data points, model adequacy may be hard to assess and difficulties may be encountered in comparing alternative models. For example, if the NBS five-parameter model is fitted to only six data points, only one degree of freedom is available to statistically test the model. The resultant test is not very powerful.

All properties which can conceivably lead to failure should be measured for obvious reasons. It appears to be common practice to measure only properties which are known a priori to give the desired results so that a particular methodology can be illustrated.

*This critique relates only to the goals of Study 4 and is not intended to reflect on the overall quality of the individual studies.

$$P = P_0 + k \log t \quad (11)$$

$$P = P_0 + k_1 \log t + k_2 \log^2 t \quad (12)$$

$$P = b_1 \exp \left\{ - \left[\left(\frac{t + b_2}{b_3} \right)^{b_4} \right] \right\} + b_5, \quad (3)$$

These choices of mathematical models serve to bring out several significant points. Only in the second case is the model mechanistic (i. e., based upon theoretical considerations, and assumes first-order degradation kinetics). It is likely that a truly mechanistic model will never be achieved. And, finally, a truly mechanistic model need not necessarily be achieved. A brief discussion might be useful.

Clearly, the ideal state one drives toward is a complete understanding of the degradation of material properties in a given environment and under a given set of operating conditions. A full understanding implies ability to formulate a mathematical aging model based on the mechanisms and rates of degradation. Extrapolation from short-term to long-term behavior can be done with higher confidence. A further implication is that the number of parameters that are adjustable is a minimum - a sought-for goal.

The scarcity of mechanistic models to date would suggest that a totally mechanistic mathematical model is difficult to achieve. While a portion of property degradation often can be assigned to specific mechanisms, and thus to assignable causes (environmental variables), the interactions of environmental variables are most often unknown and must be determined experimentally. This circumstance introduces the necessity for additional adjustable equation parameters. Some of the models noted previously attempt to take into account these possible interactions. The Weibull-type model has five parameters. Additional parameters are also likely needed when it is not feasible on an economic or technical basis to control or measure a sufficient number of properties/characteristics and environmental conditions.

But it is not necessary always to have a truly mechanistic model! If the interactions among environmental variables are many, a truly mechanistic model might be highly complex, even if the degradation is understood. Tractability could be made difficult indeed if the model, say for a material interface, contained several rates of degradations, all of which exhibited about the same value. Many separate property measurements might have to be made. Purely from the point of developing an accelerated test, a full understanding of the degradation might not be necessary, especially if one mode of degradation (one rate constant) overshadows all others. In such a case, a desirably simple empirical model is possible. For a total encapsulant system, a tractable experimental design for aging tests must take into account the known mechanisms and rates of degradation so as to help simplify the aging model by paying the most attention to the expected high-rate modes of degradation. Since the "system" has not yet evolved, initial attention

must be given to separate property changes in materials and "simple" interfaces. Under such circumstances, the models drawn from experience to date must be considered even though they do not draw heavily upon the fundamental physics of aging.

Conclusions

The best published aging studies found to date exhibit serious deficiencies relative to the goals of Study 4. As a result, building an aging model from literature data and verifying that model is impossible. What can be done is to consider the various types of deficiencies and design a better aging test to overcome the deficiencies. In spite of the shortcomings of the studies, they have indicated that an accelerated aging study, if properly designed, can predict the change in at least some properties under actual outdoor-aging conditions. The various property-versus-time models found in the literature will certainly be useful in designing the accelerated/abbreviated aging tests in this study. Also, some of the available data analyzed, although it is not generally satisfactory, can be used in evaluating portions of our methodology as it is developed during the study.

Background and Initial Development of the Methodology for Aging Tests

One of the outputs of Study 4 is to be a methodology to be used in developing specific test designs. This subsection presents some aspects of the methodology considered to date. It will serve as a brief background to some of the major features of aging tests. A "prototype aging experiment" is described, together with an example from an actual application of the procedure. Some considerations are also presented concerning the required measurement precision.

Experimental Objectives

The four primary objectives of an aging experiment are:

- (1) Measure material and performance characteristics over time and deduce their degradation rates under specified operating and environmental conditions.
- (2) Relate the degradation rates of material and performance characteristics to suitably quantified measures of the environmental and operational stresses.
- (3) Predict the times required for the amount of degradation for each material and performance characteristic to reach specified limits as functions of the environmental and operational stresses.

- (4) Verify the predicted degradation amounts and times of occurrences for each material and performance characteristic for each stress level.

The emphasis on measure, relate, predict, and verify (MRPV) simply serves to indicate the required scientific framework for aging experiments. The emphasis on "degradation rates" and "amount of degradation" serves to identify a key aspect of aging experimentation. The real challenge for aging experiments consists of measuring the time rates of change in the material/performance characteristics. Symbolically, it is not only the measurement of characteristic x at time t that is needed; it is also essential to obtain $\dot{x} \equiv \Delta x / \Delta t$. As shown later, severe measurement requirements are often associated with the measurement of a degradation rate, $\dot{x}$.

As soon as a degradation rate can be estimated from experimental data, the first primitive estimate of the amount of degradation to be expected over a specified time period can be obtained by multiplying the degradation rate by the time period of interest. That is, as soon as some measurable change, Δx , is observed in a time period Δt , the first primitive estimate of the amount of degradation to be expected in time t is given by $\Delta x(t) = \dot{x}t = (\Delta x / \Delta t)t$. This estimated amount of degradation can then be compared with the specification requirements pertaining to material and performance characteristics to determine whether or not the system is likely to meet the requirements of the specifications by the end of the specified time interval. Such "failures" to meet specifications depend, of course, on the specifications themselves. From the viewpoint of the physics of aging, the specification generally appears to be rather arbitrary. That is, the same system with the same degradation rate could be judged as a failure by one set of specifications and not by another set. This point simply serves to emphasize the need to place primary emphasis on the experimental deterioration of the degradation rates and degradation amounts, and secondary emphasis on whether or not "failure" has occurred according to some specifications.

Stress Levels

It is generally useful to conceive of the operation of a system over time as occurring under some kind of generalized stress. Although frequently difficult to define and measure, the concept of generalized stress is essential to the design and analysis of aging experiments. Some of the more important ideas related to generalized stress are:

- (1) The level of stress denotes a quantified measure of the abusiveness of the environmental and operating conditions.
- (2) A suitable definition, and a corresponding quantitative measure for stress, is usually unknown initially and must be deduced through analysis of early-life data.

- (3) Stress must be defined so that increasing levels of stress are associated with increasing degradation rates.
- (4) A normal stress constitutes the operational and environmental conditions that are equivalent to intended-use conditions.
- (5) A higher-than-normal stress constitutes either the operational stress or the environmental stress that is expected, or found, to be greater than the normal stress.

The required relation between generalized stress and degradation rate is expressed in (3) above, i. e., stress must be defined so that increasing levels of stress are associated with increasing degradation rates. If the contrary is found to hold in the experimental results, the definition of stress must be revised appropriately. In other words, there is a cause-and-effect requirement to interpret the experimental findings in such a way that stress is the cause of the observed effects – the degradation rates. Carrying the analogy still further, consider changes that occur over time and yield degraded performance. It is regarded as necessary that such changes be interpretable as generalized strains that result from the generalized stresses imposed on the system over time.

Relating Degradation Rates to Stress Levels

The objective in analyzing the data from an aging experiment consists of identifying and quantifying the relationship between the observed degradation rates and suitably constructed measures of stress. It is often difficult to achieve this objective. In general, the following observations can be made:

- (1) Degradation rates must be computed from experimental data.
- (2) The quantitative relations between degradation rates and constructed measures of stress must be derived from analyses of data using mathematical models based on physical, statistical, and engineering approaches.

Some of the mathematical approaches are described in detail in Reference⁽⁵⁸⁾, and are not elaborated on below.

On Predictions

Because of the uncertainty associated with defining and measuring the appropriate stress in an aging experiment, it is essential that predictions be made during the early-life portions of the experiment to predict degradation rates and degradation amounts that are expected to occur in late-life portions of the experiment. Such early predictions must be made in order to form a basis for learning and for correcting errors. For example, it will often be necessary to change definitions of stress, and possibly even change the number and "spacing"

of the stress levels. This problem will be seen more clearly in the discussion below concerning the prototype aging experiment.

Of special importance to the prediction problem is that predictions of the times required to achieve specified amounts of degradation are of two types:

- (1) Those predictions that are made within a stress level
- (2) Those predictions that are made across stress levels.

In general, such predictions must be generated during the experimental test program to provide a convincing "track record". Those predictions made within a stress level are made using early-life results to predict the amounts and times of occurrence of late-life degradations at the same level of stress. Such predictions, for example, should be made during the performance of an abbreviated life test performed under normal stress conditions. The predictions across stress levels occur for accelerated testing in which experimental findings at higher than normal stress levels are used to predict the amounts and times of occurrence of late-life degradations at lower stress levels. In general, it is expected that degradations will occur first at the highest level of stress used in the experiment. Those results should be used to predict results that will occur subsequently at the lower levels of stress. The predictions from higher to lower stress levels always require extrapolations of the data. In fact, obtaining a valid extrapolation from higher than normal stress to normal stress is the overall objective of accelerated testing. As always, extrapolations are hazardous. However, they are essential to accelerated testing, and knowledge of this fact has considerable bearing on how accelerated-aging tests should be designed. In general, it may be said that an accelerated-aging test should be designed to minimize the risk of invalid extrapolations of degradation rates and amounts based on experimental findings obtained at higher than normal stresses to those expected to occur at normal stress levels. The problem is intensified by the fact that data may never be obtained at the normal stress levels because the low degradation rates associated with those levels would require excessive test times, beyond the time and/or finances available.

Description of a Prototype Aging Experiment

Figure 10 shows a prototype aging experiment in schematic form. At the measurement stage, the first step shown at the top of the figure, it is seen that a material or performance characteristic, labeled property $x(t)$, is measured over time at different stress levels labeled S_0 , S_1 , S_2 , S_3 , S_4 , and S_5 . These may be one or more "normal" stresses and stresses expected to be higher than normal ("accelerating"). Each diagram at the top of the figure represents a different property. The straight lines shown on these diagrams suggest the simplest possible case in which the data points (not shown) can be well represented by the fitted, least-square regression lines. That is, the line labeled S_5 is taken to be a regression line fitted to data obtained on measurements of $x(t)$ taken at various times, t , at the highest stress level. The same property measured for

systems operated at the next highest stress level is shown by the regression line labeled S_4 , etc. The degradation rates are then estimated by the slopes of these regression lines.

The second step of the procedure consists of quantifying the measures of stress so that a mathematical relationship between degradation rate and stress level can be identified. One method for accomplishing this involves an Arrhenius-type plot (as Step 2 in Figure 10). Here, the observed degradation rates are plotted against a reciprocal measure of stress, $1/S$. Each line in the Arrhenius plot represents a different measured property, one line corresponding to each set of lines shown in Step 1. It should be noted that normal stress is considered to be a low stress, so that $1/S$ would be relatively large, as shown on the stress axis. Reading vertically from the normal stress it is seen that Property k shows the largest degradation rate for normal stress. The degradation mechanism for Property k would be called the dominant degradation mechanism at normal stress levels. The figure shows that if the stress level is changed, the dominant degradation mechanism may also change. In accelerated testing, it is frequently desirable to increase the stress level above normal as much as possible without changing the degradation mechanism. In the figure a change in dominance is shown by the circled intersection of the two rightmost Arrhenius lines.

Once the degradation rates have been measured experimentally and related to initially chosen measures of the stress levels, it is then desirable as the third step to predict of the expected times of occurrence and expected magnitudes of future degradations both within and between stress levels. Again, the simplest possible versions of these prediction procedures are shown as Step 3 of Figure 10. For linear prediction within a stress level, it is only necessary to multiply the degradation rate by the subsequent time interval of interest. This is shown by the dashed line to the point labeled S_5 with the predicted time and predicted amount of degradation shown on the left (bottom) prediction sketch. The right (bottom) sketch shows the prediction scheme for predictions across stress levels. The amount of degradation that has just been observed at S_5 , the highest stress level, would be expected to occur at some future time at S_0 , a lower (for instance, a "normal") stress level. If sufficient points have been observed to identify the curves for S_0 and S_5 , the prediction can be made as shown in the sketch.

Figures 11 through 16 show actual applications of the procedure described above. Figures 11, 12, and 13 show the regression lines fitted to the property data for three stress levels corresponding to operating temperatures of 70, 100, and 125 C for 10-Kohm, 1/2-w 120 carbon composition resistance operated at full power.

Figure 14 shows the Arrhenius-type plot with the slopes of the three regression lines plotted against reciprocal temperature. Note that each regression line gives rise to a single point on the Arrhenius plot.

1. Measure Properties Over Time To Deduce Degradation Rates At Specified Conditions

Measure material and/or performance characteristics over time at different conditions ("increasing" stress levels) in order to determine their *degradation rates* under the specified conditions. Select conditions that include the "normal" stress level and hopefully more abusive ("accelerating") stress levels that maintain the same failure mechanism.

2. Relate Degradation Rates To Measures of the Environmental/Operational Stresses

Quantify the measures of the environmental and operational stresses and determine some mathematical relationship between the degradation rate and the stress level.

3. Predict Expected Times/Amounts of Degradation Within and Between Stress Levels

Predict the expected times and amounts of future degradations both within a stress level (predict the value a property will have after a longer time at that same condition) and between stress levels (predict the time it will take at a lower stress level for a property to degrade the same amount already observed at a higher stress level).

4. Verify the Predicted Degradation Amounts and Times Using Data From Continuing Tests

FIGURE 10. SCHEMATIC OF A PROTOTYPE AGING EXPERIMENT AS DESCRIBED IN THE TEXT

FIGURE 11. AVERAGE RESISTANCE AS A FUNCTION OF OPERATING TIME FOR 120 CARBON-COMPOSITION, 1/2-WATT RESISTORS OPERATED AT FULL-RATED POWER AT A NOMINAL TEMPERATURE OF 70 C

FIGURE 12. AVERAGE RESISTANCE AS A FUNCTION OF OPERATING TIME FOR 120 CARBON-COMPOSITION, 1/2-WATT RESISTORS OPERATED AT FULL-RATED POWER AT A NOMINAL TEMPERATURE OF 100 C

FIGURE 13. AVERAGE RESISTANCE AS A FUNCTION OF OPERATING TIME FOR 120 CARBON-COMPOSITION, 1/2-WATT RESISTORS OPERATED AT FULL-RATED POWER AT A NOMINAL TEMPERATURE OF 125 C

FIGURE 14. SLOPE-TEMPERATURE RELATION FOR RESISTANCE DEGRADATION

Finally, the materials studied should be characterized completely so that, to put it quite simply, one knows what one is predicting the life of. This is especially true for polymers where a generic polymer type can encompass a wide range of molecular weights, molecular-weight distributions, degrees of branching, amounts of residual monomer, etc. Furthermore, if the materials tested are selected (within a generic polymer type) by some random process, predicted lifetimes and life distributions will be applicable to a much wider range of materials. It is desirable to have both characterization and randomization in an aging study. If this is not practical it is essential that one or the other be done.

The literature studies discussed above are compared in Table 3 according to these four criteria. The inadequacies of even the best existing aging studies with regard to Study 4 goals are quite apparent. Characterization of and/or randomization over materials is almost never seen unless it is done without being mentioned in the reports. Replication, sufficient data points, and sufficient properties are also common deficiencies. The test plan to be developed in Study 4 must be free of these deficiencies. Another glaring deficiency of published outdoor-aging studies is the failure to properly monitor outdoor-aging variables which can contribute to failure, such as UV intensity, relative humidity, average temperature, temperature extremes, pollutant levels, percent wet time, etc. This deficiency must also be taken into account in the Study 4 plan.

TABLE 3. CRITIQUE OF AGING STUDIES OF POLYMERIC MATERIALS REPORTED IN THE LITERATURE FOR SPECIFIC APPLICABILITY TO THE EVALUATIONS TO BE CONDUCTED IN STUDY 4

Investigator	Reference	Replication	Sufficient Data Points	Sufficient Properties	Characterization for Randomization Over Materials
NBS-MCA	(50, 51)	No	Yes-no	Yes	No
RAPRA	(55)	No	No	No	No
Kamal	(10)	No	Yes	No	No
Leikina, Tatevos'yan	(52, 53)	Yes	Yes	Yes-no	No
Leikina, Talevos'yan et al.	(54)	No	Yes	Yes-no	No
Lockheed	(56)	Yes	Yes	Yes	No
Hill AFB	(57)	Yes	Yes	Yes	No

Critique of Property-Versus-Time Models

The following property-versus-time models have been employed in studies discussed previously:

$$P = P_0 + b_1 t \quad (13)$$

$$P = P_0 \exp (-kt) \text{ or } \ln P = \ln P_0 - kt \quad (9, 11)$$

Figure 15 shows the acceleration factor that results from the linearity of the Arrhenius plot. In general, the figure shows that 1-hr operation of one of these resistors at a temperature of 100 C is equivalent to 4-hr operation at 70 C; operation for 1 hr at 125 C is equivalent to 14 hr of normal operation.

Figure 16 shows all of the data transferred to the same time scale appropriate for operation at 70 C. If a perfect correlation had been found, then all of these data points would have fallen on a single straight line through the origin. This figure shows a measure of the overall success in correlating the accelerated test data.

Some Preliminary Calculations

In designing an accelerated test, it is necessary to be concerned with measurement precision. Degradation rates of interest are frequently very small and very precise measurement techniques are required to detect and measure them. The calculations given below are intended to suggest the order of magnitude of the precision required; accordingly, they are based on the simplest possible assumptions.

Begin by supposing that the material or performance property decays over time in a first-order exponential manner:

$$x(t) = x^*(t)e^{-Kt}, \quad (14)$$

where

- $x(t)$ denotes a measured degraded property value
- $x^*(t)$ denotes the property value that would be obtained in the absence of degradation
- e^{-Kt} denotes a degradation factor with K a constant and t a measure of time.

By rearrangement, it follows that

$$f = x(t)/x^*(t) = 1 - e^{-Kt}, \quad (15)$$

where f denotes the fractional degradation over time t . By setting f equal to a particular value (say 20 percent) at the end of particular time (say 20 years) the corresponding value of K can then be determined from Equation (15). Table 4 shows the resulting values of K for f set equal to 20, 40, 60, and 80 percent, and t set equal to 7305 days (20 years).

FIGURE 15. ACCELERATION FACTOR AS A FUNCTION OF OPERATING TEMPERATURE

FIGURE 16. OVERALL REGRESSION LINE FOR TRANSFORMED DATA

TABLE 4. VALUES OF DEGRADATION CONSTANT FOR
SEVERAL VALUES OF FRACTIONAL
PROPERTY DEGRADATION AT THE END OF
20 YEARS FOR SIMPLE MODEL

Fractional Degradation, percent	Computed Value of K
20	0.000031
40	0.000070
60	0.000125
80	0.000220

Once K is determined, the amount of degradation that would be expected to occur at any intermediate time can be computed. Table 5 shows the fractional degradation that would be expected to occur at the end of 1, 30, 90, 180, 270, and 360 days, using the preceding K-values. The table shows, for example, that if the degradation for a system reaches 20 percent at the end of 20 years, then in the first 30 days, the system would be expected to show a degradation of only 0.1 percent (0.001 in Table 5) at 30 days, 0.6 percent at 180 days (6 months), and 1.1 percent at 360 days (approximately 1 year). With an 80 percent degradation after 20 years, these values increase to 0.7, 3.9 and 7.6 percent, respectively.

TABLE 5. FRACTIONAL DEGRADATION FOR VARIOUS ELAPSED
TIMES BASED ON K-VALUES IN TABLE 4

Assumed Fractional Degradation at End of 20 Years, percent	Fractional Degradation Expected to Occur at End of Time Shown, percent					
	1 Day	30 Days	90 Days	180 Days	270 Days	360 Days
20	0.000	0.001	0.003	0.006	0.008	0.011
40	0.001	0.002	0.006	0.013	0.019	0.025
60	0.001	0.004	0.011	0.022	0.033	0.044
80	0.002	0.007	0.020	0.039	0.058	0.076

These values indicate that very high measurement precision is required to detect and measure such degradation rates in early-life portions of an aging experiment.

It is clear that the preceding calculations do not account for any "noise" in the measurements. However, real aging tests are limited, not only by instrument precision, but also by the inability to hold environmental conditions exactly at prescribed levels over long periods of time, by gradual instrument drift, and by calibration. This means that statistical calculations must also be made in order to take explicit accounts of such measurement errors. Some sample-size formulas can be useful for this purpose.⁽⁶⁰⁾

Sources of Data

In general, three different sources of data are useful in aging experiments. These include data from field testing where experimental control is largely absent, but the exposure conditions are real; from laboratory testing where experimental control is possible, but the exposure conditions are likely to be oversimplified; and from diagnostic testing in a laboratory where destructive analyses permit very precise measurements of changes in quantities that otherwise cannot be measured. Diagnostic measurements can sometimes give advance clues to changes that are forthcoming, but have not yet resulted in measurable effects on the field or simulated conditions in the laboratory.

In an ideal aging experiment, diagnostic testing should be done on systems that are removed from test at periodic times. The removal of a good and degraded system with subsequent testing of both can give important information on the degradation mechanisms that are occurring.

Experiment Designs for Aging Tests

An experiment design (test plan) for an aging test includes the following specifications:

- (1) Material and performance degradation rates to be measured
- (2) Materials and specimen designs and numbers of specimens to be used
- (3) Stress conditions that are to be used
- (4) Measurement technique and frequency and precision of measurement required for field testing, laboratory testing (simulated environment), and diagnostic testing of good and degraded systems
- (5) Methods for data analyses to be used to generate:
 - (a) Early estimates of degradation rates

- (b) Early-life predictions of expected degradation amounts and their expected times of occurrence, both within and between stress levels
- (c) Procedures for identifying the dominant degradation processes that occur at each higher than normal stress level and those that would be expected to occur at normal stress levels.

Subject to given time and cost constraints a design for an aging test is always a compromise that focuses on the problem of obtaining the most informative allocation of resources among (1) field testing in actual environments, (2) laboratory testing in controlled environments, and (3) diagnostic testing to better identify and quantify the rates of degradation.

PLANS FOR THE NEXT QUARTER

Based on the work completed in Study 4 on the reviews of material aging behavior and on the identification and analysis of available aging data relevant to the encapsulation system, efforts are being directed toward formulating a detailed plan for the remainder of Study 4. Discussions are now underway among JPL and Battelle-Columbus personnel to detail and finalize the planned outputs of Study 4: (1) the methodology for developing aging tests and (2) the test designs for accelerated/abbreviated aging tests for selected materials and materials interfaces.

Among the tasks to be undertaken in the next quarter for these output requirements are:

- (1) Complete the development of the detailed study plan
- (2) Continue the analysis of aging data and models in order to contribute to the development of the statistical tools required in the study
- (3) Continue to develop the methodology for formulating the experiment designs for aging tests
- (4) Identify the expected performance criteria for the encapsulation system and translate these criteria into property requirements for components of the encapsulation system
- (5) Select a tentative test design for investigations to be carried out in Study 3 to furnish aging rates for use in Study 4 (The degree of success of this design will be used in developing and testing the methodology.)
- (6) Select possible "stresses" likely to bring about the dominant failure modes in the selected materials/interfaces for which aging test designs are to be developed

- (7) Analyze the precision/sensitivity required of the instrumentation to be used to measure the selected properties and stresses.

NEW TECHNOLOGY

The results of the research efforts are not yet sufficiently established to permit reporting of specific New Technology items. It is anticipated that specific items from Studies 1 and 2 may be identified in the next quarter upon conclusion of these parts of the investigation.

REFERENCES

- (1) Greenberg, S. A., McCargo, M., and Palmer, W. L., "Investigation of FEP TEFLON as a Cover for Silicon Solar Cells", NASA-CR-72970 (August, 1971), 69 pp.
- (2) Titus, J. B., "The Weatherability of Polyolefins", Plastec Report 32, (March, 1968) 84 pp.
- (3) Winslow, F. H., Matreyek, W., and Trogalla, A. M., "Weathering of Polyethylene", Acs. Div. Poly. Chem., New York Meeting, Preprint 10 (2), 1271 (September, 1969).
- (4) Carlsson, D. J., and Wiles, D. M., "Surface Changes During the Photo-Oxidation of Polypropylene", Polymer Letters, 8, 419 (1970).
- (5) Dunn, P., and Hill, E. J., "The Weathering of Polyolefins", Australian Dept. of Supply ADSSDLL, Report 421 (1971).
- (6) Shylapintokh, V. Ya., and Goldenberg, V. I., "Effect of Photostabilizers on the Rate of Photodegradation of PMMA", European Polymer Journal, 10, 679 (1974).
- (7) Davis, A., and Goldon, J. H., "Stability Study of Polycarbonate", J. Macromolecular Sci. - Reviews Macromol. Chem., C3 (1), 49 (1969).
- (8) Davis, A., and Gordon, D., "The Importance of Angle of Exposure in the Weathering of a Polymer", ERDE Technical Report 85 (1971).
- (9) Singleton, R. W., Kunkel, R. K., and Sprague, B. S., "Factors Influencing the Evaluation of Actinic Degradation of Fibers", Textile Research Journal, 35, 228 (1965).
- (10) Kamal, M. R., "Effect of Variables in Artificial Weathering on the Degradation of Selected Plastics", Polymer Engr. and Sci., 6, 333 (1966).
- (11) Komal, M. R., Private Communication (1976).
- (12) Adams, P. B., "Glass Containers for Ultrapure Solutions" in Corning Research, 1973 (reprinted from Ultrapurity, Marcel Dekker, Inc., 1972), pp 119-177.

- (13) Doremus, R. H., "Interdiffusion of Hydrogen and Alkali Ions in a Glass Surface", J. Non-Crystalline Solids, 19, 137-144 (1975).
- (14) Walters, H. U., and Adams, P. B., "Effects of Humidity on the Weathering of Glass", J. Non-Crystalline Solids, 19, 183-199 (1975).
- (15) Anderson, P. R., Bacon, F. R., and Byrum, B. W., "Effect of Surface Treatments on the Chemical Durability and Surface Composition of Soda Lime Glass Bottles", J. Non-Crystalline Solids, 19, 251-262 (1975).
- (16) Sieger, J. S., "Chemical Characteristics of Float Glass Surfaces", J. Non-Crystalline Solids, 19, 213-220 (1975).
- (17) Simpson, H. E., "Measuring the Surface Durability of Glass", Bull. Amer. Ceram. Soc., 30 (2), 41-45 (1951).
- (18) Hench, L. L., "Characterization of Glass", Chapter 8 in Characterization of Materials in Research, Ceramics and Polymers, J. E. Burke and V. Weiss (Eds.), Syracuse University Press (1975).
- (19) Tsuchihashi, S., Konishi, A., and Kawamoto, Y., "Chemical Attack of Optical Glass Surface by Formic Acid Vapor", J. Non-Crystalline Solids, 19, 221-239 (1975).
- (20) Pantano, C. G., Jr., Dove, D. B., and Onada, G. Y., "Glass Surface Analysis by Auger Emission Spectroscopy", J. Non-Crystalline Solids, 19, 41-53 (1975).
- (21) Berstein, V. A., and Nikitin, V. V., "Glass Surface Study by Means of Multiple ATR Spectroscopy", in Proceeding of the Tenth International Congress on Glass, Kyoto, Japan July, 1974, pp 105-110.
- (22) Mould, R. E., "Strength and Static Fatigue of Abraded Glass Under Controlled Ambient Conditions: IV, Effect of Surrounding Medium", J. Amer. Ceram. Soc., 44 (10), 481-491 (1961).
- (23) Wiederhorn, S. M., "Environmental Stress Corrosion Cracking of Glass", National Bureau of Standards Report 10-565 (April, 1971), AD 722692.
- (24) ASTM Test Designation C158-72, "Flexure Testing of Glass".
- (25) Wilson, R. E., Perry, H. A., and Koubeck, F. J., "Salt Water Resistance of Surface-Compression Strengthened Glass", Naval Ordnance Laboratory Report NOLTR 71-56 (October 1971).
- (26) Wiederhorn, S. M., Evans, A. G., Fuller, E. R., and Johnson, H., "Application of Fracture Mechanics to Space Shuttle Windows", J. Amer. Ceram. Soc. 57 (7), 319-323 (1974).

- (27) Wiederhorn, S. M., "Crack Growth as an Interpretation of Static Fatigue", *J. Non-Crystalline Solids*, 19, 169-181 (1975).
- (28) Weyl, W. A., Colored Glasses, Soc. Glass Technology (1951), pp 497-514.
- (29) Garg, H. P., "Effect of Dirt on Transparent Covers in Flat-Plate Solar Energy Collectors", *Solar Energy*, 15, 299-302 (1974).
- (30) Newton, R. G., "Problems Arising from the Weathering of Poorly Durable Glass", pp 49-54 in Proceedings of the Tenth International Congress on Glass, Tokyo, Japan, 1974.
- (31) Ministry of Tech., London (Eng.), Materials Div., "The Effect of Storage on the Strength of Annealed and Toughened Clear White Plate Glass", Report No. D., Mat. 153 (September, 1968), 35 pp.
- (32) Corney, N. S., Ministry of Defense, London (Eng), Directorate of Research Mat., "The Evaluation of VHR 2A and VHR 3A Glasses (Glaverbel-Mecaniver S.A.) for Aerospace Applications", Report No. DR-Mat-198 (March, 1975), 33 pp.
- (33) MIL-HDBK-17, "Plastics for Flight Vehicle, Part II. Transparent Glazing Materials".
- (34) ASTM Test Designation C225-73, "Resistance of Glass Containers to Chemical Attack".
- (35) Mendel, J. E., and Ross, W. A., "Chemical Durability of Glasses Containing Radioactive Fission Product Waste", BNWL-SA-4854, Paper presented at Annual Meeting of American Ceramic Society, April, 1974.
- (36) Simmons, J. H., Mills, S. A., and Howell, B. F., Nat'l Bur. of Standards, Washington, D. C., Inst. for Mat'l Res., "Effect of Phase Separation on the Physical and Chemical Properties of Glasses - Density and Chemical Durability", Final Tech. Report No. NBSIR-74-510 (July 16, 1974), 27 pp.
- (37) Morey, G. W., The Properties of Glass", Second Edition, Reinhold (1954).
- (38) Hagy, H. E., "Physical Properties of Glass", Section 17 in The Handbook of Glass Manufacture, Volume II, F. V. Tooley (Ed.), Books for Industry Incorporated, and The Glass Industry Magazine (1974).
- (39) ASTM Test Designation C 724-72T, "Acid Resistance of Ceramic Decorations on Architectural Type Glass".
- (40) Fitch, W. T., Motorola, 13th Annual Reliability Phys. Sym. (April, 1975). pp 58-69.

- (41) Khajezadeh, H. , and Rose, A. S. , RCA, 13th Annual Reliability Phys. Sym. (April, 1975), pp 87-92.
- (42) Brodeur, J. E. , Fairchild Semiconductor, 13th Annual Reliability Phys. Sym. (April, 1975), pp 255-256.
- (43) Lycoudes, N. , Motorola, 13th Annual Reliability Phys. Sym. (April, 1975), pp 257-259.
- (44) Perri, J. A. , "Glass Encapsulation", Microelectronic Technology, Boston Tech. Publishers, Inc., S. L. Marshall (Ed.) (1967), pp 215-217.
- (45) Solvason, K. R. , and Wilson, A. G. , "The Development of Evaluation Procedures for Factory-Sealed Double Glazing in Canada", Proceedings of a Seminar on the Durability of Insulating Glass, National Bureau of Standards, Bldg. Sci. Series Report, BSS 20 (February 1970), pp 11-16.
- (46) Gwyn, J. D. , "Manufacturers Test Methods: Correlation with Field Experience; Expected Field Life", Proceedings of a Seminar on the Durability of Insulating Glass, National Bureau of Standards, Bldg. Sci. Series Report, BSS 20 (February 1970), pp 35-36.
- (47) Mayzoni, J. R. and Bowser, G. H. , "Test Methods and Field Experience with Double-Glazed Units", Proceedings of a Seminar on the Durability of Insulating Glass, National Bureau of Standards, Bldg. Sci. Series Report, BSS 20 (February 1970), pp 37-42.
- (48) Robinson, H. E. , "An Exploratory Study of Laboratory Test Methods and Standards for Factory-Sealed Double-Glazed Window Units", Proceedings of a Seminar on the Durability of Insulating Glass, National Bureau of Standards, Bldg. Sci. Series Report, BSS 20 (February 1970), pp 49-58.
- (49) Jemian, W. A. , Wilcox, R. C. , and Hsu, A. D. T. , "Stability of Glass Fiber Reinforced Composites", Auburn University Final Report, Content DAAH01-73-C-0466, November 25, 1974 (AD/A-003499/1st).
- (50) National Bureau of Standards and Manufacturing Chemists Association, "Outdoor Performance of Plastics I through X", 1968-1972.
- (51) Clark, J. E. , "Correlation of Accelerated and Outdoor Weathering Tests of Plastics", NBS Report (1967).
- (52) Leikina, M. E. , and Tatevos'yan, G. O. , "Planning an Experiment for Studying the Light Aging of Polyethylene Film", Soviet Plastics, No. 7, 73 (1970).
- (53) Box, G. E. P. , and Wilson, K. B. , J. Roy. Statis. Soc. (B), 13, 1-55 (1951).

- (54) Leikina, M. A. , Tatevos'yan, G. O. , Kuznetsova, I. B. , and Melkumov, A. N. , "Use of Mathematical Experiment Planning Method to Investigate the Influence of Artificial Weather Factors on Certain Properties of Polymer Films", Soviet Plastics, No. 2, 41 (1971).
- (55) Thomas, D. K. , and Sinnott, R. , "Prediction of Shelf Storage Life from Accelerated Heat Aging Tests", Journal of IRI, p 163 (1969).
- (56) Myers, G. E. , "Chemical Structural Aging Effects", MANCP Report No. 297 (1974).
- (57) Dalaba, E. M. , "Minuteman Stage III Component Report", AFRPL-TR-74-58 (1974).
- (58) McCallum, J. , Thomas, R. E. , and Waite, J. A. , Accelerated Testing of Space Batteries, NASA-SP-323, Goddard Space Flight Center, National Aeronautics and Space Administration (1973).
- (59) Thomas, R. E. , and Gorton, H. C. , "Research Toward a Physics of Aging of Electronic Component Parts", Proceedings of Second Symposium on Physics of Failure (1964).
- (60) Hald, A. , Statistical Theory with Engineering Applications, John Wiley and Sons, Inc. , New York (1952), p 395.