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INTERIM REPORT

MEASUREMENT TECHNIQUES AND INSTRUMENTS SUITABLE FOR LIFE-PREDICTION TESTING OF PHOTOVOLTAIC ARRAYS

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

for the

ENCAPSULATION TASK OF THE
LOW-COST SILICON SOLAR ARRAY PROJECT

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

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

January 15, 1978

G T Noel, F. A. Sliemers, G C. Deringer, V. E. Wood,
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ABSTRACT

The validation of a service life of 20 years for low-cost photovoltaic arrays is a critical requirement in the Low-Cost Silicon Solar Array Project that is being conducted by the Jet Propulsion Laboratory for the Department of Energy, Division of Solar Technology Of necessity, this validation must be accomplished through accelerated life-prediction tests A methodology for such tests has been developed in a preceding study at Battelle for the LSSA Project Remaining needs before such tests are carried out are the identification, assessment, and experimental evaluation of diagnostic techniques and instruments which make possible the measurement of failure-related degradative property changes over a short time period with sufficient precision to allow the prediction of life over 20 years

A two-phase study is being conducted addressing these needs Phase I, the results of which are discussed in this report, consists of the initial identification and assessment of all known measurement techniques and instruments that might be used in these life-prediction tests. Phase II will consist of experimental evaluations of selected techniques and instruments

Array failure modes, relevant materials property changes, and primary degradation mechanisms are discussed as a prerequisite to identifying suitable measurement techniques and instruments Candidate techniques and instruments are identified on the basis of extensive reviews of published and unpublished information These methods are organized in six measurement categories – chemical, electrical, optical, thermal, mechanical, and "other physicals". Using specified evaluation criteria, the most promising techniques and instruments for use in life-prediction tests of arrays are then selected

These recommended techniques and their characteristics are described in the report. Instances are identified in which experimental evaluations are necessary to provide a basis for selecting among techniques with overlapping capabilities. Recommendations are made regarding establishment of the adequacy, particularly with respect to precision, of the more fully developed techniques for this application, and regarding the experimental evaluation of promising developmental techniques Measurement needs not satisfied by presently available techniques/instruments are also identified Investigations of some of the recommended techniques (within the level-of-effort of the study) are being planned for Phase II

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Hugh Maxwell of the Jet Propulsion Laboratory is the Technical Manager for this study and Cliff Coulbert of JPL is the Manager of the Encapsulation Task of the Low-Cost Silicon Solar Array Project for which this study was performed. Their helpful guidance and technical input to the study are gratefully acknowledged.

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MEASUREMENT TECHNIQUES AND INSTRUMENTS SUITABLE FOR LIFE-PREDICTION TESTING OF PHOTOVOLTAIC ARRAYS

SUMMARY

The results are reported for the first phase of a study to evaluate instruments and techniques for the quantitative measurement of degradation-related changes in the properties of photovoltaic materials and arrays, which are precursors to the failure of such arrays. The focus of the study is on techniques and instruments that are suitable for measurements to be made in aging tests for the purpose of array-lifetime prediction. The need for improved measurements of rates of degradation was identified in a preceding study, also conducted by Battelle for the Low-Cost Silicon Solar Array Project, on the development of a "Methodology for Designing Accelerated Aging Tests for Predicting the Life of Photovoltaic Arrays" (Report No. ERDA/JPL-394328-77/1).

The selection of suitable instruments and techniques for lifetime-prediction testing requires an understanding of (1) observed and projected array degradation/failure modes and their causative/contributing factors, (2) the fundamental degradation mechanisms associated with these failures, and (3) the property changes that may be early precursors of this degradation.

Failure Modes and Factors Affecting Array Performance and Lifetime

Array degradation/failure modes and array lifetime depend upon the individual and combined effects of array design, materials of construction, processing/fabrication methods, and environmental stress factors. The combined effects of the various degradation reactions that occur within the different materials that make up the array (as a result of exposure to key environmental factors such as heat, ultraviolet radiation, moisture, and wind) are the primary concern of studies directed toward array-lifetime prediction.

Observed and projected failure modes for arrays can, for purposes of organization, be related to changes in the values of the components of the lumped-constant photovoltaic device/array model (i.e., current generator, ideal diode, series resistance, and shunt resistance, as shown in Figure II-1). These can, in turn, be related to major degradative changes in specific elements or combinations of elements of the module/array, and ultimately to the microscopic (and, in some cases, macroscopic) chemical and physical changes that are the earliest precursors to degradation and failure. Key factors (see Figures II-2 through II-5) are optical losses (e.g., due to discoloration, delamination, etc.) that are reflected in the light-generated current; corrosive attack or fracture of contacts, connections, and interconnects, which affect the series resistance; surface-region and pottant conductance changes that result in shunt resistance effects; and fundamental cell-junction characteristic changes that would result in diode losses. This last type of loss is not expected to be significant in normal terrestrial service.

Microscopic and Macroscopic Property Changes Associated with Primary Mechanisms of Degradation that Lead to Failure

The identification of early environmentally induced molecular alterations and other minute property changes that are clearly correlatable with observed degradation rates and failure modes is an important and difficult task in the development of a methodology for projecting the operational lifetimes of encapsulated photovoltaic modules/arrays. A major factor contributing to the difficulty of the task is the large number of potential variables (e.g., the large number of candidate materials, materials combinations, and structural designs; and the range of environmental conditions that might be experienced). A second and more fundamental factor is the lack of theoretical relationships and/or experimental data on quantitative correlations between observed molecular-level or microscopic changes and observed degradation/failure modes for the majority of materials and materials combinations. A third and equally fundamental area of difficulty is the lack of a sound scientific basis for predicting the nature and quantity of the microscopic-level changes that will be produced by specified levels of environmental stresses, particularly in cases where synergistic effects involving several environmental factors are involved (as will certainly be the case in actual operation).

The lack of hard data and the immediacy of the needs of the DOE test and demonstration efforts necessitate that, for purposes of this study, preliminary judgments be made as to which of the possible environmentally induced property changes are the most relevant and sensitive indicators of photovoltaic array/module degradation and failure modes. In this context, the major environmental factors contributing to degradation/failure are considered to be ultraviolet radiation, thermal energy, water, oxygen, mechanical and thermal stress, pollutants, and abrasives. It is the quantitative link between these environmental factors (including their combinations) and the degradation *rates* which is the ultimate objective of the life-prediction process

Environmental aging of *polymeric materials* is considered to be primarily the result of photooxidation processes that ultimately result in embrittlement, discoloration, and increased dielectric loss *Glasses* are primarily susceptible to surface attack involving moisture and pollutants of an acidic or alkaline nature. Both polymers and glasses may be subject to abrasive attack from airborne or waterborne particulates. Cell *contact metallization and electrical interconnects* are subject to attack by various corrosive agents that might penetrate through or evolve from the encapsulating materials. Universal among these are water and oxygen. Degradation of the basic *cell* (exclusive of deposited layers such as the metallization and optical control coatings) is believed to be unlikely because of the attack resistance of silicon and the remoteness of the possibility of experiencing temperatures high enough to affect diffusion profiles or result in significant indiffusion or redistribution of impurities. Other array/module components such as the *substrates, frames, and edge seals* are likely to be subjected to corrosion or stress-induced changes that will degrade their ability to protect the cell and other electrically and optically functional constituents from environmental factors.

Materials Properties, Techniques, and Instruments for Detection and Measurement of Failure-Related Degradation

Potentially useful techniques and instruments for degradation measurements were identified through an extensive literature search and through discussions with knowledgeable technical personnel at Battelle and other industrial research laboratories, government laboratories, universities, and instrument manufacturers. For the purposes of the study, the techniques and instruments were organized into six measurement categories – chemical, electrical, optical, thermal, mechanical, and "other physical". The identified techniques and instruments were then screened and evaluated by Battelle researchers in each of the categories, and across categories, using the criteria given in Table IV-2. The resulting recommendations of techniques/instruments made for each of the categories are listed below. (All techniques investigated are listed in Table IV-1, and each of the techniques recommended is described in Section IV of the report.)

Chemical Measurement Techniques

The recommended techniques/instruments in this category are

- Fourier Transform Infrared Spectroscopy (FTIR)
- Electron Spectroscopy for Chemical Analysis (ESCA)
- Auger Electron Spectroscopy (AES)
- Chemiluminescence
- Gel Permeation Chromatography (GPC)
- Mass Spectrometry/Gas Chromatography Combination (MS/GC)
- Surface Energetics.

Of these recommended chemical techniques, all but chemiluminescence and surface energy analysis are suitable in their present state of development. The FTIR technique (including Attenuated Total Reflection, ATR) is potentially one of the most powerful tools available for studying degradative changes in polymers at their earliest stages. GPC and the MS/GC combination are also potentially powerful techniques for investigating degradative changes due to chain scission, while ESCA and AES will probably find their major applications in destructive teardown analyses. More data should be obtained on precision for all of the recommended tests.

Electrical Measurement Techniques

The recommended electrical measurement techniques are

- Cell/Module/Array Current-Voltage Characteristics, Including Spectral Response Measurements
- Dielectrometry
- Electrical Conductance
- Electrical Noise Measurements
- Special Detectors.

Spectral-response measurements will play a key role in testing of devices and modules involved in aging and degradation studies. In order for illuminated I-V characteristics to play a significant role in the quantitative assessment of degradation processes, periodic characterization of the illumination-source spectral characteristics will be required. The quality of the information currently derived from the diagnosis of I-V characteristics is not adequate for service-life prediction for modules having 20-year lifetimes, the goal of the LSSA Project. A study to optimize the sensitivity, precision, and accuracy specifically for life-prediction testing is recommended.

Current noise (1/f) measurements are recommended for use in studying contact and interconnect corrosion. Dielectric and electrical conductivity measurements can be used to study several types of degradation-related changes in materials. The incorporation of special detectors or test patterns in arrays is also recommended for further investigation.

Optical Measurement Techniques

Recommended techniques for optical measurements for possible use in life-prediction studies are

- Reflectometry
- Ellipsometry
- Holographic Interferometry
- Light Scattering
- Microscopy
- Spectral Transmission.

The suitability of simple reflectance measurements for evaluation of first-surface deterioration needs to be determined experimentally for a variety of candidate first-surface materials Ellipsometric studies should continue with emphasis on problems involved in detecting delamination and on materials and structures of primary importance. Holographic interferometry experiments should be considered with the objectives of determining the trade-offs between the area scanned and the overall sensitivity and reliability of the technique, and of determining whether strain-birefringence changes, precursory to delamination, can be detected in this way. Optical measurements performed on complete modules or arrays should be limited to a few simple tests, such as spectral transmitted intensity, possibly at only a few selected wavelengths (including UV). Final array designs will play a key role in determining specific measurement procedures.

Thermal and Mechanical Measurement Techniques

The recommended techniques and instruments in the thermal- and mechanical-properties categories are:

- Differential Thermal Analysis (DTA)
- Differential Scanning Calorimetry (DSC)

- Torsion Pendulum
- Forced Vibration Viscoelastometer
- Ultrasonic Pulse-Echo
- Infrared Thermovision.

Since the properties of polymers are in some cases very sensitive to the value of the glass transition temperature (T_g), it will be useful to measure this property by a suitable means. The simplest and most rapid methods for measuring T_g appear to be differential thermal analysis and differential scanning calorimetry. In the absence of any information on the relative accuracies of these two techniques with regard to measurement of T_g, DSC measurements would be preferred since the resulting thermograms can be interpreted quantitatively. An alternative method for obtaining T_g is dynamic mechanical measurements, such as torsion pendulum and viscoelastometer. This family of techniques also yields potentially valuable data on the mechanical behavior of the materials. Dynamic mechanical measurements would thus be recommended over DTA or DSC in cases where both types of measurements are available. Since temperature is a more important variable than frequency for dynamic mechanical measurements, any of the techniques described in the text may be used, depending upon availability and ease of measurement.

The applicability of infrared thermovision in diagnosing solar cell modules merits further testing. The infrared transmission of the various cover and adhesive materials needs to be examined over the wavelength range to which the instrument is sensitive. Also, evaluations need to be made on the spectral emittance of opaque materials and on the possibility of radiation from these materials being propagated through the cover and adhesive materials. Infrared thermovision has already been demonstrated as being of value in detecting the presence of defects, as evidenced by certain areas of modules being hotter or colder than surrounding regions. It is recommended that further testing should be conducted to establish quantitative relationships, such as apparent temperature differences versus a quantitative measure of the degree of the defect.

The applicability of ultrasonic techniques also requires further testing and evaluation. A theoretical analysis appears necessary in order to interpret the various echo signals that may be received. Some experimental testing will be needed in order to select optimum transducers and locations. It is considered that ultrasonic methods have good potential for applicability in this area, and thus tests should be conducted on encapsulated cells with and without defects in order to establish the potential magnitudes of changes in ultrasonic signals that may be experienced.

Other Physical Measurement Techniques

Other physical measurement techniques recommended are

- Profilometry
- Photoacoustic Spectroscopy (PAS)
- Vapor and Gas Permeability.

Profilometry, when combined with computer processing of the data, could be a powerful tool for quantitative assessment of changes in surface roughness over large areas, such as those that might occur as a result of abrasive attack of photovoltaic module covers. Photoacoustic spectroscopy offers some potentially unique capabilities in studying optical, thermal, and possibly bonding characteristics of polymers; evaluations should be continued to demonstrate its capabilities in studies of photovoltaic-module materials degradation. Permeability measurements of polymeric materials are important for establishing their barrier properties against potential corrosive agents; they could also be useful in diagnosing chemical and structural changes associated with degradation mechanisms in the polymers. Developmental work and experimental evaluations to demonstrate the capabilities are being conducted in another investigation.

Selection Criteria and Comparative Analysis of Techniques/Instruments

Adequate experimental data for making comparative assessments, on the basis of precision, of techniques having potentially overlapping capabilities have not been found. This does not exclude interim selections on the basis of other attributes (e.g., availability, field-use capability) but does preclude the recommendation of a preferred technique for measurement, for example, of changes in some polymer properties.

The problem of determining how accurately one can expect to predict the lifetime of a photovoltaic module/array extends beyond the question of the precision associated with a given measurement technique or instrument. Given that, for example, the glass transition temperature T_g can be measured with a known precision, one is still faced with uncertainties in the values of primary derived quantities such as percentage of crystallinity or molecular weight, or in secondary derived quantities that are more directly relatable to module power-degradation rates (e.g., optical transmission). Comprehensive experimental work will be required to establish these relationships.

Recommendations

Three categories of recommendations are addressed.

Establishment of the Adequacy of Existing (Developed) Techniques

In order to establish the limits of the techniques that are more fully developed for this application, the following recommendations are made.

- A determination of the precision for measured properties should be made for ESCA, FTIR, and the MS/GC combination, also, ESCA and FTIR should be compared for measuring surface carbonyl concentration using the Mandel sensitivity-ratio criterion.

- A major effort should be directed toward establishing quantitative correlations between key measurable properties (e.g., polymer molecular weights and glass transition temperatures, T_g) and degradation/failure modes

- A set of experiments to determine the relative precision of the thermoanalytical and dynamic mechanical techniques for measuring T_g should be conducted.

- Techniques for measuring the current-voltage characteristics of encapsulated cells/modules should be refined to optimize sensitivity, precision, and accuracy for degradation studies.

Potentially Useful Developmental Techniques

The techniques recommended for development, in addition to surface energetics, photoacoustic spectroscopy, and polymer permeability which are already under investigation, are as follows

- Electrical noise measurements, electrical-conductivity measurements (polymers), reflectometry and light-scattering measurements, dielectrometry, chemiluminescence, and the use of special detectors for in-situ measurements, are recommended for preliminary experimental evaluations.

- Holographic interferometry and infrared thermovision should be considered for investigation on a high-risk, high-return basis.

Measurement Needs Not Presently Satisfied

- A technique for in-situ determination of changes in the mechanical strength of encapsulation materials would be a useful tool in degradation studies

- An adequate means for measuring changes in the breaking strength or static fatigue of glass needs to be developed.

- A reliable, reasonably inexpensive method is needed for making in-situ spectrophotometric measurements with high precision and over relatively long time periods.

Phase II of this study will be an experimental evaluation of techniques selected on the basis of these Phase I recommendations regarding techniques and additional needed information. Experimental investigations of some of the recommended techniques, within the level-of-effort of this present study, are currently being planned and submitted for JPL approval for inclusion in Phase II.

It should be noted that summary tabulations of the recommended techniques in each of the property-measurement categories, along with values and comments for key selection criteria and other attributes, are given in Section VI (Conclusions and Recommendations) of this report in Tables VI-1 through VI-5. Also in that section, recommended techniques are tabulated according to the degradation-related areas to which they are applicable (Tables VI-6 and VI-7) and according to their suitability for laboratory versus in-situ field measurements (Table VI-8).

I. INTRODUCTION

I. INTRODUCTION

The development of a suitable encapsulation system for terrestrial photovoltaic arrays is a key requirement for the realization of the array cost and lifetime goals of the Low-Cost Silicon Solar Array (LSSA) Project(I-1, I-2) of which this study is a part. The long-term integrity and stability of the encapsulation system will determine the operational lifetime of the array. And the materials that provide this protection must be low in cost and must not significantly decrease the performance of the solar cells (I-3) There is, then, an urgent need for establishing reliable tests for characterizing the weathering behavior of present and future encapsulation materials and systems.

A previous investigation by Battelle for the LSSA Project was on the development of a "Methodology for Designing Accelerated Aging Tests for Predicting Life of Photovoltaic Arrays". The investigation (which is described in Report No. ERDA/JPL-954328-77/1), defined the need for and provides considerable background information for the study described in this report That investigation developed an advanced methodology for designing life-prediction aging tests for terrestrial solar arrays that meet the LSSA array-lifetime goal of 20 years. The existence of suitable instruments for measuring property changes associated with the degradation of array materials is an essential prerequisite to the successful application of any such methodology.

Instruments suitable for this application must provide sufficient sensitivity and precision to allow projections of ultimate system lifetime, and of performance over that lifetime, from short-time natural and/or simulated weathering tests. Sufficient confidence is required to allow selection among alternative designs and materials and to allow widespread use of such arrays Further, the diversity of candidate materials and designs, and the variety of potential environmental-stress combinations(I-4), degradation mechanisms, and failure modes will require that a number of combinations of measurement techniques be identified which are suitable for characterizing various encapsulation system-environment combinations. To this end, currently used and potentially useful standard and developmental instruments and techniques are being examined to determine their applicability in lifetime-prediction aging tests

A. OBJECTIVE

It is the objective of this study to identify and evaluate instruments and techniques for measuring degradation-related changes in the properties of encapsulation materials and other module components which are precursors to array failure; techniques are required which can be used in accurate quantitative assessments of degradation rates for life-prediction studies As part of this objective it is intended to.

- Assess the adequacy of existing instruments and techniques for meeting the diagnostic needs of lifetime-prediction studies
- Identify potentially useful techniques whose applicability requires further evaluation through experimental testing
- Identify diagnostic needs, if any, not adequately met by existing instruments and techniques or minor modifications thereof.

The measurement techniques and instruments listed and discussed in this report are not intended to constitute an exhaustive coverage of measurement possibilities. Only those techniques and instruments which were believed to offer enough potential for this application to warrant detailed investigation and evaluation have been included in this study Many others were considered but were rejected during initial screening as being clearly not applicable to the development of high-sensitivity quantitative data on degradative changes in materials and encapsulation systems associated with photovoltaic modules.

This study is being conducted in two phases. The *first phase*, the results of which are reported in this interim report, consists of a review and evaluation of potentially useful techniques on the basis of published literature, patents, reports, and discussions with expert technical personnel. The *second phase* will be an experimental evaluation of those selected techniques which are believed to have potential for this application but whose applicability requires further evaluation through experimental testing.

B. APPROACH

For the purposes of the review and analysis of instruments and techniques which might be useful in array-degradation studies, six general measurement-technique categories were established (chemical, electrical, optical, thermal, mechanical, and "other physical"). Each of the measurement technique categories was assigned to a researcher knowledgeable in that area. This interdisciplinary team approach was used to ensure coverage of all potentially applicable techniques in the study. The researchers were then responsible for collecting and reviewing published and unpublished information in their assigned areas, and subsequently for analysis of the applicability of the various techniques to array-life-prediction testing Key project staff provided direction and close coordination of the team activities and statistical analyses and comparisons of techniques in the different categories. The information-gathering activities included computerized data-base searches, discussions with experts in specific instrument and technique areas, and a review of current periodicals and books.

The computerized data-base searches included a generalized search as well as searches specific to each of the measurement categories. Key words and search strategies were generated by the researchers responsible for the various categories. The data bases searched in the computer-assisted effort were:

Chemical Abstracts
DDC
Engineering Index
INSPEC
NTIS.

The search identified approximately 9500 potentially relevant documents. Key words and abstracts from these documents were reviewed by the researchers and approximately 500 of them were selected for in-depth review.

The information acquired through the computer-assisted data-base searches and the personal searches of current literature was augmented and amplified by discussions with experts and equipment manufacturers for the key techniques (e.g., ultrasonics, chemiluminescence, and dynamic mechanical) identified. The information developed from all of these sources provided the basis for the discussions and evaluations of the measurement techniques by the researchers for this report.

In the overall approach to this study, it was necessary to assume that the focus was on measurement methods and instruments suitable for life-prediction testing and, specifically, for photovoltaic arrays That is, the study could not cover the complete field of measurements and instruments, nor could it risk missing any diagnostic method that could be important to this specific use. To accomplish this, the interdisciplinary project team of experts in measurement techniques, materials, and photovoltaics pursued as a group the following steps

(a) Identification of all observed and projected *failure types/modes* for photovoltaic arrays and materials

(b) Organization and breakdown of major failure types, identifying all possible subtypes and the *degradation factors* and *causes* involved in the failures

(c) Identification of the microscopic *degradation mechanisms* possibly leading to each of the types of degradation and failure

(d) Definition of the microscopic and macroscopic *property changes* that might be associated with these degradation mechanisms

(e) Identification and analysis of the *measurement techniques/instruments* which might be used for early detection of these degradation-related property changes

This approach is reflected in the report which first discusses the failure types/modes [Steps (a) and (b)], then describes the associated degradation mechanisms and property changes [Steps (c) and (d)], and finally reviews the pertinent measurement techniques/instruments [Step (e)] in the remainder (bulk) of the report. The organization of the report is further outlined below.

C. ORGANIZATION OF THIS REPORT

This report is organized into six sections, Section I being this introduction. Modes of failure (i.e., factors which can directly cause a reduction in cell/module output below acceptable levels) and their contributing causes are discussed briefly in Section II. This leads, in Section III, to a discussion of the state of knowledge regarding the microscopic and macroscopic property changes and mechanisms of degradation which lead to the failure of photovoltaic modules. An identification of these factors is essential in meeting the objectives of this study as listed above. The discussion in Section III also includes consideration of the key environmental stress parameters which produce these changes.

In Section IV, measurement techniques in six categories (chemical, electrical, mechanical, optical, thermal, and "other") are discussed in detail and their applicability to the characterization of specific types of property changes is delineated. The techniques discussed in this section are those that were selected and recommended within each of the six categories after detailed evaluation against an established set of technical and economic criteria which are given in Table IV-2. Some techniques which, after careful examination, were felt not to be useful for these studies (or to be clearly superseded by another technique in the measurement category) are discussed briefly in Section VIII – Appendix.

It should be emphasized at this point that the focus of this study and report is on techniques and instruments suited for testing aimed at lifetime prediction. While there is some overlap among techniques suited for this type of testing and techniques useful in qualification, acceptance, performance, and other types of tests, there are many techniques that are well suited to these latter tests but not applicable (or at least are not best suited) to lifetime-prediction testing. These techniques may have been eliminated during the early screening (and therefore are not covered here), or they may have been examined in detail before rejection for this application (in which case they appear in Section VIII – Appendix). Where techniques have been found to be primarily suited for qualification, acceptance, etc., testing, they have been so identified in the discussion. There was, however, no attempt or intention to make a comprehensive study of techniques and instruments suitable for these types of tests.

In Section V, a discussion of the selection criteria and statistical considerations applicable to this study is followed by a discussion of cross-category (e.g., mechanical versus electrical) assessment of instruments and techniques based on the established criteria. A selection is made, where possible, among techniques which offer redundant capabilities in terms of the property changes measured.

Specific recommendations based on these Phase I evaluations are summarized in Section VI of the report, including the establishment of

- The adequacy of existing (developed) techniques
- Potentially useful developmental techniques
- Measurement needs not presently satisfied.

Many documents, including reports, publications, and patents, were used in compiling the information required to make these assessments. A listing of these which includes many documents not specifically referenced in this report is available upon request

II. FAILURE TYPES AND FACTORS AFFECTING ARRAY PERFORMANCE AND LIFETIME

II. FAILURE TYPES AND FACTORS AFFECTING ARRAY PERFORMANCE AND LIFETIME

A DEGRADATION AND ARRAY PERFORMANCE

Life-prediction studies are concerned with the time dependence of degradation.(II-1) The loss of power output that has occurred up to any point in time during the operational lifetime of a solar array is usually due to, and provides a measure of, significant materials-related degradation that has taken place in the array. This degradation may have occurred in one or a combination of the materials of construction of the array, i.e., the polymerics, the glasses, or the metallics. It may be a result of the design, materials, or processing per se, and/or the environmental exposure, where ultraviolet radiation, temperature, humidity, mechanical stress, and their combinations may be causative. That is, array degradation is dependent on the individual and combined effects of

- Array design
- Materials of construction
- Processing/fabrication methods
- The environment to which the array is exposed.

The effects of these are discussed below

1. Array Design Effects

Array design, independent of its effect on materials selection and processing/fabrication requirements, will influence the rate and extent of degradation in a number of ways. The access route of foreign penetrant gases and liquids will be dictated by the design features employed in end sealing the array, by the thickness of the cover material, by the method used in putting the electrical leads through specific parts of the encapsulant, etc. Also, design will determine the locations and magnitudes of stresses produced by high wind loads, by temperature and humidity cycling, etc. Here again, design features such as component thicknesses and structural reinforcement will be critical.

2. Construction Materials Effects

Materials selection is of major importance in controlling array performance and lifetime. Major requirements in the materials selection are, in addition to cost, the initial values of the optical, mechanical, and electrical properties and the stability of these properties when exposed to hostile weathering environments for prolonged time periods. In this latter case, the properties of polymeric encapsulation materials are of particular concern since they are often significantly affected by the environment. It is, therefore, extremely important that the deleterious effects of the environment on long-term polymeric-materials properties (bulk, surface, and interface) be established.

3. Processing and Fabrication Effects

The materials processing and array fabrication steps can also be important contributing factors in problems related to short- and long-term array reliability. If array failure rate, as defined in terms of some specified level of degradation, is plotted against time, a troughlike ("bathtub") curve generally will result. The failure rate/time relationship is characterized by a high initial rate, primarily because of failures associated with processing/fabrication inadequacies, followed by a long period of array stability (characterized by a slow degradation rate) with few failures, and finally by a return to high rates as the arrays begin to "wear out". Those failures associated with processing/fabrication *inadequacies* are likely to take the form of delaminations (ineffective bonding of one array component to another), losses of electrical contact (lead and interconnect breakage), gas/liquid entrapment (associated with reactions of components or with residual volatiles in polymeric components), etc. Minimization of such events will, of course, require the implementation of stringent quality-control procedures for use on incoming lots of array components and on array fabrication procedures

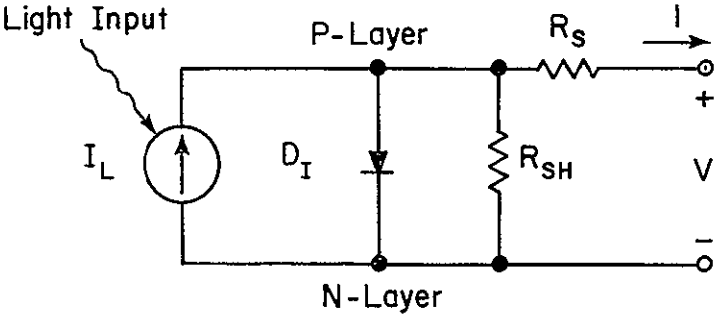
4. Environmental-Exposure Effects

Finally, there is the environmental exposure factor. Array degradation rates can be extremely low if the array is maintained in the dark at constant, moderate temperature and humidity. In actual use, however, when the array is exposed to the sunlight with the accompanying environmental factors of heat, ultraviolet moisture, and wind, various chemical reactions occur and continue to occur within the different materials that make up the array. The combined effects of these reactions constitute the processes of degradation which are the primary concern of array-lifetime-prediction studies.(III-3)

B. FAILURE TYPES

In the context of array performance and degradation, a "failure" is generally considered to be a change in the properties of the cell/module/array which results directly in a reduction in its power output below a specified minimum level for the particular application and system design. Such a change can occur either catastrophically or gradually. A given failure mode can have many different causes, some of which may be the direct result of degradative changes in the optical or electrical properties of materials or encapsulation systems, while others may reflect indirect contributions from degradative changes in the ability of the encapsulation system to isolate the cells from environmental and mechanical stress factors.

The "lumped-constant" model of the photovoltaic cell, shown in Figure II-1, has been found useful in these studies to organize failures due to degradation into four types based on the components of this model. This provides a convenient framework for discussing the basic failure modes and their contributing causes. Such a discussion is a useful prelude to an identification of the environmental-stress-related microscopic and macroscopic changes in the properties of materials and structures which are precursors to such failures, and which might therefore be usefully monitored in lifetime-prediction studies.



Components of the model·
I_L = Light-generated current source
D_I = Ideal diode
R_S = Series resistance
R_{SH} = Shunt resistance

FIGURE II-1. LUMPED-CONSTANT SOLAR CELL MODEL

The lumped-constant model consists of four basic components – a current source (representing the light-generated current), an "ideal" diode, a shunt resistance, and a series resistance. The failure of a cell or module corresponds, in effect, to a significant change in the value of one or more of these four components; correspondingly, changes in the effective values of these lumped-constant components can be traced to major degradative changes in specific elements or combinations of elements of the module/array and ultimately to the microscopic (and in some cases macroscopic) chemical and physical changes in materials, which are the earliest precursors to degradation and failure. The state of knowledge regarding the latter is discussed in Section III. This present discussion is intended to outline the correlation between failure types and the various degradation mechanisms that might be observed.

Figure II-2 is a first-level breakdown showing the four failure types based on the solar cell model and potential causative degradation factors. In the illustration, degradation effects that could lead to a reduction in the light-generated current include optical-transmission losses, increased minority-carrier recombination at surfaces or in the bulk silicon, and the rather special case of fragmented cells. It is appropriate here to note that it is the assumption of the authors that environmental conditions severe enough to affect the bulk properties, diffusion profiles, etc., of the silicon cells are not likely to be experienced during normal array operation. It is anticipated, therefore, that junction and bulk-semiconductor changes will not be a significant factor in determining the lifetime of terrestrial photovoltaic modules. The potential causes of diode losses, as shown in Figure II-2, include any changes in the junction which will result in deviation from the ideal. (This should not be a significant factor in lifetime prediction.) Degradation factors contributing to reductions in the shunt resistance include changes in the conductivity of pottants or adhesives, junction damage, and the presence of foreign agents which could result in increased surface-state conduction. Causative factors for increased series resistance are erosion/corrosion/debonding of contact structures, lead fracture, and changes in the surface-layer sheet resistance or bulk silicon resistivity.

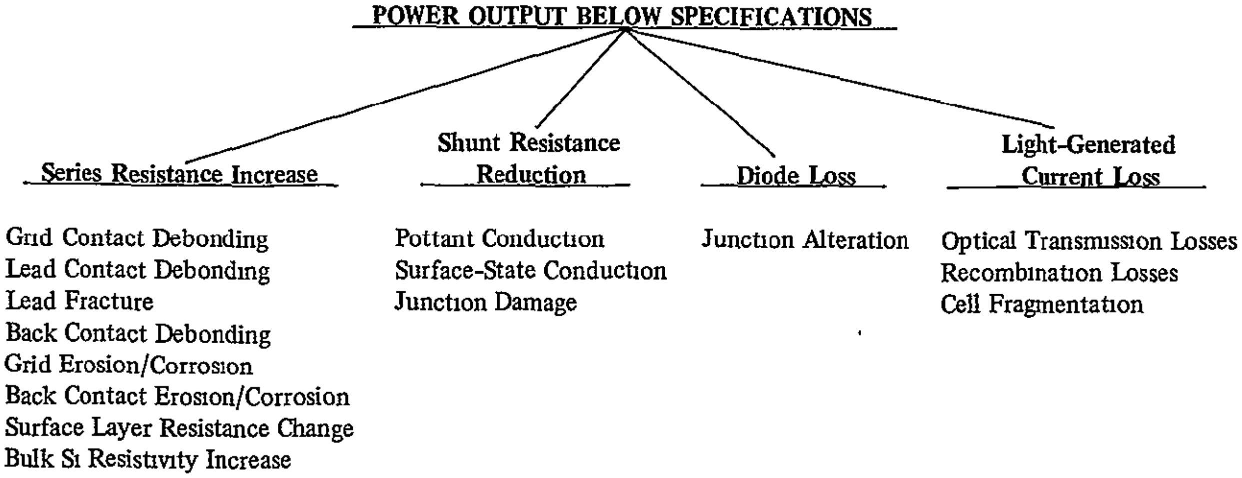


FIGURE II-2. FOUR FAILURE TYPES BASED ON THE FOUR COMPONENTS OF THE LUMPED-CONSTANT CELL MODEL (FIGURE II-1) AND A FIRST-LEVEL BREAKDOWN INTO CAUSATIVE DEGRADATION FACTORS

The degradation factors shown in Figure II-2 for each of the four types of failures are believed to include the primary potential *power* degradation modes (i.e., factors which, if changing, will have a direct and measurable effect on the power output and I-V characteristics) for photovoltaic cells and modules. The following subsections will trace these degradation factors to the next level of breakdown to provide a transition to the discussions in Section III. These subsections focus primarily on those factors that will play a key role in determining the operational lifetime of a photovoltaic array.

1. Light-Generated Current Losses

As noted above, a decrease in the light-generated current will probably be due to optical losses. Figure II-3 shows a second-level breakdown of the degradation factors that could contribute to degradation of the power output by reducing the percentage of the incident radiation that enters the photovoltaic device. These factors fall into four basic categories – factors resulting in losses due to reflection of a portion of the insolation, factors resulting in losses due to absorption of radiation, factors which result in transmissive scattering of the insolation (and which may not, even in the presence of large amounts of scattering, contribute significantly to losses), and factors which might effectively reduce the incident energy per unit area by altering the orientation of the module/array. These factors for the most part relate to key properties of the bulk, surface, and interfacial regions of those components of the encapsulation system which are required to be transparent. These key properties and attributes include indices of refraction, absorption coefficients, surface textures, numbers of surfaces affected (by delamination for example), accumulation of foreign particulate matter, etc. Changes in these properties can, in most instances, be correlated with microscopic-level changes directly related to environmental stresses.

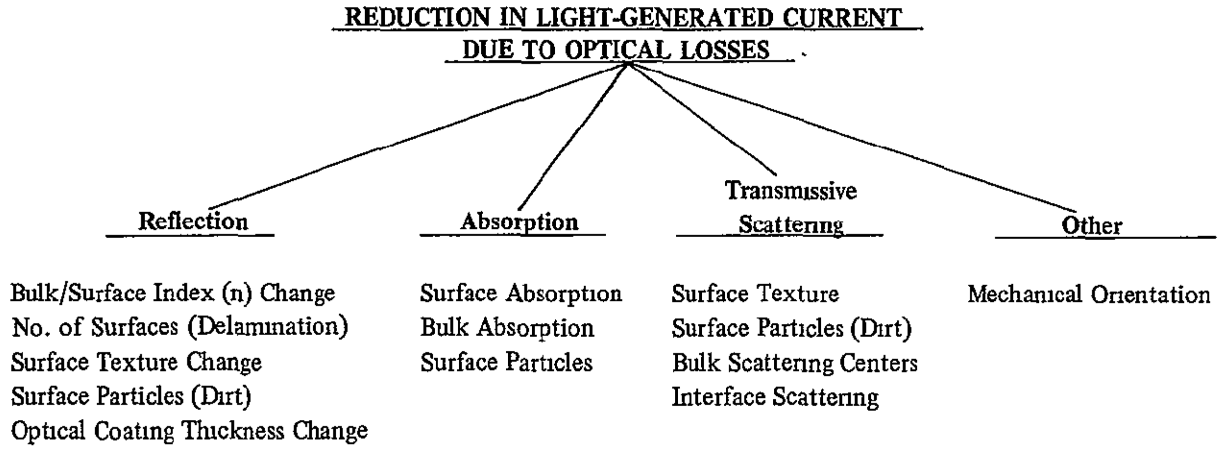


FIGURE II-3. BREAKDOWN OF DEGRADATION FACTORS CONTRIBUTING TO OPTICAL LOSSES WHICH CAUSE A DECREASE IN THE LIGHT-GENERATED CURRENT

2. Series Resistance Increases

Several of the important degradation-related factors result in internal (i.e., to the array) dissipation of power through increased series resistance, as shown in the breakdown in Figure II-4. The key elements in this type of degradation/failure are the front- and back-surface contact metallization of the solar cells, the interconnects between cells or modules, and the connection points where the interconnects are attached (by soldering, welding, etc.) to the cell metallization. These elements are, in many cases, vulnerable to chemical attack and/or mechanical stress as indicated. Other factors shown in the figure relate to changes in cell properties which, as noted above, would not be likely to occur under anticipated normal operating conditions. Certain patterns of cell cracking or fragmentation could, however, result in an effective increase in the apparent series resistance of a cell.

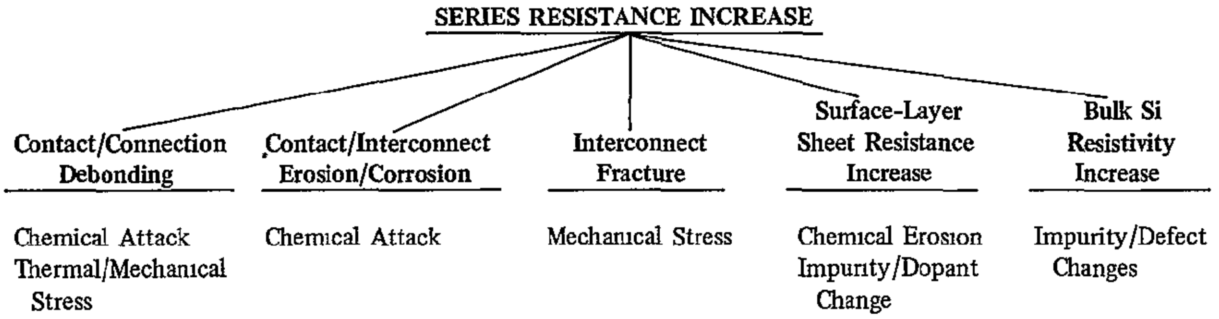


FIGURE II-4. DEGRADATIVE CHANGES MANIFEST AS SERIES RESISTANCE INCREASES

3. Shunt Resistance Decreases

Figure II-5 lists degradative changes which could result in increased internal power dissipation by effectively lowering the shunt resistance in the lumped-constant model. The major degradation-sensitive factors controlling losses due to shunt conductance are the conductivity of the pottant material and the presence of surface conduction states or regions at the junction edges.

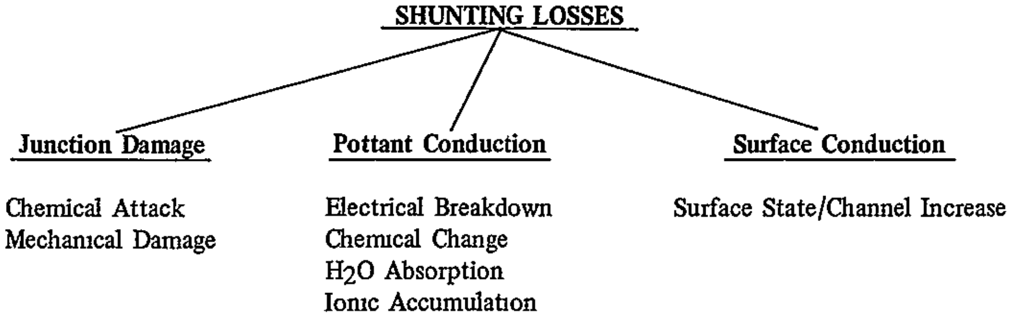


FIGURE II-5. DEGRADATION FACTORS CONTRIBUTING TO LOSSES BY SHUNT RESISTANCE DECREASES

4. Ideal Diode Losses

Diode losses due to changes in the junction characteristics which would affect the performance (e.g., increased generation/recombination currents in the junction region) are not anticipated, as discussed above.

In the next section, these types of failures and degradation factors are related to associated microscopic and macroscopic mechanisms which might be measured as part of lifetime-prediction testing.

III. MICROSCOPIC AND MACROSCOPIC PROPERTY CHANGES ASSOCIATED WITH PRIMARY MECHANISMS OF DEGRADATION THAT LEAD TO FAILURE

III. MICROSCOPIC AND MACROSCOPIC PROPERTY CHANGES ASSOCIATED WITH PRIMARY MECHANISMS OF DEGRADATION THAT LEAD TO FAILURE

A. BACKGROUND

1. General

One of the most important and most difficult tasks in the development of methodologies for predicting the operational lifetimes of encapsulated photovoltaic modules is the identification of *early, environmentally induced, molecular changes and other minute property changes that can be clearly correlated with the observed degradation rates and failure modes of the encapsulated module* or its components. There are three major factors that contribute to the difficulty of the task.

One major factor is the multitude of possibilities that must be considered. As mentioned earlier in this respect, degradation mechanisms and failure modes will vary with the materials and material combinations used in fabricating the module/array, the specific module design, the module fabrication processes, and the environment in which the array is operating. At present, there are a large number of candidate materials for each of the components (e.g., cover, pottant/adhesive, substrate, etc.) of the module, and the number of potential compositional combinations and structural designs for modules is also large. Potential environmental conditions are also quite varied in several respects, including temperature extremes and range, humidity, rainfall and condensation, types and magnitudes of pollutants, abrasive exposure (e.g., blowing sand), etc. The need to consider a wide range of environmental conditions is a fixed requirement that can be changed only by the designation of certain geographic or climatic regions as unsuitable for terrestrial photovoltaic applications. The uncertainties of materials, materials combinations, and structural designs are not likely to be reduced in the near future due to the continuing effort to reduce module and array costs that meet the sequential goals established by the DOE.

A second and more fundamental factor contributing to the difficulty of the task is the lack of theoretical relationships and/or experimental data on *quantitative* links between observed molecular level or microscopic changes and observed degradation/failure modes for the large majority of the candidate materials and materials combinations. This is especially true in the case of the polymers, which are at present the most environmentally vulnerable array constituents. Some of the major degradation modes have been established (e.g., delamination, embrittlement, discoloration, etc.), although these have been observed over relatively short exposure times and, hence, there is the possibility that other modes will be important in longer-lived modules. Similarly, at least some of the microscopic level property changes that occur as a result of environmental exposure (chain scission, carbonyl formation, radical formation, etc.) are known, but the factors that link these to the observed degradation modes have not been clearly established.

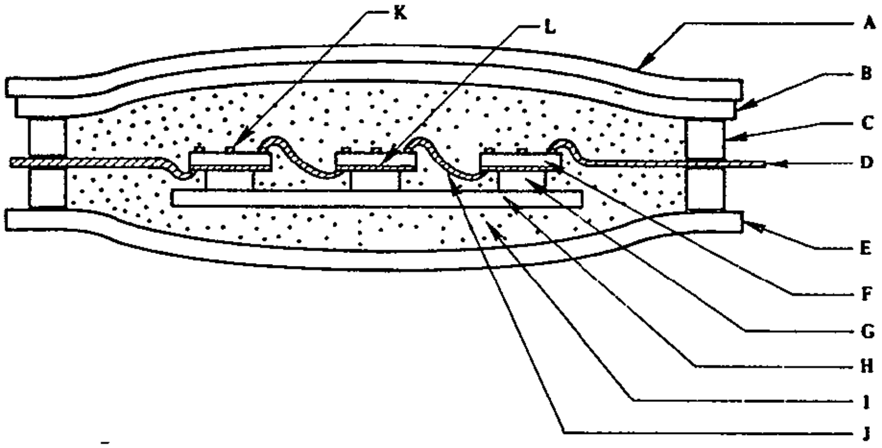
A third, and equally fundamental area of difficulty, is the lack of a sound, scientific basis for predicting the nature and quantity of microscopic level changes that are produced by specified levels of environmental stresses, particularly in cases where synergistic effects involving several environmental factors are involved (as will certainly be the case in actual operation). Credible projections of lifetime and life cycle performance for a given array at a variety of locales cannot be made without this information.

The informational needs cited above can be filled only by a series of focused research programs such as those currently mounted. The time frame in which satisfactory and complete answers will be forthcoming from these efforts is uncertain, as is generally the case in such research efforts. However, the need for this information in the context of the DOE's test and demonstration efforts is immediate. Consequently, the situation necessitates that, for the purposes of this study, some judgments be made as to *which of a large number of possible environmentally induced property changes are the most relevant and sensitive indicators of photovoltaic array/module degradation and failure modes* and, as such, those changes that should be studied to establish essential quantitative correlations. These judgments can be modified as research efforts develop. The discussions in this section of the report are concerned with identifying those changes which, on the basis of the present state of knowledge and the exercise of reasonable technical judgment, are felt to be sensitive precursors to failure-oriented degradation. These identifications in turn provide the basis for identifying instruments and techniques that can quantify the microscopic changes and ultimately provide the data that will allow array lifetime and life cycle performance projections. The latter identifications (i.e., techniques and instruments) are the major focus of the study and are discussed in detail in Section IV. The identifications made here are, however, very important in the overall study, and considerable thought and discussion preceded these assessments. Identification of these relevant properties and microscopic changes was a necessary requirement before selecting measurement techniques and instruments. It is not intended that the following material cover all conceivable property changes, but only those which, after due consideration, are felt to be of major significance and relevance to this project.

2. Encapsulated Module/Array Components

The designed functions of the ancillary constituents of the photovoltaic module/array are to protect the cells and their interconnects from environmental attack and stress and to provide a convenient means for handling and mounting. There are additional requirements that are essential in selecting materials for these components; i.e., components between the cell surface and the incident radiation (1) must have high solar spectrum transmittance, (2) must have no effect on the electrical output of the module/array, and (3) must not, themselves, stress other components of the module/array beyond prescribed limits. During the course of field operation, a reduction in the ability of these components to provide protection from environmental factors or to meet the additional requirements listed above is a degradation of the integrity of the encapsulation/support system that could ultimately lead to failure (if the performance of the module/array falls below specified limits).

Figure III-1 is a schematic of a hypothetical module$^{(III-1)}$ illustrating encapsulation-system components. The major components include the cells (with metallization and antireflection coatings), interconnects (metal ribbons, wires, metallized plastics, etc.), pottants/adhesives (polymerics), substrates (glass, anodized aluminum, PC board, etc.), and sheet or film coverings (glass or polymer). Other possible constituents include various types of coatings for surface-property enhancement and insulating meshes. There are many possible module configurations, or encapsulation-system designs, which use various combinations of components and materials. The major types of module/encapsulation designs based on both polymer and glass front covers are illustrated schematically in Reference (III-1) The model shown in Figure III-1 is quite general, being adopted for the purposes of subsequent discussions of degradation and failure modes and associated property changes. Table III-1 lists some typical materials employed or considered for use as module constituents.



A Antireflective or abrasion/impact-resistant coating
B Top cover
C Adhesive sealant for lead wire
D Lead wire
E Bottom cover
F Silicon cells
G Adhesive for bonding cell to substrate
H. Substrate
I Pottant
J Interconnects
K Metallization collector grid
L Metallization, bottom

FIGURE III-1. SCHEMATIC OF HYPOTHETICAL ARRAY MODULE IDENTIFYING ENCAPSULATION-SYSTEM COMPONENTS

TABLE III-1. ROLES OF MATERIALS IN PHOTOVOLTAIC MODULES

	Component			
Material	Interconnects	Pottants/Adhesives	Substrates	Cover Sheet
Polymers		Epoxies Silicones Polyurethanes Polyesters Polyamides	Epoxies Melamines Phenolics Polyesters Urethanes	Acrylics Fluorocarbons Polycarbonates Polyesters Composites
Glasses			Borosilicate Soda-lime	Borosilicate Soda-lime
Metals	Copper Aluminum Beryllium-copper Kovar Molybdenum		Aluminum Steel	

3. Environmental Factors That Cause Degradation/Failure

There are a large number of environmental factors whose effects, acting either singly or in concert, could result in the degradation and ultimate failure of the photovoltaic module/array. The key factors and their combined effects vary considerably with the geographic location of the array as well as with the season, time of day, etc. The environments to which arrays are exposed in various geographic locations based on 10-year historical data have been characterized in a previous study at Battelle as part of the LSSA Project. This analysis includes climatic, solar radiation, and other environmental data and *combinations* of environmental factors (I-4)

The environmental factors that are generally considered to be of primary importance in the initiation and evolution of degradative changes (not catastrophic failures, like lightning) are:

- Ultraviolet Radiation – The wavelength range of importance for terrestrial exposures is between approximately 290 nm and 400 nm. Radiation in this wavelength range is sufficiently energetic to break some of the weaker chemical bonds in polymers. In addition, the selective absorption of photons in this energy range can result in excited states and ionized molecules through interaction with defects, impurities, etc. These in turn result in other types of degradation-related chemical reactions.

- Thermal Energy – Heat is generally a contributing rather than an initiating factor in the degradation processes, since temperatures sufficient to produce scission and/or cross-linking are generally not experienced by operating modules. Heat is, however, a factor of primary importance because it is a major controlling factor in determining the rate at which various reactions and degradative changes take place.

- Water – H_2O in liquid or vapor form can directly or indirectly contribute to the degradation of several of the components of the module. One of the functions of the encapsulation system is to prevent significant amounts of water from penetrating to corrosion-prone elements. Water (alone or in the presence of certain pollutants and/or impurities) can degrade encapsulant materials through hydrolysis, leaching, swelling, dissolution, etc A combination of high humidity and temperature degrades many polymers.

- Oxygen – "Normal" oxidation in polymers (i.e., at normal temperatures and in the absence of light) is generally a fairly slow process requiring relatively long time periods before detectable effects are observed. However, when oxygen is coupled with ultraviolet radiation and/or elevated temperatures, synergistic effects occur, resulting in degradation rates that are orders of magnitude higher than those observed under "normal" conditions.

- Physical Stress – Mechanically and thermally induced stresses are major contributors to the fracture of the more brittle constituents of the module (glass covers, cells, hard plastics) and to bonding failures at interfaces. Failures due to normal (i.e., design value) stresses are generally preceded by weakening or flaw generation resulting from other degrading mechanisms. Temperature extremes, frequency of wide temperature excursions, wind forces, etc., are important factors.

- Pollutants – Pollutants such as NO_x, SO_2, O_3, particulates, etc., are potentially significant degrading agents in certain industrial and urban areas. Synergistic effects involving the combined effects of these pollutants with light, water, and heat are of

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primary long-term concern. Specific degradation paths associated with pollutants are sometimes difficult to identify since they involve catalytic effects, multiple interdependent chemical reactions, etc.

- Abrasives and Dirt – Dirt, blowing sand, and dust, hail, etc., are known degrading agents that can contribute to degradation directly through alteration of the optical properties of cover-material surfaces and indirectly through the initiation of surface flaws that provide nuclei for other degradation and failure modes.

These are the primary factors that give rise to the property changes whose detection and quantification are the focus of this study, and it is the quantitative link between these environmental factors (including combinations) and the *degradation rate(s)* that is the ultimate objective of the life-prediction process. The present state of knowledge regarding the specific effects of the above environmental factors on specific module constituents has been, necessarily, our primary guide in identifying microscopic-level changes that are most probably correlatable with degradation/failure modes. The correlation at present is empirical and qualitative at best. It may remain empirical for some time to come, however, it is the objective of this study to provide the means to render it quantitative.

B. PROPERTY CHANGES ASSOCIATED WITH ENVIRONMENTAL EXPOSURE

1. Polymeric Materials

The environmental aging of plastics is primarily a photooxidation process and ultimately results in changes in mechanical (embrittlement), optical (discoloration), and electrical (increased dielectric loss) properties. Embrittlement results from molecular and/or morphological changes due to chain scissions and cross-linking reactions. Discoloration is associated with the formation of polyene chromophores. Dielectric loss increases with increases in polar-group concentration produced by reactions with oxygen and other reactive species.

The principal steps in the degradation process may be described as:

(1) Absorption of energy

(2) Chain scission (dissociation) and free-radical formation

(3) Free-radical chain reactions (with and without oxygen)

(4) Radical combination to form new products (polymeric and nonpolymeric, with and without oxygen-containing groups).

Since most polymeric materials contain additives (stabilizers, plasticizers, processing aids, etc.), changes in these low-molecular-weight materials also contribute to the degradation process. An example is the stabilizer system. It may contain one or several materials of relatively small molecular size, and serves, through one of several mechanisms, to prevent available energy from reacting with the polymer. However, with time, it is consumed and the degradation rate of the polymer accelerates. Moreover, as it is consumed, like most other additives, by-products can be formed that adversely affect materials properties. Molecular defects or impurities in the polymer also may be regarded as additives in the sense that they cause atypical polymer performance and accelerate degradation.

Degradation in polymers can be defined in terms of the occurrence of one or more of a number of primary events within the material that produce changes *at the molecular level.* Principal among these primary events are chain scissions, cross-linking reactions, development of unsaturation, depolymerization, molecular rearrangement, volatile-product formation, and attendant reactions with foreign moieties (oxygen, water vapor, etc.). Certain events also can be anticipated in the low-molecular-weight additives present in the formulation. These are mainly of the latter three types mentioned here.

Within the polymer, the occurrence of the events may be random, i.e., scattered throughout the bulk of the material or, more commonly, concentrated at exposed surfaces of the polymer. The location at which primary events occur will be dependent on the nature of the degrading elements. UV degradation, for example, will be nonrandom. Degradation due to ionizing radiation, on the other hand, might be random.

In addition to primary events within and/or at the surface of materials, molecular-level changes at materials interfaces within the encapsulant system of the array also must be considered. Here, primary events of the types identified above will occur during the degradation process. However, because of multimaterial involvement, these are somewhat more complex and, therefore, less understood than those associated with individual polymers. Further, mechanically induced stresses are more relevant precursors to failure at such interfaces.

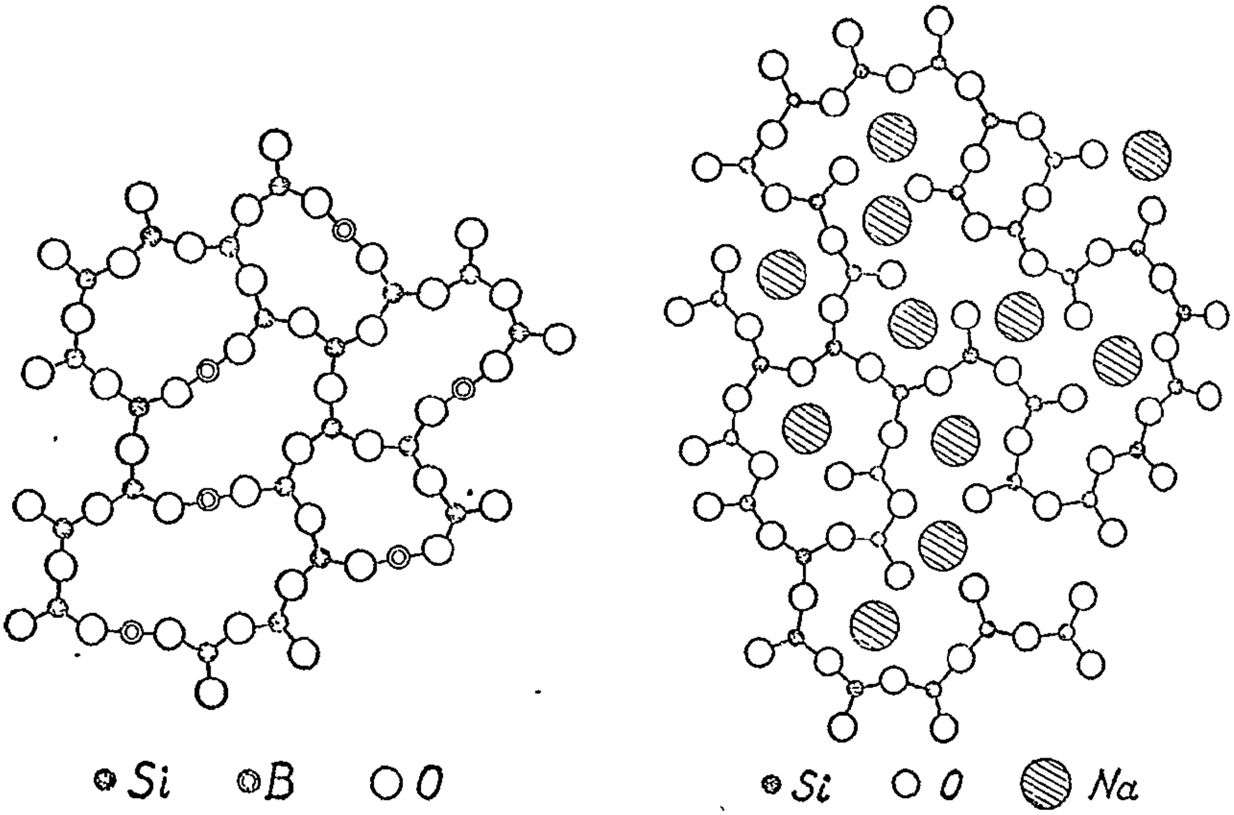
Polymeric materials, as well as glasses (discussed below), are also susceptible to abrasive attack when used as outer covers.

2. Glasses

Glasses are generally considered to be long-lifetime materials, although they are susceptible under certain conditions to weathering by chemical attack or abrasive particles. The two types of glasses of primary interest in this study are borosilicate glass and soda-lime glass (including both float and sheet, having low iron content that is commonly referred to as "water-white"). Two-dimensional schematics of the structures of these materials are presented in Figure III-2. The primary constituents are summarized in Table III-2.

Borosilicate glass is highly corrosion resistant, highly transmissive for the solar spectrum, and has a lower thermal expansion coefficient than soda-lime glass. It is also the more expensive of the two types and has a lower design stress limitation. Soda-lime float glass is the cheaper of these glasses. It is also weather resistant, with the tin-rich surface being more resistant than the silica-rich top surface.(III-2) It does, however, exhibit higher light absorption than either the borosilicate or the soda-lime, low-iron, "water-white" sheet. The latter exhibits low light absorption and is of intermediate cost.

The important weathering agents for glasses include condensed moisture, acidic air pollutants, alkali, sunlight, and airborne particulates that can accumulate on and/or abrade the surface. The major area of attack is the surface of the glass, although solarization (photochromic effects) may, in general, exert a bulk effect.(III-3)



a. Borosilicate Glass

b. Soda-Lime Glass

FIGURE III-2. TWO-DIMENSIONAL SCHEMATIC OF THE STRUCTURE OF BOROSILICATE GLASS AS COMPARED TO THAT OF SODA-LIME GLASS

TABLE III-2. COMPOSITION OF GLASSES

	Composition, weight percent								
Glass	SiO_2	Na_2O	K_2O	CaO	MgO	B_2O_3	Al_2O_3	Fe_2O_3	PbO
Soda-lime-silica (plate glass)	72·5	13·0	0·3	9·3	3·0		1·5	0·1	
Borosilicate (Pyrex)	80·6	4·2		0·1	0·05	12·6	2·2	0·05	

Note: Fe_2O_3 content of low iron "water-white" sheet glass is $\sim$0.01 weight percent.
Fe_2O_3 content of PPG float glass (1975 analysis) is $\sim$0.09 weight percent.

Moisture is a key ingredient in the weathering of glass surfaces, both in the static fatigue associated with hydrated layer formation and in chemical attack associated with ionic solutions. The nature of the attack will depend on the types of ions present in surface moisture. Acidic solutions attack the surface through a leaching mechanism involving the exchange of sodium and hydrogen ions, as illustrated by the following reaction:

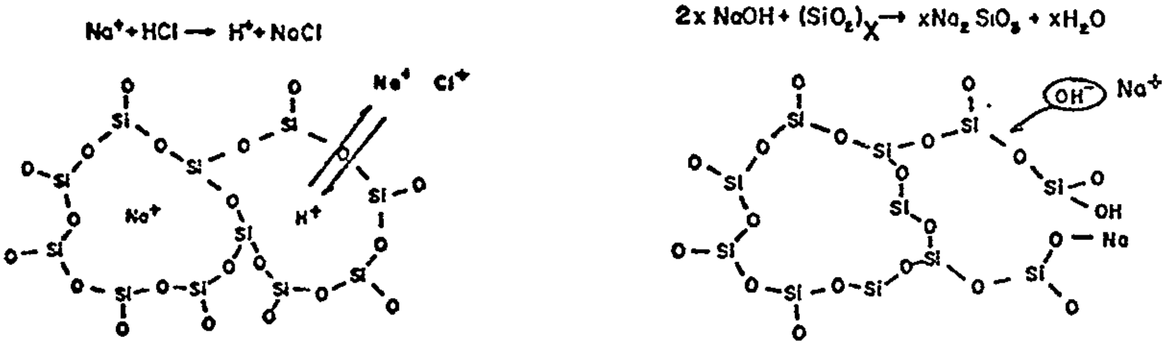
$$Na^+ + HCl \rightarrow H^+ + NaCl \quad .$$

The rate of attack increases with the acidity of the solution. A schematic of this mode of attack is shown in Figure III-3a. The leaching process results in a depleted layer on the surface of the glass. The attack rate will be dependent (after the initial depletion) on diffusion through the depleted surface layer.

Alkaline solutions have an etching effect on glass in which the silicon-oxygen bond is attacked in a manner illustrated by the following reaction:

$$2X\ NaOH + (SiO_2)_X \rightarrow X\ Na_2SiO_3 + X\ H_2O \quad .$$

This process is illustrated in Figure III-3b. If residue-buildup effects are not significant, the reaction rate is linear with time and increases by a factor of 2 to 3 per unit change in pH.(III-3) The rate of attack for most glasses is considerably higher in alkalies than in acidic solutions, however, alkali attack is seldom encountered in weathering situations except where strong detergents are used for cleaning. The resistance of soda-lime glasses to acidic corrosion may be improved by chemical treatment (surface dealkalinization or fluoride treatment); such treated glass has a potential for high corrosion resistance at low cost.



a. Acidic Ion Exchange Corrosion of Soda-Lime Glass

b. Alkaline Corrosion of Glass in Which the SiO Bond is Attacked

FIGURE III-3. SCHEMATICS OF DEGRADATIVE REACTION FOR GLASS

If antireflective coatings are used on the glass (or polymer) covers of modules, the corrosion resistance of the cover then depends primarily upon the chemical nature of the antireflective coating. As the development and application of these coatings progresses, it will be necessary to identify key environmental factors affecting them to ensure that appropriate diagnostics are brought to bear.

In solarization, the interaction of solar radiation with impurity ions present in the glass results in valence changes and associated increases in absorption in the solar spectrum (and attendant changes in the color of the glass). Typical valence changes of this type may be illustrated by:

- Mn^{+2} (weakly colored) + UV photons → Mn^{+3} (pink to purple) + e^-
- Fe^{+2} (blue-green) + photons → Fe^{+3} (yellow-green) + e^-.

Solarization can be avoided by minimizing the amount of iron and other multivalent impurity ions present in the glass and is not likely to be a common problem in glass-encapsulated modules. Testing to detect unacceptable levels of impurities of this type should be part of the qualification and/or acceptance testing routine.

Dirt accumulation can have a very significant, albeit reversible, effect on the apparent optical properties of glasses. The effect is the direct result of reflection, scattering, and absorption of solar radiation by the accumulated particulate material. Dirt-accumulation rates are a function of the angle of inclination of the glass surface and the specific environment in which the solar array is operating. In the absence of etching or abrading of the glass surface, the effect is relatively independent of the type of material involved. This would tend to indicate that either the accumulated dirt acts like a black body in absorbing solar radiation (e.g., through light entrapment due to a porous structure) or that particle-size controlled light scattering is a significant contributor. As indicated above, dirt-accumulation effects that do not involve chemical interaction with the glass are essentially fully reversible through proper cleaning.

Abrasive attack of glass surfaces is also strongly dependent on the specific operational environment. Causitive agents for this effect include wind-blown and water-borne particles. Washing or cleaning techniques are a potential contributing factor. The effect of abrasive attack is the localized removal of material from the surface region, resulting in defect introduction (including microcrack initiation) and surface irregularity or roughness.

3. Contacts, Connections, and Interconnects

The cell contact metallization and the electrical interconnects between cells are susceptible to attack by corrosion associated with the penetration of water, oxygen, and other corrosive agents through the protective encapsulation system (also, conceivably, by chemical compounds evolving from the encapsulating materials themselves). These elements of the photovoltaic module are also subject to damage by thermally and mechanically induced stresses (III-3)

Ideally, degradation of the metallization and interconnects should be preceded by degradation or failure of one or more of the other elements of the module, assuming the adequacy of the basic module design for providing environmental and stress protection. Early diagnosis of changes in these elements of the module would, ideally, identify potential module/array degradation before the occurrence of detectable changes in the metallization and interconnects. The availability of diagnostic tools adequate for the early detection of encapsulation systems changes that can lead to contact and interconnect degradation, particularly in the case of stress-related changes, is not clear at this stage of the investigation. (The Phase II evaluations should provide additional insight in this area.) The early detection of changes in these metallic components of the system could assume major importance if a suitable means for detecting their precursors in other encapsulation-systems components are not available.

The cell contact metallization generally consists of a gridlike pattern that covers a small fraction of the active area on the front surface, and a large area contact on the back surface. Common metallization systems used or considered for use in fabricating these contacts include.

- Vacuum deposited Ti-Ag (with or without solder coat)
- Vacuum deposited Ti-Pd-Ag
- Screen printed silver
- Screen printed aluminum
- Screen printed copper
- Electroless nickel or copper plating (with or without solder coat).

Sintering of the contact at elevated temperatures is generally required at some stage in each of these fabrication processes to ensure adequate mechanical and electrical properties. For the Ti-Ag metallization system without solder coating, corrosion has been clearly demonstrated to be a potential problem, although even here the details of the mechanism of the corrosion process are not generally agreed upon.(III-4) It is, however, clear that elevated temperatures and the presence of moisture are key factors, and that the process is accompanied by the generation of hydrogen and results in the production of an amorphous and relatively weak TiO_2 layer at the original Ti-Ag interface. The end result is a loss of mechanical adhesion and an increase in the series resistance of the device, culminating in blistering and peeling of the contacts. The use of palladium as an interface between the titanium and the silver, or the use of a solder overcoat to prevent penetration of moisture through the relatively porous silver appear to be effective ways of eliminating or reducing this problem to tolerable levels for space use cells during their earth-storage period. Whether these approaches are equally effective for cells operating 20 to 30 years in a terrestrial environment remains to be seen. Other corrosion processes for this system and key corrosion processes for other candidate contact metallization systems have not been identified or characterized well enough to permit an assessment of their nature and potential impact on array lifetime. Discoloration of contact metallization in some modules under field test conditions has been observed, but information permitting speculation on the chemical origin and extent (e.g., as to whether it is confined to a surface layer that blocks continued attack) of the changes associated with this discoloration is not generally available. Identification of optimum diagnostic tools specific to a given corrosion process requires the identification of the corrosive agents and the corrosion products. Some of the sensitive surface-analysis techniques available today could provide this information in cases where corrosion has been observed, however, the tests will likely require destruction of the module. Until such information is available, early detection and diagnosis of corrosive attack on cell metallization systems in modules will have to rely on sensitive measurements of property changes that are ancillary to the corrosion processes (e.g , changes in electrical characteristics and possibly changes in optical or "appearance" characteristics) and that commonly accompany all such processes.

Connections between the leads or cell interconnects and the cell contact metallization are generally made by either soldering, welding, ultrasonic bonding, or thermocompression bonding. These connection points are potentially high-stress areas under thermally or mechanically induced movement. Design features that affect these stresses are well known (i.e., those that minimize thermal mismatches, use stress-relief loops in interconnects, etc.), and designs that are in principle adequate for "normal" conditions can generally be developed. Conditions that can lead to early failure under "normal" operational stresses are well known and well documented as a result of the use of cells in the space program. These conditions (e.g., improper soldering, improper interconnect loops, etc.) should be detectable during quality-control inspections or qualification and acceptance testing and, hence, should not play a significant role in the long-term degradation of photovoltaic modules/arrays. Under continual thermal cycling and mechanically induced flexure over a 20 to 30 year period materials and designs that were initially adequate could eventually fail. The early symptoms that might be precursors of failure at such a connection or joint include defect buildup or work hardening, creep, and microcrack initiation. These processes will be very difficult to detect (let alone quantify) early in the degradation process without destructive tear down since, in many cases, these connection areas are not readily accessible to close and careful inspection or mechanical testing in situ. Similar symptoms would accompany overstress or abnormal stress conditions that could result in failure at a connection. In this case, early detection and diagnosis of changes (e.g., hardening of pottants or adhesives) that cause stresses beyond design values would, hopefully, provide the key to analyzing and correcting the condition when necessary to meet operational-lifetime requirements.

The electrical leads or interconnections between cells in a module can have several forms, including wire, wire mesh, metallized plastic films and PC boards, and metal ribbons or strips of various (and sometimes elaborate) forms. Materials that have been used as interconnects for photovoltaic modules/arrays include:

- Copper – unplated or silver plated
- Silver
- Beryllium copper
- Aluminum – unplated or silver plated
- Kovar-nickel/copper/solder or silver plated
- Molybdenum – silver plated.

Platings or claddings are used to increase corrosion resistance and to enhance conductivity in some cases. The current state of knowledge regarding corrosive attack of interconnects is similar to that for the cell contact metallization (excepting the known effects on unprotected Ti-Ag contacts) in that very little information is available. Discoloration of interconnects has been observed on some field-tested and humidity-tested modules and is attributed to "probable corrosion"; however, details of the reactions involved are not generally known. The nature of some of the materials used would imply that processes other than straightforward oxidation would be required for large-scale corrosive attack of these structures.

As with the contact metallization, tests to identify active corrosive agents and symptomatic corrosion products will probably require destructive tear down of modules to allow inspection and analysis of surface materials. Monitoring of electrical characteristics or optical properties that will be affected by corrosion-associated changes could provide a means for the general detection and rate characterization of corrosive attack. Corrosive agents, corrosion processes, and corrosion products will vary with the interconnect material. The identification of specific interconnect corrosion mechanisms that are applicable to photovoltaic modules and that could have an impact on the operational lifetime of such modules will require further experimental evaluations. Once these identifications have been made, a sound basis for recommending the most sensitive techniques for measuring the rate of corrosive attack can be developed.

Stress damage to interconnects resulting from thermal cycling or periodic mechanical deformations will be manifested initially in work hardening of the metal and ultimately in the partial or complete fracture of the interconnect. These processes will be accompanied by changes in the electrical properties of the instrument. Work hardening would also produce changes in the microstructure of the interconnect that could be detected and characterized during destructive-tear-down tests. The earlier stages of fracture would also be clearly observable during such tests.

4. Solar Cells

Degradation of the silicon cells (as contrasted with materials deposited on the cells) is considered to be unlikely under terrestrial conditions. The resistance of silicon to attack by the chemical elements and compounds that would normally be present under such circumstances will probably preclude corrosive attack of the cell itself. It is also unlikely that temperatures high enough to significantly affect diffusion profiles or impurity migration within the bulk silicon will be experienced. (If such temperatures were experienced for significant time periods, the damage to other module constituents would probably have a more immediate and catastrophic impact on performance.) Extremely high temperatures could arise in some concentrating systems if, for example, a coolant circulation system were to fail. Whether such catastrophic failures should be considered degradation is questionable. If, for some unanticipated reason, degradative changes in the cells should occur during terrestrial operation, the factors that are important in determining cell performance (e.g., minority-carrier diffusion lengths, junction characteristics, or surface recombination) are well understood, and techniques for analyzing and measuring changes in these factors are firmly established. Because it is unlikely that cell degradation per se will play a significant role in limiting the operational lifetime of photovoltaic arrays and because adequate means for measuring the property changes that would accompany cell degradation are well known, an extensive treatment of cell-degradation mechanisms and techniques for measuring them has not been included in this study.

One portion of the cell structure that might be subject to long-term degradation is the antireflection coating. Antireflection coating materials that might be used in terrestrial photovoltaic modules include silicon oxides or silicon oxide – titanium oxide combinations, silicon nitride, and tantalum pentoxide. Techniques for producing antireflection coatings on photovoltaic cells include vacuum deposition, chemical vapor deposition, and spin-on or spray-on deposition. The long-term effects of combinations of thermal cycling and humidity on the adherence and optical properties of films of the above material (particularly films deposited by potentially low cost techniques such as the spin-on approach) have not been fully assessed. Speculation on microscopic changes that might be involved has no basis at present, however, the macroscopic effects of significant changes would clearly be either alteration of the index of refraction of the coating, alteration of its optical-absorption characteristics, and/or delamination. The presence of impurity ions could give rise to photochromic effects (solarization) similar to those discussed for glass); however, this should properly be considered a quality-control or acceptance testing problem rather than a problem involving degradation of normal module constituents.

Fracture of a photovoltaic cell due to stresses beyond design values is a potential failure mode. Such failures are generally not preceded by long-term changes in cell properties that would allow projection of cell or module operational lifetime for this mechanism. Changes in the properties of other module constituents (e.g., substrate or pottant) will probably be more fruitful areas for early projections of failure due to cell fracture.

5. Substrates, Frames, and Edge Seals

Module designs generally incorporate either a rigid substrate or superstrate as a base for mounting the cells in fixed positions. In addition to providing a base for mounting the cells, this module component also supplies rigidity and strength to the module. Superstrates generally also serve as the front cover sheet of the module and must be made of either glass or a transparent polymer. Substrates may or may not serve as the back covering for the module. A wide range of materials has been considered at one time or another for use as substrates These include various types of plastic sheet, glass, plywood, fiberglass, masonite, transite, aluminum honeycomb, anodized aluminum sheet, porcelainized steel, and several others. The varied nature of these materials precludes generalized statements about degradation on a microscopic level in substrates. The property changes and degradation mechanisms in polymers and glasses which were discussed earlier in this section will apply equally when these materials are used as substrates. Fatiguing or loss of strength and moisture barrier properties will be primary concerns, although, in cases where transmissive substrates are used to provide lower array operating temperatures, degradation of substrate optical properties could also assume significant importance.

Metallic substrate materials could be subject to corrosion or stress-induced changes similar to those discussed for interconnections. Early detection and diagnosis of damage from corrosion and stress in substrates will almost certainly require destructive tear down of modules and analysis and inspection by chemical and metallurgical techniques. Metallic substrates will generally incorporate some coating or interface material to ensure electrical insolation from the cells and the interconnects. Changes in the electrical properties of these layers which could lead to arcing could also be important degradation modes. Probable property changes that would precede such arcing in the harder, less permeable coatings (e.g., the porcelain layer in porcelainized steel) include the initiation of cracks or voids in the layer, possibly due to stress. Additional property changes likely to be important primarily for polymeric interface materials include increases in ionic content and water-vapor content, and structural (chemical) changes which will result in increased electrical conductivity.

Some module/array designs incorporate metal-backed foils as edge sealants to provide a barrier against moisture penetration through the edge region: These components are unlikely to be altered significantly in this respect by the normal action of light, heat, or H_2O. Puncture or rupture of the foil as a result of unusual stresses or the presence of unanticipated corrosive agents are potential damage modes. Changes in the adhesive layer (see discussion of polymerics, Section III.B.1) between the foil and the module which could lead to delamination of the foil will be equally important. This is another component of the module in which damage will be difficult to assess without some disassembly, since framing components generally prevent ready access and inspection.

The framing of the module/array, in designs which use this type of structure, consists of a metal channel (e g., aluminum) and appropriate gaskets and/or sealants. The frame is a key factor in establishing the mechanical strength of the module/array and hence its resistance to mechanical stresses. Factors that could impair the ability of this structural member to fulfill its function are, as with most of the other metallic components of the system, corrosive attack and various types and degrees of mechanical damage (e.g., creep, work hardening, stress rupture). As the metal frame is an external component, changes which are externally manifest (surface damage due to corrosion, dimensional changes or distortions, etc.) can be detected and to a limited extent analyzed to deduce degradation rates without removal of the module from its operational emplacement or disassembly. Highly precise analyses of these effects and very early detection of structural (microscopic) changes due to linear or cyclic stresses will probably require destructive examination of some samples with the use of metallurgical techniques to study their microstructure.

IV. SELECTED MATERIALS PROPERTIES, TECHNIQUES, AND INSTRUMENTS FOR DETECTION AND MEASUREMENT OF FAILURE-ORIENTED ARRAY DEGRADATION

IV. SELECTED MATERIALS PROPERTIES, TECHNIQUES, AND INSTRUMENTS FOR DETECTION AND MEASUREMENT OF FAILURE-ORIENTED ARRAY DEGRADATION

A. OVERVIEW – TECHNIQUES AND CRITERIA

1. Techniques Selected and Their Categories

This section contains summary descriptions of those techniques and instruments which have been found, as a result of the extensive surveys and evaluations conducted in this study, to be directly applicable or potentially useful in photovoltaic-array-lifetime prediction. The selected techniques and instruments discussed in this section are the survivors of a detailed examination of a large number of candidates which were identified by the researchers on the basis of their expertise in the field, the computerized literature searches, and consultation with numerous experts in specific appropriate fields. Table IV-1 lists all of the techniques given detailed consideration in the course of the study. Brief comments and descriptions for some of the techniques appearing in Table IV-1 which are not recommended for use in weathering/aging tests or for further evaluation are contained in Section VIII. An inspection of the table reveals obvious overlap and cases where a given technique could well fit into another category. It should be noted that the categorization system chosen for classifying the techniques and instruments is simply a convenient means for dividing the activities of the study while insuring that potentially useful techniques would not be overlooked in the literature searches. It was not intended nor attempted to develop a unique division of the identified techniques and instruments.

2. Focus of the Selection and Evaluations of Techniques

Molecular-level degradative changes in polymerics are, at some total integrated level, generally accompanied or followed by changes in morphological properties (e.g., such properties as crystallinity and orientation). The latter may be thought of as property changes at the microscopic level. At still higher levels of degradation, these molecular- and microscopic-level changes manifest themselves as macroscopic changes, e.g., changes in tensile strength, elongation, hardness, and heat distortion temperature.

As has been indicated earlier, measures of molecular- and microscopic-level changes, both of which occur earlier in the degradative process than macroscopic changes, are generally of more importance as early predictors of degradation. Consequently, diagnostic tools that manifest such changes must, at the same level of instrument sensitivity/precision, be of prime importance in studies directed toward prediction of service life. Thus, in such studies it is important that diagnostic tools be identified that can be used to quantify materials changes which are clearly precursors to failure *extremely early* in the degradation process, i.e., primarily at the molecular and morphological (microscopic) levels. Moreover, *a number of such tools* must be available so that each of the principal modes of potential failure of the key materials and materials subsystems within the array can be followed.

TABLE IV-1. TECHNIQUES, INSTRUMENTS, AND PHENOMENA INVESTIGATED FOR APPLICABILITY TO MEASUREMENTS IN LIFETIME-PREDICTION STUDIES

Chemical

Chromatography
Wet Chemistry
Mass Spectrometer
Emission Spectrometer
EPR
NMR
Mossbauer Effect
Thermal/Vacuum Analytical Techniques
SIMS
Neutron Diffraction
X-Ray Diffraction
Electron Microprobe
IR Techniques (FTIR, etc.)
Auger
Chemiluminescence
XPS/ESCA
Fluorescent Probe
Electron Stimulated Desorption Spectroscopy
ISS
LEED
Raman Spectroscopy

Electrical

Dielectrometry
Resistivity
Noise Effects
Dark and Light I-V
Cell Patterning (including passive and active devices)
Electron Tunneling Spectroscopy

Mechanical

Rheology
Bond Strength
Elasticity
Tensile Tests
Impact Tests
Acoustical Effects
Flexural Strength

Optical

Spectroscopy
Microscopy
Haze/Gloss Measurements
Optical Wave Guide Effects
Ellipsometry
Reflectance
Absorptance
Scattering Phenomena
Photoelasticity
Magneto-Optical Effects
Piezo-Optical Effects
Laser Diffraction
SEM
Holography
Optical Multichannel Analysis

Thermal

Thermal Conductivity
Thermal Expansion Coefficient
Heat Capacity
Thermal-Analytical Techniques (DSC, DTA, etc.)

Other Physical Techniques

Water Vapor and Gas Permeability
Profilometry
Photoacoustic Spectroscopy

In considering potentially applicable tools, candidates have been identified that are likely to be useful in providing information on molecular- and morphological-level changes within and at surfaces and interfaces of the various array materials. Selected instruments and methods for monitoring macroscopic-level events have also been identified, since measurements of these events serve important supplemental and in-situ measurement requirements for lifetime-prediction studies as well as provide "first line" indication of changes when instrument sensisitivity, precision, and accuracy are adequate.

In this section, the specific types of degradation modes and mechanisms which are best suited to measurement by a given instrument or technique are identified. In this study, the researchers made use of the most current available information to identify the most important degradation and failure modes and their microscopic precursors as discussed in Section III. Sources of information used include the reports and discussions of personnel from JPL, MIT-Lincoln Laboratories, and NASA-LeRC based on their experience with acceptance and field testing, and discussions with experts, internal and external to Battelle, on the properties (including degradation thereof) of polymers and glasses. The investigation of techniques then focused on identifying and evaluating techniques (and instruments) which would provide the most sensitive and direct means of characterizing the key degradation-related factors identified from these sources.

3. Evaluation Criteria Used in the Study

The evaluations of the techniques and instruments (once their basic applicability had been established) were based on a series of technical and economic criteria which were established, for the most part, during the conceptual stage of this study. The basic criteria are listed in Table IV-2 These criteria also play a key role in the evaluations of Section V where cross-category assessments of measurement techniques are discussed. More detailed consideration of some of the key criteria are presented in that section.

The following discussions of the selected instruments and techniques are divided in accordance with the original categorization, i.e., chemical, mechanical, optical, thermal, electrical, and "other physical".

TABLE IV-2. INSTRUMENT AND TECHNIQUE EVALUATION CRITERIA

Properties Measured

Areas of Applicability (material classes, bulk or surface, environments, etc.)

Measured Property Value Ranges and Sensitivity in Ranges

Accuracy in Ranges

Precision in Ranges

Required Form of Test Specimen

Effect of Measurement on Test Specimen (destructive or nondestructive)

Suitability for In-Situ Measurements

Instrument Cost

Ease of Measurement (equipment and specimen preparation, set-up time, run time, monitoring, etc.)

Cost of Test (power and environmental requirements, operator skill level, etc.)

Instrument Portability (size, power requirements, special environmental or cooling requirements, etc.)

Calibration Requirements and Reproducibility Among Instruments

Availability of Instruments

B. CHEMICAL MEASUREMENT TECHNIQUES SELECTED

1. Background

In the chemical-techniques category, analytical instruments capable of detecting chemical changes related to degradation of photovoltaic-array components were investigated These include such things as carbonization of polymeric surfaces due to oxidation, chain scission of polymers, chemical leaching of glass surfaces, and metal corrosion. It was recognized from earlier studies that information on precision would be difficult if not impossible to find. For this reason part of the literature search focused on the identification of such information. This search was successful in finding precision studies on two of the key tests being recommended: gel permeation chromatography and Auger electron spectroscopy. Information on sensitivity was found rather easily in most cases, while information on accuracy was limited; however, since it is not absolutely necessary for accurate measurements of degradation rate*, in most cases, this was not of major concern.

The following analytical instruments in this category are considered most suitable for detection of degradation of photovoltaic-array components

- Fourier Transform Infrared (FTIR) Spectroscopy including Attenuated Total Reflectance (ATR)
- Electron Spectroscopy for Chemical Analysis (ESCA), X-Ray Photoelectron Spectroscopy (XPS)
- Auger Electron Spectroscopy (AES)
- ESCA, or XPS, and AES in conjunction with ion sputtering for depth profiling
- Chemiluminescence (CI)
- Gel Permeation Chromatography (GPC)
- Combination of Mass Spectrometry/Gas Chromatography (MS/GC)
- Surface Energetics.

Discussions of each of these instruments and their areas of applicability follow.

2. Fourier Transform Infrared (FTIR) Spectroscopy

Infrared spectroscopy is based upon the interaction of infrared electromagnetic radiation with matter. This interaction results in absorption of certain wavelengths of radiation, the energy of which corresponds to the energy of specific transitions between various rotational or vibrational states of the molecules or groups of atoms within the molecule. The IR-absorption spectrum of

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*Measurement of rate of change involves the difference between two measured values The inaccuracies in each are cancelled out upon subtraction. This, of course, is true only if test bias is constant.

a material is a measure of the fraction of the incident radiation absorbed as a function of wavelength. The magnitude of the absorption can be related to the concentration of specific absorbing groups and, therefore, IR spectroscopy is a quantitative tool. In polymeric systems, infrared spectroscopy can be used to measure the degree of regularity of the arrangement of macromolecules (i.e., degree of crystallinity or orientation of stretched film or fibers). Number average molecular weight and degree of branching can also be determined.

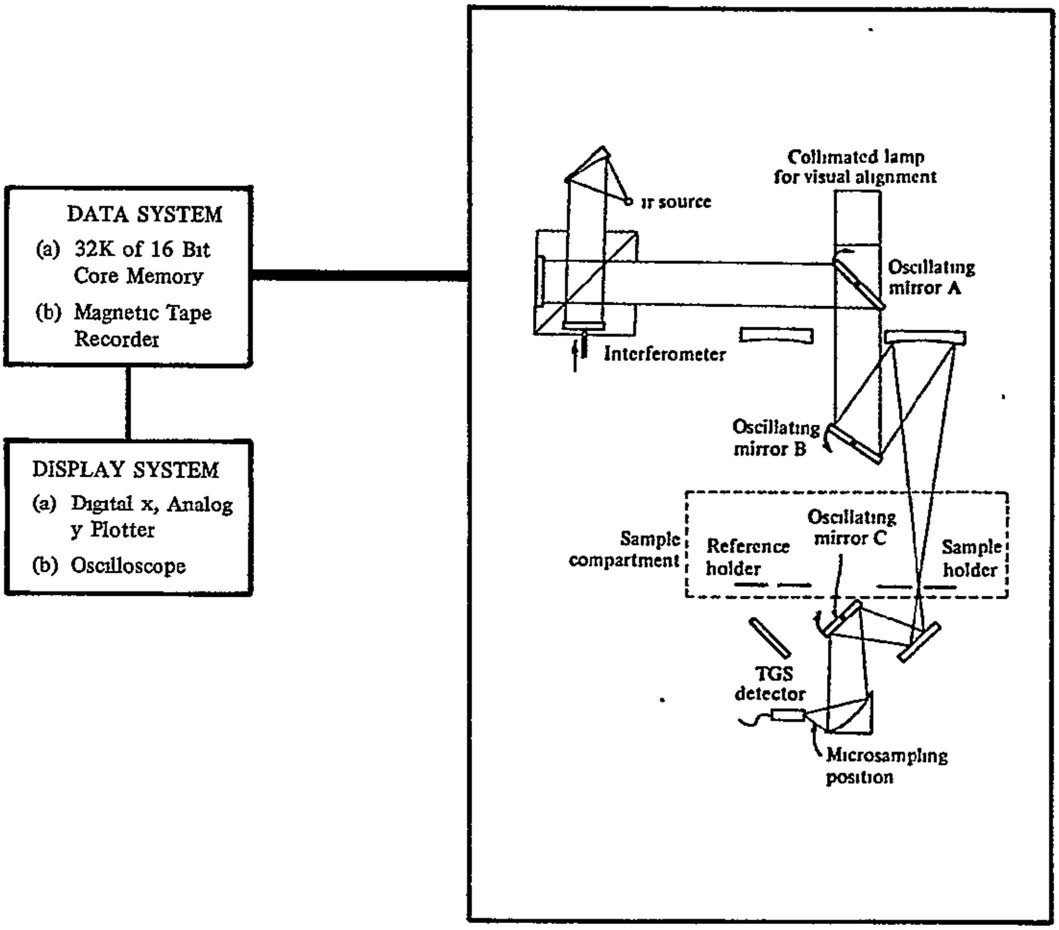
Conventional IR spectroscopy can be used as a quantitative tool for studying degradative changes; however, Fourier transform infrared spectroscopy offers the potential for significantly higher precision in characterizing the small changes that could be encountered in the LSSA-lifetime studies.

FTIR Apparatus and Measurements

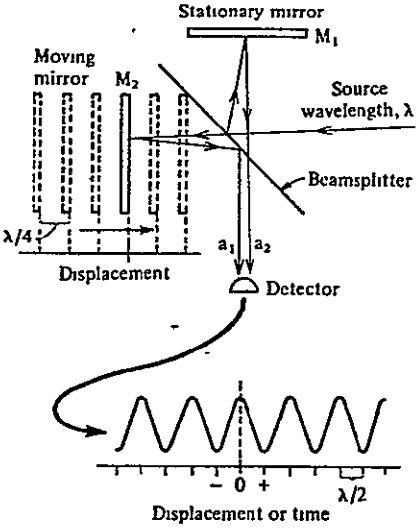
A schematic representation of the configuration of the FTIR apparatus is given in Figure IV-1. Modulated light from the source is collimated and passed to the semireflecting mirror of the interferometer. The interferometer consists of two fully reflective plane mirrors (one movable) at right angles to each other and the semireflecting mirror oriented at 45 degrees to the other two mirrors. The semireflecting mirror splits the collimated light into two equal beams for the other two mirrors. When these two mirrors are located such that the optical paths for both beams are equal, the beams will be in phase when they return to the beam-splitting mirror and will constructively interfere. Displacing the movable mirror by a distance equivalent to one-quarter wavelength (for monochromatic light) will result in destructive interference of the beams. Continuous linear movement of the mirror (in either direction) will result in a continual cycling of the illuminated field from light to dark as the mirror displacement goes through quarter-wavelength multiples. When the mirror is moved with a velocity ν, and using light of wavelength λ, the signal from a detector will have a frequency $f = 2\nu/\lambda$. Plotting detector signal against mirror distance yields a pure cosine wave. If polychromatic light is used, the result is the sum of all of the cosine waves, which is the Fourier transformation of the illuminating spectrum. The intensity at each wavelength is modulated by a frequency f as given above. Performing an inverse transformation of the interferogram then yields the spectrum. This is accomplished through the use of digital computer techniques. In summary, the Fourier transform IR spectrometer performs a frequency transformation, instead of dispersing the polychromatic light, in order to achieve wavelength discrimination and uses a dedicated digital computer (with appropriate analog conversion devices) to effect rapid analysis of the data. These factors lead to the following two major advantages of FTIR over conventional infrared spectroscopy

- The use of an interferometer results in a substantial gain in energy or light throughput as compared with a monochrometer. This gain in energy results from the fact that all wavelengths of light are examined simultaneously in an interferometer (i.e., the light is not dispersed to provide wavelength discrimination) and energy losses of the magnitude of those occurring in a dispersive instrument, which examines the light one wavelength at a time, are not experienced. This additional energy can be used in one of several ways. (a) for faster scan speeds (as fast as 0.6 second), (b) for up to a 30-fold increase in signal-to-noise ratio, or (c) for 10^2 to 10^3 greater sensitivity.

- The availability of a dedicated computer offers several major data-handling advantages. Spectra ratios can be compared and the spectra manipulated to remove absorption bands arising from background materials, and the computer can be



a. Apparatus configuration



b. Interferometer mirror movement and resultant signal

FIGURE IV-1. ILLUSTRATION OF FTIR APPARATUS used to perform spectral arithmetic. Thus, spectra can be added or subtracted from each other and also multiplied or divided. In this way, the spectra can be adjusted in size, and unwanted components can be removed from the spectra without the necessity of chemical separation. A conventional IR spectroscopic setup could of course incorporate a dedicated computer and thereby gain similar capabilities for data manipulation. The ability to easily compare different sets of data and detect differences is of key relevance to accelerated testing and degradation studies.

Examples of the use of FTIR systems are given in the following paragraphs. The sensitivity of FTIR systems is illustrated by the fact that it has been possible to get usable spectra on 25 nanograms of material (using a Digilab FTS-14 system), whereas 1 microgram has been the limit with dispersive infrared spectroscopy (Perkin-Elmer 521 infrared spectrophotometer). Analyses can be done in aqueous systems that are difficult, if not impossible, to do with dispersive spectroscopy. In this area it has been possible to detect and identify drugs in water in the 100-ppm range.

Another example of the sensitivity of FTIR systems is presented in Figure IV-2 which shows the spectra of thin films of stearic acid deposited on an internal reflection crystal (ATR, or attenuated total reflection). It suffices to say that spectra can be easily obtained on very thin films (25 Å ≅ a monomolecular layer) and that differences between these thin films can easily be detected. Thus, an ATR technique could be devised which would permit spectra of materials to be obtained on a monomolecular film or less (partial surface coverage)

In Figure IV-3, the sensitivity of FTIR is emphasized even more. Here the spectrum obtained on the Digilab FTS-14 system (Figure IV-3B) is of much higher quality (even without scale expansion) than even the 10X scale-expansion spectrum obtained on the Perkin-Elmer dispersive spectrophotometer. From results such as these, it has been estimated that Fourier transform infrared systems are inherently 10 to 100 times more sensitive than dispersive spectroscopy.

An illustration of the value of the computer is shown in Figure IV-4. This figure shows the transmission spectrum of a film of low-density polyethylene (Figure IV-4A) and of the same type of low-density polyethylene after weathering (Figure IV-4B). While the film thickness is not identical, it is still apparent from Figures IV-4A and IV-4B that there are no visual differences between the spectra of the two films. However, when the spectra of Figures IV-4A and IV-4B are stored in the computer file and then subtracted, the result is shown in Figure IV-4C. Here it is apparent that there is a real difference between the two films which can be seen better when the spectrum of Figure IV-4 is scale expanded (Figure IV-4D). The infrared absorption bands marked "O" (Figure IV-4D) indicate the expected oxidation effects upon weathering. Surprisingly however, those bands marked "S" clearly demonstrate that the weathered polyethylene also contains a silicone grease. In this instance, a silicone grease was used as a mold release agent when the films were cast. For the weathered polyethylene, a little more silicone grease (trace amount) was used than for the unweathered polyethylene film. Since silicone grease can affect weathering performance, even a trace quantity like that seen in Figure IV-4 could affect the weathering results.

Figure IV-5 repeats the subtracted transmission spectra of weathered and unweathered polyethylene (shown in Figures IV-4C and IV-4D). This figure shows subtracted spectra of the same two polyethylenes except that the original polyethylene spectra (before subtraction) were obtained via the ATR technique rather than by transmission methods (with ATR, only absorption near the surface is measured). Comparison of the ratio of bands due to oxidation with those due to silicone in Figures IV-5A and IV-5B indicates that the silicone is dispersed throughout

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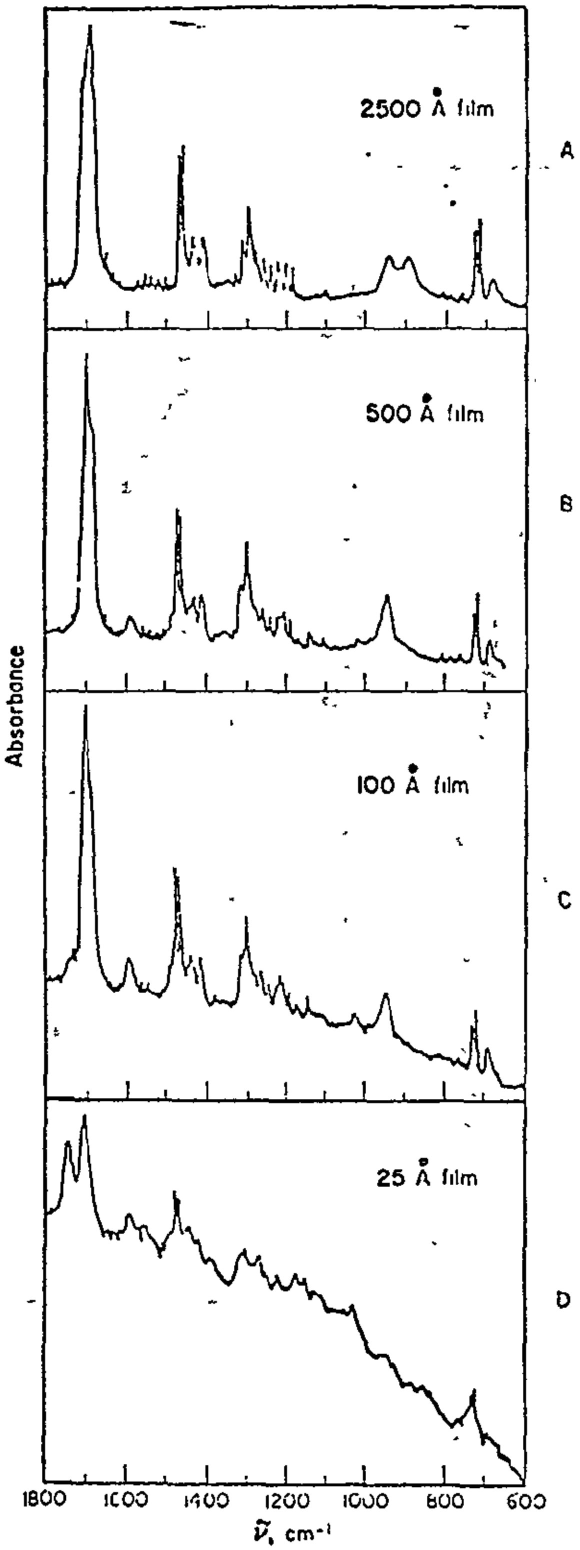

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FIGURE IV-2. FTIR SPECTRA OF STEARIC ACID ON KRS-5 CRYSTAL, SPECTRA OBTAINED USING THE DIGILAB FTS-14 FTIR SYSTEM

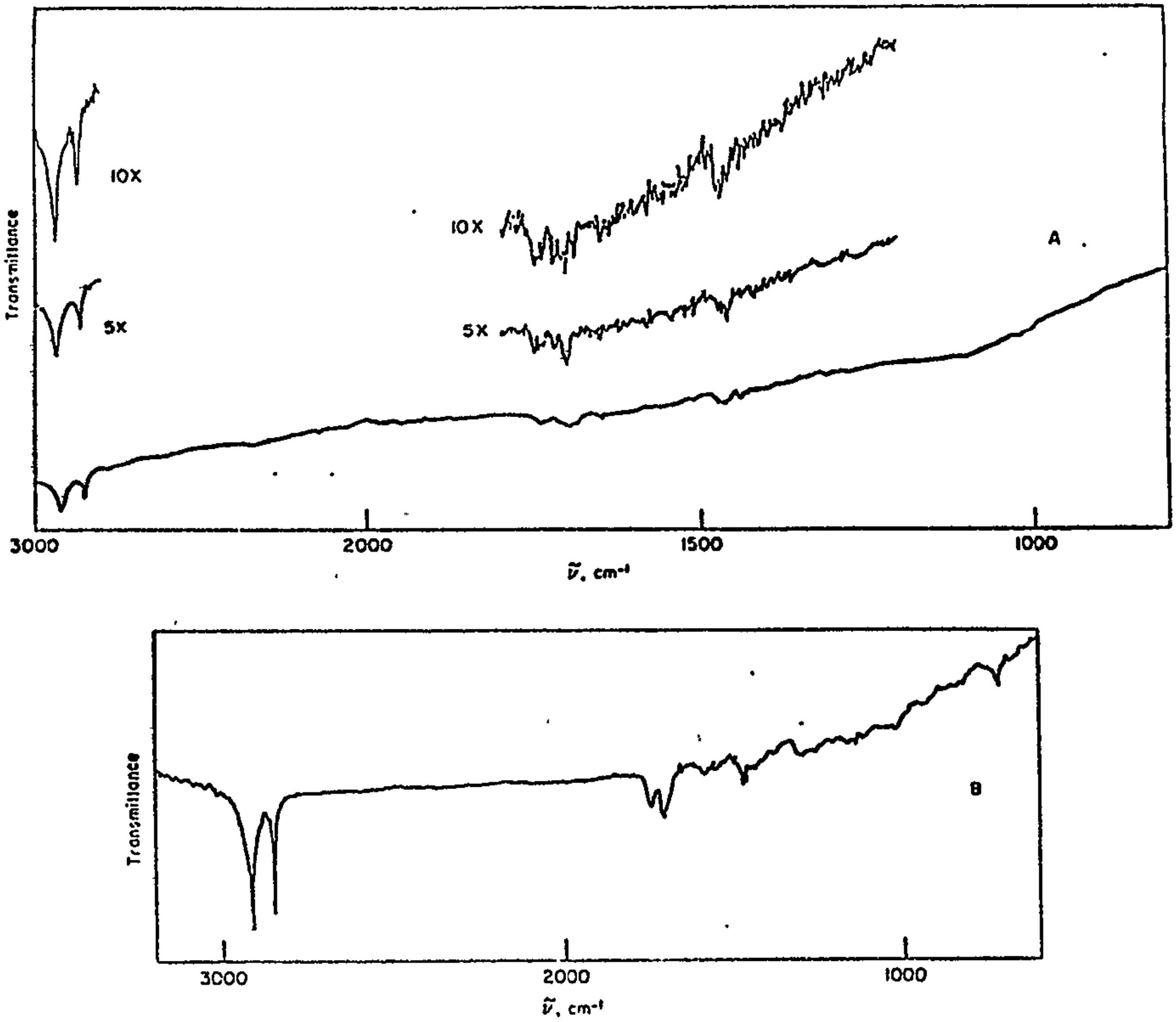

FIGURE IV-3. STEARIC ACID (25 Å) ON KRS-5 CRYSTAL, OBTAINED ON (A) PERKIN-ELMER 521 SPECTROPHOTOMETER; (B) DIGILAB FTS-14 FOURIER TRANSFORM INFRARED SYSTEM

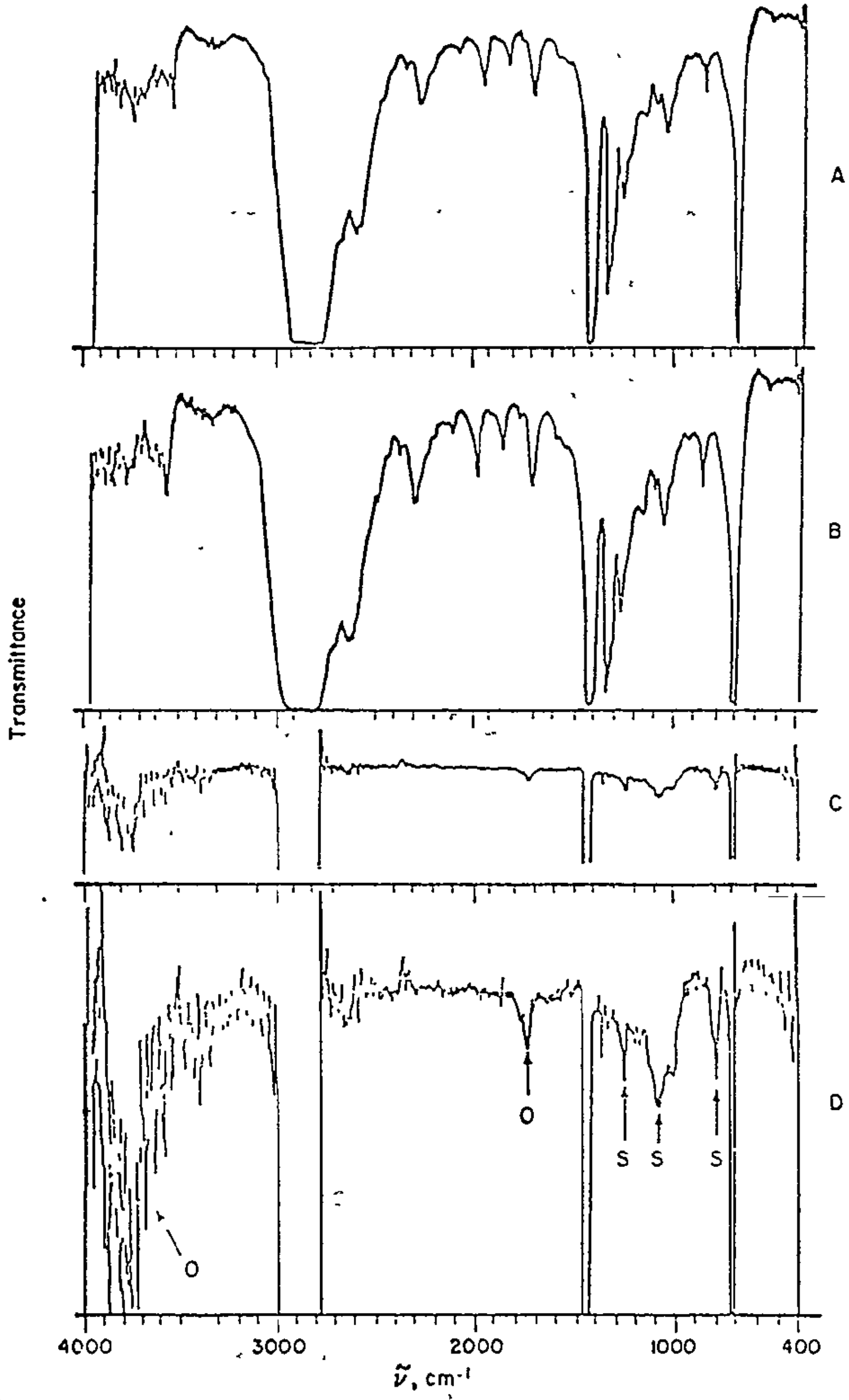

FIGURE IV-4. FTIR SPECTRA OF LOW-DENSITY POLYETHYLENE BEFORE (A) AND AFTER (B) WEATHERING; (C) SPECTRUM B MINUS SPECTRUM A; (D) SAME AS SPECTRUM C AFTER SCALE EXPANSION

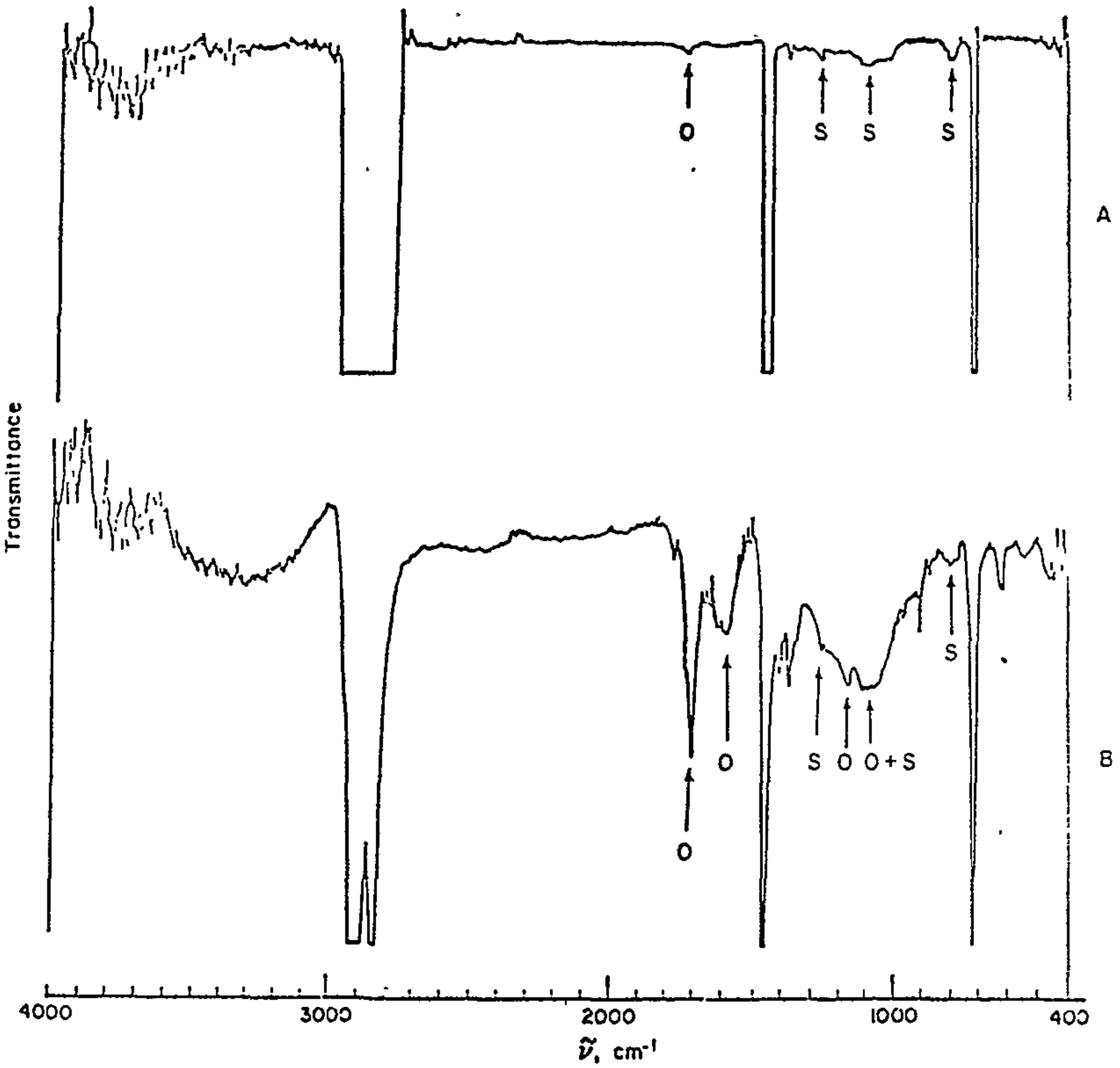

FIGURE IV-5. FTIR SUBTRACTION SPECTRA OF LOW-DENSITY POLYETHYLENE (WEATHERED SAMPLE MINUS FRESH SAMPLE) OBTAINED ON THE DIGILAB FTS-14 FTIR SYSTEM BY (A) DIRECT TRANSMISSION AND (B) ATTENUATED TOTAL REFLECTANCE (ATR) TECHNIQUE

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the film, while the bulk of the oxidative effects occur on or near the surface of the polyethylene film. Thus, a great deal of information can be obtained from a few spectra, using the ability of the computer to perform arithmetic.

Measurements Applicable to Modes of Failure

The photodegradation of most organic polymers results in the formation of carbonyl groups. Since the oxidation is diffusion controlled, the carbonyl concentration is higher at and near the surface than in the bulk of the material. Carbonyl can be easily detected by FTIR and ATR-FTIR can be used to measure carbonyl close to the surface. Carbonyl concentrations as low as approximately 0.01 to 0.1 percent can be detected by FTIR but calibration is required for absolute quantification. The minimum amount of carbonyl *change* detectable has not been determined. Increases in carbonyl can be detected after a relatively short time of outdoor exposure for many organic polymers. Since the formation of carbonyl groups is felt to be a precursor to failure caused by higher levels of oxidation, FTIR should prove quite useful in service-life prediction. It is applicable to any organic polymeric material used in the photovoltaic array but appears particularly applicable to polymeric cover materials such as polycarbonate, polyvinylfluoride, and polymethyl methacrylate. Aside from its ability to detect carbonyl groups, FTIR can also be used to follow changes in crystallinity and by using polarized light is also capable of measuring orientation changes. These capabilities are important because both types of change can occur as the result of outdoor degradation of polymeric materials and both could conceivably lead to failure.

Cost and Other Information

An FTIR apparatus costs approximately $120,000, including the computer, and is manufactured by several companies including Beckman Instruments and Digilab, Inc. It is a nondestructive test but sample size requirements will necessitate module destruction in the case of a module test. The test is not portable.

3. Electron Spectroscopy for Chemical Analysis (ESCA)

With ESCA, also known as X-ray photoelectron spectroscopy (XPS), the sample of interest is exposed to a 10 kv source of monochromatic X-rays. This is followed by analysis of the energy spectrum of the resulting photoelectrons emitted from the sample. The method is capable of detecting elements present at an atomic fraction of 10^{-2} to 10^{-3}. The penetration depth is 5 to 15 Å for metals, 15 to 25 Å for inorganic compounds, and 50 to 100 Å for organic compounds. ESCA provides measures of binding energies of the electrons in both the deep-lying shells and valence bands, and these in turn provide information of a chemical nature about the bulk sample and, in particular, about its surface. The experiment is carried out in ultrahigh vacuum and samples are generally solids–small plates, powders, or frozen liquids. The instrument is illustrated schematically in Figure IV-6.

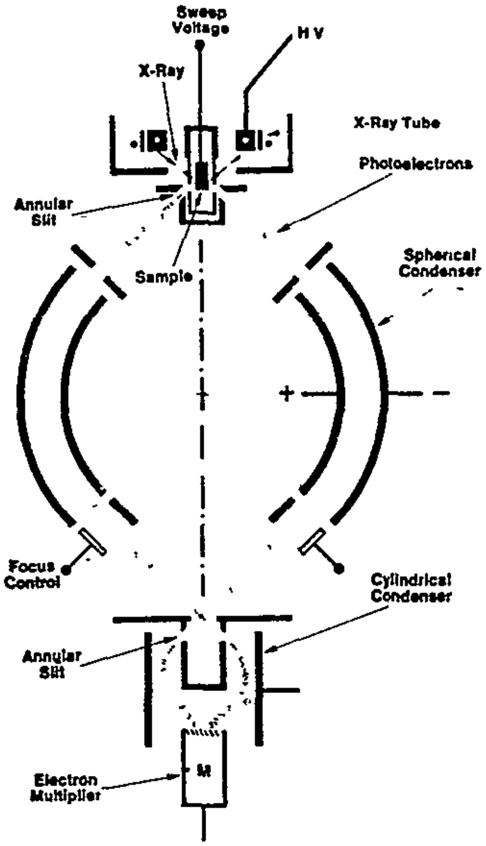

FIGURE IV-6. CROSS SECTION OF AN X-RAY PHOTOELECTRON SPECTROMETER, XPS (OR ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (ESCA)

With ESCA, the information content per spectrum is unsurpassed by any other spectroscopic technique. The levels of available information are, as pointed out by Clark(IV-1), the following:

(1) Absolute binding energies, relative peak intensities, shifts in binding energies. Element mapping for solids, analytical depth profiling, identification of structural features, etc.

(2) Shake up-shake off satellites. Monopole excited states. energy separation with respect to direct photoionization peaks, relative intensities of components of "singlet" and "triplet" origin.

(3) Multiple effects. For paramagnetic systems, spin state, distribution of unpaired electrons (analogue of ESR).

(4) Valence energy levels.

(5) Angular dependent studies. For solids with fixed arrangement of analyzer and X-ray source, varying take-off angle between sample and analyzer provides means of differentiating surface from subsurface and bulk effects. Variable angle between analyzer and X-ray source yields angular dependence of cross sections, asymmetry parameter β, symmetries of levels.

However, if information from any one of these levels obtained by ESCA is compared with that available from the most competitive of the other available spectroscopic techniques, ESCA almost invariably has sensitivity.

Unlike all of the other surface spectroscopic tools employing an excitation beam and an analyzer such as AES, SIMS, LEED, and SSP, ESCA can be applied to polymeric systems. Because the ESCA dose rate is several orders of magnitude smaller than that of the other surface methods, it is essentially a nondestructive test when applied to polymers

Much of the ESCA work done to date on polymers has been done by Clark.(IV-1) He lists the following advantages of ESCA in studying polymeric materials.

(1) Technique essentially nondestructive.

(2) High sensitivity and modest sample requirement.

(3) Large number of information levels available from a single experiment.

(4) For solids, unique capability of differentiating surface from subsurface and bulk phenomenon. Analytical depth profiling possible.

(5) Information level such that ab-initio investigations are feasible.

(6) Data often complementary to that obtained by other techniques Unique capabilities central to the development of a number of important fields.

(7) Theoretical basis well understood; results of considerable interest to theoreticians and may be quantified.

Measurements Applicable to Modes of Failure

For polymers used in the photovoltaic arrays, ESCA is particularly useful for measuring surface carbonylation, which is frequently considered to be an early precursor to several kinds of failure. It has already been mentioned that these surface carbonyls can be measured with FTIR with the aid of attentuated total reflectance. Actually, however, ATR-FTIR measures to a depth of 100 to 200 Å whereas ESCA measures 5 to 100 Å. ESCA, therefore, might be more appropriate for failure modes concerned with surface and not bulk changes.

For glass covers, ESCA should be useful for detection of Na^+ depletion due to erosion by acidic solutions Most other types of surface films or deposits caused by pollution, rain, UV, etc., can also be detected with ESCA

Since ESCA is a surface tool it cannot, of course, be used for in-situ interfacial analyses. It should be helpful, however, in diagnosing failure modes after tear-down or "autopsy" analysis of failed units providing the exposed interface is not too thick.

ESCA is also useful in conjunction with ion sputtering for determining depth profiles, i.e., plots of concentration versus depth into the polymer surface. Such information is expected to be particularly useful for interfacial tear-down failure analyses. For an interfacial failure, both surfaces could be depth profiled as an assist in the determination of the cause of failure. For example, in a delamination involving two polymeric materials, depth profiling of the surfaces may help to differentiate between failure due to a low-molecular-weight species migrating to the surface and that due to thermal stressing. Depth profiling with ESCA would also be useful in monitoring any changes in the antireflective coating on the glass or polymer cell cover.

Test Variability, Sensitivity, Etc.

Data on test variability, such as variation of replicates and variation between laboratories, instruments, and operators of instruments, do not appear to be available. ASTM Committee E-42 on Surface Analysis, however, is in the process of conducting a round-robin test to obtain such information.

Cost and Other Information

The cost of an ESCA unit is presently in the vicinity of $200,000, depending upon the desired options. ESCA units have been manufactured by DuPont, Hewlett Packard, and Physical Electronics Industries, Inc. However, only Physical Electronics still produces the unit commercially. The unit is quite large and heavy, especially with its dedicated computers, and is therefore not portable. It is a specialized instrument and requires a fair amount of skill in its operation.

4. Auger Electron Spectroscopy (AES)

In Auger electron spectroscopy, an electron beam (2 to 300 ev) is directed onto the surface of a test specimen where it excites electrons in the surface and near surface atoms of the sample. This excitation results in the removal or freeing of some inner shell electrons from the atoms, creating vacant states. These states are subsequently filled by outer shell electrons, and this relaxation process is accompanied by the ejection of electrons with energies characteristic of the specific energy levels (and, hence, atomic species) involved. These electrons are called Auger electrons. An Auger spectrum consists of a plot of the derivative of the energy distribution of the ejected electrons versus energy.

AES is capable of detecting as little as 0.1 percent of an atomic layer and has a penetration depth of only a few atomic layers.

AES has become a well-established technique for the qualitative analysis of surfaces, particularly metals. Its acceptance as a quantitative technique, however, has been less widespread owing to the difficulty of establishing suitable calibration standards and to the lack of a comprehensive quantitative theoretical analysis. Most attempts to quantify AES have been empirical owing to lack of knowledge of ionization cross section, effects of diffraction, chemistry, and surface roughness, the enhancement of Auger signals by backscattered electrons, the variation in average escape depth for electrons of different energies and inability of commonly used detectors to measure absolute Auger currents.

Many papers, nevertheless, report quantitative uses of AES. These results are based on suitable calibration of the Auger signal strength relative to some independent technique such as electron microprobe, ellipsometry, piezoelectric thickness monitors, and low-energy electron diffraction. West[IV-2] has shown that the long-term (112 days) reproducibility of AES data in a study of alloys of known composition is in the vicinity of ±20 percent. In other work, Chang(IV-3) reported variations in the reciprocal sensitivity factor of up to 30 percent from sample to sample and in different materials. These results suggest that AES is not capable of detecting the minute degradative changes of interest in the LSSA program. It may, however, be quite useful for detecting the onset of corrosion on the leads and metallization as well as other tear-down testing. Gutsche and Hill(IV-4) have reported such an investigation.

When used in conjunction with ion sputtering, AES is capable of producing a depth profile, i.e., a plot of concentration versus depth into the specimen. Such information should be especially useful in tear-down testing for failure modes For example, in polymer-metal delaminations, an oxide film may be detected between a polymer layer and a metallization layer indicating poor adhesion between the polymer and the metal oxide.

5. Chemiluminescence

The chemiluminescence technique measures light, generally of very low intensity, which is emitted in the course of a chemical reaction, particularly a reaction involving oxidation or degradation of materials, e.g , hydrocarbon oxidation. In these instances, part or all of the energy change of the reaction goes to activate an electronic state in some molecule rather than appearing as heat. The activated molecule returns to the normal state by emitting the excess energy as radiation. Chemiluminescence measurements are capable of giving kinetically and mechanically significant results for reactions too slow to measure by other means. The extreme sensitivity (down to reaction rates as low as 10^{-15} moles/year) of the chemiluminescence technique makes it unexcelled in cases where very slow reactions must be detected. This nondestructive technique should be useful in determining reaction rates associated with degradation of the polymeric materials in an array such as the cover, the encapsulant, adhesives, and pottants. In general, for transparent materials, the technique measures degradation of the bulk material. If the sample is opaque, it measures surface degradation. Theoretically, the technique is applicable to polymer-polymer interfaces by first measuring chemiluminescence of the interface and then measuring the separate components. Whether this can be done in practice remains to be seen.

The Chemiluminescence Apparatus

An artist's rendition of the chemiluminescence apparatus is presented in Figure IV-7. The heart of the apparatus is an RCA Model 4501/V4, 12-stage photomultiplier whose output can be displayed in analog (strip-chart recorder) or in digital (photon second) form. Below the photomultiplier head are a sequence of shutters, focusing lens, and a wheel containing filters. The sample is placed in the inner chamber of a two-compartment oven. The inner chamber is provided with electric heating elements, while the outer chamber is cooled continuously to avoid heating the aluminum box that contains mechanical controls. Provisions are included for metering-in two gases into the sample oven at rates read from flow meters.

Background counts with no sample in the oven are found to be a function of temperature (increasing with increasing temperature) and are larger in oxygen than in argon. This increase is not significant because the sample counts generally exceed those from the background by several orders of magnitude.

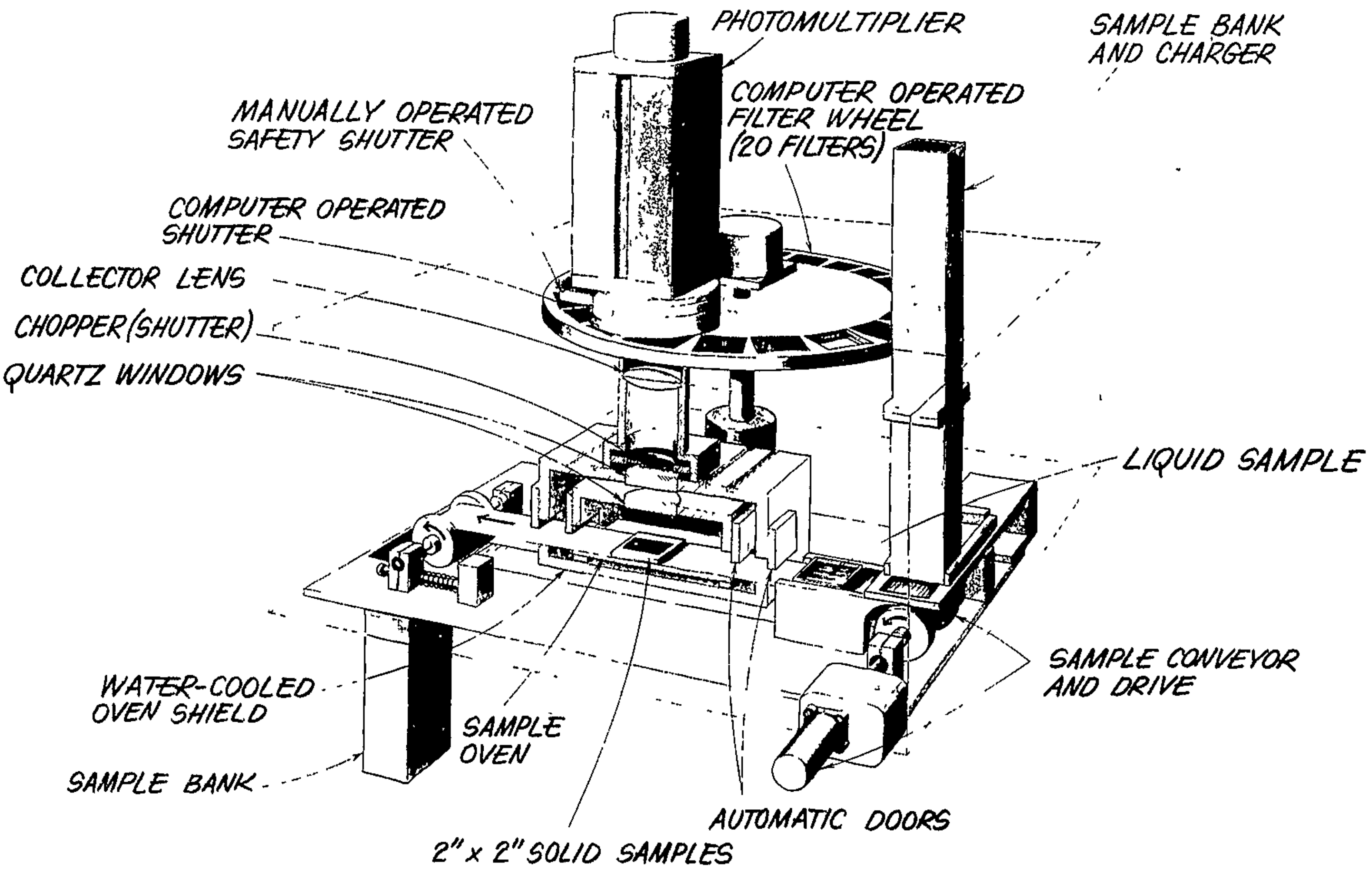

FIGURE IV-7. PHOTON COUNTING APPARATUS FOR CHEMILUMINESCENCE MEASUREMENTS OF SOLID OR LIQUID SAMPLES

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Test Repeatability

For most materials of interest, photon emission rates are 1 to 10^6 per second. The data are obtained as arithmetic means of the count in approximately a 10-second interval and the count can be automatically recorded or fed directly into a minicomputer for data treatment. If the individual count data have a standard deviation of σ, then by a theorem in statistics the standard deviation of a mean of N measurements is $\sigma/\sqrt{N}$. Thus, any desired level of precision can be obtained simply by using an appropriate sample size, N. For example, if extreme precision is necessary, the sample can be run overnight, over a weekend, etc., with the computer doing the data collection and statistical evaluation. Thus, a single sample can be measured with any desired precision.

Comparisons between samples, however, have in some instances shown differences too great to be attributed solely to the inherent variability of the instrument. Further testing will be required to determine whether such events are due to actual sample variability or instrument drifts. Variability among instruments and laboratories has not been determined

Cost and Other Information

Components are manufactured by RCA, Products for Research, and NJE Corporation. The instrument described was constructed by Battelle at a total cost of approximately $50,000.

The instrument weighs about 40 pounds and can be made portable. Optimal sample size is a 3-inch-diameter sample of any thickness, but smaller samples can be accommodated. The sample can be solid, liquid, or powder. The apparatus is extremely simple to run since it involves only placing the sample in the test chamber and taking the photon counts off a recorder

6. Gel Permeation Chromatography (GPC)

Gel permeation chromatography is used to measure the molecular-weight distribution of polymers. It involves selective adsorption of the polymer onto various size gel particles packed in a column. A differential refractometer detector and strip-chart recorder are used to record the resulting chromatogram. It is potentially useful for detection of molecular-weight reduction in polymers due to degradative chain scission. Low-molecular-weight additives such as plasticizers and residual monomer are also detectable, since the test output is an entire distribution curve.

Precision and Accuracy

Quano(IV-5) estimated precision of GPC for polydimethylsiloxane and polystyrene, the former with a broad molecular-weight distribution, the latter with narrow distribution His results are shown in Table IV-3. Estimating the standard deviation as one-third of the mean, coefficients of variation (i.e., standard deviation divided by mean) were calculated for the six table entries. For $\overline{M}_w$ and $\overline{M}_n$ (weight and number average molecular weights, respectively) they ranged from 5 to 7 percent and for $\overline{M}_w/\overline{M}_n$ from 1 to 2 percent. Accuracies were also estimated by Quano by comparing his results with suppliers specifications. Results are shown in Table IV-4.

TABLE IV-3. REPLICATE RUNS FOR ESTABLISHING THE PRECISION OF GEL PERMEATION CHROMATOGRAPHY (GPC)

Polymer	$\overline{M}_w \times 10^{-3}$			$\overline{M}_n \times 10^{-3}$			$\overline{M}_w/\overline{M}_n$		
	Max Value	Mean Value	Min Value	Max Value	Mean Value	Min Value	Max Value	Mean Value	Min Value
PS-97,200	105	98	91	99	91	84	1.08	1.07	1.06
Polydimethylsiloxane #145C-03	1,353	1,218	1,083	709	659	610	1.91	1.85	1.78
Polydimethylsiloxane #145C-02	142	132	123	59	54	49	2.50	2.45	2.39

TABLE IV-4. AGREEMENT BETWEEN SUPPLIERS DATA AND EXPERIMENTAL DATA FROM GPC

Polymer Sample	Suppliers Spec.		Molecular Weight Detector		
	$M_w \times 10^{-3}$	M_w/M_n	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
PS-97,200	97.2	1.06	98	91	1.07
PS-161,000	160	1.06	188	162	1.16
PS-411,000	411	1.06	387.6	364.9	1.06
PS-1.8 x 10^6	1,800	1.20	1,792	1,470	1.22
Polydimethylsiloxane (145C-02)	165.7	3.52*	132	54	2.45
Polydimethylsiloxane (145C-03)	609.4	4.05*	1,218	659	1.85
Polymethyl methacrylate	105	2.15*	99	35	2.80
Polycarbonate (053C-04)	47.9	2.65*	51	26.7	1.91

*Obtained by standard GPC techniques.

Although suppliers specifications are generally not a good standard for accuracy determination, they are sufficient for an approximate estimate. Overall, on the basis of suppliers' specifications, accuracy was generally poorer than precision, with deviations from suppliers' values as high as 20 percent, ignoring the spurious $\overline{M}_W$ values for polydimethylsiloxane. Quano indicated that precision could be considerably improved with a better pumping system and computerized data smoothing.

In spite of its apparent lack of ultrahigh precision, gel permeation chromatography provides much information on low-molecular-weight additives and provides a method of separation of components for use in infrared, mass spectrometry, etc. If one considers the principal types of changes that are likely to occur in a polymer during aging and looks at tools for the study of these changes, only GPC appears relevant for following chain scission and variation in low-molecular-weight nonvolatile components.

7. Gas Chromatography – Mass Spectrometry

Gas chromatography, a well-known technique for separating volatile organic compounds, can be applied both qualitatively and quantitatively to a wide variety of materials The technique involves the separation of components of a mixture by passing it through a column containing a stationary phase, either solid or liquid. Usually a gas is used to transport the mixture through the column. The separation is caused by differential adsorption of the various components. The detection of these components as they exit from the column may be accomplished in many different ways. This section deals only with mass spectrometric detection Whatever type of detection is used, gas chromatography is a very powerful tool because throughput can be effected very rapidly and compounds with only very minor physical or chemical differences can be separated.

In *mass spectrometry*, molecules of the material to be analyzed are introduced into a vacuum chamber, where they are then ionized. The resultant ion mixture is then resolved on the basis of the mass to charge ratio (m/e), usually by a magnetic sector analyzer, and the so-called mass spectrum – ion intensity versus m/e – is recorded. Usually the ionization is produced by impact of low energy (50 to 100-volt) electrons on the vapor molecules. In some cases, the ions formed originally may degrade to fragment ions and neutral species. Occasionally the parent ion is so unstable that it can be detected only indirectly by analysis of the major fragments. So-called chemical ionization may sometimes be useful in avoiding such cases. In this technique a reagent gas is introduced into the ion source at a pressure of about 1 torr. Some of the reagent gas molecules are ionized by electron impact and these ions then cause ionization of the sample molecules.

Mass spectrometry is useful in itself and also in combination with gas chromatography, where it can serve as a very sensitive detector. In either case the use of modern data-processing technology increases the power and usefulness of the technique. Two types of computer-based MS/GC analysis are used· repetitive scanning and selected ion monitoring. In the first, the mass analyzer repeatedly scans over a mass range selected by the operator. Scans take from 2 to 4 seconds. In a typical MS/GC run of 30 minutes, 400 or more spectra are stored in the computer. At the completion of the run a total ionization chromatogram is obtained by computer plot of the summation of the ion intensities for each scan versus scan number. The primary use of such plots is to determine which scans contain mass spectral data corresponding to each component of interest. However, since all of the data are stored in the computer, they can be examined and plotted in many different ways. A typical example is selected ion monitoring, in which the ion current at selected masses is plotted versus time (or spectrum number). These plots can be obtained either by having the computer extract the data acquired by repetitive scanning or by having the mass spectrometer continuously monitor selected ion masses. The latter technique has the advantage of better quantitative reliability and sensitivity at least 100 times better.

The usefulness of MS/GC in the study of molecular processes leading to possible degradation of solar-cell performance depends critically on the generation of volatile fragments as the polymer component of the cell degrades and on whether available apparatus is sufficiently sensitive to detect and measure the material that is exuded. In the case of the photolytic degradation of PMMA at room temperature(IV-6), several volatile products have been detected. In addition to CH_4, H_2, CO, and CO_2, methyl formate, methanol, and methyl methacrylate monomers have been detected. Studies of vacuum photodegradation at 30 C(IV-6) have shown that at least one molecule of carbon monoxide is produced per chain scission. The work cited in Reference (IV-6) provides encouragement to the concept that degradation of polymeric materials does produce detectable quantities of volatile products. In order to apply MS/GC to the detection of these volatile materials, specimen solar cells would have to be exposed to typical ambient temperatures and radiation in closed chambers. A constant flow of air or other gas would be maintained to sweep the volatile materials into the inlet of a MS/GC apparatus, either directly or after concentration by cold traps.

Sensitivity and Precision

Most modern MS/GC systems should be able to generate routinely good-quality spectra from 10 to 100 nanograms (ng) of material. State-of-the-art instruments are able to generate complete mass spectra on considerably smaller quantities (about 0.1 ng). In the selected ion monitoring mode, a MS/GC system should be capable of detecting subnanogram quantities of most volatile compounds.

Selected ion monitoring has been used to obtain quantitative analyses of biologically important compounds at concentrations below 1 ng/m.(IV-7) However, this sensitivity is not routinely obtained. Routinely, quantitative results can be expected down to about 10 ng/ml.(IV-8) Precision information has not been found and will have to be developed. The MS/GC combination looks promising enough to tentatively consider as a candidate test method for degradation studies.

Available Instrumentation

At present there exists a large variety of mass spectrometers, gas chromatographs, computers, and ancillary equipment. If MS/GC is eventually selected as a technique for monitoring solar-cell degradation, specific systems optimized for such monitoring can be assembled from commercially available components. Some typical systems that have been assembled are described below. All of the gas chromatographs that can be used on these systems are designed to use either conventional packed GC columns or high-performance glass capillary GC columns.

MS/GC Systems. The Finnigan Model 4000 gas chromatograph/dual electron impact (EI) and chemical ionization (CI) mass spectrometer system is capable of high sensitivity in either mode of ionization over a mass range of 1 to 1000 Daltons. The Model 4000 MS/GC is coupled to a Finnigan/Incos Model 2300 data system which includes a 32K memory Nova 3 computer, a high-speed Versatec 800-A electrostatic printer plotter, a 9-track magnetic tape system, and a Tektronix 4010 graphic display terminal.

The Finnigan Model 3200-E MS/GC system is used for CI mass spectral analyses. It is coupled to a Finnigan Model 9500 biomedical-type gas chromatograph. Control of the mass scan and data processing is handled by a System Industries Model 150 data system, consisting of a Digital Equipment Corporation (DEC) 16K PDP8M computer with EAE, a Diablo single-platter disk drive, a Tektronix 4010 graphic display terminal, and a Houston digital plotter.

One of the Finnigan Model 3200-F MS/GC systems has ion sources for either CI or EI ionization. It is also coupled to a Finnigan Model 9500 gas chromatograph and a System Industries Model 150 data system.

High-Resolution Mass Spectrometry. A typical high-resolution instrument is the A.E.I. MS-9 double focusing mass spectrometer, which can be updated so that it meets most of the specifications of the newer MS-902 Model. It has a demonstrated resolution capability of over 30,000 ($M/\Delta M$, 10 percent valley definition), although most high-resolution spectra are obtained at an effective resolving power of about 15,000. The MS-9 is coupled to a digital data system which permits on-line digital recording of high-resolution mass spectra at scans as fast as 10 seconds per mass decade. The system includes a 125-kHz analog-to-digital converter, peak detection and threshold logic, a digital tape recorder, and digital control logic necessary to provide data output in the form of gapped, computer-compatible digital magnetic tape records. Final computer processing is done on a large central computer. The instrument time and total man-hours required to obtain computer printouts of complete high-resolution mass spectra are very little more than those required to obtain a normal oscillographic recording of low-resolution mass spectra. Utilization of a large, high-speed computer for final data processing results in maximum versatility in the type and complexity of data processing obtainable.

8 Surface Energy Analysis

Wettability measurements combined with proper mathematical analysis of the data provide an excellent means of determining the cleanliness and bondability of surfaces which are to be adhesively bonded. A good example of the usefulness of the method is seen in some recent work by D H Kaelble.(IV-9) In this investigation the degradation with time of cleaned aluminum alloy surfaces was followed under various controlled relative humidities. The specific measurements made were determination of contact angles of several liquids having various surface tensions and polar-nonpolar properties. In the analysis it is assumed that the various interfacial energies can be represented as the sum of a component due to polar forces and a component due to dispersion forces. The quantity of interest γ_{SV}, the surface free energy of a solid in contact with a vapor phase (in this case, air plus water vapor), is not directly measurable. However, it can be determined by means of a procedure described by Kaelble in the cited publication and other publications. The analysis is summarized below

For a drop of liquid in contact with a solid, the following equations are valid:

$$W_a = (1 + \cos\theta)$$

$$W_a = 2[\alpha_L\alpha_S + \beta_L\beta_S]$$

$$\gamma_{LV} = \gamma_{LV}^d + \gamma_{LV}^p = \alpha_L^2 + \beta_L^2$$

$$\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p = \alpha_S^2 + \beta_S^2$$

$$W_a/2\alpha_L = \alpha_S + \beta_S(\beta_L/\alpha_L) \quad ,$$

where W_a is the work of adhesion, θ is the contact angle, γ_{LV} and γ_{SV} are the interfacial energies for the liquid-vapor and solid-vapor interfaces, and $\alpha_{L(S)}$, $\beta_{L(S)}$ are the square roots of the dispersion and polar contributions to the respective interfacial energies of the liquid-vapor and the solid-vapor interfaces.

In practice, γ_{LV}^d and γ_{LV}^p are known, θ is measured, and W_a is calculated from the first equation above. α_L and β_L are obtained from the square roots of γ_{LV}^d and γ_{LV}^p respectively, and a plot of (β_L/α_L) versus $W_a/2\alpha_L$ is made. This plot usually gives a straight line of slope β_S and intercept α_S.

Kaelble's work on aluminum alloys was successful in showing that surface energy analysis is applicable to detailed studies of metal surface degradation. Decreases with time were observed for the polar components of γ_{SV} and a strong dependence on relative humidity of the characteristic degradation time was found.

Because of its demonstrated utility in following the degradation of surface energy and, consequently, bondability of solid surfaces, surface energy analysis should be very useful in the fabrication of solar modules in that it provides a method for insuring proper bonding between the various components of the modules. However, the usefulness of surface energy analysis in studying failure modes and degradation rates of solar modules remains to be demonstrated. The technique can be used to detect changes in surface conditions on the outer face of the modules. If the detected changes can be shown to be related to one or more failure modes of the cells, then the technique is applicable. The fluids used to measure interfacial energies must not interact chemically with the solid under study if the equations cited above are to be valid. Much further research is needed to clarify these points Furthermore, information on precision, accuracy, sensitivity, etc., is not available and would have to be evaluated.

It is recommended that this test be tentatively considered as a candidate test and be studied further.

9. Summary — Chemical Measurement Techniques

- Of the recommended instruments, all but chemiluminescence and surface energy analysis are suitable in their present state of development. Chemiluminescence is adequately characterized only if the exact degradation kinetics are known. When they are not known, the data are treated empirically by calibration against another test method of known reliability.

- FTIR (including ATR) is one of the most powerful tools for studying degradative changes in polymers at their earliest stages.

- ESCA and AES will probably find their major application in destructive tear-down analyses

- GPC and the MS/GC combination are also powerful techniques for investigating degradative changes due to chain scission, etc.

- More information is needed on precision for all of the recommended tests, including interlaboratory precision, day-to-day precision, and interoperator precision. Further, a sensitivity analysis such as that developed by Mandel(IV-10) should be run for comparison of ESCA and FTIR for measuring carbonylization of polymers

C. ELECTRICAL MEASUREMENT TECHNIQUES SELECTED

1. Background

The electrical measurement category includes: (1) measurement techniques which involve monitoring the electrical output or characteristics (I_{SC}, V_{OC}, P_{max}, etc.) of the photovoltaic cell/module/array; (2) techniques which measure the electrical properties (carrier transport and polarization related phenomena) of the individual module/array constituents (i.e., other than cells), and (3) techniques which involve monitoring the electrical characteristics of special active or passive devices which, because of their sensitivity to degradation processes or products (e.g., ions), might be usefully incorporated into the module/array structure as detectors.

Electrical measurements are in principle applicable to the detection and diagnosis of environmentally related property changes in the majority of the constituents of the photovoltaic array, although their sensitivity may not be as high as alternative techniques in some cases. High-sensitivity measurements of the current-voltage (I-V) characteristics of environmentally stressed modules could reveal degradative changes in those components of the system which can affect the input of solar energy to the cells by reflection and/or absorption of the incident radiation (i.e., cover sheet, pottants, adhesives, other protective and optical control coatings) and in those which can affect the extraction of power from the module due to series resistance and shunting effects. However, in many cases, these measurements would not detect changes which might be early precursors to failure. Discrimination among several possible degradation modes which might affect a given module property (e.g., optical transmission) will, in general, not be possible from measurements of the I-V characteristics alone. Combinations of several measurement techniques will most likely be required for this type of assessment. Correlation of I-V characteristic changes with "first cause" molecular or atomic level changes is also unlikely without the assistance of other measurement techniques.

A key focus in the evaluation of all of the measurement techniques has been the need to identify techniques which can detect and quantify property changes in materials which are related to but precede obvious degradation or failure in the performance of the module. Direct measurement of the electrical properties of individual module constituents (e.g., cover sheets, pottants, interconnects) could lead to early identification and characterization of changes which are precursors to failure in these materials. These measurements may, however, require special arrangements (e.g., embedded electrodes), specially designed equipment, or destruction of the module. Here also, the initial identification of specific molecular- or atomic-level changes which are the cause for the measured changes in electrical properties will, in general, require supplemental measurements by other techniques which are more specific to the unique and distinctive properties of such species.

In summary, the property changes (either degradative or "degradation related") for which electrical measurement techniques offer significant potential for detection and quantification are:

- Changes in optical transmission (solar spectrum) of components in the light path between the cell and the incident radiation
- Changes in the types and densities of polar species in dielectric components
- Presence and changes in density of ionic species in dielectric components
- Corrosive attack of contacts, connections, and interconnects

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- Structural changes which affect carrier (i.e., electrons and holes) drift and diffusion in materials with measurable conductivities
- Changes in the glass transition temperature (T_g) of polymerics (This in turn can be related to more fundamental molecular-level changes. A detailed discussion of the relation appears in the thermal and mechanical techniques portion of this section of the report.)
- Degradative changes in the cell itself (This is felt to be an unlikely occurrence)

The specific electrical measurement techniques that are recommended as a result of this study and which are applicable either immediately or potentially to the measurement of the types of changes described above are

- Cell/module/array current-voltage characteristic measurements including dark and illuminated, forward and reverse, spectral response, and attendant analyses of key parameters
- Measurement of electrical noise associated with current crowding and carrier trapping effects
- Dielectric property measurements including determinations of dielectric constants and dielectric loss factors and their temperature and frequency dependence
- Electrical conductance measurements including surface and bulk conductance, thermal dependence, and photoconductance
- The use of specially incorporated passive and/or active electrical devices as selective and sensitive detectors.

These techniques and their immediate or potential areas of applicability are described in this section. Inelastic tunneling spectroscopy (IETS) was also investigated as a candidate electrical technique; however, its application to studies of degradation in photovoltaic-module components poses significant difficulties and it is not felt to be a strong candidate at this stage. A description of this technique including its principles and limitations for the present application is given in Section VIII.

2. Current-Voltage (I-V) Characteristics of Cells/Modules

Device and array I-V characteristics are the most commonly measured parameters in assessing the performance of photovoltaic devices and diagnosing the causes of degradation/failure. Virtually all photovoltaic installations and all laboratories investigating photovoltaic devices and modules incorporate some type of capability for making this most basic measurement. The technique is familiar enough to personnel working in the photovoltaic area to justify a relatively cursory description of the basic equipment.

The basic components of an I-V characteristic measurement installation are an illumination source, a variable load for the photovoltaic device, a "current sensing" resistor, and some means of reading and recording the measurement. A schematic of a relatively simple form of such a setup is presented in Figure IV-8.

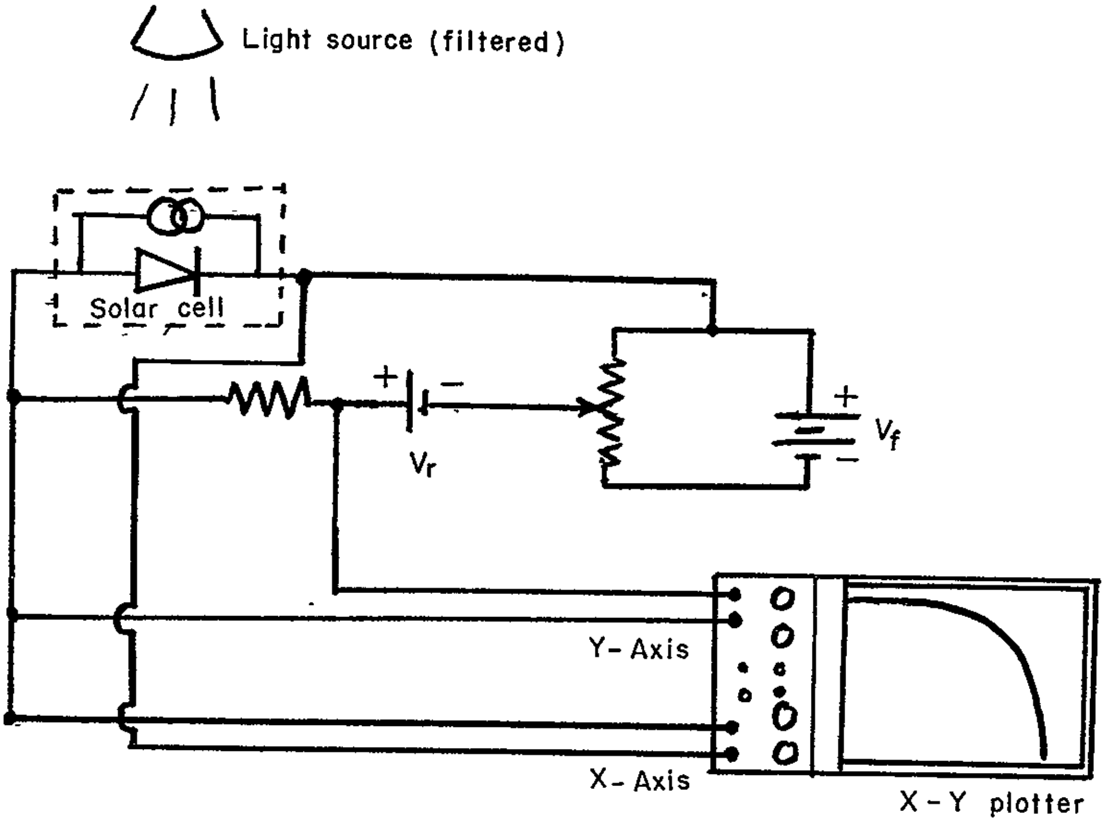

FIGURE IV-8. SCHEMATIC OF SIMPLIFIED SETUP FOR MEASURING CURRENT-VOLTAGE (I-V) CHARACTERISTICS

Light Sources

Light sources which are commonly used for these measurements include tungsten halide lamps (either in conjunction with a water filter or directly incorporating a dichroic filter to allow elimination of unwanted infrared portions of the lamp spectrum), steady-state xenon arc lamps, pulsed xenon lamps and direct sunlight. Carbon arc sources generally contain too much ultraviolet radiation for this application although this radiation can in principle be controlled by filtering. In general, xenon illumination sources, with proper filtering, provide a better match to the actual solar spectrum than other types. They are also the most readily adaptable to uniform large-area illumination (up to 5.5-m-diameter circle for pulsed xenon arc sources)(IV-11), but are the most expensive. Direct sunlight is obviously the most desirable illumination source; however, lack of control of temporal availability, intensity variations, and, to some extent, spectral-content variations (which may be important in degradation studies) dictate the use of simulation sources supplemented with direct solar calibrations for many analytical applications.

The light source controls the short-circuit current of the photovoltaic cell. (Strictly speaking, it controls the light-generated current, however, the two are essentially synonymous except in cases of extreme internal power dissipation.) Since the short-circuit current (I_{SC}) is the most critical parameter to be established in accurate and precise solar-cell-performance measurements, the characteristics of the light source are critical factors in determining the limits of precision and accuracy that can be expected in such measurements. The temporal and spatial variations of the light source, including intensity and spectral (temporal only) variations are the principal factors limiting the precision, accuracy, and repeatability of contemporary illuminated I-V characteristic measurements.

Spatial uniformity of beam intensity varies with the optical system used, with the manufacturer, and with the test plane area. A typical tolerance figure for a good-quality, large-area, xenon-arc illumination system is of the order of ±2 to ±3 percent. Poorer quality equipment yields tolerances of ±5 to ±10 percent even for considerably smaller illumination areas. Quoted values for beam power stability are generally in the range ±1 percent for periods of 100 milliseconds to 24 hours. This figure degrades as the tube ages and can approach ±3 percent as the tube nears the end of its useful life.

Data on spectral variability and spectral stability of illumination sources are much more difficult to find. Data on lamp-to-lamp spectral variability for the tungsten halide, dichroic, filter-type lamps are not available, although a manufacturer noted that lamp intensity variations of up to 30 percent for the UV and visible portions of the output are known to occur. The situation is equally obscure for the variability of xenon lamps as fabricated, although here one manufacturer of xenon-arc solar simulators gave an estimate (no hard data) of ±10 percent per spectral interval. Variations in spectral energy distribution with age are not well documented for either type of lamp; however, in this case there is general agreement among users and manufacturers both on the type of trend one might expect and the qualitative magnitude of the trend over the life of the lamp.

The tungsten halide lamps tend to degrade by two somewhat compensating mechanisms: (1) localized changes in the filament that manifest as series resistance increases and that result in increases in the color temperature at one or more points on the filament and (2) changes in the resistance of the lamp base which tend to shift the lamp spectrum toward the longer wavelengths. These changes are projected to occur near the very end of the lamp's life and significant changes in the spectral energy distribution of these lamps are not projected during any major portion of their operational lifetime. This projection is in agreement with a NASA LeRC study(IV-12) on the time variation of the output of one such lamp.

The primary changes which accompany the aging of xenon-arc lamps are the deposition of tungsten on the envelope of the tube and changes in the operational conditions of the lamp associated with increasing arc gap and, in some cases, internal pressure changes. The latter two are generally felt to be less important than the former. These changes are projected to have an impact on the shorter wavelength portion of the lamp spectrum, and the net effect over the lifetime of these lamps is, in general, felt to be small. Quantitative data to support this contention have not been found.

One of the primary reasons for the past lack of serious concern over the spectral variability of solar simulators in the photovoltaic field is that the use of standard cells with spectral response characteristics reasonably well matched to the devices being tested to calibrate the intensity of the source negates the impact of spectral differences on the measurement. This argument is soundly based for normal devices; however, for devices or modules undergoing degradation modes which result in shifts in the spectral response, the degree of match with standard cell spectral response may not be adequate. A significant alteration of performance due to degradation would still probably be detectable under such conditions, however, the quantitative interpretation of the effects of the change as related to some reference set of conditions (e.g., AM 2) would be questionable. Similar questions could arise in attempts to relate degradative changes to commonly based reference conditions when the illumination source is natural sunlight, since significant variations in spectral distribution can arise here also (although sunlight measurements are generally made under the best of conditions, i.e., clear days, sun near zenith).

The major conclusion from the above observations is that spectral response measurements will play a key role in studies on devices and modules involved in aging and degradation studies. This point is addressed again in the discussion of light-generated current measurements later in this section. If illuminated (solar spectrum) I-V characteristics are to play a significant role in the quantitative assessment of aging and degradation effects having an impact on the optical properties of key transmissive components, more attention will have to be focused on the periodic characterization of the spectral energy distribution of the illumination source.

Solar simulators incorporating an illumination source, filters, and other necessary optical components are commercially available from Spectrolab, Inc., Sylmar, California; Oriel Corporation of America, Stamford, Connecticut; and Schoeffel Instrument Corporation of Westwood, New Jersey; costs range from about $3,000 up to $50,000 or more, depending on size, optical accessories, etc.

I-V Characteristic Measurement Equipment

Several degrees of sophistication are available in constructing I-V characteristic measurement installations The most basic loading scheme uses a bank of fixed-value load resistors which are inserted one at a time or in successive appropriate combinations to obtain discrete point I-V plots. The most sophisticated installations incorporate a computer-controlled power supply with automatic data acquisition and analysis by the computer. Between these extremes are various versions of manually and automatically controlled variable power supplies with readouts ranging from meters with hand recording of data through high-quality X-Y plotters and thermal recorders. Detailed descriptions of such installations and the precautions necessary to insure accurate data (e.g., control and recording of temperature, four-wire connections, and minimizing lead lengths) are contained in publications and reports by a number of investigators and thus will not be elaborated on here. The reports of the NASA Lewis Research Center Solar Energy Group are good sources of information in this area.(IV-13, IV-14) If reasonable care is exercised in the design and construction of the measurement system, then high degrees of sensitivity, precision, and accuracy are, in principle, achievable. The measurement system will not, in general, be the limiting factor for precision, accuracy, etc., in illuminated I-V characteristic measurements. Measurement-system (i.e., exclusive of light source effects) accuracies of the order of a few tenths of a percent or better should be achievable in practice for this type of measurement.

For dark I-V characteristic studies, banks of high-accuracy, high-stability resistors coupled with a good constant voltage source will generally provide the highest accuracy and repeatability. Using current specifications for high-quality voltmeters and special-order resistors, calculated accuracies of the order of hundredths of a percent can be determined for these measurements. In practice, various noise sources may preclude the realization of accuracies of this order, particularly at the lower current levels.

I-V Characteristic Diagnosis

Environmentally induced changes which degrade the performance of the encapsulated cell/module will manifest themselves in three primary areas

- Reduced light-generated current
- Increased series resistance
- Reduced shunt resistance

Analytical studies of measured I-V characteristics can provide quantitative information on changes associated with these three degradation modes Figure IV-9* provides a qualitative indication of the effects of relatively large changes in series and shunt resistances on the forward and reverse characteristics of solar cells Deviations from the ideal characteristic which could arise from poor cell fabrication are also illustrated. Analysis of dark and illuminated forward characteristics can provide valuable information on quality-control problems of this type. I-V characteristic measurement and diagnostic techniques which can be used in developing quantitative assessments of each of the above degradation modes are discussed below.

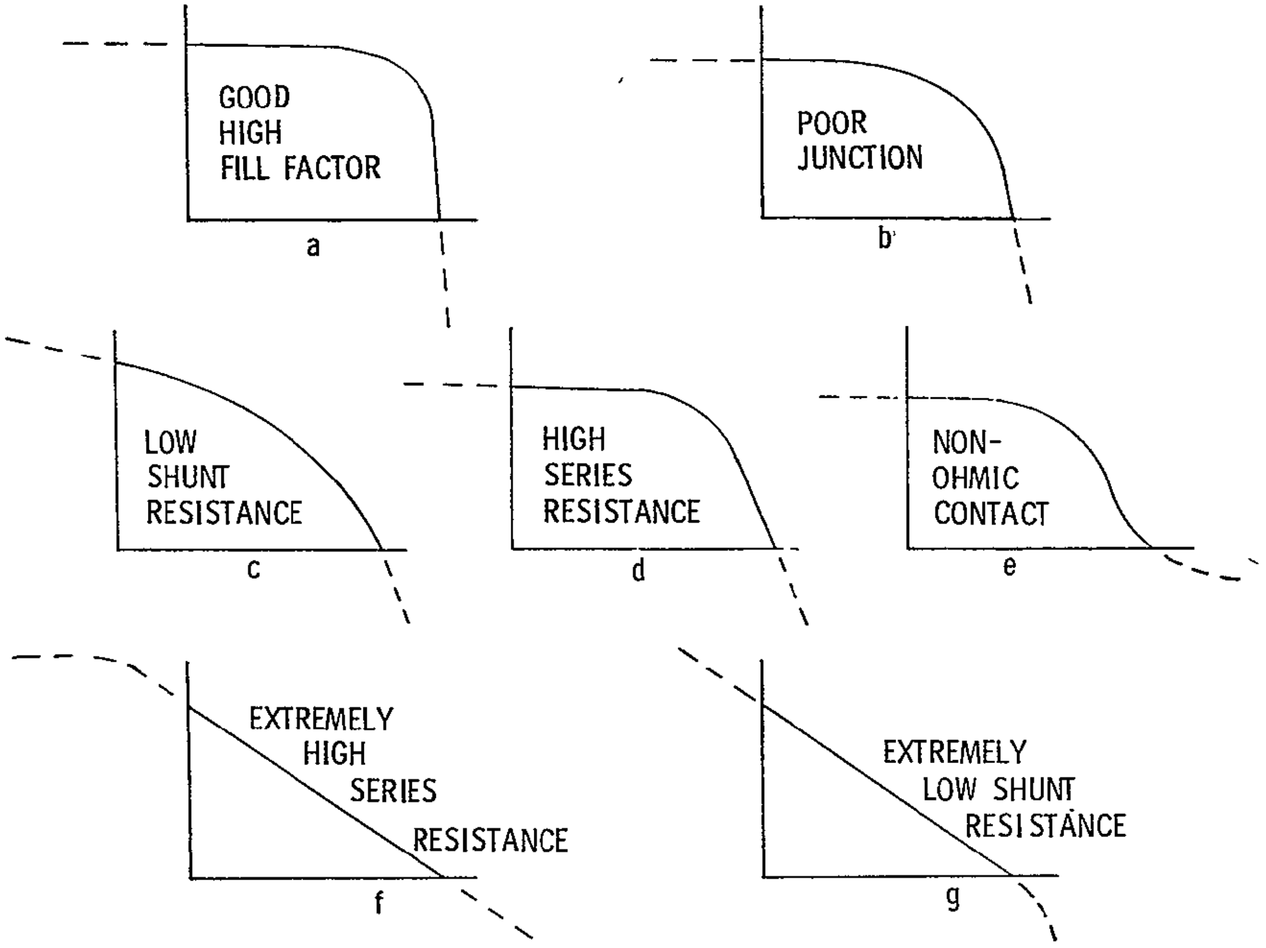

FIGURE IV-9. SOLAR CELL I-V CHARACTERISTICS – EFFECTS OF UNDESIRABLE FACTORS

Reduced Light-Generated Current. The light-generated current (I_L) is a measure of the light which reaches and is absorbed in the photovoltaic cell. Reductions in the light-generated current can be related to degradation-associated transmission losses (due to reflection and absorption) in the components of the module between the cell and the incident photons. (It is

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*Adapted from Reference (IV-13)

ORIGINAL PAGE IS
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assumed that degradation of intrinsic cell factors, e.g., minority-carrier lifetime, will not occur.) Light-generated current is normally determined by measuring the output current of the illuminated cell near the zero bias (short circuit) condition. When extremely high series resistance is present it may be necessary to reverse bias the cell in order to obtain the light-generated current. Under natural or simulated sunlight illumination, the light-generated current reflects the total integrated contribution over the entire spectrum of the illumination source. In aging studies involving the degradation of the optically critical components of the module, it will be necessary to make comparative measurements and assessments on encapsulated devices whose spectral characteristics (i.e., spectral response) may be changing with time and may ultimately vary significantly from those of the standard cells used in calibrating light sources. Further, it will be necessary in these studies to compare measurements which are widely separated in time. Meaningful assessments and comparisons under these conditions will require that either (1) the spectral match between the illumination source ("natural" or simulated sunlight) and the reference solar illumination conditions (e.g., AM1 or AM2) is close and can be demonstrated not to vary significantly with time (e.g., due to light-source aging or replacement) or (2) the spectral characteristics of both the test device and the illumination source be fully characterized in conjunction with each measurement. As is pointed out in the discussion of light sources for solar simulation earlier in this section, there appears to be a significant lack of hard data on the spectral stability and variability of present-day illumination sources. It is clear that significant spectral variations, unless identified and characterized, could confound the interpretation of life-testing data. Additional soundly based information on this aspect of performance testing is needed to assess the requirement (for the purposes of degradation studies) for periodic measurement of the spectral characteristics of light sources. It is also clear that measurements of the spectral response of modules whose optical properties are degrading will be essential in any quantitative assessment of the degradation and in the interpretation of its effects under various reference or actual operational conditions. For example, the comparison of measurements made under differing illumination conditions (i.e., "natural" or simulated sunlight) by transformation to reference conditions (e.g., AM1) requires a knowledge of the spectral response of the module and the characteristic spectral distributions of the various illumination conditions. Spectral-response measurements should be made a routine part of testing in degradation studies unless it is known that optical properties of key components will not be affected by degradation or unless the spectral impact of the degradation is already well characterized.

Spectral-response measurements are measurements of the light-generated current of the device as a function of the wavelength of illumination. The two commonly used illumination sources in these measurements are monochromators and narrow-band-pass filters in conjunction with conventional light sources. These types of setups and variations using white-light bias and chopped-light sources are described in Reference (IV-11). Monochromators provide continuous coverage of the spectrum but are limited in intensity, beam size, and uniformity. The use of the band-pass-filter approach overcomes these limitations but sacrifices the continuous scanning feature. Absolute accuracy in spectral response is a substantial problem.(IV-11) Peak accuracies are projected as being no better than ±5 percent at present, with errors of ±20 percent being not unusual in practice. This is highly important in degradation studies, where it may be necessary to measure changes of the order of tenths of a percent with high precision. In view of the importance of spectral-response measurements in evaluating optical degradation, as cited above, efforts to improve spectral-response measurement techniques or to develop more suitable techniques seem warranted. One concept which might prove suitable is the development of a spectral-response measurement system using the Fourier transform interferometric principle presently employed in FTIR studies (see discussion on chemical techniques in Section IV-B). The potential advantages in sensitivity, resolution, etc., of the Fourier transform spectral-response (FTSR) technique need to be evaluated.

Increased Series Resistance. Increases in series resistance will degrade module performance through increased internal dissipation of power. Increases in series resistance can result from corrosive attack of contact metallization and electrical interconnects or from stress-induced work hardening and fracture of connections and interconnects. In principle, then, the analysis of the I-V characteristics to determine series resistance can be a means of quantitatively evaluating degradative changes in these components due to corrosion or stress

There are four basic techniques which are generally used to determine the series resistance from I-V characteristics. The most widely used technique at present is the method published by Wolf and Rauschenbach(IV-15), which is based on the fact that under two levels of illumination any difference in the voltage across the load, under conditions of constant diode current, must be due to differences in the voltage drop across the series resistance associated with differences in the magnitude of the load currents. Another commonly used and somewhat simpler technique is to measure the slope of the forward characteristic. Assuming the lumped constant model as described in Section II of this report, the I-V characteristic is given as

$$I = \frac{R_{sh}}{R_s + R_{sh}} \left[I_L - I_o \left(e^{\lambda(V + IR_s)} - 1 \right) - \frac{V}{R_{sh}} \right]$$

The second derivative can be obtained as

$$\frac{d^2I}{dV^2} = \frac{\lambda^2 I_o R_{sh} e^{\lambda(V + R_s)}}{R_s + R_{sh} + \lambda I_o R_s R_{sh} e^{\lambda(V + IR_s)}} \left(1 + R_s \frac{dI}{dV} \right)^2 \quad .$$

Setting this equal to zero, the slope extremum corresponding to the higher voltage portion of the forward characteristic is obtained as

$$\frac{dI}{dV} = -\frac{1}{R_s} \quad .$$

As long as the determination is made on the linear portion of the forward characteristic the voltage region chosen for the slope determination is not critical.

A third, and probably the most accurate, technique is to determine the short-circuit current (I_{SC}) and open-circuit voltage (V_{OC}) for a range of intensities and to plot these pairs as individual points on an I-V curve. This gives a characteristic which is free of the effects of series resistance (again assuming $I_L = I_{SC}$). This characteristic may then be compared with either the dark forward or the normalized (by subtracting I_L) light forward characteristic to determine the series resistance.

The fourth approach is the use of computerized curve-fitting techniques to determine parametric values which will result in a match of the measured I-V data to theoretical diode curves.(IV-16) This method permits accurate determination of reverse saturation currents and junction factors (A_1), as well as series and shunt resistances in cases where the theoretical relationship fits the experimental data. However, difficulties can be encountered when multiple effects of approximately equal magnitude are superimposed. The ultimate accuracy and precision of this method for aging studies needs to be evaluated through comparison with the results of other methods.

It is not clear whether or not any of the described techniques for determining series resistance will provide adequate sensitivity, accuracy, and precision to allow detection of corrosion or stress-induced changes in their earliest stages, although advanced stages should be clearly identifiable. Since long-term stability of light sources is not a factor in these determinations, the principal limitations should be those associated with the measurement instrumentation. Measurement errors can, in principle, be reduced to tenths or possibly hundredths of a percent as discussed above. The practical problems of making series resistance measurements that meet the demanding requirements of photovoltaic module aging tests have yet to be addressed. It is apparent however that more care and attention to detail than has previously been exercised in such measurements will be required for this application.

Reduced Shunt Resistance. Shunting of the cells could result from changes in the conductivity of surrounding media due to increased ion concentrations, electrical breakdown, or other factors affecting carrier transport properties. The determination of the shunt resistance of cells and modules from I-V characteristics is usually made from the slope of the reverse characteristic at some fixed reverse bias point. For devices whose characteristics conform to the theoretical relation given above, the slope of the reverse characteristic approximates

$$\frac{dI}{dV} \sim \frac{1}{R_s + R_{sh}} \quad .$$

In practice, the reverse characteristics of solar cells are often found to be "soft" and not in conformance with the ideal diode characteristic. This makes the absolute determination of shunt resistance by this method difficult, and the results of this type of measurement are generally interpreted as qualitative rather than quantitative indicators of device merit. The computerized curve-fitting techniques cited above offer an alternative means of evaluating the shunt resistance, although deviations from the ideal diode characteristics will present equally formidable difficulties in this approach.

While presently used analytical techniques are not adequate for absolute determination of the shunt resistance, the possibility of quantitative assessments of *changes* in this parameter is not necessarily precluded. Comparison of initial values, determined by the slope of the reverse bias characteristic, for example, with values measured after aging or environmental stress could provide a quantitative indication of the progress of degradative changes affecting this parameter. This possibility needs to be evaluated. Direct measurement of the electrical properties of encapsulants could also provide a means for the early detection and characterization of changes leading to shunting effects. This technique is discussed later in this section.

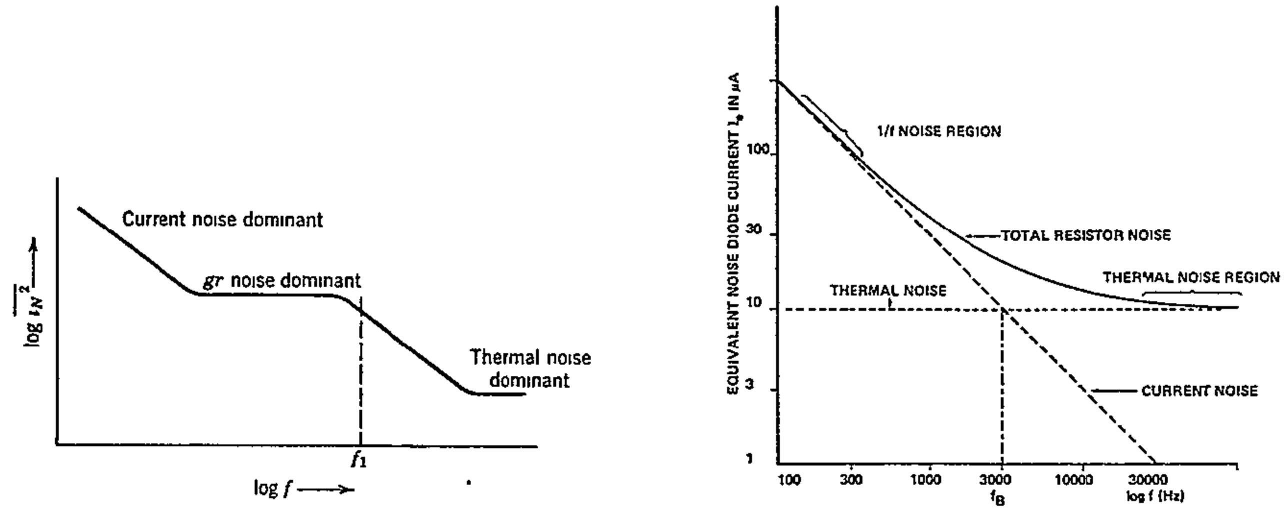
3. Electrical Noise

Microscopic random fluctuations in the flow and density of electrons result in measurable "noise" currents in electrical components and devices. These noise currents arise from several sources, including thermal motion of the charge carriers (thermal or Johnson noise), the randomness associated with the transport of carriers across a barrier or discontinuity such as a diode junction (shot noise), and the trapping and emission of individual carriers in the bulk semiconductor (generation-recombination noise). The spectral density of the above types of noises is "white" (i.e., independent of frequency), although in some cases (e.g., generation-recombination noise) an upper limit cutoff frequency is observed. There is another type of noise associated with the flow of current through components and devices. This noise is called current or 1/f noise and has a power spectrum of the form

$$\overline{i_N^2} = \frac{AI^2\Delta f}{f} \quad ,$$

where $\overline{i_N^2}$ is the mean square noise current in the band width Δf, I is the dc bias current, f is the frequency at which the measurement is made (or centered), and A is a proportionality factor. Current noise with a 1/f-type power spectrum has been observed to occur under a number of different circumstances, including the flow of current through bulk semiconductor materials(IV-17), through film-type resistors(IV-18), and through defective contacts(IV-17), and in the presence of surface and edge currents in junction devices(IV-19).

Noise current spectra for a semiconductor(IV-20) and a thick-film resistor are shown in Figure IV-10. At the lower frequencies, the current noise is the dominant contribution. The presence of unusual conditions such as cracks and other defects in the bulk semiconductor material or defective contacts results in increases in the low-frequency noise above normal levels. The potential applicability of current noise measurements as a diagnostic tool for electronic device and component quality control and acceptance testing has received considerable attention in the 1960's and 1970's and some limited use of the technique in this regard has resulted. The National Bureau of Standards has established a standard method (Method 308 of MIL-STD-202B) for measuring the noise characteristics of resistors and there are two major manufacturers of equipment that is intended for the measurement of electrical noise associated with current flow through electrical components and devices (the Quan-Tech Division of Scientific Atlanta, Inc., and Hewlett Packard).



a. For Semiconductors

b. For 5000-Ohm-Thick Film Resistor

FIGURE IV-10. NOISE CURRENT SPECTRA

An example of an instrumentation arrangement for measuring the noise frequency spectrum of a component or device is shown in Figure IV-11. In biasing the component/device under test, it is essential that a low noise power supply be used. Lead acid batteries are commonly employed for this purpose in laboratory noise-measurement systems. The basic measurement system consists of a low-noise preamplifier coupled to a wave analyzer and an averaging circuit with an appropriate meter for displaying the output. Standard noise sources are available from several manufacturers (e.g., Sylvania makes a Type 5722 noise diode) and provide a means of calibration for the system.

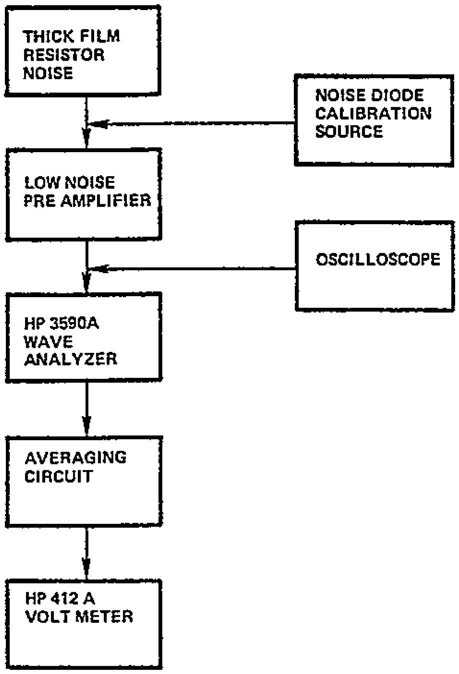


FIGURE IV-11. BLOCK DIAGRAM OF THE NOISE MEASUREMENT SYSTEM

Measuring changes in the low frequency 1/f noise is a potentially sensitive means for the early detection and characterization of corrosive attack of the contact and interconnect metallization. The technique should be directly applicable to the detection of contact corrosion involving the interface between the silicon surface and the contact metallization such as has been observed in the unprotected Ti-Ag contacts. The use of the technique to evaluate the corrosion of interconnects will probably require a more indirect approach because the sensitivity of the noise-measurement system is lower for low-impedance test samples. A possible approach in this case would be to incorporate thin-film resistive elements, using the interconnect metal as the resistive material, into the module strictly for the purpose of monitoring corrosive attack of the interconnect material.

Current noise has been found in many cases to be highly sensitive to defects in components and devices, with variations as great as several orders of magnitude between normal and abnormal units being observed. However, attempts to gain some insight into the magnitude of the effect one might anticipate for the present application through discussions with equipment manufacturers and authorities in the field revealed no published or unpublished information on experimental investigations of the quantitative correlation between changes in 1/f noise and progressive deterioration of device contacts. Opinions were uniformly positive concerning the feasibility and potential of the concept; however, it was felt that experimental data to support (or refute) these judgments do not currently exist and tests would be required to establish ideal measurement conditions, sensitivity, etc., for this application.

In summary, it is felt that the use of current noise measurements to detect and quantitatively track the progress of corrosive effects in photovoltaic devices is of sufficient potential to warrant further investigation. Commercially available composite noise measurement units are available at costs in the range \$3 K to \$15 K with quoted accuracies of the order of ±0.5 dB and precisions of ±1 dB (noise figure). These units are generally not suitable for the evaluative measurements required here, and a custom-built system similar to that illustrated in Figure IV-11 would be more appropriate. Costs of custom-built systems can vary considerably, however, an adequate system could be established for approximately \$10 K.

4. Dielectrometry

Dielectrometry has proven to be a useful tool for in-process monitoring of the degree of cure of polymeric materials.(IV-21, IV-22) Dielectrometry is also of potential interest in studies of polymeric degradation and its relation to the lifetime of photovoltaic arrays. In addition to being sensitive to several of the factors associated with degradation processes (e.g., absorbed H_2O, ions, polar polymeric breakdown products), it is nondestructive and applicable to all dielectric materials.

The major parameters of interest in dielectrometry are the dielectric constant, ϵ', and the dielectric loss tangent or dissipation, D, given by

$$D = \mathrm{Tan}\ \delta = \frac{\epsilon'}{\epsilon''} \quad ,$$

where δ is the dielectric loss angle and ϵ'' is the imaginary part of the complex dielectric constant

$$\epsilon = \epsilon' - i\epsilon'' \quad .$$

The dielectric constant is defined as the ratio of the permittivity of a dielectric material to the permittivity of free space. It is, then, a measure of the polarizability and, hence, of the presence of polar species in the material. The loss tangent is a measure of the energy dissipated in the material as a consequence of the attempt of dipoles, contained therein, to follow the variations of an impressed ac electric field. It is, then, sensitive to factors which determine the mobility of polar species, including the properties of the surrounding medium. Either of these parameters (ϵ' and D) can, under proper conditions, provide a means for detecting and identifying specific polar groups which might be present as a result of environmentally induced degradative changes, impurity absorption/diffusion, etc. The loss tangent is generally the more sensitive of the two. The dielectric loss tangent is somewhat analogous to the loss tangent in dynamic-mechanical-property measurements and exhibits similar characteristics behavior (e.g., temperature dependence of peaks, sensitivity to glass transition temperatures, etc.) in many cases.

A study of the sensitivity of the loss tangent to the presence of known quantities (determined by IR analysis) of specific polar groups, including carbonyl groups, methyl groups, hydroxyl groups, and terminal vinyl groups in polyethylene (a nonpolar polymer) has recently been published.(IV-23) Other studies demonstrating the basic applicability of the technique to structural investigations and degradation studies(IV-24) have also been published. Information that would permit a general assessment of the capabilities of the technique in diagnosing degradation in materials and structures associated with photovoltaic modules, particularly its sensitivity, accuracy, etc., for providing quantitative assessments of changes is not available. However, the potential is sufficiently apparent to warrant some consideration of an experimental effort to develop some of this information.

Techniques used in measuring dielectric constants and dielectric loss generally fall into one of two categories – null methods and resonant circuit methods. The various types of capacitance bridges use null methods whereby the unknown in one arm of the bridge is balanced out against impedance elements in other arms. The resolution of the balance arms and the sensitivity of the balance indicator are key factors in the accuracy of this technique. Null-type measurements are generally suitable for measurements in the frequency range of 0 to 10^7 Hz. At higher frequencies, resonant circuit techniques are more suitable. In this technique the unknown is incorporated into a tunable microwave resonator which is then tuned through resonance. The loss is measured by the width of the resonance curve. An interesting discussion of one approach to resonant circuit measurements of dielectric properties of polymers appears in Reference (IV-25).

The key variables in dielectric spectroscopy studies are frequency (of the ac electric field) and specimen temperature. As the frequency is scanned from very low to higher frequencies, gradual steplike drops in the dielectric constant accompanied by peaks in the loss curve are observed at specific frequencies. These correspond to resonances of specific dipole species as they reach a point where maximum energy is absorbed from the field. At higher frequencies these species can no longer respond fast enough to follow the field and, hence, their contribution to the dielectric constant drops out. The presence of ions in a material can significantly alter the low-frequency loss characteristic. Varying the temperature while monitoring dielectric characteristics at a fixed frequency allows the identification of phase changes and crystal structure changes through their effects on molecular mobility. These also will be manifested as inflection changes in the dielectric constant and loss curves.

Systems for studying the dielectric properties of materials over the lower frequency regions are available commercially. Some of these units can be adapted for varying both frequency and temperature and they sell for $10 K to $20 K. Instrumental setups for resonant cavity-type measurements are generally custom built. In general, the sensitivities, accuracies, and precision that these instruments provide in measuring dielectric parameters are difficult to ascertain, although accuracy figures of the order ±1 percent for loss tangent have been quoted. Testing to develop a reasonable data base in these areas is advisable.

5. Electrical Conductivity/Resistivity

As with dielectrometry, dc electrical-conductivity measurements have been used to monitor curing cycles in polymeric materials.(IV-26) The volume conductivity of dielectric materials is sensitive to the presence of mobile ionic species and moisture, and monitoring of this parameter could provide a sensitive means of detecting significant changes in these factors as precursors to corrosive degradation, electrical shunting effects, etc. The basic principles of conductivity (or resistivity) measurements are familiar enough to warrant no further elaboration. Detailed procedures for measurements on high-resistivity dielectric materials such as glasses and polymers are available from published test standards and procedures.(IV-27) Since these materials can have extremely high volume resistivities, care must be exercised in electrode arrangements to allow distinguishing between surface and volume conductive effects. Four-point contacting is recommended where feasible.

Sensitivities, costs, etc., of instruments for measuring electrical conductance measurements are discussed earlier in this section. Measurements in the higher resistivity ranges will sacrifice some of the quality (e.g., accuracy, precision) obtained at lower resistivities, and in some cases grounding and shielding requirements will increase.

The conductivity of dielectrics can be highly sensitive to temperature so this parameter must be monitored and/or controlled during such measurements. The temperature dependence of the conductivity of dielectrics can also reveal significant information about the conductive species present, their activation energies, etc.(IV-28) Glow-curve-type measurements, in which excited carriers frozen into trapping levels associated with structural defects and discontinuities are gradually released by raising the temperature, thereby giving discrete peaks in the conductivity at characteristic temperatures, can also be used to derive information about the nature and density of microscopic defects.(IV-28, IV-29) This type of measurement could be useful in degradation diagnostic studies, although other available laboratory techniques might provide more direct and easily interpretable identifications.

Simplicity and portability of instrumentation are major features of electrical-conductivity measurements. These characteristics allow consideration of its use for monitoring dielectric materials in on-site situations. Metal electrode patterns and buried electrodes of appropriate geometries could be incorporated as integral parts of photovoltaic modules for field-test purposes. This could be an important role for electrical-conductivity measurements in array-lifetime studies. As a calibration step to allow proper interpretation of data obtained in the field, there is a need for some preliminary (or possibly parallel) measurements to establish baseline properties and sensitivities to controlled impurities (e.g., specific types and quantities of ionic species) for materials which are being or will be used in photovoltaic modules.

6. Special Detectors

The incorporation of special detectors, test patterns, and test structures as integral parts of field-installed arrays is mentioned in several contexts in this session (e.g., under optical techniques). There are several electrical devices of this type which might be usefully included in the module/array design. Some of these are alluded to in the preceding sections (e.g., in the discussion of electrical noise measurements for corrosion detection). Other possibilities suggest themselves, and it is appropriate at this point to briefly mention the general concept of special electrical detectors and some specific candidates.

The incorporation of special patterns and devices has been used extensively in the electronics industry and has been discussed for use in process monitoring(IV-30) in conjunction with the LSSA Project. The extension to degradation monitoring and lifetime-prediction studies is a logical one. The basic concept is to incorporate, as an integral part of the fabricated array, devices which exhibit high sensitivity to anticipated degradation processes and products In the electrical measurements category, both active and passive electrical devices can be considered as candidates. The desired attributes of special detectors include:

- Test devices should offer significant advantage in sensitivity to degradative factors over conventional measurements (i.e., solar cell I-V characteristics)
- Incorporation of the device should not significantly affect module/array design or baseline performance (including localized operating temperature)

- The test device and ancillary connections should not, themselves, contribute to the degradation or contamination of the module.
- Test devices should be kept as simple as possible for maximum reliability.

Devices and structures whose electrical resistance (as measured by current flow at a fixed bias) is markedly affected by degradation-related factors constitute the major class of potential special detectors in the electrical measurements category. A typical example of a simple device might consist of a thin film (to maximize sensitivity) of a metal or other conductive material which is subject to corrosive attack by suspected alien species. The rate of change of the resistance of the device will be proportional to the rate of corrosive attack and, hence, to the amount of the corrosive species present. Materials sensitive to water or oxygen are obvious candidates. Others which might suggest themselves as chemical products resulting from degradation of specific encapsulant materials are identified. Field-effect devices which are sensitive to the presence of ions at their surfaces offer another detector possibility, as does the incorporation of strategically located miniature strain gages.

Many of these devices can provide high sensitivity by choosing proper geometries. The fact that, in the case of resistive devices for example, well-developed electrical measurement instruments (i.e., current and voltage meters) are used further ensures high sensitivity, precision, and accuracy (see earlier discussion of I-V measurements in this section).

7. Summary – Electrical Measurement Techniques

- Spectral-response measurements should be used in a key role to study devices and modules involved in aging and degradation investigations.
- Periodic characterization of illumination source spectral characteristics will probably be required if illuminated I-V characteristics are to play a significant role in the quantitative assessment of degradation processes.
- The quality (e.g., sensitivity, precision) of the information currently derived from the diagnosis of I-V characteristics (e.g., series resistance) is not adequate for diagnostic studies of degradation in devices or modules having lifetimes approaching the goals of the LSSA program. The potential for improvement to an adequate level needs to be examined.
- Current (1/f) noise measurements offer a promising means for studying contact and interconnect corrosion. Experimental evaluation will be required to establish their full capabilities and limitations.
- Dielectric and electrical conductivity measurements, including the use of special electrical detectors, can be used to study degradation-related changes in materials used in photovoltaic module structures.

D. OPTICAL MEASUREMENT TECHNIQUES SELECTED

1. Background

This category includes principally those techniques which relate to what may be termed macroscopic optical properties of materials Those measurements specifically related to changes in the electronic properties of particular molecular groups are excluded. The latter group of methods, broadly classed as "spectroscopic", is more appropriately classed with chemical techniques and is discussed in that subsection. A couple of examples should make the distinction clear. Measurement of the amount of light of a given wavelength reaching the solar-cell surface for a particular encapsulation falls in the present category, while measurement of the strength of a particular infrared line indicating the presence of water vapor is a "chemical technique". Use of light scattering to detect changes in polymer structure is "chemical", its use to detect surface abrasion is discussed in the present section. Some arbitrary divisions have had to be made; the topics and phenomena discussed in this section are explicitly enumerated below

The capabilities and limitations of these optical techniques for measurement of environmentally produced changes of the type of interest here may perhaps be brought out by some elementary discussion of optical instruments in general. Fundamentally, there are only one or two broad categories of these optical instruments. An input beam (or set of beams) characterized by a particular wavelength, intensity, polarization state, and direction impinges on some sample. Some or all of the same characteristics are measured on an output beam (or beams) reflected, transmitted, or scattered by the sample. If the input and output beams are reasonably coherent, their relative phase can also be determined, leading to the interferometric class of instruments. In principle, with a sufficiently large set of measurements, rather complicated sample systems can be analyzed optically; that is, from our point of view, the important environmentally induced changes in optical properties of the materials in the sample system can be detected and correctly differentiated. In practice, for systems of the complexity of those to be dealt with in this program, determining just what has happened in a particular experiment may be rather difficult unless it is known from prior experience what the principal changes are likely to be For example, in any interferometric experiment, anything occurring to cause a change in optical-path length anywhere in the system will cause a phase difference at the detector. Such a path-length change might be due to flow-induced change in strain birefringence of a polymer, to delamination, to a refractive-index change caused by a chemical reaction, or to thermal expansion. As another example, in a simple absorption measurement, a change in transmitted intensity might result from a darkening of one or more components induced by UV exposure, from an increase in light scattering owing to abrasion of the first surface*, or from a change in reflectivity caused by delamination or possibly by a change in strain birefringence. The various contributing effects might be separated out by additional measurements. In the second example, UV-induced yellowing would have a fairly characteristic spectral signature, light scattering could be monitored directly, and one could measure specularly reflected as well as transmitted light. But it is not desirable to make all of these measurements, and possibly more, in every test. Moreover, abrasion-induced scattering will affect the measured reflectivity, delamination in small spots will affect the measured scattering (so will absorption if it is large enough), and so forth This deconvolution problem is complicated by the paucity of baseline data which would help in

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*The "first surface" is defined as that which is ordinarily exposed to the atmosphere, and which is the first system interface encountered by the incident beam.

setting up optical experiments in the optimum way – for example, the geometry of delamination is not known, quantitative data on yellowing are available only for very few polymers, and so on. Also, as repeatedly stressed in this report, it is desired to measure these changes at the lowest possible levels as well as at levels where obvious cell deterioration occurs in order to make the most reliable possible life predictions and to indicate areas where preventive measures may be required. On the basis of these arguments, the following conclusions have been reached; these are stated here rather than at the end of this section because they have strongly influenced the subsequent discussion:

- For cells or assemblies to be exposed to a variety of influences, such as by natural weathering, only the simplest optical measurements are likely to be useful.
- There is a need for a test program aimed not only at evaluating instruments and measurement techniques, but also at providing some useful baseline data on components and interfaces that are presently deemed most likely to see service in solar photovoltaic arrays. Some of this latter information will be obtained as a natural part of the testing of instruments; however, a comprehensive program to provide needed information in this area is not within the scope of the present effort.

As the reader may have gathered from the foregoing discussion, the primary focus is the application of optical techniques to the study of environmental deterioration of the transparent optical components of the array as prepared for practical use. The component materials considered include

- Glasses or plastics used as cover plates
- Adhesives or pottants if in light path
- Antireflection layers, wherever located
- Interfaces, particularly those due to delamination
- Other layers in the light path, used for protective or surface-property-enhancement purposes.

Changes specifically not considered include changes in the optical properties of the cell itself, of metallizations, or of interconnects, except insofar as reflections from these materials might be used in investigating properties of the enumerated materials classes. Degradation of the cell itself is not being addressed in this discussion of optical techniques, and changes in optical properties of the metallic constituents relatable to deterioration in their electrical properties are likely to be difficult to discern at low levels, particularly if the changes take place beneath the electrodes as is the case in some observations of corrosive attack of contact metallization, and because irregularity of the surface will considerably complicate optical observations in the case of the interconnects. In all probability, measurements will be required on complete cell and array assemblies, on subassemblies, principally two transparent layers bonded together; and on individual materials. First, optical tests on individual materials and, particularly, on simple subassemblies should be considered. Such tests would not only determine the potential of various techniques for measuring lifetime-related degradation, but also should be helpful in selecting materials and determining their mutual compatibilities.

There are a number of ways to discuss systematically the degradation-dependent properties of possible significance and optical methods to assess them. However, after some consideration, it seemed clearer to present the following short list of phenomena that might be studied optically, which includes both some specific types of degradation phenomena and some that might be more accurately described as "degradation related".

(a) *Overall spectral transmission.* It is of fundamental importance to know the intensity and spectral distribution of light reaching the solar-cell surface in order to be able to ascertain what part of a change in cell or array output may be attributed to optical property changes and what part to other causes. Measurements at a few wavelengths might suffice. In view of the importance of such measurements, we believe that it is appropriate to emphasize them. It is well to recognize that provisions for making such measurements feasible may eventually have to be part of array design.

(b) *First-surface damage.* Damage to the first surface may be a serious factor in degradation of output. It might result from abrasion by wind-driven particles, by chemical attack by atmospheric constituents – SO_2 for instance – or even from repeated washing.(IV-32) Included in this category are "remediable" occlusion of the surface by dust, dirt, or grime.

(c) *Delamination.* This may be defined as the formation of voids at interfaces. It appears to be emerging as one of the principal degradation phenomena in the current generation of test arrays. The details and fundamental causes are still unclear, but considered simply as a phenomenon, it is certainly one that can be studied optically. Within this category the production of bubbles or striae of any type, whether or not at interfaces, can be included.

(d) *Discoloration* The principal types of discoloration that may be encountered are UV-induced yellowing of polymers and photochromism in glasses. Observable yellowing of polymers upon long UV exposure appears(IV-33,34) to represent the "tail" of stronger absorption changes occurring at the shorter wavelengths It should be detectable well in advance of any obvious degradation effects simply by measuring the change in UV absorption. As described earlier, the photochromic changes of most importance in glasses involve light-induced valence changes of iron and manganese ions. Interactions between ions may also be important; for example, UV-induced oxidation of Mn^{2+} to Mn^{3+} may promote reduction of nearby Fe^{3+} ions to Fe^{2+}. These ions all have characteristic spectral signatures fairly independent of the glass composition, and in favorable circumstances can be detected optically. As has been mentioned earlier, these determinations are of primary concern in quality control and acceptance testing.

(e) *Oxidation.* Permeation of water vapor or other gases may induce chemical changes, for instance, the formation of carbonyl bonds in polymers or additives. The extent to which optical techniques of the type discussed in this section can detect such changes needs to be assessed.

(f) *Strain* Changes in strain, and thus in birefringence, are obviously likely to occur wherever interfaces occur, particularly in the presence of thermal cycling, clamping, or gas permeation. The changes in strain of greatest interest for the present program will be those – if they generally exist – that are precursors of delamination. Distinguishing these from other sources of birefringence change promises to be a challenging task.

The degradative mechanisms and phenomena of probable chief importance are believed to be included in the above list. Some changes in polymers that may take place through curing processes – for instance, change in average molecular weight or in degree of crystallinity – have not been explicitly discussed, but could be studied by the techniques described below (and others) if necessary. Optical measurement methods selected for studying each of these six "degradation categories" are described below.

Methods suitable for several of the categories are described where first appropriate and then referred back to. Only those methods selected as showing some promise are discussed here. Other methods which have received consideration are described, or at least listed, in Section VIII. Because of the lack of fully applicable data concerning degradation rates of materials of interest, simple calculations have frequently been used to estimate the levels at which various effects might be observed optically. While an attempt has been made to be realistic about interpreting these, it should be borne in mind that such calculations tend to make things look easier to detect than they actually are. On the other hand, it is possible in some cases to discern by such methods the kinds of degradation for which optical techniques of the type discussed here are not satisfactory.

2. Optical Methods for Measuring Overall Spectral Transmission

The objectives of this measurement are (a) to determine changes in the light intensity per unit spectral range reaching the solar-cell front surface and (b) to determine the change in absorption coefficient with time. The first measurement, an absolute measurement, is useful in determining at any given time what part of a change in cell output results from optical factors and what part from electrical factors. The absorption measurement, a relative measurement, is needed to predict the useful life of the cell and is essential in determining the true impact of the optical-property degradation on cell/module performance and for transformations to reference conditions (e.g., AM1 or AM2) for comparative purposes. An effective absorption coefficient can be determined by comparing intensity transmitted through the cover layers in a given spectral range with that from the same source without the cover layers. This will be an effective, rather than "true", absorption coefficient since, intentionally, no corrections are to be made for reflection or scattering. The absolute change in transmissivity to be detected (i.e., required sensitivity) will depend on the planned allowable degradation in optical quality over the life of the cell, and thus on the entire system design; for this reason the design requirements for transmissivity-degradation measurement techniques are difficult to specify. It is not too early, though, to consider the problems involved, since they could be substantial. In some scenarios, as little as 10 percent overall degradation in optical throughput to the cell over a life of 20 years is required for system feasibility. In such circumstances, it would be necessary, in accelerated life testing and in field testing, to detect absolute changes in transmission of 1/2 percent, and preferably smaller, occurring over periods up to 1 year in order to meet the first objective, and relative measurements of about the same accuracy to meet the second. Particularly in view of the fact that the overall transmission will naturally be large by design, there is a difficult long-term precision problem to be solved – the transmission at 500 nm, say, is 90 percent today, while 1 year from now it may be 89.5 percent. For short and long wavelengths, the precision necessary will not be as great, but then neither will detector response unless very complicated and expensive multidetector measurements are resorted to. The most natural way to make the measurement is to use a white-light input and to measure the spectral transmittance with a spectrophotometer*, since these instruments are widely available in designs well suited for field use. In the following, potential experimental setups are described and then the characteristics of the measuring systems are discussed

All experimental arrangements will start with the white-light source and simple optics to produce a well-collimated beam normally incident on the first surface. To minimize difficult registration problems, the beam will have to be either small or large compared with the detector area, it will be taken as small, since that appears overall to be a somewhat better arrangement The simplest detection arrangement, alluded to above, involves putting a few holes through the array to the level of the silicon front face, the transmitted light can then be measured with a fiber-optic probe imbedded in these holes. The setup is sketched in Figure IV-12a Instead of the fiber-optic probe, which may introduce orders of magnitude loss in sensitivity(IV-35), a telescope output might be used, as in Figure IV-12b. Standard attachments for converting spectrophotometers to telespectrophotometers, such as those manufactured by Gamma Scientific, Inc., or by EG & G, Inc., among others, would probably be suitable. Alternatively, a close-up lens might be used. Imbedding probes or telescopic attachments in the array might be avoided by measuring at the back of the array (Figure IV-12c) if the material near the back is known not to degrade much and if the array does not have an opaque backing. Alternatively, a reflective arrangement (Figure IV-12d) might be tried – a highly reflective layer could be incorporated in a cell, or perhaps the edge of the metallization could be used In all these arrangements, it should be noted that there are surfaces that must be protected from serious environmental damage over the life of the experiments – the base of the borehole, the reflector, and the collecting optics surfaces.

However, any of these arrangements requires, for absolute measurements of the type described above, a stability in the detecting system which is at the least very difficult to come by. Quoted precision values are not nearly good enough – "±2 percent", "±1 percent over 6 months", "±0.3 percent over 1 month" are typical statements There are at least 30 U.S. sources for spectrophotometers, and it has not been possible to survey all of them**; moreover, many manufacturers do not discuss long-term precision in their literature. The problems appear to lie largely in drift of the electronics and in bias to the detectors. Recalibration is not feasible since the accuracy of absolute calibration is lower – typically 2 to 5 percent – owing to the difficulty of obtaining standard light sources. Broad-band photometers/radiometers suffer from the same general precision problems as spectrophotometers, so there is no advantage to using such an instrument with the wavelength selection at the input beam. As far as relative absorption measurements go, short-term precision of ±0.1 percent or so is generally available, so a change in absorption coefficient big enough to be taken seriously should be readily determinable, however, gathering several points as a function of time in order to make a reliable extrapolation would not be easy.

Thus, there does not seem to be any way of making this a routine test, and to devise any kind of reliable test at all is going to require careful thought. Resorting to "identical" pairs of samples, one of each pair sheltered insofar as possible from environmental stresses and the other "weathered", might be considered, but this clearly has its drawbacks Detector precision problems should be borne in mind in the following sections whenever long-term measurements not of a null nature are discussed

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*More properly, a spectroradiometer, since measurements beyond the visible range will be of interest

**Among the manufacturers of research-quality instruments are Optronic Laboratories, Inc , Silver Spring, Maryland, EG&G, Boston, Massachusetts, International Light, Newburyport, Massachusetts, and Alphametrics, Ltd , Winnipeg, Manitoba, Canada

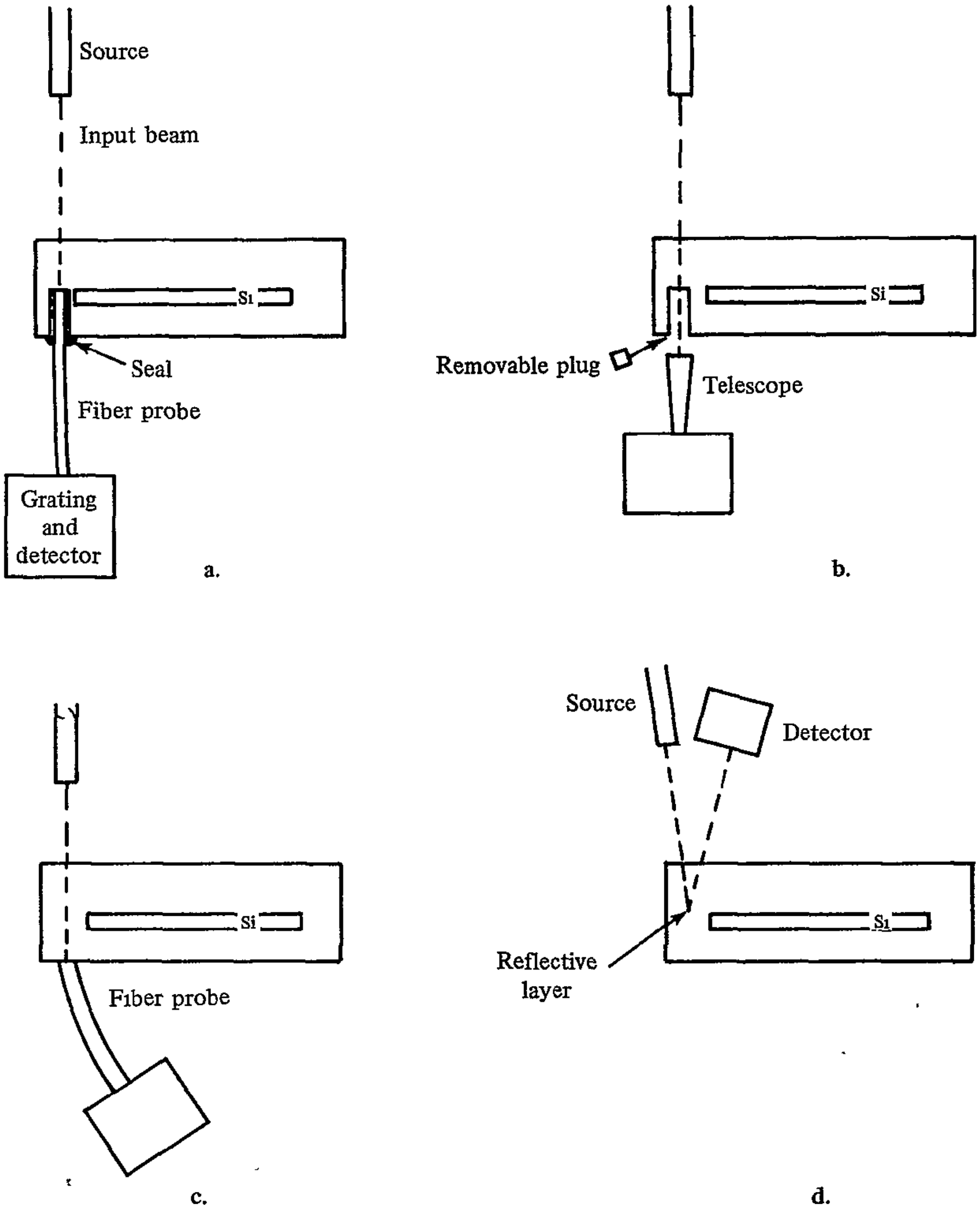

FIGURE IV-12. SIMPLIFIED SKETCH OF ENCAPSULATED SOLAR CELL INDICATING WAYS INCIDENT LIGHT INTENSITY AT LEVEL OF CELL FRONT SURFACE MAY BE MEASURED

3. Optical Methods for Measuring First-Surface Damage

As mentioned above, the principal mechanisms of first-surface degradation will be abrasion, chemical attack, and occlusion. The principal optical effect of any of these mechanisms is an increase in scattered light, which suggests one obvious line of investigation. The principal optical methods of studying first-surface damage may be categorized as follows:

- Direct optical observation – principally microscopy
- Enhanced direct observation – enhanced by chemical enlargement or by decoration of defects
- Scanning electron microscopy
- Specular reflectivity, which will be reduced by the increase in scattering
- Direct measurement of scattered light.

Each of these is discussed below.

Direct Optical Observation

Straightforward observation of surface changes by conventional microscopy is both too broad and too familiar an area to warrant extensive discussion. Remarks on a few instruments which might be particularly helpful follow.

The first of these is a hand-held anamorphic* microscope(IV-36) with its own light source (Figure IV-13). This instrument was developed for the rapid analysis of roughening of steel surfaces prior to painting, but should also work fairly well on glass or plastic. By the optical sectioning method (imaging the oblique reflection of a slit), average roughness to a level of around 15 μm over an aperture of 7.5 mm may be estimated. Something of this sort, which can be held and operated with one hand, might be convenient for the rapid surveying or sampling of surface damage to arrays in situ. A microscope of this type is supposed to be in commercial production in England, but no information from the manufacturer has been received.

Of the various types of phase and interference microscopes**, the most generally useful commercially available type is the Nomarski differential interference contrast microscope (Figure IV-14). In this instrument, the incident light is passed through a Wollaston prism, producing two perpendicularly polarized beams traveling at a small angle to one another. After passing through a condensing lens, these beams pass through or are reflected from the sample, go through the magnifying optics, and pass through another Wollaston prism bringing them to the same polarization so they may interfere. The result is an image closely approximating gradients in the optical path. For the case of reflection from a rough surface, these gradients just result from the different distances adjacent rays travel before reflection, and one obtains a sharp topographic picture of the surface with excellent depth of field. Besides being

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*That is, one which magnifies predominantly in one dimension, for the instrument described here, 50X vertical to 10X horizontal.

**A description and comparison of various types of interference microscopes is given by Claussen (IV-37)

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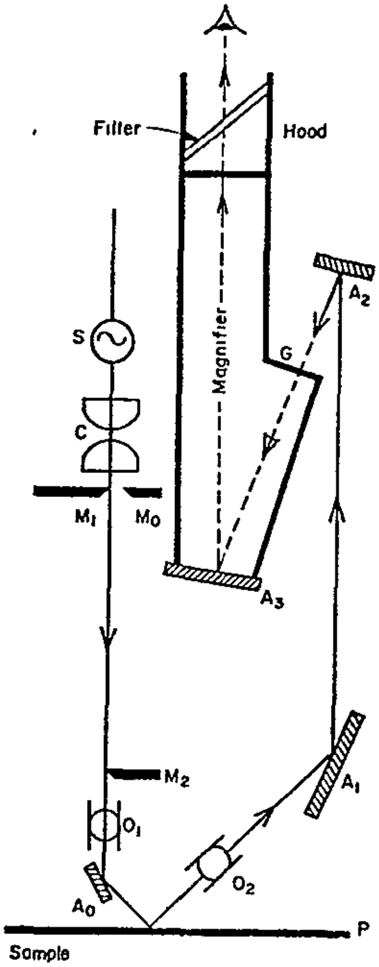
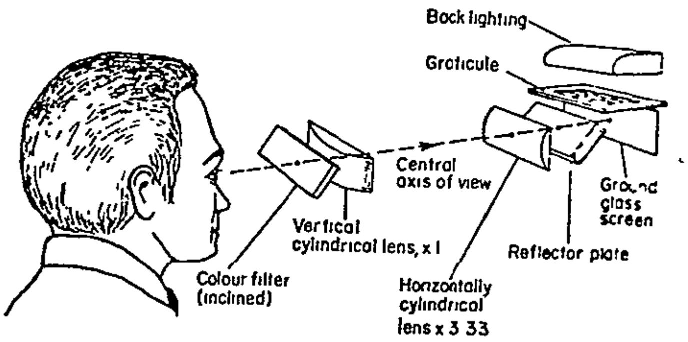
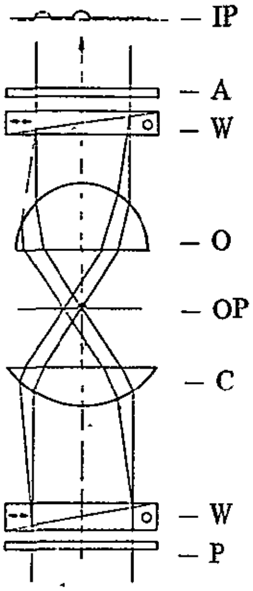


a. Instrument Layout



b. Optical Elements of Magnifier

FIGURE IV-13. SCHEMATICS OF LAYOUT OF AN ANAMORPHIC SURFACE-PROFILE MICROSCOPE



P: polarizer
A: analyzer
W. Wollaston prism
C: condenser
O objective
OP: object plane
IP. image plane

FIGURE IV-14. SCHEMATIC DIAGRAM OF NOMARSKI DIFFERENTIAL PHASE INTERFERENCE MICROSCOPE FOR TRANSMISSIVE SAMPLE

useful as a laboratory instrument for qualitative assessment of the extent of damage, this type of microscope is useful for distinguishing different types of surface damage and for determining just what the effect on the surface has been. Binocular Nomarski microscopes with magnifications up to 1000X are available from Carl Zeiss, Inc., for around \$6000*, independent of recording or display cost. The instrument can also be used as a conventional bright-field or dark-field microscope.

Among the direct optical techniques, multiple beam interferometry should be mentioned. With this technique, fairly abrupt surface topography features, such as steps, in the 30 to 50 Å range may be observed and measured. To apply this technique, the surface to be investigated generally must be silvered to obtain good reflectivity. This of course requires care, is time consuming, and must generally be considered destructive, and thus the technique has not found wide popularity.

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*Because of the modular character of most optical instruments, prices vary tremendously, depending on accessories chosen Prices given represent rough approximations or typical ranges.

Enhanced Optical Observation

Since the object of optical examination of the specimen surfaces is to reveal defects at the lowest level possible, anything that will enhance the visibility of the defects will be welcome. Nondestructive methods are clearly preferable, but not absolutely necessary. The most obvious technique to try is etching; besides being destructive, this will be successful only in limited circumstances, particularly on noncrystalline materials such as glass or plastic. An example in which etching is not particularly effective is afforded by the careful work of Tomandl(IV-38), who studied sandblasted and etched glass by both light scattering and SEM. Calculation of shapes of pits etched with HF from stereo-SEM pairs showed that these pits were shallow ellipsoidal depressions Upon further etching, these depressions appear just to gradually enlarge without change of shape, as the light-scattering measurements show. On the other hand, such things as composition variations can cause changes in etching behavior and also be associated with incipient defects, as shown by Lopez(IV-39) for SiO_2 films on silicon. Much attention has been given to degradation of thin SiO_2 and other glassy films on silicon because of their role in ensuring the reliability of integrated circuits. In such films, "surface" defects extend, or often can be made to extend, entirely through the thin dimension. This provides the opportunity for a number of specialized techniques for enhancing the observability of these defects, which have been reviewed by Kern and Comizzoli.(IV-40) Among these, electrophoretic decoration of the defects with phosphor particles and electrostatic corona charging to selectively deposit surface ions ("developed" by neutralization with charged carbon black particles from a dielectric liquid) are attractive as essentially nondestructive methods. Cracks and pinholes in the micron range, and probably smaller, can be reliably detected by the latter method. These methods, however, are suitable only for thin films (up to a few microns thick) on conducting substrates, and are thus not likely to be generally useful in the present program.

Scanning Electron Microscopy

Under the most favorable circumstances, features as small as 2000 to 3000 Å may barely be resolved using optical microscopy. To discern smaller features, scanning electron microscopy (SEM) has become the method of choice, despite the high cost of the instrument (at least $60,000, and generally more for a research-grade system), because of its simplicity and versatility. Only "conventional" SEM for study of surface topography is considered here, other uses being more chemical or electrical in nature. Present-day commercial instruments, when properly maintained, have a lateral resolution in the range 50 to 100 Å. Because these microscopes have great depth of field, resolution in depth is of the same order of magnitude, with a suitable "viewing angle". By the use of more than one viewing angle, the detailed topography of pits, microcracks, and other surface features can be reconstructed to a high degree of accuracy, as mentioned above. Scanning electron microscopes which can generate stereo photographs in real time are now available. For SEM of dielectric materials, it is generally necessary to lightly metallize (with gold, usually) the surface to be studied in order to avoid charging it. While glass surfaces can be investigated to some extent without metallizing, although the signal-to-noise is very poor, plastics cannot be since the electron beam causes volatilization at the surface, with untoward consequences for both the sample and the microscope. Metallization of the sample cannot really be considered a nondestructive technique, since the characteristics of the surface and thus its future degradation rates are likely to be altered by the film deposition and removal processes. Aside from perhaps making it possible to observe the progress of surface damage resulting from weathering at an earlier stage than otherwise possible, the chief use of SEM is to provide the detailed information which can assist in developing an interpretation of the nature of the damage process. SEM is not suitable for investigating defects in depth because of the charging problem and the energy straggling of the electron beam inside the solid material.

Specular Reflectivity

As stated above, the principle of these measurements is simply that light which is scattered is not specularly reflected, and the drop in reflectivity is generally large enough to measure This is particularly true of metallized surfaces – an rms surface roughness of only 28 Å is sufficient to produce a 0.5 percent drop in reflection for light of wavelength 0.5 μm.(IV-41) But even on glass the change can be readily observed – data of Howes(IV-42) indicate that only 30 g of SiC dropped 1 meter onto a microscope slide is sufficient to cause a 14 percent reduction in near-normal reflectivity at 0.633 μm. Howes' abrasion-test procedure is similar to ASTM D968-51(IV-43), but the powder-dropping apparatus dimensions differ, and, as mentioned, silicon carbide is used rather than sand. Abrasion of other glasses and plastics could be measured in the same way.(IV-42) These results arouse hopes that effects of weathering abrasion and chemical attack on the surface could be measured easily, though not completely characterized, by a simple reflectivity measurement. A few simple measurements to verify and extend these results seem called for. Heterodyne detection(IV-41) to obtain a small viewing angle seems like a good idea. If the reflectivity changes prove to be fairly large in some cases, the technique might be adapted for in-situ measurements. A fiber-optic reflectometer would be useful for such measurements, such an instrument, with accuracy better than 1 percent, is available from PBL Electro-optics Inc., West Newbury, Massachusetts, for about $800.

Direct Measurement of Scattered Light

The most obvious technique for this purpose can be carried out successfully by straightforward bistatic reflectometry(IV-38) or by a number of other techniques surveyed by Eastman(IV-41). In reflectometry, the surface is generally metallized(IV-38), both to increase the reflectance and to eliminate problems from scattering from other interfaces and bulk materials in the system. This and the other methods generally require very careful work and/or very specialized instruments in order to get reliable quantitative scattering data. Even given the data, relating it to the statistical surface roughness is a difficult task, as a review(IV-44) of the theoretical approaches that have been tried reveals. Overall, a combination of the other methods described seems more generally useful than direct scattering studies. Small-angle forward scattering measurements are of special interest though, since light scattering owing to first-surface deterioration is likely to complicate the study of light scattering due to other causes, such as delamination. It is possible that the first-surface scattering might be studied under controlled conditions by use of the optical multichannel analyzer for detection, as described in the following section, whether its effects can adequately be separated from other sources of scattering is another question.

To summarize, simple specular reflectivity measurements may be satisfactory for observing the presence of first-surface deterioration at fairly low levels. Some simple experiments to verify and quantify this should be performed. Optical and electron microscopy and light-scattering measurements on the same samples would provide more detailed information on the nature of the damage, which should improve the predictive capability of the technique. These other methods might also be generally useful in their own right for assessing first-surface damage, however, no particular research on them is needed at this time.

4. Optical Methods for Detecting Delamination

The seriousness of delamination as a failure mode has been already referred to several times. It is not only of consequence in itself, but also as a precursor of other modes of degradation and failure, since delamination may open pathways for chemical attack, and delamination between the silicon and adjacent materials may lead to peeling of the metallization.

From the optical standpoint, the simplest delamination model consists of replacing a plane interface, between say Materials A and B (Figure IV-15a), with two interfaces separated by distance d with "vacuum" between them (Figure IV-15b). Actually, separations of this sort virtually never occur, the usual situation being more like that in Figure IV-15c, i.e., with the break being entirely in one material or the other. Also, in its incipient stages the delamination may not occur uniformly over a sizable area, but rather may take place at numerous small spots (Figure IV-15d). Still, the delamination model in Figure IV-15b will be adequate for estimating the separation d at which observation of the delamination can be made by various techniques.

Since relatively little is known about the details of delamination failures, particularly in their early stages, in present-day arrays, the best course at present is to perform some simple calculations to indicate the level at which delamination failures might be expected to be observable by various optical techniques – providing, as always, that concomitant effects do not overly interfere with the observation – and to suggest a limited experimental program for studying this failure mode under controlled conditions. In the following discussion, it is assumed for purposes of illustration that the delamination is between two transparent layers. However, most of the possible optical test methods described can be adapted without great difficulty to investigate delamination between a glass or plastic and silicon or a metal.

The methods that have been examined for optical observation of delamination are

- Specular reflectivity
- Ellipsometry
- Holographic interferometry
- Light scattering
- Strain birefringence.

Light scattering will obviously be useful only if the initial delamination is in the form of numerous small voids or possibly if the delaminated surfaces are particularly rough. The procedure of the previous section is followed and each of these methods are discussed in turn below, except for the last, which is discussed under measurement methods for "strain". It is appropriate to remark here, however, that it is possible that measurable and characteristic changes in birefringence may precede actual delamination, and thus provide a possibility for detecting delamination before it even starts. The techniques described in this section can all also be more or less sensitive to birefringence changes; whether this is a blessing or a curse remains to be seen.

a. Undelaminated Surface

b. Idealistic Model

c. More Realistic Situation

d. Possible Incipient-Stage Situation

FIGURE IV-15. MODELS OF DELAMINATION

Specular Reflectivity

From the standpoint of the reflectivity measurer, delamination is just another problem in the optics of multilayer films. An attempt has been made to estimate the level at which delamination might be noticeable in reflectivity measurements under favorable conditions by calculating a variety of cases using an available computer program. Some typical results are shown in Figure IV-16 In this calculation, an incident-medium refractive index of 1.543 and a substrate index of 1 538 were assumed, and the change in reflectivity for various angles of incidence and degrees of separation d was calculated. Results for the s-polarization for 45-degree incidence are shown, the change being larger than for p-polarized light. For the situation described, the reflectivity at the interface before delamination is very small, and one might be able to discern a slight delamination less than 100 Å thick. In general though, it will be necessary to measure the change in a relatively strong reflection, and at least a 0.5 percent change in reflectivity during short-term experiments, and perhaps a 5 percent change in long-term studies, will be needed; in the former case, delamination would begin to be observable at about 200 Å, and in the latter at 400 or 500 Å. While there is some advantage in sensitivity in going to a relatively large angle of incidence, there may be disadvantages from greater difficulty in assessing the importance of complicating effects, such as surface damage, nonplanarity, or birefringence changes, when two different areas of the specimen under test are sampled by the light path.

The advantages of straightforward reflectivity measurements of this type for the study of delamination are obviously

- A relatively simple and inexpensive setup
- The capability for determining where in the plane of the sample defects are located.

The disadvantages include

- Possible problems with reflection or scattering from the first surface reaching the detector
- Sensitivity to first-surface deterioration
- Necessity of scanning point by point to find localized defects
- Less sensitivity than some other methods
- Difficulty in determining between which two layers the delamination has occurred.

The last difficulty can in principle be overcome with enough measurements at different incidence angles or wavelengths, but in practice it is not so easy. Numerous reflectometers are available commercially, but for exploratory laboratory measurements of the type discussed here it will be better to construct a system from components, the more easily to modify it as experience dictates. No suggestions are made as to specific experiments in this area, but it is emphasized that any that may be undertaken should be carefully controlled, particularly with regard to having only one solid-solid interface in the system and in eliminating first-surface deterioration.

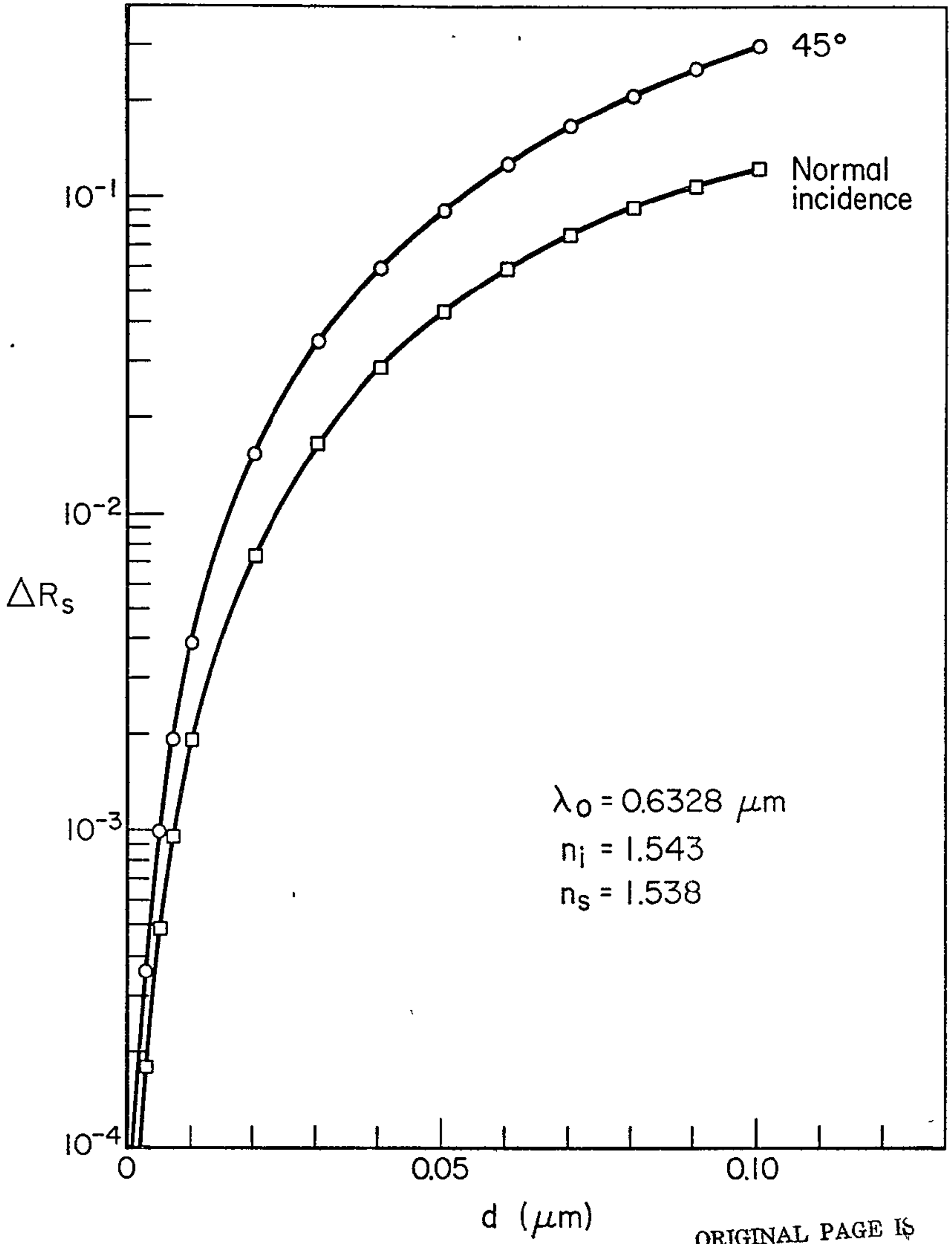

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FIGURE IV-16. CALCULATED CHANGE IN REFLECTIVITY ON DELAMINATION

Aside from the simple reflectivity setup discussed so far, a multiple-internal-reflection setup for studying delamination and other film characteristics might also be considered Either reflection of a broadened beam in an optically thick layer, or excitation of an optical guided wave in a thin layer might be considered. The three possibilities are illustrated schematically in Figure IV-17. These methods might be also used in studying absorption in surface layers. These techniques have high sensitivity for detecting degradative changes occurring over extensive regions, but a number of problems with their practical implementation have precluded recommending them in general. The difficulties include

- Restriction to layers with higher index than surroundings, placing artificial restrictions on encapsulation system design
- Problems in coupling into layers, particularly where long test periods are involved
- Reduced dynamic range.

Also, it is felt that, in general, multiple-reflection techniques increase the difficulty of interpretation of the results. Still, there might be very special circumstances where they would be useful. Techniques and applications not too remote from the delamination problem are discussed by Harrick(IV-45) for thick films and by Swalen et al.(IV-46) for thin films.

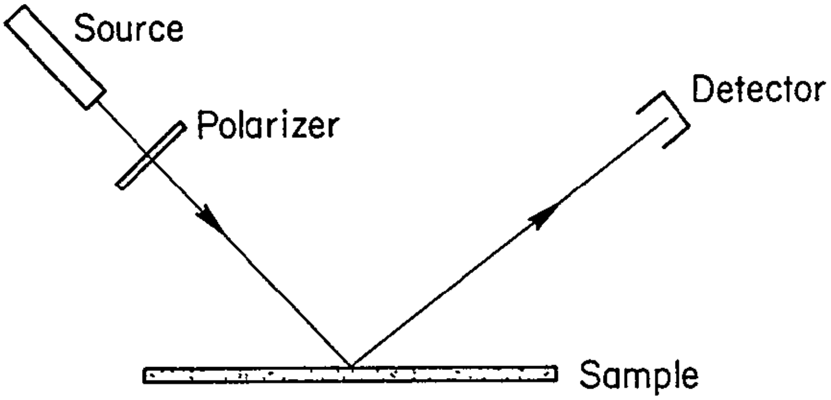
Ellipsometry

Reflected light is in general altered from incident light in polarization as well as in intensity, a simple reflectivity measurement determining only the relative intensity of the reflected beam thus does not make use of all the available information in the beam. Ellipsometry remedies this defect. A schematic of an ellipsometer is shown in Figure IV-18. Linearly polarized light is in general elliptically polarized in reflection; in most ellipsometers the converse effect is used – a polarizer and quarter-wave plate produce elliptically polarized light which is adjusted until the reflected beam is plane polarized; this permits a null detection scheme with a crossed analyzer. With excellent quality polarizing prisms and precise mechanical arrangements for measuring the angles involved (to the hundredth of a degree, typically), ellipsometry is capable of remarkable accuracy and precision in the measurement of optical properties of surfaces and of transparent films, and it is furthermore extremely well suited to measuring changes in these quantities. Thickness and thickness changes in thin films are also regularly measured this way. The degree to which any of these factors can be measured, though, is somewhat hard to specify in a general way, since it is a large calculational step, generally involving a computer program as well as a large number of assumptions about the nature of the system of materials and interfaces being studied, to get from the angles measured experimentally to the optical constants and/or thicknesses it is desired to determine. Ellipsometry has been used considerably as a tool in design of solar cell-coatings(IV-47), but it is only beginning to be investigated for the study of delamination and other types of optical degradation(IV-48).

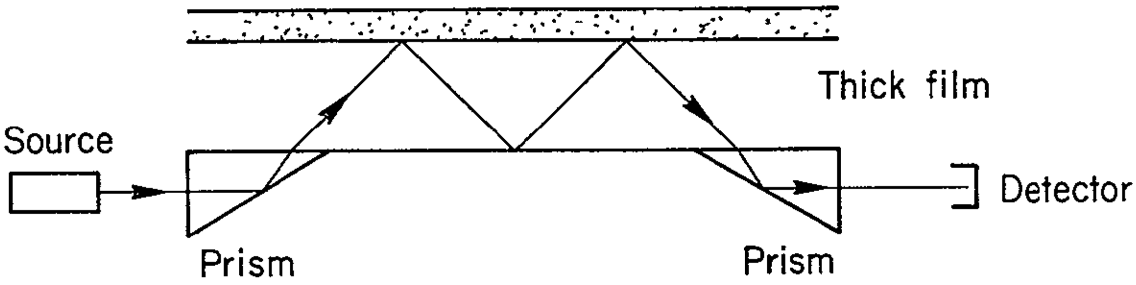
The capabilities of ellipsometry for identifying a simple delamination were investigated by running a standard ellipsometry analysis program for various sets of hypothetical data, including the example analyzed in the reflectivity discussion. If other effects do not interfere with the observations, ellipsometry should be capable of detecting delaminations between transparent materials at the level of 10 Å or less. However, this should not be taken to mean that the thickness of a delamination can always be measured to within 10 Å; it is characteristic of the method that there are regions of lower accuracy. To some extent this difficulty may be overcome by

C-2

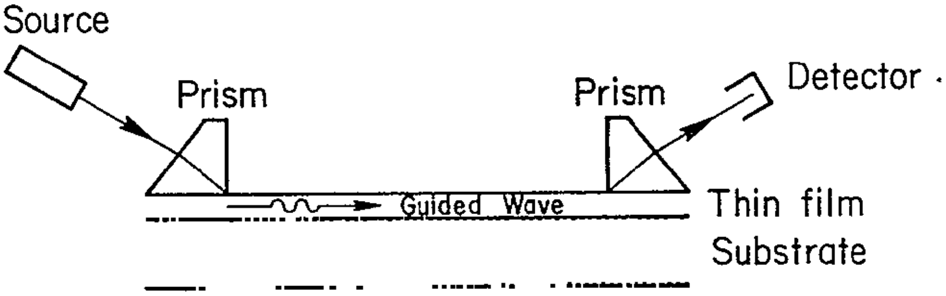
REFLECTOMETRY
VISIBLE WAVELENGTHS



I. Simple Reflectometer



II. Internal Reflection



III. Optical Waveguide

FIGURE IV-17. THREE TYPES OF REFLECTOMETERS

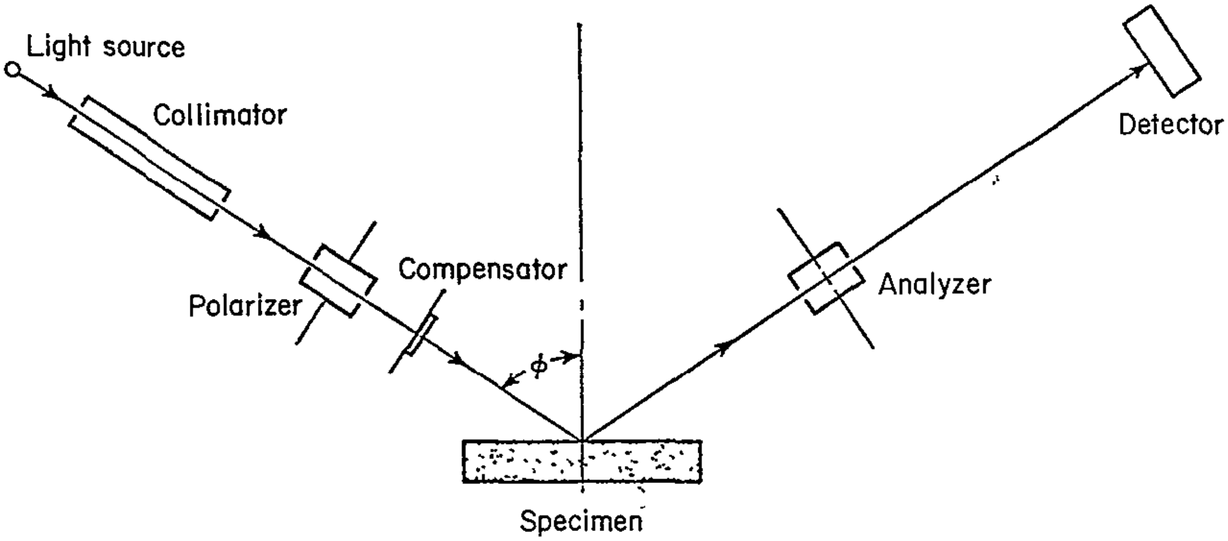


FIGURE IV-18. SCHEMATIC OF ELLIPSOMETER

making measurements at two well-separated wavelengths. Numerical experimentation of the type used here can also be used to determine, approximately, the best set of experimental conditions (incidence angle, wavelength) for a particular test, once the properties of the test specimen are specified.

Ellipsometry's chief advantage is obviously the great accuracy of which it is capable It suffers from all the problems described above in connection with reflectometry. In addition, interpreting the results requires experience; it is no job for beginners. Besides a thorough understanding of the optics involved, familiarity with thin-film technology is necessary for the experimenter to be aware of the various changes that may occur in the sample during the life of a test and of the optical changes to which these may lead.

Ellipsometers are manufactured by Gaertner Scientific Corp., Chicago, Illinois, and by Rudolph Research, Fairfield, New Jersey, at prices ranging from around $10,000 to $50,000. The more expensive models have automatic data input to a minicomputer, permitting immediate determination of the optical constants in a variety of situations.* Ellipsometers are not suitable for field use, and should not be long exposed to damp or corrosive atmospheres Rather large samples (up to 1 square foot) can in principle be examined, given enough time.

Inasmuch as experiments are in progress on ellipsometry as a tool for investigating delamination and the other degradative mechanisms of interest here, we have no particular recommendations to make except to repeat our suggestion that all experiments be directed as soon as possible to the materials and subsystems of greatest interest to the program.

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*An automatic ellipsometer in the $10,000 price range has quite recently been announced by Rudolph. Details on the capabilities of this machine have not yet been received

Holographic Interferometry

The technique of holographic interferometry has been widely used in nondestructive testing, including accelerated life-testing applications, albeit not at the sensitivity level nor over the time scale of interest here. A wide variety of experimental arrangements have been used, the basic setups are shown in Figures IV-19 and IV-20. At the beginning of the experiment, with the sample in place, the holographic recording material at the beam intersection is exposed, and then whatever processing steps are necessary to develop the hologram may be carried out (in so-called real-time interferometry) or may be deferred until the end of the experiment (in "double-exposure" or "time-lapse" interferometry) The recording material may produce an amplitude hologram (as with conventional film) or a phase hologram [as with DuPont photopolymer(IV-49)]. In principle, a material producing a thick phase hologram is best, since this can have a diffraction efficiency approaching 100 percent, while with amplitude holograms efficiency is limited to around 7 percent.(IV-50) If the recording material is removed for processing, it must be replaced with great accuracy, an advantage of photopolymer is that it may be processed in place. Next, whatever steps are involved in accelerated testing of the sample are carried out (in situ, if at all possible – reregistering both the film and the sample will be particularly difficult). Then a phase shift of approximately 180 degrees is introduced into one arm of the interferometer*, in order to produce destructive interference along light paths that are unchanged**, and a new hologram is formed at the recording plane. This is simply viewed through the exposed hologram (real-time interferometry) or is allowed to further expose the recording material (double-exposure interferometry), which is then developed and viewed with the reference beam. In either case, it should be possible to observe any sample regions that have changed in optical path, whether because of delamination, change in birefringence resulting from flow, or from altered stress, or whatever.***

The advantage of holographic interferometry of this type is that it is quite insensitive to the presence of roughness on other scattering sources in the light path. However, changes in microstructure producing scattering will lead to high spatial frequency interferences(IV-51) which greatly complicate the interpretation of the observed pattern. Microcrystallinity_changes of this type, and possibly strain birefringence changes, both resulting from room-temperature variations, probably contributed to difficulties encountered in some early experiments(IV-52) in making holograms of some kinds of plastics. Details of the relative merits of real-time and double-exposure interferometry are not presented; instead the reader is referred to texts.(IV-51,IV-52) The double-exposure technique is capable in principle of somewhat greater accuracy, but is limited in practice to relatively short stress times on the sample (perhaps an hour at the outside) if phase-sensitive recording is used.

We can bracket the range of sensitivity to optical-path changes that may be observed by finding a theoretical lower limit to what can be observed using double-exposure phase holography and referring to practically determined lower limits for real-time amplitude holography. For the former case, a simple vector-addition argument(IV-54) shows that the contrast ratio between spots where there has been a phase change θ and spots where nothing has occurred is given by

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*For an amplitude hologram in photographic film, this step is unnecessary, since a negative image is formed in the film processing.

**The phase change may conveniently be accomplished by mounting one of the mirrors on a piezoelectric mount, rather than by placing a compensator (such as an electrooptic modulator) in the beam

***The conventional thing to do for extended life testing by holography is to add an extra stress during one of two exposures after the sample has completed the life test For instance, one may compare, by either the real-time or the double-exposure method, the sample at an elevated temperature with itself at room temperature. Something along these lines might be successful in the present circumstances, although it would be difficult to implement successfully where plastics are involved.

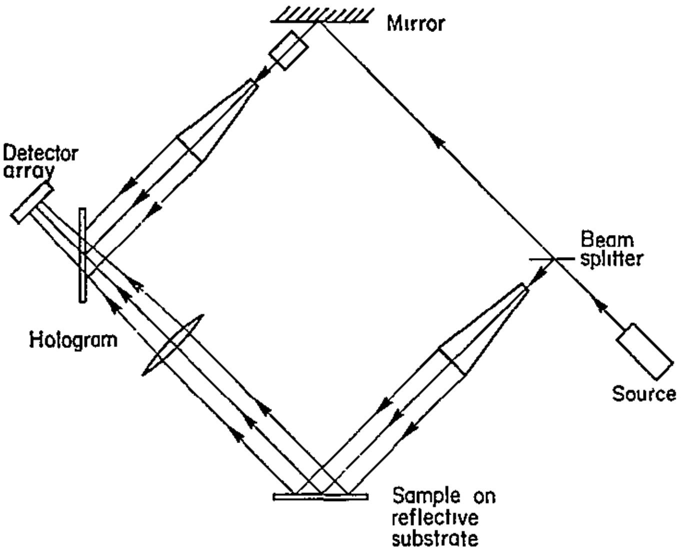

FIGURE IV-19. EXPERIMENTAL ARRANGEMENT FOR HOLOGRAPHIC INTERFEROMETRY, REFLECTIVE SAMPLE

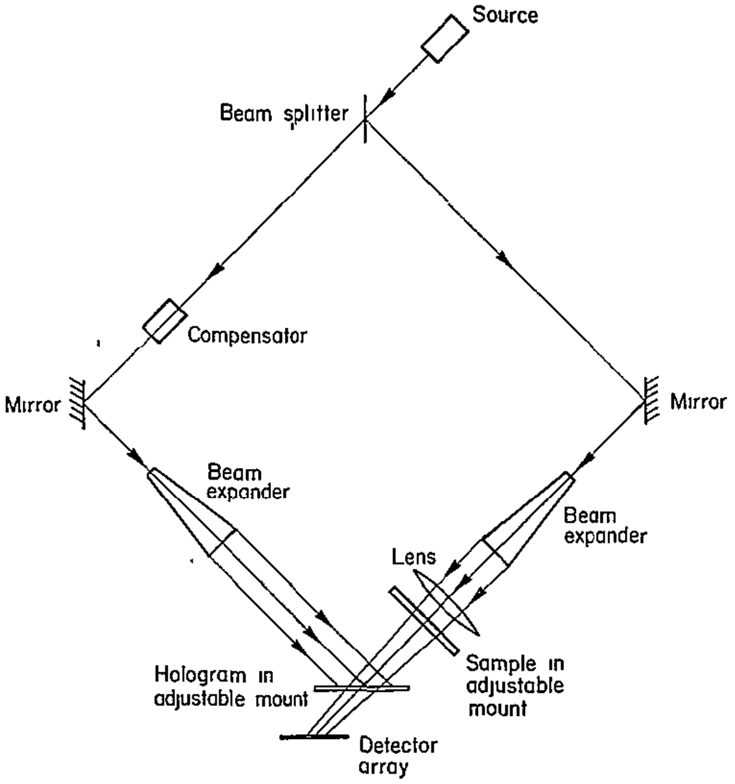

FIGURE IV-20. EXPERIMENTAL ARRANGEMENT FOR HOLOGRAPHIC INTERFEROMETRY, TRANSMISSIVE SAMPLE

$$c = \frac{K + 1 + 2\,K^{1/2}\cos(\Psi - \theta)}{K + 1 + 2\,K^{1/2}\cos\Psi} \quad ,$$

where Ψ is the phase shift introduced into the reference beam between exposures and $K = A^2/B^2$, where A and B are the recorded amplitudes of the initial hologram and of the second hologram in the background regions, respectively. A and B are assumed to have the same spatial variation across the hologram plane. If things could be arranged so that K were unity and $\Psi = \pi$, then the contrast ratio would be infinite and visibility of changed regions would be limited only by the sensitivity of the detector. However, the characteristics of the recording media available make this very difficult to achieve in practice, with care one might achieve K = 0.8 reproducibly. When K is not one, i.e., the reference-beam phase shift for maximum contrast is not π, it should be noted. If 10 percent is taken as the change in contrast ratio that could easily be detected (quite a conservative assumption), then it is found that, for an incident light wavelength of 0.633 μm, delaminated local areas smaller than 40 Å might be detected if Ψ is set at 180 degrees, and areas smaller than 12 Å if Ψ is optimized (at around 172 degrees). Several things should be borne in mind in assessing these calculations First, relatively uniform changes in optical path extending over large areas will usually be "compensated out", and therefore not noticed. Second, defects which are small in area compared with the holographic fringe spacing will be hard to detect reliably. This means that there is a trade-off, accomplished through selecting the angle between the input beams, between ease of registration of the second-exposure pattern and size of defect observable. The minimum observable defect diameter would generally lie in the 10 μm to 50 μm range. Finally, other sources of error in the system will inevitably make the achievable sensitivity less than calculated here.

To bracket the sensitivity at the other end, practical data on what can be done on a routine basis are needed, rather than theoretical estimates of what might be achieved. For amplitude holograms on photographic film, the minimum path difference change reliably detectable is around half a wavelength, or 2500 to 3000 Å. This is partly due to reregistration difficulties, but mainly results from film shrinkage in processing.

Between these limits, the capabilities of holographic interferometry for investigating delamination and similar defects presumably lie. It would take a rather extensive research program to find out just what the capabilities, if any, of holography might be in this area, but in view of its apparent desirable features, some effort appears warranted It should be recognized that only the simplest possible conditions have been discussed. Various ingenious methods, involving two separate reference beams and the polarization characteristics of the beams, have been devised(IV-55) for enhancing the sensitivity of holographic interferometers, and should obviously be explored.

The advantages of holographic interferometry for the present type of work are.

- A fairly large area may be surveyed at once.
- Defects are located within the plane of the sample.
- The method is capable in principle of fairly high sensitivity.
- Sample imperfections are automatically compensated for.

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OF POOR QUALITY

A number of disadvantages are also obvious

- One must work on a stable, well-isolated optical table.
- Carefully controlled processing of some kind of the recording material is required.
- Defects are not localized in depth, at least not without a great deal of additional work.
- As with many other optical techniques discussed, anything contributing to a change in optical-path length will have an effect; these effects may be hard to sort out.
- There will be problems associated with proper registration of the recording material and the sample relative to the light beams.

In view of the severity of these difficulties, it seems very risky to recommend work in this area; still, it has unique advantages, and at the very least should be given some additional thought and some simple experiments to see whether there is a chance it can be made to work. Holographic-interferometry setups are available from Newport Research Corp., Fountain Valley, California, Jodon Engineering Assoc., Ann Arbor, Michigan; Apollo Lasers, Los Angeles, California, and Rottenkolber Holo-System GmbH, Obing-Allertsham, Germany, at prices in the $30,000 range. The Rottenkolber system can use phase-sensitive thermoplastic film; the others use conventional photographic film. For exploratory work of the type that would be required in the present program, however, a system assembled from components would be preferable on the basis of versatility.

Light Scattering

Small-angle elastic scattering of photons is a well-known method of determining the presence and concentration of small regions with optical properties differing from the bulk. In the event that delamination occurs in such a way as to produce such regions, small in all dimensions compared with the wavelength of light, scattering would be a good way to study the phenomenon. For delaminations optically thin in one dimension and thick in the others, some of the other methods discussed would be better, unless guided waves could be used. Light scattering would also be useful in determining the presence of any other similar inclusions within the materials being used. Measurements at several wavelengths are necessary if concentrations of defects are to be determined; the possibility of defects of more than one size must be borne in mind.

The most satisfactory present-day method of measuring small-angle forward scattering is to use a tunable laser, or several lasers, as the light source and an optical multichannel analyzer as the detector. This versatile instrument could also be used in other areas of the present program where parallel acquisition of optical data is desirable, as in holographic interferometry. Basically the instrument may be thought of as an array of 500 x N (N = 1–256) parallel detectors, with associated memory, display, and data-processing electronics. The detector channels are 25 μm wide and 25 x 256/N μm in height. A variety of detectors are available for various wavelength and sensitivity ranges, the associated electronics is such that with the most sensitive extremely large dynamic ranges – as much as 80 dB in the most sensitive wavelength range – are possible, making it possible to measure small amounts of scattered light without blocking the forward channels. The memory and data-processing features, which allow the reduction of noise by repeating measurements and also subtracting out an initial spatial spectrum so that only changes with time are displayed, make these instruments almost ideal for light-scattering studies, so despite their cost (around $10,000 to $40,000), they are rapidly coming into use. Princeton Applied Research Corp., Princeton, New Jersey, is the principal manufacturer. A variety of older instruments for studying scattering are surveyed by Lundberg et al.(IV-56)

In the absence of specific information on the type of delaminations to be expected, it is difficult to fully assess the usefulness of scattering studies for this specific purpose. However, it should be recognized that optical scattering studies of materials and interfaces of interest will probably form a part of any well-rounded accelerated testing program

To summarize this discussion of delamination and similar defects, ellipsometry is probably the most sensitive technique and deserves experimental evaluation. However, each of the techniques described has its advantages and disadvantages, one of the principal difficulties in all cases being the separation of competing effects, which will be very difficult to do under all but the most rigidly controlled experimental conditions; moreover the suitability of any of the techniques for measurements throughout an extended life test remains to be demonstrated.

5. Optical Methods for Measuring Discoloration

The question that comes to mind concerning discoloration is whether the color changes involved can be detected at low levels by some method other than direct measurement of the absorption changes involved, such as by changes in reflectance or by ellipsometry. Some numerical estimates have indicated that the answer to this question would generally be in the negative.

To get a feeling for the time scales involved, the results of Oster et al.(IV-33) on absorption of 12-μm-thick Saran film irradiated with UV at 2540 Å for various times were considered. The solar UV radiation reaching the earth's surface will of course be peaked at longer wavelengths and thus will have a lower quantum efficiency in producing yellowing than the source used in the experiments. To avoid problems in extrapolating the data to long wavelengths, a measurement wavelength of 4750 Å was assumed. Neglecting a small background absorption, the absorption cross section at this wavelength is approximately 0.67 x 10^{-22} cm^2/photon. If all air mass 2 solar photons with wavelengths shorter than 3200 Å were as effective in darkening the plastic as the 2540 Å photons were, a 12-μm Saran sheet would become completely opaque (<0.1 percent transmission at 4750 Å) in about 16 months' outdoor exposure, assuming no other chemical changes. Since the actual quantum efficiency will be much lower, obvious yellowing over a 5 to 10-year life range may be anticipated, showing the desirability of accelerated tests Some data on exposure of polystyrene (very photosensitive) and polymethyl methacrylate to sunlight for 5 to 31 months are given by Winslow.(IV-57) Epoxy adhesives are particularly apt to degrade in sunlight, according to data of Mauri.(IV-58)

To see whether absorption changes below the level of obvious yellowing could be detected by reflectivity or ellipsometric measurements, the standard computer programs previously discussed were run for a wavelength of 0 633 μm and an optically thick sample of a hypothetical material with a refractive index of 1.54 and various absorption coefficients. It was found that ellipsometry, although not really well suited to this type of measurement, was still more sensitive than reflectivity, but that in either case, by the time one had a reliably detectable change in these optical characteristics, the absorption even for a 12-μm-thick film had increased enough for the change to be easily measurable directly. Thus, these methods are not suitable for detecting color changes. By far the best thing to do, particularly in the laboratory environment, is just to monitor the absorptance of the materials of interest at some wavelength in the ultraviolet (say 0.3 μm) where the optical density changes from UV exposure are much greater than those in the visible spectrum. If the data on Saran is any guide, it should be possible to detect color changes this way in a time span of 10 to 20 percent of that required to observe them directly in the visible spectrum.

The more highly colored states of photochromic ions in glasses generally have fairly characteristic spectral signatures by which their concentrations may be roughly estimated at about those levels where they begin to become a problem. If, however, photochromic darkening is observed in accelerated testing, what is really required is chemical analysis of the glass to determine the total concentration of switchable ions, so that the total darkening over the practical cell life may be predicted and a decision on whether a better material is necessary may be reached.

6. Optical Methods for Measuring Oxidation

The major concern here is oxidation of polymers as a result of vapor permeation Formation of oxide films on metallizations and interconnects is likely to be a problem, but it is not one that can be studied easily by optical techniques, except possibly in portmortem examinations The problem with the metallizations is that materials likely to oxidize are next to the silicon, and not very accessible to a probe beam. With the interconnects, the problem is unfavorable (that is, nonplanar) geometry; some qualitative changes might be noted, though.

The oxidation of polymers proceeds by a complicated and imperfectly understood chain of reactions(IV-57), requiring radiation to produce free radicals as well as oxygen or another oxidative reactant. The reaction propagates, though without multiplying; so one initial radical may lead to consumption of hundreds of oxygen molecules. Fortunately, it is not necessary to address the reaction details, but only to consider the net effect, which is to replace one hydrogen attached to a carbon with a hydroperoxide (OOH) radical. At the interfaces where we expect oxidation primarily to occur, these peroxide radicals will be very unstable and will soon be replaced by more stable doubly bonded oxygen (with evolution of water) or possibly by a hydroxyl group (with reevolution of oxygen). Such characteristic groups could of course be detected by infrared absorption spectroscopy; the possibility of detecting them by their effects on the refractive index in the visible spectrum will be examined here.

Such changes are easily estimated for polymers by using the concept of molar refractivity. There are various approaches to this concept; the Lorenz-Lorentz type formulation is used here.(IV-59) According to this formulation, the refractive index of a polymer at some characteristic wavelength (usually 0.589 μm) is given by

$$n = \left(\frac{1 + 2Z}{1 - Z}\right)^{1/2} ,$$

where $Z = R\rho/M$, where R is the sum of tabulated(IV-59) universal molar refractivities for one repeat unit of the polymer, ρ is the bulk density, and M is the molecular weight of the repeat unit. As a simple example, the refractive index of polyethylene in which various small percentages of C=O or HCOH groups were substituted for CH_2's was estimated, assuming that the density changes could be neglected. It was found that for 1 percent of the repeat units altered in one of these ways, the index change expected would be 0.005 to 0.007. In a bulk sample, this would be easily measurable, but here it is just a change in the first few molecular layers at the interface, and is well below detection by any of the methods so far discussed – this at a rather heavy degree of oxidation. The conclusion is obvious – measurement of optical properties in the visible spectrum is not a suitable way to study interface oxidation effects, at least not unless much larger secondary effects are associated with them.

7. Optical Methods for Measuring Strain

As mentioned several times previously, sizable strains are likely to be present in the composite systems of interest here, and these strains will change with time, both as a result of environmental exposure and through slow relaxation mechanisms. Strains which might be precursors of delamination, either between transparent layers or between the metallization and the silicon, are of particular interest. The presence of strain is recognized optically by the presence of strain birefringence. In this section, factors involved in measuring changes in this quantity are discussed.

Polymers, as is well known, show birefringence even when they are not being stressed. This birefringence depends on the polymer production method and its whole thermomechanical history. In particular, it may result from(IV-60)

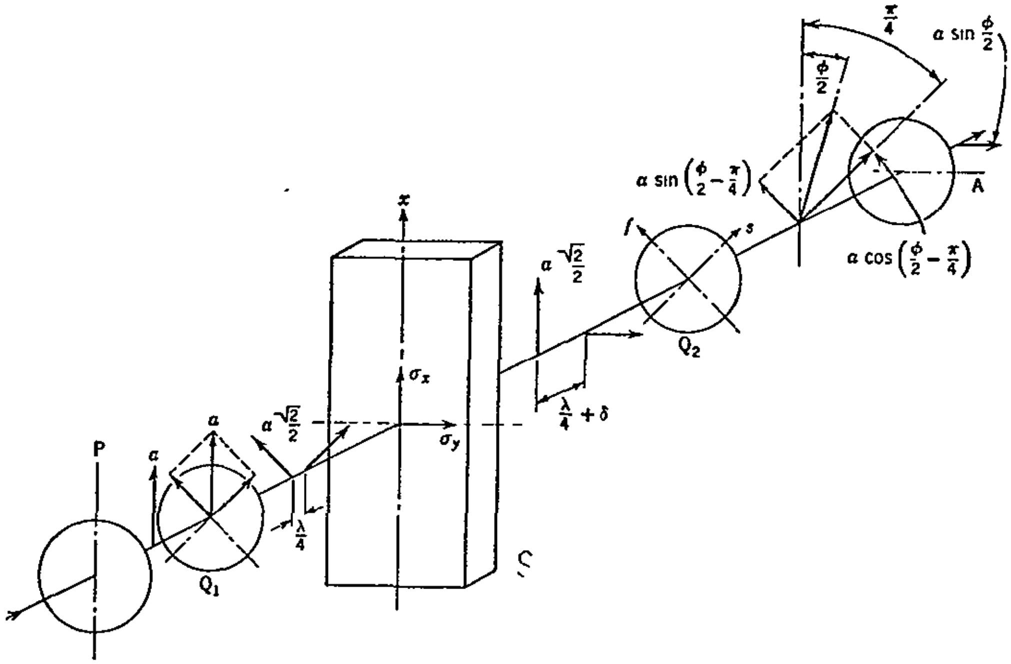
- Preferential chain alignment from high-temperature shear
- Bond distortion from low-temperature stress, including scratching
- Presence of crystalline or semicrystalline regions
- Presence of boundaries between different types of material, as in block copolymers.

These effects may be loosely referred to as strain or intrinsic birefringence.

When a polymer sheet is bonded to another material, a stress birefringence will be added to the intrinsic birefringence. In principle, the former property could be distinguished from the latter by its characteristic dependence on the geometry of the sample and the bond, but it is not known that this has been demonstrated Even if this composite is not subjected to any environmental stress, the birefringence may in many cases change with time as the polymer tries to relieve the mechanical stress on it. If there are environmental effects in addition – say just moderate temperature cycling – there will be thermally produced irreversible changes in the mechanical properties of the sample, leading to changes in the stress and strain birefringence. In addition, there will be thermal changes in the basic refractive indices and stress-optic coefficients to consider if measurements are to be made at other than room temperature The problems involved in performing and interpreting this kind of experiment for just a single polymer, not bonded to some other material, are well set forth by Kovacs and Hobbs.(IV-60) The field of investigation where measurements at temperature are involved is called thermooptical analysis It is still in its rudimentary stages. The present circumstance presents a rather more complicated situation to study than those generally attacked so far, even if experiments are limited to measurements at room temperature. As has been repeatedly stressed, many of the optical measurements so far discussed will be more or less sensitive to these birefringence changes. However, some part of these birefringence changes may be characteristic of internal strain changes (which must occur) preliminary to delamination; so it might be possible to obtain useful data along these lines from any of these measurements, or perhaps from more conventional birefringence studies, discussed below.

The usual instrument for studying photoelastic birefringence in the main is the polariscope. Various types are discussed in detail by Redner.(IV-61) The most suitable type for quantitative measurement of changes is the circular polariscope*, in which any given point in the field may be selectively nulled (Figure IV-21). Without going into the details of operation, in these instruments, inhomogeneous strain birefringence is revealed in the distortion of a pattern of interference fringes The conventional polariscopic arrangement, looking through the broad face of the sample perpendicular to the interface, would yield an extremely complex pattern, difficult to interpret. Of course the phase changes are of similar complexity with the other optical methods described, such as ellipsometry and holographic interferometry, but in those cases the point by point sampling with the prior method and the possibility of effectively nulling large regions of initial birefringence in the latter make them seem more capable of some rational interpretation. Conventional photoelasticity of this sort is not capable of any higher resolution than the other methods; all in all it does not seem like a technique worth experimenting with at the present time.

A somewhat different technique for studying the stress effects from bonding materials is to measure birefringence with the light paths parallel to the bond interface.(IV-62) In this procedure, it is best to use a small probe beam and a compensator to get results of high accuracy, rather than to employ the polariscope arrangement What is investigated is the birefringence



P: polarizer
A: analyzer
Q: quarter-wave plate
S sample

FIGURE IV-21. SCHEMATIC DIAGRAM OF CIRCULAR POLARISCOPE

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*Such instruments are available from Gaertner Scientific Corp at prices in the $10,000 range, and with fields of view up to 8 inches.

produced by the long-range strain due to the presence of the interface Meaningful measurements cannot be made close to the interface because the stress pattern sampled will be too complex. This is unfortunate because changes of interest are likely to be first noticeable near the interface. In reasonably hard materials, though, a change in the long-range strains indicative of yielding at the interface and thus of incipient delamination might conceivably be noted as a result of a change in long-range strain birefringence. No particular work along these lines is suggested at present, but it should be kept in mind if other approaches prove to yield data too difficult to interpret.

8. Summary – Optical Measurement Techniques

- Optical experiments to be carried out in the second phase of this program, as well as other studies, should be directed partly toward obtaining relevant optical data on materials and combinations of materials likely to be used in solar photovoltaic arrays, as well as toward evaluating instruments and measurement techniques.

- Light-scattering measurements should be made on some materials of interest to determine whether first-surface deterioration, delamination, and some polymer aging characteristics can be detected and differentiated by this technique, alone or in combination with other measurements.

- The suitability of simple reflectance measurement for evaluation of first-surface deterioration through abrasion, etching, etc , should be determined experimentally for a variety of likely first-surface materials. Data on probable rates of surface deterioration in various locations should be gathered in order to allow useful-life predictions to be made.

- Ellipsometric studies should continue with emphasis on problems involved in detecting delamination and on materials and materials combinations of primary importance.

- Holographic interferometry experiments should be considered with the objectives of determining trade-offs between area scanned and overall sensitivity and reliability of the technique; and determining whether strain birefringence changes, possibly precursory to delamination, can be detected in this way.

- Optical measurements performed on complete modules or arrays should be limited at first to simple tests, such as spectral transmitted intensity (including UV), possibly at only a few selected wavelengths. Development of specific measurement procedures must await final formulation of array designs, but the instrumentation problems involved deserve early consideration.

E. THERMAL AND MECHANICAL MEASUREMENT TECHNIQUES SELECTED

1. Background

This category includes the thermal and mechanical properties of materials and related diagnostic techniques. Many of the potential array failure modes are related to changes in the mechanical properties of the module materials, especially the polymeric and glass encapsulation materials caused by environmental stresses. Mechanical properties of interest here include the elastic moduli, yield strength, ultimate strength, impact strength, fatigue, elongation, hardness, creep, and bond strength. This category also includes rheological measurements which may be useful both as an analytical tool for developing data on engineering properties, and in detecting flaws such as delaminations.

Failure modes relating to changes in thermal properties are less clearly defined. The thermal conductivity, specific heat, and thermal contact resistances will determine module operating-temperature distributions. Mechanical stresses will then be determined in part by differences in coéfficients of thermal expansion. The contribution of changes in these properties to module failure is not clearly established. In addition to the usual thermal properties, this category also includes the thermal analytical tools, such as differential thermal analysis, differential scanning calorimetry, thermogravimetric analysis, and thermomechanical analysis, and special techniques such as infrared thermography.

The thermal properties and thermal analytical tools would be applicable mainly to single materials, while infrared thermography is anticipated as being a useful diagnostic tool for assembled modules.

Glass-Transition-Temperature Properties in Polymers

Characteristics of major importance in polymers include the changes in properties associated with various transition temperatures, the primary ones being the glass transition temperature (T_g) and the crystalline melting temperature (T_c). Some of the properties of polymers which change significantly at these transitions are identified in Figure IV-22.(IV-63) Below the glass transition temperature, the materials are hard, rigid glasses, while above T_g, the individual molecules are mobile and rearrange themselves to form soft and flexible (amorphous) segments with or without attendant regularly structured hard (crystalline) segments. Thus, any material degradation which shifts the glass transition temperature through the operating-temperature range of a module has the potential of seriously altering the performance of the module and may lead to failure.

Many factors affect the glass transition. The most important morphological factor is the chain stiffness or flexibility. Other chemical factors include the molecular polarity and backbone symmetry. Structural factors include molecular weight, degree of cross linking, and amount of plasticization. Nielsen(IV-64) gives some empirical rules for estimating changes in T_g. In the range of practical molecular weights, T_g is given by

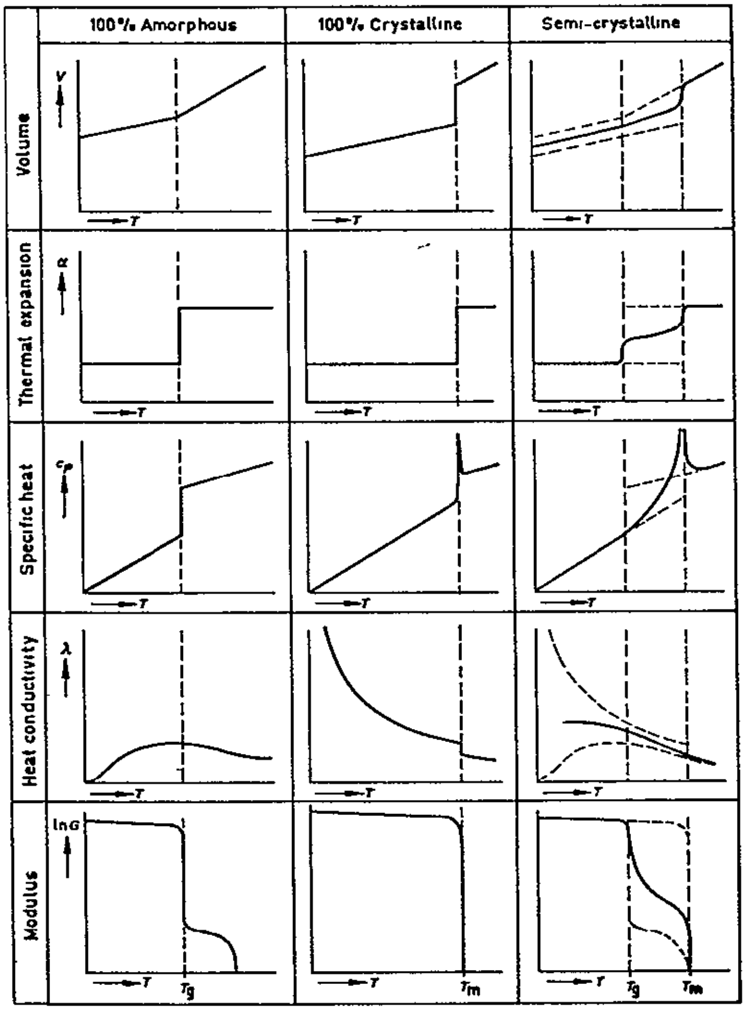


FIGURE IV-22. BEHAVIOR OF SOME POLYMER PROPERTIES AT TRANSITION TEMPERATURES

$$T_g = T_g{}^o - \frac{K}{\overline{M}_n} \quad ,$$

where $\overline{M}_n$ is the number average molecular weight, $T_g{}^o$ is the glass transition temperature at infinite molecular weight, and K is a constant which is characteristic of a given polymer. For polystyrene, $K \simeq 1.75 \times 10^5$, and using $T_g{}^o = 100°C$, the following numerical values may be obtained:

M_n	T_g, °C	$\frac{d\overline{M}_n}{dT_g}$
10^6	99.83	5.7×10^6
10^5	98.25	5.7×10^4
10^4	82.5	5.7×10^2

The effect of *cross-linking* on T_g is given by the equation

$$T_g - T_{g_o} = \frac{3.9 \times 10^4}{\overline{M}_c} \quad ,$$

where T_{g_o} is the glass transition temperature of the uncross-linked polymer having the same chemical composition as the cross-linked polymer, and $\overline{M}_c$ is the number average molecular weight between cross-linked points. Numerical values for the shift in T_g may be tabulated as follows:

$\overline{M}_c$	$T_g - T_{g_o}$, °C
10^6	0.039
10^5	0.39
10^4	3.9
10^3	39
10^2	390

As may be seen from the literature, shifts in T_g of more than 80 degrees are not unusual for systems such as thermosetting resins.

Plasticizers are low-molecular-weight liquids (and occasionally solids) which are purposely introduced to lower the glass transition temperature. The loss of these plasticizers during environmental exposure can have a significant effect on the glass transition temperature. Mixture rules for predicting T_g for a plasticized material are

$$T_g = T_{gA}\Phi_A + T_{gB}\Phi_B$$

and

$$\frac{1}{T_g} = \frac{w_A}{T_{gA}} + \frac{w_B}{T_{gB}} \quad ,$$

where T_{gA} and T_{gB} are the glass transition temperatures of the base polymer and the plasticizers, respectively, Φ_A and Φ_B are the volume fractions and W_A and W_B are the weight fractions. Typical values of T_{gB} are between -50 and -100°C, so that the T_g of the mixture may vary anywhere from T_{gB} to T_{gA}, depending upon the amount of plasticizer.

Because of the importance of the glass transition temperature, diagnostic methods based on the measurement of this quantity should be particularly useful in degradation studies. Techniques which can be used to measure T_g include:

- Differential thermal analysis
- Differential scanning calorimetry
- Thermomechanical analysis
- Dynamic mechanical analysis.

Thermal-Stress Properties in Polymers

Thermal stresses usually involve quantities such as $E\alpha\Delta T$, where E is the modulus of elasticity, α is the linear thermal expansion coefficient and ΔT is the temperature change from an unstressed condition. Any changes in either E or α are thus likely to change the thermal stress patterns. Empirical rules which relate the volume coefficients of expansion above and below T_g to T_g are:

$$\beta_\ell T_g = 0.16^{(IV-63)}$$

$$(\beta_\ell - \beta_g) \simeq 0.113^{(IV-64)} \quad ,$$

where β_ℓ and β_g are the coefficients of expansion above and below T_g, respectively. These rules taken together predict that $\frac{\beta_\ell}{\beta_g} \simeq 3$ to 4. While this change in expansion coefficient may be significant, it may be overshadowed by the much larger changes that can occur in the modulus of elasticity as the T_g is shifted.

Nielsen(IV-64) has presented graphs which show the effects of several variables on the shear modulus of polymers. Figure IV-23 shows the effect of molecular weight on the modulus-temperature curve for an amorphous polymer such as normal atactic polystyrene. At the glass transition temperature, the modulus drops by about three orders of magnitude. Below T_g, molecular weight has practically no effect on the modulus. For sufficiently high molecular weights, T_g and the drop in modulus are also independent of molecular weight. Above T_g, the molecular weight has a larger influence, as the tendency for viscous flow becomes more pronounced.

The effect of *cross-linking* on the modulus-temperature curve is shown in Figure IV-24. Several effects of cross-linking are evident. First, the modulus above T_g is greatly increased as cross-linking progresses. Second, the glass transition temperature shifts to higher values with increased cross-linking, as was discussed earlier. Finally, the transition region is broadened with increased cross-linking. Below T_g, cross-linking has little effect on the modulus. The effect of crystallinity on the modulus-temperature curve is shown in Figure IV-25. The shear modulus is essentially unaffected by crystallinity below T_g but increases markedly with increasing degrees of crystallinity above T_g. For the most part, polymeric encapsulation candidates will be noncrystalline since most semicrystalline materials are opaque (ruling out top-cover applications) and have

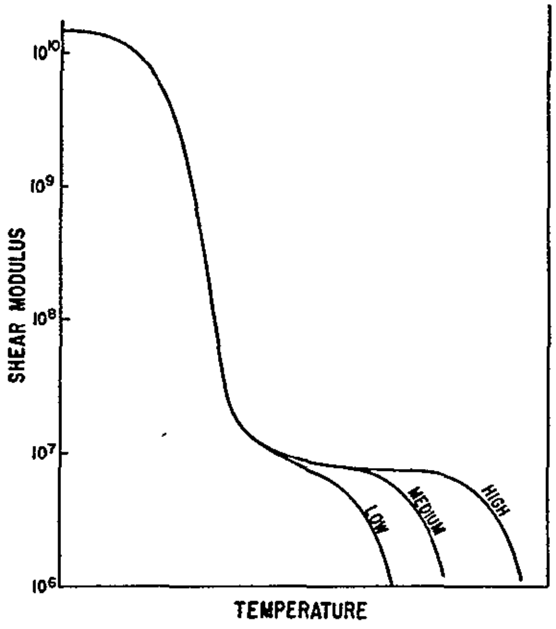


FIGURE IV-23. EFFECT OF MOLECULAR WEIGHT ON THE MODULUS-TEMPERATURE CURVE OF AMORPHOUS POLYMERS

Modulus is given in dynes/cm^2.

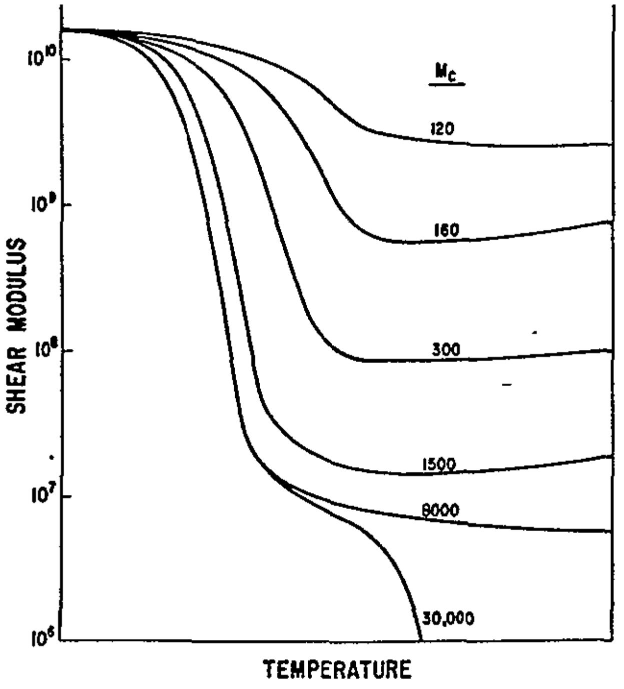


FIGURE IV-24. EFFECT OF CROSS-LINKING ON THE MODULUS-TEMPERATURE CURVES OF AMORPHOUS POLYMERS

The numbers on the curves are approximate values of $\overline{M}_c$. The value of 30,000 refers to an uncross-linked polymer with a molecular weight of roughly 30,000 between entanglement points. Modulus units = dynes/cm^2.

properties which are particularly sensitive to thermal history. However, where crystalline or crystallizable polymers are used, the effect of crystallinity on modulus and other physical properties will be significant.

The effects of *plasticization* and *copolymerization* on the modulus are shown in Figure IV-26. The principal effect is a shift in the glass transition temperature.

The response of a solid under the influence of an oscillating or otherwise time-dependent forcing function is governed by a complex modulus $G^* = G' + iG''$. The imaginary term gives rise to a *damping* or dissipation of energy, while for small to medium damping, the real term is the same as the modulus measured by other methods. The ratio of the loss modulus, G'', to the real modulus, G', is called the loss tangent and is defined by

$$\tan \delta = G''/G' \quad .$$

Another convenient damping term is the logarithmic decrement Δ which is related to the peak amplitudes of successive damped natural vibrations A_1 and A_2 by

$$\Delta = \ln \frac{A_1}{A_2} \quad .$$

In terms of the complex modulus, Δ is given by

$$\Delta \simeq \pi \frac{G''}{G'} \text{ for } \Delta < 1 \quad .$$

For a given polymer, the complex dynamic modulus depends on both the temperature and the frequency of oscillations as illustrated in Figure IV-27.(IV-64) For most polymers, T_g and the damping peak are increased about 7°C for an order of magnitude increase in frequency.

Nielson gives approximate equations by which dynamic mechanical data taken over a range of frequency can be used to calculate the creep compliance and stress-relaxation modulus, which are useful engineering properties.(IV-64)

The effect of molecular weight on damping is illustrated in Figure IV-28. Above T_g, the damping depends strongly on molecular weight, and the value of damping at the minimum in the curve may be used as a measurement of the number average molecular weight. The extreme sensitivity of damping to changes in degree of cross-linking is illustrated in Figure IV-29.(IV-64) Qualitatively similar results are obtained for the damping with changes in plasticizer content.

Many polymers exhibit additional damping peaks at temperatures below T_g. These are called secondary glass transitions. Prominent secondary glass transitions are usually found for tough, ductile, glassy polymers and those with high impact strength, so that changes in these secondary transitions may be indicators of changes in ductility and impact strength.

The *melt viscosity,* while probably not of significant engineering importance in relation to module performance, is nonetheless extremely sensitive to changes in molecular weight.(IV-63) Above a critical molecular weight, M_{cr}, the melt viscosity may be represented by the equation

$$\log \eta = 3.4 \log \overline{M}_w + A \quad ,$$

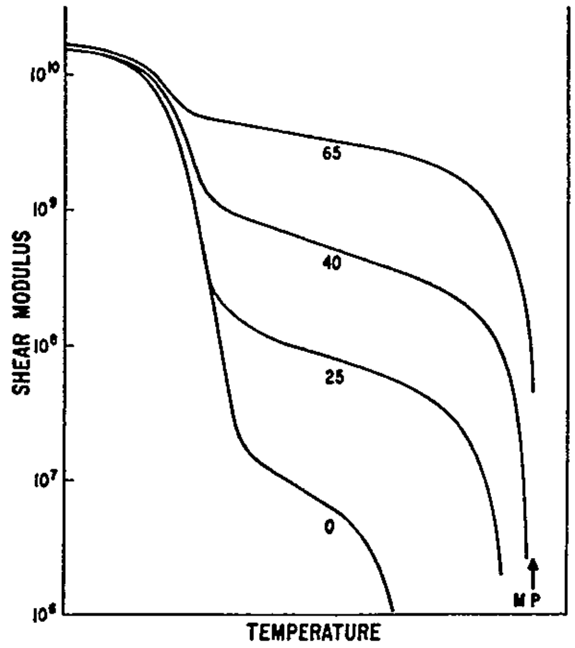


FIGURE IV-25. EFFECT OF CRYSTALLINITY ON THE MODULUS-TEMPERATURE CURVE

The numbers on the curves are rough approximations of the percent of crystallinity. Modulus units = dynes/cm^2.

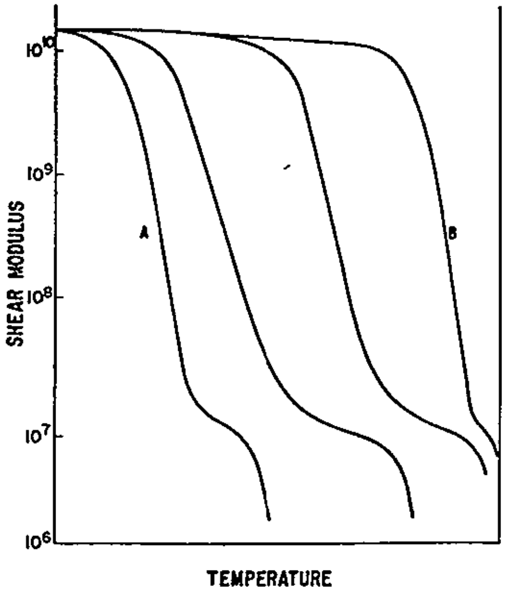


FIGURE IV-26. EFFECT OF PLASTICIZATION OR COPOLYMERIZATION ON THE MODULUS-TEMPERATURE CURVE

The curves correspond to different plasticizer concentrations or to different copolymer compositions. B is unplasticized homopolymer. A is either a second homopolymer or plasticized B.

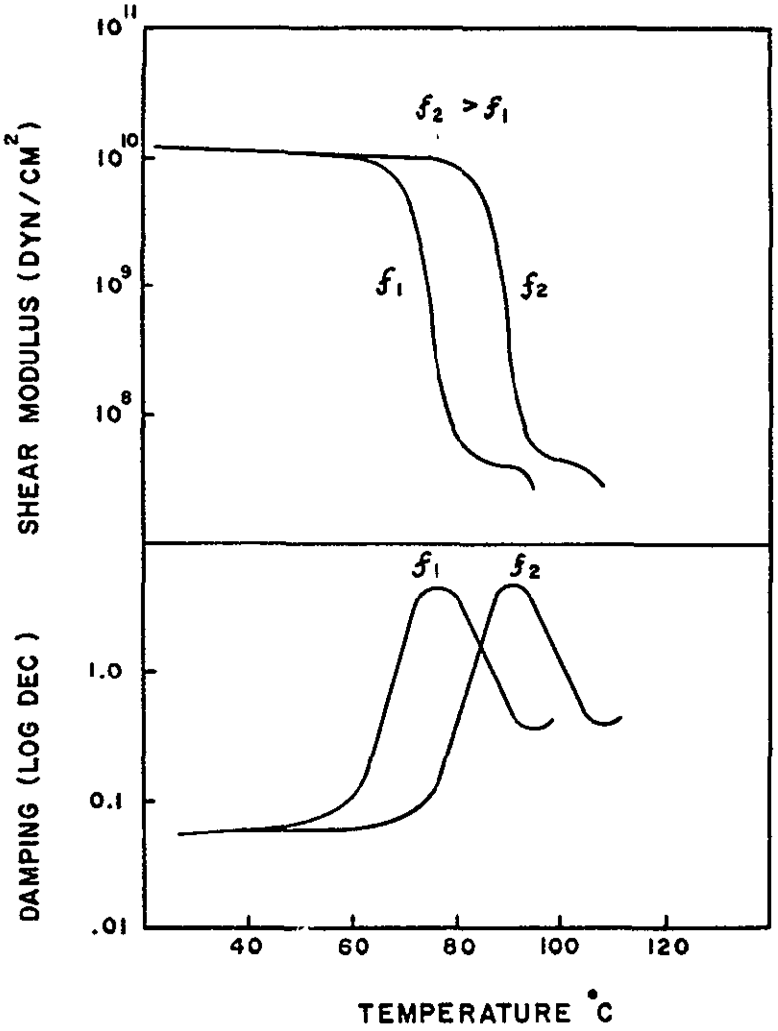


FIGURE IV-27. THE MODULUS AND DAMPING OF A TYPICAL AMORPHOUS POLYMER AS A FUNCTION OF TEMPERATURE AT TWO FREQUENCIES

Frequency f_2 is greater than f_1.

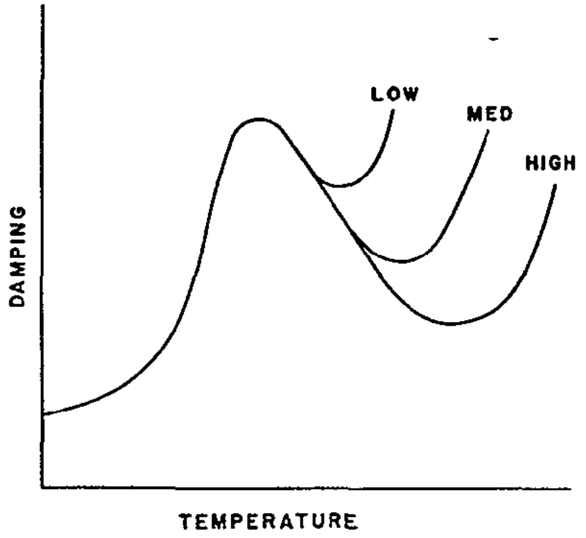


FIGURE IV-28. DAMPING VERSUS TEMPERATURE FOR A POLYMER OF THREE DIFFERENT MOLECULAR WEIGHTS where A is a constant which is characteristic of a given polymer, but is independent of molecular weight. The critical molecular weight depends upon the structure of the polymers and may vary from 2000 to 60,000. For low molecular weights, two empirical expressions are given for the viscosity:

$$\log \eta = n \log \overline{M}_w + B \quad ,$$

where $n \simeq 1$ and B is a constant, and

$$\log \eta = C_1 \left(\overline{M}_w\right)^n + C_2 \quad ,$$

where $n \simeq 1/2$ and C_1 and C_2 are constants.

A similar situation exists for the viscosity of concentrated polymer solutions. Below a critical molecular weight, the viscosity is proportional to M, while above M_{cr}, the viscosity is proportional to $M^{3.4}$. Thus, for sufficiently high molecular weights, a small percentage change in M produces a substantially larger change in η, and measurements of η would be a sensitive detector of degradation by modes in which the molecular weight is changed.

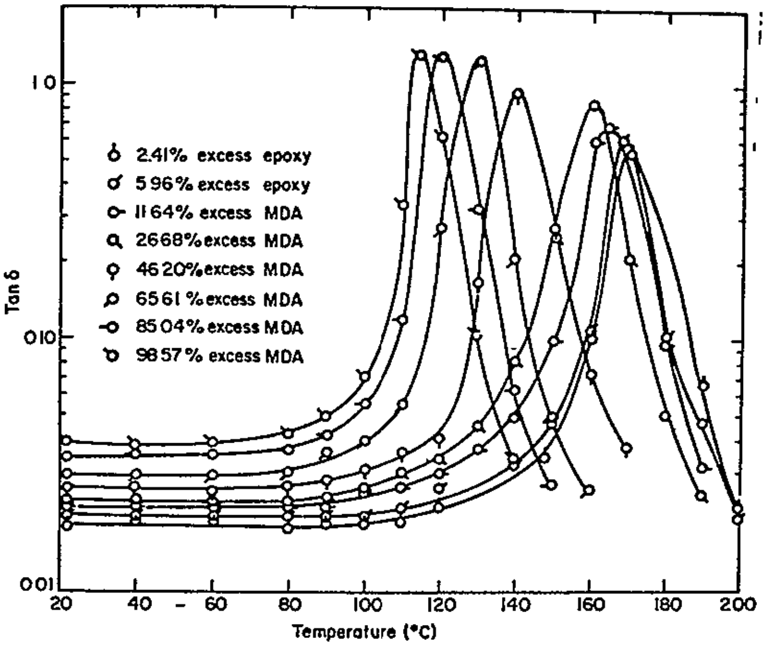


FIGURE IV-29. DAMPING OF EPOXY RESINS WITH INCREASING DEGREE OF CROSS-LINKING

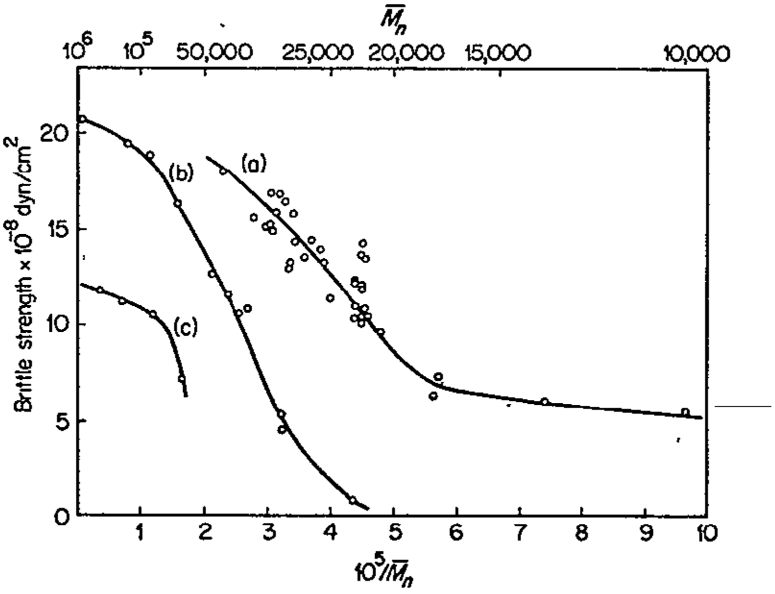
Cross-linking increases as the ratio of the components approaches the stoichiometric value. [Reprinted from Murayama and Bell, J. Polymer Sci., A2, 8, 437 (1970).]

The dependence of many polymer properties upon molecular weight may be described by the relation.

$$X = X_\infty - \frac{A}{\overline{M}_n} \quad ,$$

where X_∞ is the value of the property X at infinite molecular weight and A is a constant for a given polymer. Many properties, including density and specific heat, attain their asymptotic values at molecular weights well below the real polymer range. On the other hand, the tensile strength does vary significantly with $\overline{M}_n$ within the range of real macromolecules.(IV-64, IV-65) Figure IV-30 shows the dependence of tensile strength on molecular weight for a few polymers.(IV-66)

In addition to tensile strength, other features of the stress-strain relationship for polymers may be sensitive to degradation. The elongation at break is a frequently measured property which changes with aging. An example of this is shown in Figure IV-31.(IV-67)



Legend
(a) – Polythene
(b) – Polymethylmethacrylate
(c) – Polystyrene

FIGURE IV-30. EFFECT OF NUMBER AVERAGE MOLECULAR WEIGHT, $\overline{M}_n$, ON BRITTLE STRENGTH(IV-66)

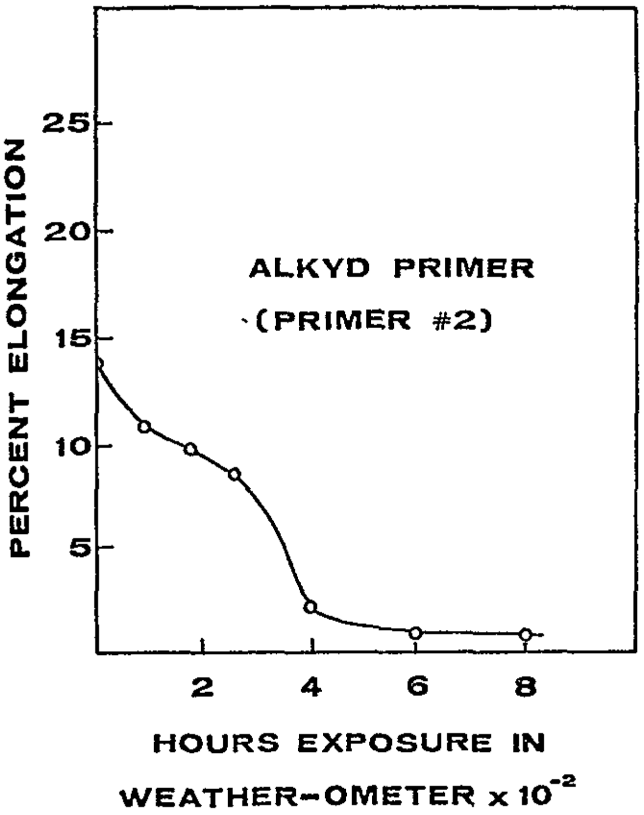


FIGURE IV-31. PERCENT ELONGATION AT BREAK VERSUS EXPOSURE TIME IN THE WEATHER-OMETER FOR AN ALKYD PRIMER (PRIMER #2)

Surface Effects in Glass

With regard to the thermal and mechanical properties of glass, degradation appears to affect mainly those properties which are intimately connected with the condition of the surface. The breaking strength of glass is determined largely by surface-flaw structure and by ionic exchange at the surface. The related property of static fatigue is also influenced largely by the surface structure. Ionic exchange may also affect the mechanical damping or internal friction.(IV-68)

Recommended Thermal and Mechanical Property Measurements

The following selected methods and instrumentation for measurement of pertinent mechanical properties of array materials and components are discussed in the succeeding sections:

- Torsion Pendulum and Torsion Braid
- Rheovibron Viscoelastometer
- Weissenberg Rheogoniometer
- Other Dynamic Mechanical Analyzers
- Ultrasonic Techniques.

In subsequent sections, the following recommended thermal measurement techniques which are pertinent to this application are discussed:

- Thermal Analytical Techniques
- Differential Thermal Analysis
- Differential Scanning Calorimetry
- Thermogravimetric Analysis
- Thermomechanical Analysis
- Infrared Thermovision.

2. Torsion Pendulum and Torsion Braid

These techniques discussed below are types of dynamic mechanical measurements, which may be separated into two categories. In the first category, the response of a sample to free or natural oscillations is measured, while in the second category, the response to forced oscillations is measured. Strains imposed upon the samples are usually small so that the sample may be assumed to be in the linear viscoelastic region. The applicability of some of the instruments to the measurement of viscosity is also discussed.

The two most important free-oscillation techniques are the torsion pendulum and the torsion braid Among all the dynamic mechanical analysis instruments, only the torsion pendulum is recognized as an ASTM method (D-2236).(IV-70) The torsion pendulum was pioneered in this country by Nielsen(IV-69), among others. Schematics of the torsion pendulum are shown in Figure IV-32.(IV-70) The specimen is clamped at each end. One end is rigidly fixed, while the other is clamped to an inertia bar and is free to move. The specimen may be either rectangular or cylindrical. Rectangular specimens are to be 0.015 to 0.10 inch in thickness, 0.10 to 0.60 inch in width, and 1 to 6 inches in length (exclusive of material in the grips). Cylindrical specimens are to be less than 0.30 inch in radius and to have the same length as above. At least 1/4 inch of specimen is to be held in each grip.

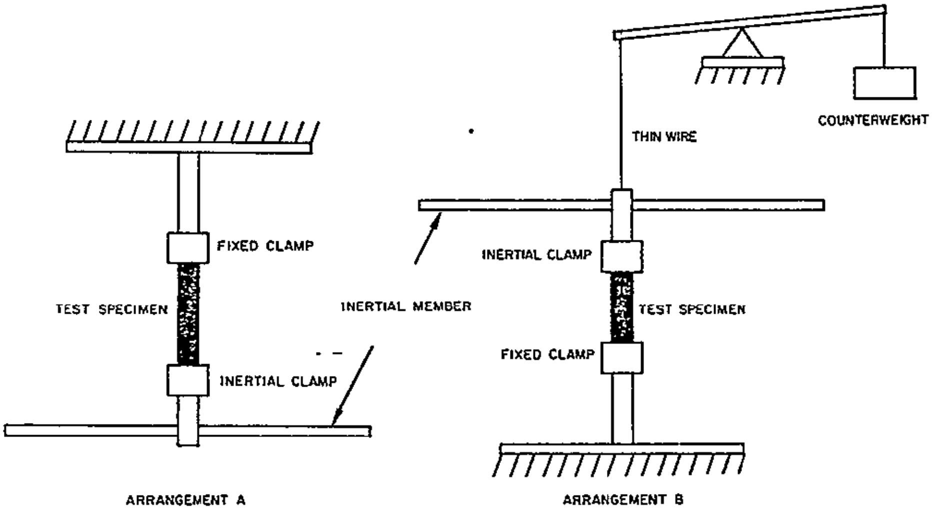


FIGURE IV-32. SCHEMATICS OF TORSIONAL PENDULUM APPARATUS

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In operation, the inertia member is given an initial angular displacement of less than 2.5 deg/cm of specimen length. The resulting damped harmonic oscillation is recorded by some suitable means such as linear variable differential transformers(IV-69), rotational variable differential transformers(IV-71), or optical techniques(IV-72). A recording of the damped oscillation will resemble that shown in Figure IV-33. The logarithmic decrement is calculated from the amplitudes of two succeeding peaks by

$$\Delta = \ln (A1/A2) \quad .$$

The real part of the dynamic shear modulus is calculated from a measurement of the frequency of oscillation, the moment of inertia of the inertia member and the geometry of the specimen.

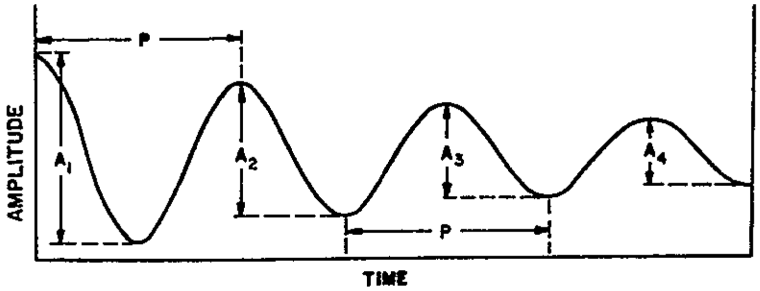

FIGURE IV-33. RECORDING OF DAMPED OSCILLATION IN TORSION PENDULUM TECHNIQUE

The useful temperature range of this technique is 4.2 to 600°K.(IV-73) The frequency of oscillations is not generally an independent variable, but rather is determined by the properties and geometry of the sample and the moment of inertia of the inertia bar. However, a normal frequency range of 0.1 to 100 Hz may be given. Since only about ten cycles of oscillation need to be observed, a given test will take at most 2 minutes.

Estimates of the precision of the technique may be obtained from the results of an ASTM interlaboratory round robin.(IV-70) With 15 laboratories participating, the interlaboratory precision was: for G' below T_g, ±7 percent, for G' in the glass transition region, ±30 percent; for G'' and Δ above T_g, ±20 percent; and for G'' and Δ below T_g, ±10 percent. Using the measured values of G' and G'', or Δ, the glass transition temperature could be determined to within ±3°C. It was found that the values for intralaboratory precision were about half those for interlaboratory precision.

Although torsion pendulums have usually been laboratory-constructed devices, a commercial model is now available from Plastic Analysis Instruments, Inc., of Princeton, New Jersey for about $40,000. This model is automated and with a computerized data acquisition system, the precision and accuracy is improved over that quoted above. Precisions of a few tenths of 1 percent may be possible with this instrument.(IV-74) This instrument is described in Reference (IV-72), and is shown schematically in Figure IV-34.(IV-72) In addition to the usual torsion pendulum mode, the instrument may also be used for torsional braid analysis. Here, the usual film specimen is replaced by an inert braid which is dipped into a polymer solution and then the solvent is removed.

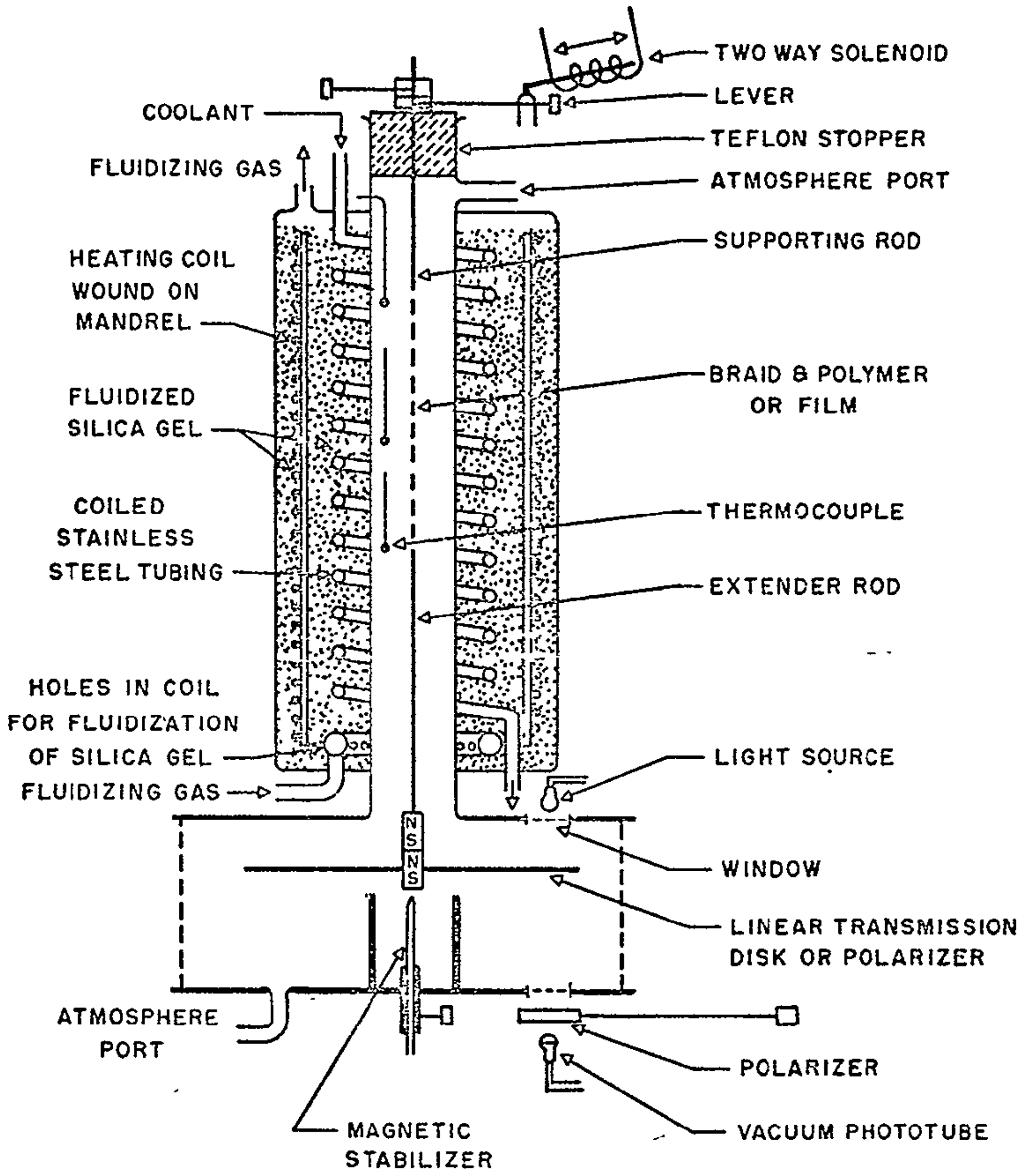

FIGURE IV-34. TORSIONAL PENDULUM AND TORSIONAL BRAID ANALYZER

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3. Rheovibron Viscoelastometer

The most widely used forced vibration viscoelastometer is the Rheovibron, a schematic of which is shown in Figure IV-35. The specimen in the form of a film or bar is held in tension by a pair of grips. An oscillating strain of a known frequency is imposed on one end of the specimen. The resulting stress is measured at the other end. From the magnitudes and phases of the stress and strain, the complex dynamic tensile modulus and the loss tangent are computed. The loss tangent may be read directly off a meter.

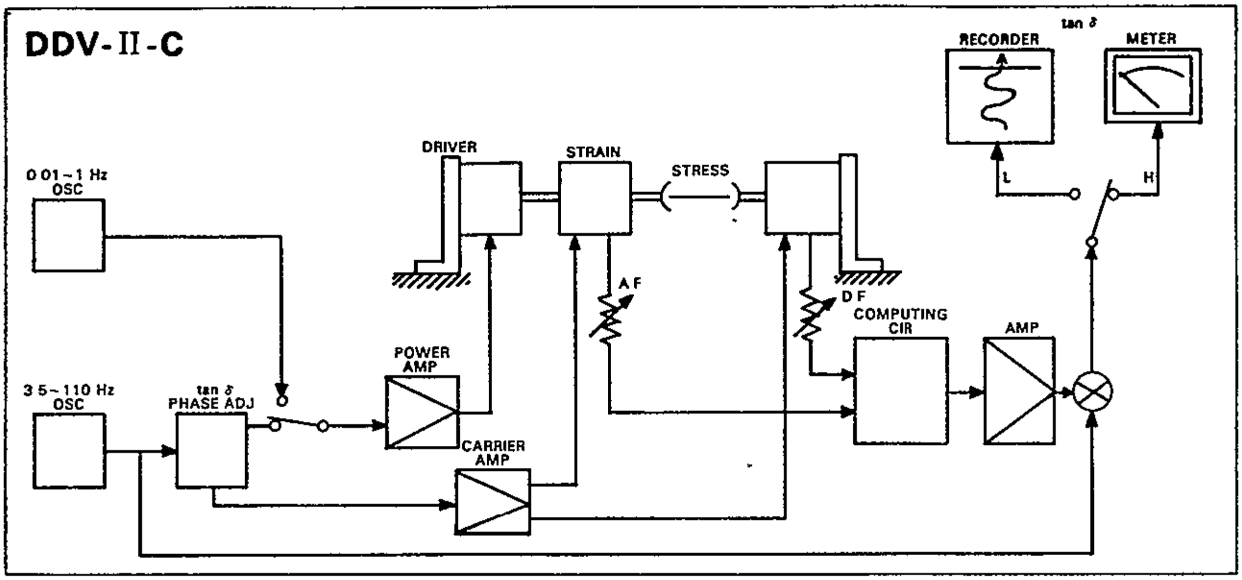


FIGURE IV-35. SCHEMATIC OF RHEOVIBRON VISCOELASTOMETER

The temperature range of this instrument is from -150°C to 250°C. Discrete frequencies of 3.5, 11, 35, and 110 Hz and continuously variable frequencies between 0.01 and 1 Hz may be imposed on the specimen. Two models are available. Maximum specimen sizes are 0.05 x 0.4 x 5 cm for Model DDV-II-C and 0.5 x 1 x 7 cm for Model DDV-III-C. The ranges of dynamic modulus which can be measured are 10^6 to 10^{12} dynes/cm^2 for DDV-II-C and 10^7 to 10^{12} dynes/cm^2 for DDV-III-C. The range of loss tangent measurable is about 0.001 to 1.7.

Massa(IV-75) has analyzed a mechanical model for the DDV-II, and has derived expressions for the moduli to take into account the effects of system compliance, sample yielding within the tensile grips, and system inertia. He showed that these effects require a correction to the raw data of 20 to 30 percent for glassy polymers. The correction factor was found to vary significantly with temperature, frequency, and sample width and thickness, and among different polymers. When appropriate corrections are taken into account, Massa estimates the accuracy of dynamic modulus values to be around 5 percent.(IV-76) Accuracy is partially limited by the inability to obtain perfectly uniform specimen cross sections and by problems in mounting the samples in order to obtain uniform strain across the sample. Precision of dynamic modulus measurements is somewhat better, possibly around 1 to 2 percent. It is difficult to assign an accuracy or precision value to the loss tangent, except to note that 10^{-3} is the lower limit of detection. A new automated system is available which uses computerized data reduction and thus increases the precision of the measurements.

Provided no damage is done to the specimen by the gripping arrangements, the measurement has no effect on the sample, so that the same sample may be remeasured after various degrees of degradation. Specimen setup time is about 10 to 15 minutes, and with a temperature scan rate of 2°C/min, a complete scan from -150°C to 250°C at a given frequency will take about 3-1/2 hours.

This is a laboratory instrument and as such is generally not portable. The instrument is produced by the Toyo Baldwin Co., Ltd., of Japan and is distributed in the United States by IMASS of Accord, Massachusetts. The costs for the basic instruments are $13,750 and $24,750 for the DDV-II-C and DDV-III-C models, respectively. A sweep accessory for the low-frequency range costs about $4000, and temperature chambers range in price from about $1000 to $2700.

Several descriptions of modifications to the Rheovibrŏn have appeared in the literature. Murayama and Silverman(IV-77) have adapted the instrument to allow measurement in a gas medium, while Lowton and Nurayama(IV-78) have extended this modification to a liquid medium. Massa(IV-75) has developed a new sample holder to adapt the Rheovibron from a tensile geometry to a flexural geometry. Shah and Darby(IV-79) described a parallel-plate modification of the sample holders to obtain oscillatory data in the shear mode for several high-density polyethylene melts.

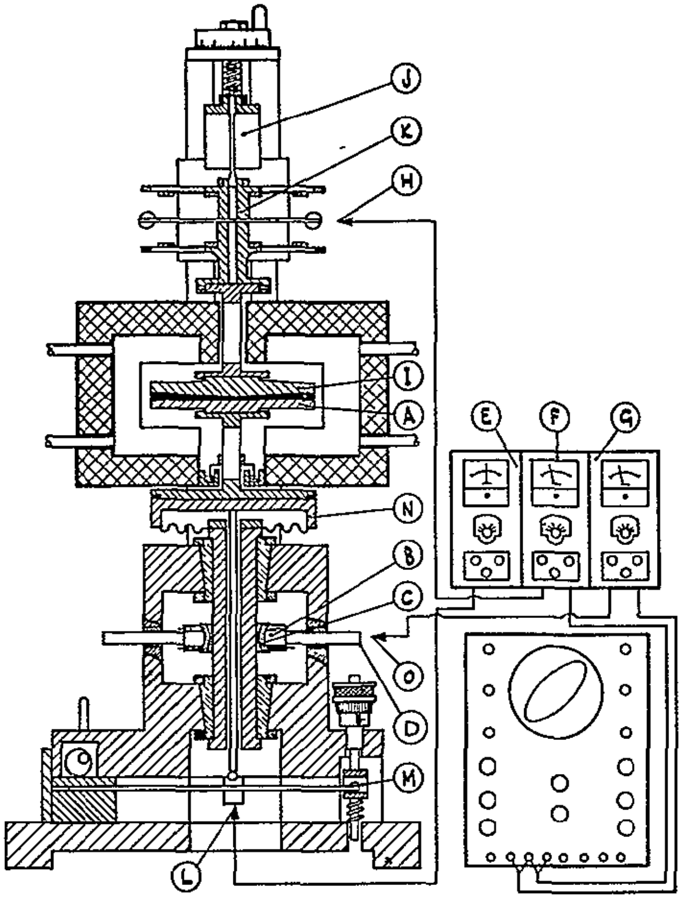
4. Weissenberg Rheogoniometer

The Weissenberg Rheogoniometer is a versatile instrument which may be used for rheological measurements on a variety of materials including melts, solutions, emulsions, suspensions, liquid mixtures, gels, pastes, and solids. A schematic of the instrument when used in the cone and plate viscosity mode is shown in Figure IV-36.(IV-80)

The fluid specimen (volume usually about 1 cubic centimeter) is held between the lower plate A and the upper surface I. Power enters the measuring head through shaft D, and through a worm and gear, a vertical shaft drives the lower surface. The upper surface is held by a torsion bar J which is clamped to the head K. An inductive transducer H detects the tangential shear stress by measuring the torsional displacement of the bar. The drive input can be pure rotation, or pure oscillation, or a combination of rotation and oscillation. When the input is oscillatory, a transducer O measures the input oscillation, while the lower plate A measures both the amplitude and phase angle of the oscillation that is transmitted to the upper surface. The plate and cone shown for use with fluids may be replaced by a set of clamps for measurements on solid specimens.

In the case of fluids, viscosities in the range 10^{-4} to 10^{8} poise can be measured. Shear rates may vary between 8 x 10^{-3} sec^{-1} and 10^{4} sec^{-1}, and provides the capability for testing of non-Newtonian fluids.

When used for measurements on solids as a dynamic mechanical analyzer, the measured quantities are the shear modulus and the loss tangent, since the specimen is oscillated in torsion. The frequency range which may be covered is 10^{-3} to 60 Hz. Solid specimens are usually in the form of bars about 2 mm x 2 mm x 2 cm. A temperature controlled chamber allows measurements to be made over the temperature range 77 to 620 K. The act of measurement has little effect on the test specimens, provided measurements are not extended to temperature or environmental conditions where degradation may occur. Precision of the technique is estimated to be about 3 percent, while the accuracy is estimated to be between 5 and 10 percent. A part of the inaccuracy is associated with the measurement of specimen dimensions.



(b)

FIGURE IV-36. DIAGRAMMATIC SECTION OF THE MEASURING HEAD OF THE RHEOGONIOMETER

Setup time may vary from 15 minutes up to about 1/2 day, while the measurement at several frequencies for a given temperature may take about 1 hour. A moderate to highly skilled operator must continuously monitor the measurements. The instrument requires power at 220 V and 10 A, and depending upon the temperature range, may require liquid nitrogen or water cooling. The instrument is a laboratory device and is not generally portable. It is manufactured by Sangamo Weston Controls, Ltd., and costs between $25,000 and $50,000, depending upon the options chosen.

5. Other Dynamic Mechanical Analyzers

Other instruments in this category are the DuPont Dynamic Mechanical Analysis System which is a module for their Thermal Analysis System, the Rheometrics instrument, the Dynastat Transient and Dynamic Viscoelastic Analyzer (sold by IMASS), and a new instrument developed by Professor Sternstein of RPI.

6. Ultrasonics Techniques

Techniques based upon the propagation of ultrasonic waves are widely used in nondestructive testing. When an ultrasonic wave traveling in one medium reaches an interface with another medium having a different acoustic impedance, a fraction of the incident wave is refracted. For a wave incident normal to the interface, the power reflection coefficient is given by

$$R = \left(\frac{\rho_1 C_1 - \rho_2 C_2}{\rho_1 C_1 + \rho_2 C_2} \right)^2 .$$

where ρ_1 and ρ_2 are the densities of the two media and C_1 and C_2 are the acoustic velocities in the two media. This reflection is the basis for the pulse-echo flaw-detection system, shown schematically in Figure IV-37.(IV-81) Here, an ultrasonic transducer bonded to the surface of the material under test emits a pulse which travels through the material. At each interface that the pulse encounters, a certain fraction of the energy is reflected and is picked up by the transducer. This technique requires that the transducer be acoustically coupled to the material. The coupling can be effected by various means, such as cements or thin films of water or oil.

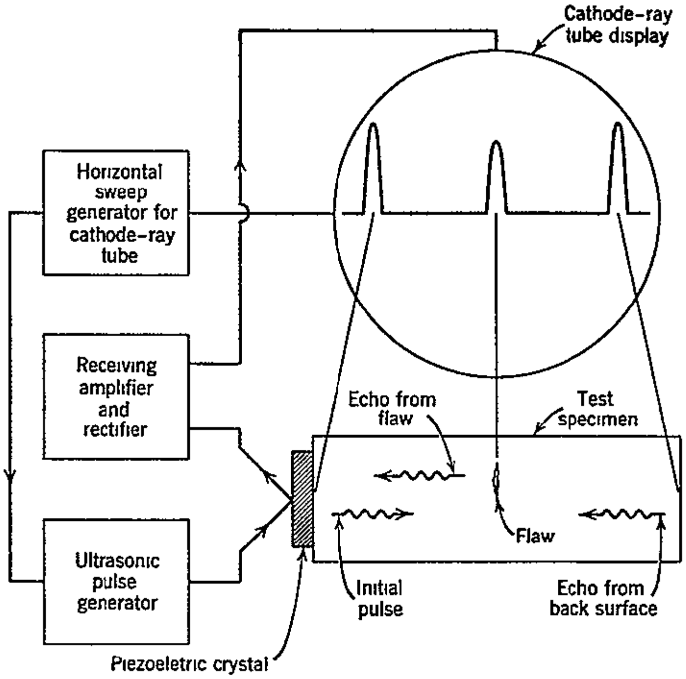


FIGURE IV-37. A SCHEMATIC OF A SIMPLE PULSE-ECHO FLAW-DETECTION SYSTEM USING A CONTACT-TYPE TRANSDUCER

An alternative pulse-echo test is the immersion-type test which is shown schematically in Figure IV-38. Here the material is immersed in a tank of water and the ultrasonic waves travel through a depth of water before impinging on the material. In this case, an echo is produced at the first surface of the material.

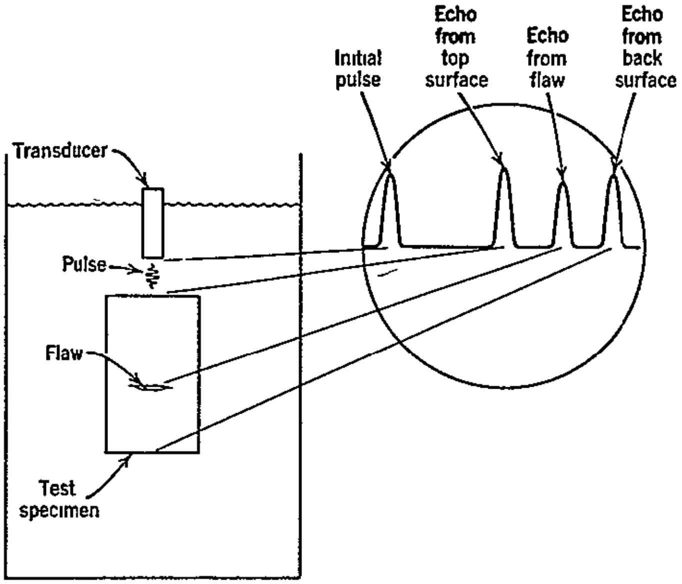


FIGURE IV-38. A SCHEMATIC OF AN IMMERSION-TYPE TEST

Inspection systems utilizing two transducers may also be used, in which a pulse is produced by one transducer and is detected by a second transducer. A two-transducer reflection system is shown in Figure IV-39, while a two-transducer transmission system is shown in Figure IV-40.

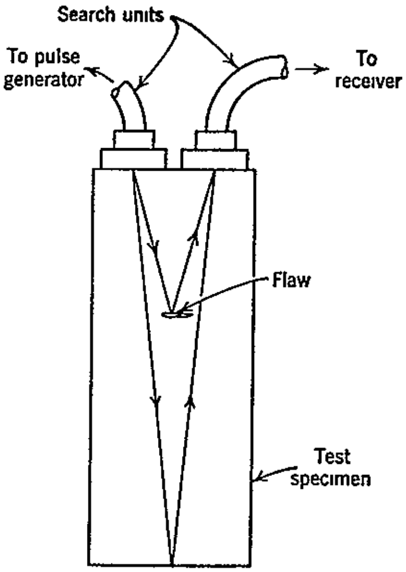


FIGURE IV-39. A TWO-CRYSTAL INSPECTION SYSTEM

As an alternative to pulses, continuous waves may be used in resonance methods of flaw detection. A single transducer is placed on the surface of the test piece and is used to produce a standing wave having an integral number of half-wavelengths, as shown in Figure IV-41.

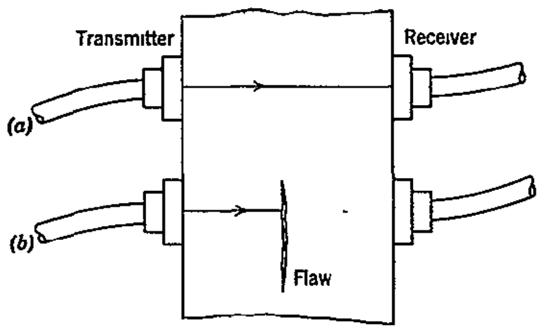


FIGURE IV-40. A TWO-CRYSTAL SYSTEM CAN BE USED FOR DETECTION OF LAMINAR DEFECTS IN PLATE MATERIAL

Transmission occurs at position (a). There is no transmission at (b).

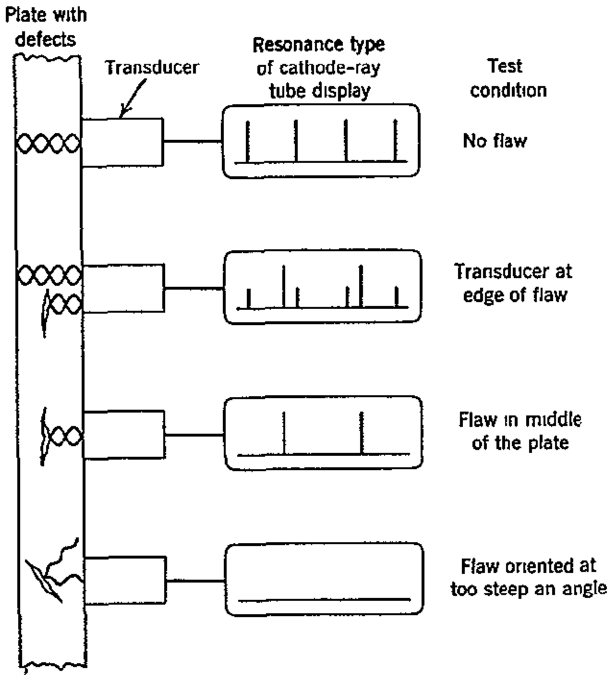


FIGURE IV-41. DETECTION OF FLAWS IN A METAL PLATE BY THE USE OF THE RESONANCE METHOD

Equipment for ultrasonic inspection usually consists of three basic items:

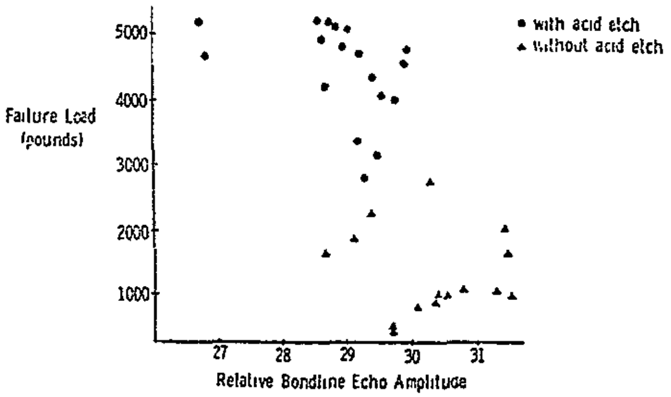
- One or more ultrasonic transducers, possibly combined with a mechanical scanning device
- Electronic signal processors which generate and detect the ultrasonic pulses or waves and other reference signals, and which convert the signals into usable data
- Units for displaying and/or recording the various signals.

Instrumentation would probably be assembled in modular form, with applicable equipment being available from such companies as Krautkramer-Branson, Panametrics, Automation Industries (Sperry Division), Nortec Corporation, Sonic Instruments, and Balteau Electric Corporation. It is estimated that equipment costs would be in the neighborhood of $5,000. Some pieces of equipment are portable and might be used for field inspections Setup and scan times may be as low as several minutes.

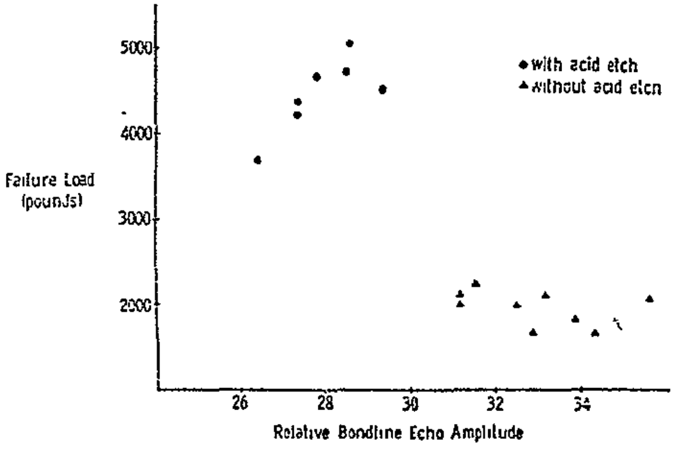
An assessment of the applicability of ultrasonic techniques to the evaluation of solar-cell modules will require a study of the details of materials properties and geometries. However, a few judgments may be made. First, immersion techniques may not be suitable in some cases because of the possibility of unwanted effects due to the immersion medium. Through-transmission techniques cannot be used in any structure which includes wood or similar material in the substrate, because of the difficulty of propagating ultrasound through such materials. It is judged that resonance techniques have limited usefulness in many of the bonding materials. The pitch-catch technique using two transducers on the same surface as in Figure IV-39 appears to be the most promising technique. In addition to delaminations (which cause enhanced reflections), material degradation which alters the ultrasonic velocity and attenuation may be detectable. It is difficult to give a quantitative estimate of an accuracy or sensitivity of this technique for measuring changes in the various effects. It is considered that a combined analytical and experimental program would be needed to provide such quantitative information.

While ultrasonic techniques have been used for many years to detect the presence of disbonded regions or delaminations in adhesively bonded systems, it is only recently that these techniques have been applied to the quantitative determination of the quality of an adhesive bond prior to actual disbonding. J. L. Rose and his associates at Drexel University have been working on a 5-year program which started in January, 1973, with the objective of developing ultrasonic procedures for a quantitative determination of adhesive bond strength.(IV-82) Most of the work has been directed at predicting the failure load of aluminum-aluminum step-lap joints, although the work is to be extended to metal-to-composite structures. Mathematical models were developed to allow a study of the basic ultrasonic wave interaction mechanisms with an adhesive bond.(IV-83) The models studied were identified as the reference bond model, the material property gradient model, the surface preparation model, and the combined property gradient and surface preparation model. The reference bond model considers the adhesive layer as a homogeneous, isotropic layer with isotropic substrate layers on either side. The material property gradient model is based upon the expectation that chemical migration, gas entrapment, and cure variation problems will cause a variation of mechanical properties across the thickness of the adhesive. This variation would then affect the transmission and reflection of ultrasonic waves through the adhesive. To make calculations, the adhesive was artificially subdivided into up to five layers having different acoustic properties. The surface preparation model is based on the expectation that surface contaminants may result in microscopic points of nonbonding uniformly distributed over the adhesive-substrate interface. This model then assumes that the interface consists of many points of contact separated by microscopic voids. The use of computer programs was necessary to obtain quantitative results. The results showed that variations in ultrasonic reflections may be small and that a careful signal analysis is necessary to avoid overlooking these small variations.

An experimental evaluation of these ideas was performed on aluminum-FM-47-aluminum step-lap-joint adhesive systems.(IV-84) The specimens were tested in an immersion tank, and the amplitude of the interfacial echo was measured. After ultrasonic testing, the specimens were loaded to failure in an Instron tensile testing machine. Different qualities of adhesive bonding were obtained either by using or by eliminating the recommended acid etching of the substrates. The results of this study are shown in Figure IV-42. As can be seen from the figures, it was observed that as the quality of the interfacial bond decreased, the amplitude of the interfacial reflection also decreased. Also, as shown by the difference in Figures IV-42 (a) and IV-42 (b), the choice of transducer appears to have a large effect on the sensitivity of the results, the 20 MHZ transducer producing a much better sensitivity than the 10 MHZ transducer. Although the correlations between failure load and bondline echo amplitude are reasonable, it is clear from the figures that predictions from a single test would not be very precise.



(a) Using 10 MHZ transducer



(b) Using 20 MHZ transducer

FIGURE IV-42. CORRELATION OF BOND FAILURE WITH BONDLINE ECHO AMPLITUDE(IV-84)

7. Thermal Analytical Techniques — General Description

Thermal analysis involves the use of a family of techniques by which the response of some material property is studied as a function of temperature. The most widely used techniques include differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and thermomechanical analysis (TMA). Other techniques in this family may include dynamic mechanical analysis (DMA), torsional braid analysis (TBA), thermooptical analysis (TOA), thermoacoustical analysis (TAA), electrical thermal analysis (ETA), thermometric titrimetry, and thermal evolution analysis (TEA). In this section, only those techniques used for measuring thermodynamic effects and weight changes are discussed; those techniques used for measuring changes in mechanical properties are discussed in another section.

All thermal analysis techniques have four main components. (1) a transducer to measure the response of the material, (2) a programmer which controls the heating and cooling rates of the material, (3) an amplifier which conditions the transducer signal, and (4) a recorder which yields a permanent record of the transducer response as a function of temperature. Various temperature scanning rates may be used and, depending upon what effects are being looked for, total running time may vary from about 10 minutes to 2 hours or so. A medium-skilled operator is required to run the instrument, but more experienced and knowledgeable personnel are needed to interpret the thermograms. Frequent calibration is needed, generally with materials of known melting point, heat capacity, etc. The instruments are usually suited for the laboratory and are not generally portable. As such, they are not suited for in situ measurements. Only a nominal amount of power is required. Liquid nitrogen is generally required for runs below room temperature, although some refrigeration units are available. Bottles of gases may be needed for purging or for atmospheric control.

8. Differential Thermal Analysis (DTA)

In differential thermal analysis, the temperature of a sample and a thermally inert reference material are measured as a function of temperature. The quantity which is recorded is the temperature difference. A schematic of a typical DTA instrument is shown in Figure IV-43.(IV-85) Here the transducers are thermocouples, which are individually placed directly within the sample and the reference material. The sample and reference are placed in identical chambers in a block, the temperature of which is automatically controlled. As the block is heated, any transition which the sample undergoes will be accompanied by either liberation or absorption of heat, with a corresponding increase or decrease in the sample temperature with respect to the reference material. A record of this temperature difference (ΔT) as a function of programmed temperature (usually the sample temperature) gives information about the temperatures at which transitions occur and whether the transition is exothermic or endothermic. The area under the ΔT curve gives a rough indication of the amount of heat transferred in or out of the sample, but is not generally used for quantitative purposes.

Since the thermocouples are embedded directly within the sample, DTA provides the highest thermometric accuracy of any of the thermal analysis techniques, and thus can be used to study small changes in transition temperatures which may be associated with other physical properties. Sensitivities of approximately 0.002°C are common for ΔT. However, this precision may not be realized in practice in measuring absolute temperatures of thermal events. Thermograms resulting from DTA runs generally show a number of peaks (associated with first-order transitions such as the melting point) and baseline shifts (associated with second-order transitions, such as the glass transition). Furthermore, there is inevitable rounding of the peaks and shifts so that various extrapolation techniques must be used to obtain transition temperatures. The shape of the DTA curve is influenced by two general types of variables instrumental factors and sample characteristics.(IV-86) Instrumental factors include furnace atmosphere, furnace size and shape, sample-holder material, sample-holder geometry, wire and bead size of thermocouple junction, heating rate, speed and response of recording instrument, and thermocouple location in sample. Sample characteristics include particle size, thermal conductivity, heat capacity, packing density, swelling or shrinkage of sample, amount of sample, effect of diluent, and degree of crystallinity. It is thus imperative that as many as possible of these factors be held constant when searching for small changes in transition temperatures. It should also be noted that the act of scanning a sample through a certain temperature range may lead to irreversible effects, such as those due to thermal degradation. In fact, a common practice is to erase a sample's previous history by performing one scan and then another. Such a procedure must be used with caution in degradation studies in order to avoid confusion between service degradation and changes induced by the actual measurement.

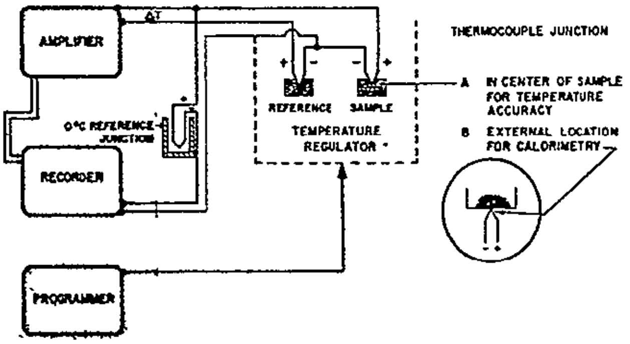


FIGURE IV-43. SCHEMATIC OF TYPICAL DTA INSTRUMENT

The use of thermal analysis in the determination of transition temperatures of polymers is covered by ASTM Designation D3418-75. Results of an interlaboratory round-robin showed that duplicate determinations of first and second-order transition temperatures on two specimens of the same sample by the same analyst should not differ by more than 1.5°C and 2.5°C, respectively. Similarly, duplicate determinations of first and second-order transition temperatures on specimens of the same sample analyzed in different laboratories should not differ by more than 2.0°C and 4.0°C, respectively.

DTA instruments are produced by a number of companies(IV-87), with DuPont and Perkin-Elmer being perhaps the better known ones. Many of these instruments are modular in design, with one basic programmer and recorder being used with separate modules for DTA, DSC, TGA, etc. As an example of costs, the DuPont programmer and recorder sell for about $13,000 while DTA modules costs range from about $6000 to $11,000. A wide range of operating temperatures is available, usually about -190°C to 1600°C. Samples may be run in a variety of gaseous atmospheres and in a variety of gaseous pressures (from about 10^{-6} torr to about 4000 psig) Various forms of specimens may be used and sample sizes may vary from 0.1 to 100 mg. A Stone DTA is available for use at Battelle's Columbus Laboratories.

Numerous applications of DTA to polymers have been reported in the literature (IV-88) From the viewpoint of this study, the most important application appears to be the determination of shifts in the glass transition temperature. One example of this use is the study of the curing and thermal degradation of thermosetting resins by monitoring T_g.(IV-89) In this study, changes of over 80°C in T_g were noted. Another potential use may be for determining the degree of crystallinity through measurements of the melting point.(IV-85)

9. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry is somewhat similar to DTA. However, DSC is more quantitative than DTA in regard to measurement of quantities of heat, i.e., DSC has a higher calorimetric accuracy than DTA. The dependent variable on the output curve of a DSC is proportional to the difference in rates of heat transfer between the sample and the reference material. The two factors which are necessary to the generation of quantitative energy data are (1) a controlled heat path into the sample and reference materials and (2) location of the temperature sensors external to the sample. Two approaches to these requirements appear to have been taken. The approach used by Perkin-Elmer, among others, is shown in Figure IV-44.(IV-90)

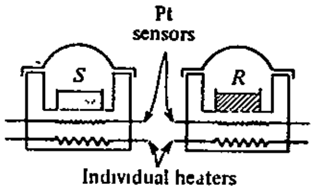


FIGURE IV-44. SCHEMATIC OF PERKIN-ELMER-TYPE DSC CELL

With this arrangement, the sample and reference material are provided with both separate temperature sensors and heaters. As the temperature is scanned, the sample and reference temperatures are continuously maintained at the same level by adjusting the power which is supplied to them. The differential power input is then recorded as the ordinate on the output chart. The second approach is that used by DuPont (see Figure IV-45).(IV-85) Here, a thermoelectric disk of closely controlled dimension and configuration acts as the major path of heat flow into the sample and reference. The disk provides one leg of a thermojunction while the other leg is made by attaching thermocouple wires to the disk. Then, under operating conditions, the differential of heat flow into the sample and reference materials is proportional to the differential temperature

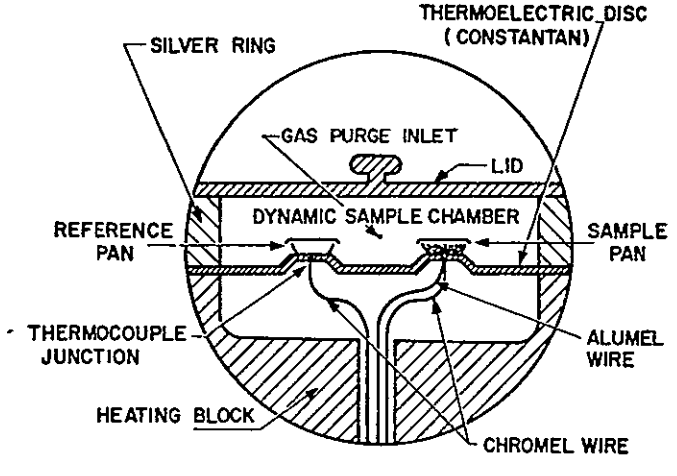


FIGURE IV-45. SCHEMATIC OF DuPONT DSC CELL

Calorimetric sensitivities as low as 3 μcal/sec have been reported (for DuPont Model 910).(IV-91) Also, a calorimetric precision of ±1 percent and a calorimetric accuracy of ±0.2 percent have been given.(IV-91) It is not clear why the accuracy is shown to be better than the precision. Temperature-calibration reproducibilities are ±0.5°C for the Perkin-Elmer instrument and ±1°C for the DuPont instrument.

As with DTA, many DSC instruments are modular. The DuPont DSC cells cost about $7,000 (programmer and recorder cost about $13,000). Temperature ranges for DSC's are -190°C to 725°C. Again, samples may be run in a variety of gaseous environments ranging from 0.01 torr to about 1000 psig. Sample sizes range from about 0.1 to 100 mg. As with DTA, the act of thermally scanning a sample may or may not produce irreversible changes.

One primary use of DSC is in the measurement of heats of transition at first-order transitions. An example of this is the heat of fusion; also, the degree of crystallinity may be correlated with the heat of fusion. The DSC may also be used to determine specific heats and heat effects associated with material decomposition, polymerization, and curing of thermosetting resins.

10. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is a technique whereby the change in weight of a sample can be measured as a function of temperature. A schematic of a TGA instrument is shown in Figure IV-46.(IV-92) Many of the commercial instruments use Cahn electrobalances. These are null-type balances, in which beam displacements caused by weight changes are detected with a light beam-shutter-photocell arrangement. A schematic of the Cahn RG electrobalance is shown in Figure IV-47.(IV-87) Changes in sample weight cause the beam to deflect momentarily. This motion produces a change in the phototube current which is amplified and fed to the coil attached to the beam. The change in coil current while in the field of the magnet produces a torque on the beam which restores it to its original position. The coil current thus serves as an indicator of weight change. The Cahn RG electrobalance has a capacity of 2.5 g and a sensitivity of 0.1 μg. A number of companies, including Perkin-Elmer, make TGA's based on Cahn-type thermobalances.

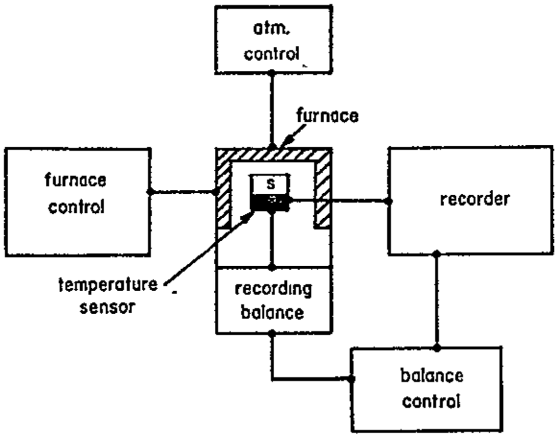


FIGURE IV-46. SCHEMATIC OF TGA INSTRUMENT

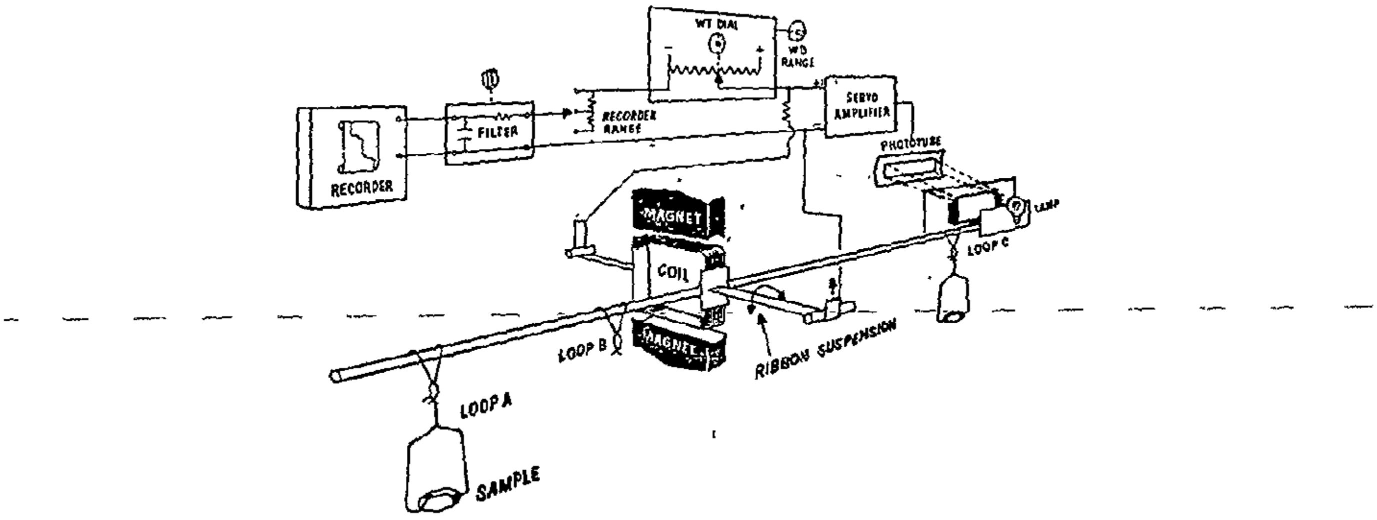


FIGURE IV-47. SCHEMATIC OF CAHN RG ELECTROBALANCE

DuPont makes a somewhat different TGA, a schematic of which is presented in Figure IV-48. The horizontal configuration, used to avoid buoyancy and aerodynamic effects, permits axial flushing of the furnace tube with various gases. This instrument has a capacity of 1 gram and a sensitivity of about 1 μg. The temperature range is room temperature to 1200 C, and the pressure range is 1 torr to 1 atmosphere pressure. The TGA is a module for the thermal analysis system and costs about $8,500. Precision and accuracy of weight measurements are 0.4 and 1.0 percent of full scale, respectively. Depending upon the sample size, as little as 0.5 percent of the sample weight may be displayed full scale.

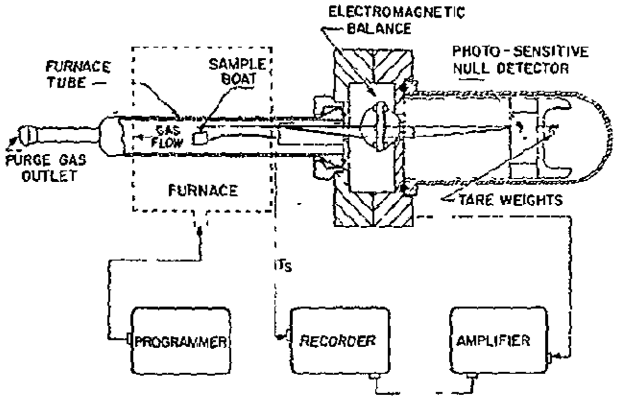


FIGURE IV-48. SCHEMATIC OF DuPONT THERMO-GRAVIMETRIC ANALYZER

As with DTA, many factors can influence the shape of a TGA curve.(IV-86) Instrumental factors which are important are furnace heating rate, recording or chart speed, furnace atmosphere, geometry of sample holder and furnace, sensitivity of recording mechanism, and composition of sample container. Important sample characteristics are amount of sample, solubility of evolved gases in sample, particle size, heat of reaction, sample packing, nature of the sample, and thermal conductivity. These factors must be considered when attempting to look for small changes in weight associated with degradation. The method is necessarily destructive of the sample.

TGA should be useful in degradation studies in determining changes in amounts of additives such as plasticizers and UV stabilizers. The effluent from the gas purge may be further analyzed by gas chromatography, mass spectrometry, etc.

11. Thermomechanical Analysis (TMA)

Thermomechanical analysis is one of the newest of the thermal analysis techniques. A schematic of the DuPont TMA module is shown in Figure IV-49. The transducer in the TMA is a linear variable differential transformer that detects linear movement of a probe in contact with the sample. Various types of probes may be used for detecting different thermomechanical properties as the sample's temperature is scanned. These probes are shown in Figure IV-50.(IV-85)

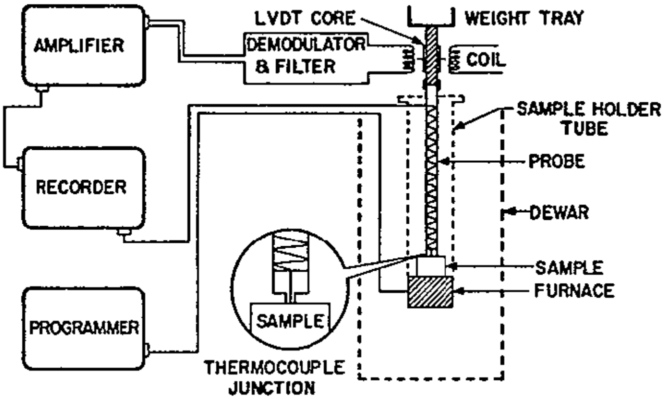


FIGURE IV-49. SCHEMATIC OF DuPONT TMA MODULE

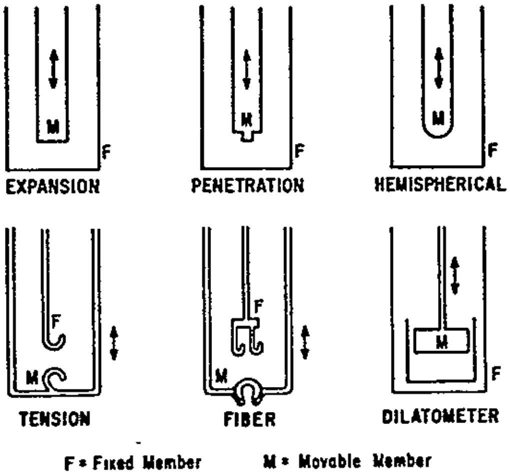


FIGURE IV-50. TMA PROBE CONFIGURATIONS

In the expansion mode, changes in sample length are measured directly. The slope of the resulting curve is the coefficient of thermal expansion. The glass transition temperature may be observed by the change in slope of the expansion curve, while the melting temperature can be observed as a sudden change in dimension. The temperature range of operation is -160°C to 1200°C. The maximum sensitivity is 50 μm. of probe deflection per inch of chart paper. Linearity is ±1/2 percent up to ±0.05-inch total displacement. Various size samples up to 0.375 inch in diameter may be used.

With other probe configurations, the TMA may be used to obtain softening temperatures, tensile modulus, compression modulus, shrink temperatures, viscosity, and stress relaxation. The price for the DuPont TMA module is about $7,000. It uses the same programmer and recorder as that used with the DSC and other instruments.

With regard to degradation studies, TMA should be useful in detecting changes in glass transition temperatures, as well as in providing quantitative data on changes in coefficient of the thermal expansion.

12. Infrared Thermovision

Infrared thermovision is a name applied to several commercial instruments which are used for detecting temperatures or temperature differences by measuring the infrared thermal radiation emitted by objects. A schematic of the instrument's sensing system is shown in Figure IV-51. Radiation emitted by an object is collected by a lens system, the object being scanned by a system of prisms. The radiation is then focused onto an infrared detector, the voltage output of which is sent to a television-type display unit. The display may be either black and white, in which lighter areas represent higher temperatures, or colored in which different colors represent different temperatures.

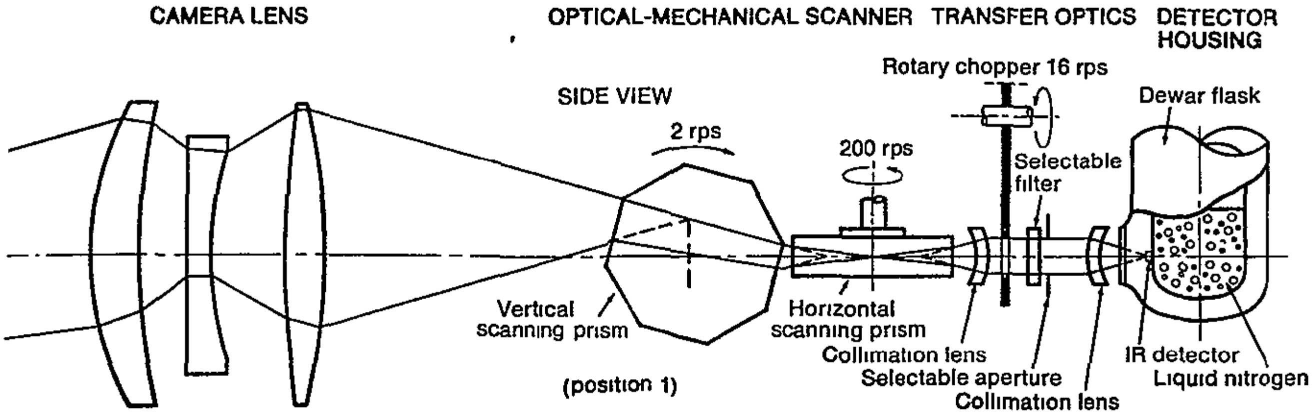


FIGURE IV-51. SCHEMATIC OF SENSING SYSTEM OF INFRARED THERMOVISION SYSTEM

One of the most popular instruments is the AGA Thermovision Model 680. This instrument utilizes an indium antimonide detector, which is sensitive to radiation in the wavelength range 2 to 5.6 microns. This instrument is capable of measuring temperatures between -30 and 2000°C. Temperature resolution is better than 0.2°C for an object temperature of 30°C. For higher object temperatures, the resolution generally increases. These resolutions depend upon the object being a black-body radiator. If the object being viewed is not a black body or is partially transparent over the wavelength range 2 to 5.6 microns, measured values of temperature or temperature differences must be carefully evaluated to obtain correct values.

Spatial resolution is on the order of 1-mm spot sizes. The system, including the camera, display unit, and carts, weighs around 140 pounds. The units are mounted on wheels and would thus be fairly portable. Electrical power and liquid-nitrogen cooling for the detector are required. The instrument may be set up in a short amount of time and scans may be taken rapidly. With the AGA system, the time-consuming part is the data reduction.

AGA Thermovision systems have already been used in testing solar cells. The system was used to monitor hot spots caused by a shorting path mode of degradation in copper sulfide-cadmium sulfide, thin-film solar cells.(IV-93) Another study was conducted on silicon solar cells which were covered with 0.006-inch-thick silica coverslides cemented to the cells with Silgard 182.(IV-94) The following defects were purposely introduced separately into the modules: (1) tabs on the solder bar were unsoldered, (2) the solar cell was broken in one corner, (3) the mesh interconnects were disconnected from the back of a cell, (4) the solar cell was not bonded to the substrate, and (5) a cell was partially shorted via a grid to the substrate. An attempt at using the system with the module being illuminated with a solar simulator was unsuccessful because of multiple infrared reflections. The technique was successful when the modules were viewed in an IR quiet area, with the cells being heated by passing a reverse current through them. Defects that were easily picked up were broken, debonded, shorted, and disconnected cells. The cells with defects were either hotter or cooler than other cells, depending upon the nature of the defect.

While some successful results have already been obtained, it is judged that further work would need to be done to determine the applicability of such a system to measuring quantitative changes in performance. The complications noted above for non-black-body radiators and partial transparency in the wavelength range of interest would have to be considered. On the whole, it is felt that this technique may have considerable merit in monitoring solar-cell modules.

In addition to AGE, thermovision instruments are manufactured by Barnes Engineering, Texas Instruments, Dynarad, and Spectrotherm, among others. AGA also makes a Model 750 which is more portable but also less versatile than Model 680. The cost of Model 680 is about $45,000.

13. Summary – Thermal and Mechanical Measurement Techniques

- Since the properties of polymers are in some cases very sensitive to the glass transition temperature, it is recommended that this property be measured by a suitable means. The simplest and most rapid methods for measuring T_g appear to be differential thermal analysis and differential scanning calorimetry. In the absence of specific information regarding the accuracies of these two techniques with regard to measurement of T_g, DSC measurements are recommended since the resulting thermograms can be interpreted quantitatively.

- An alternative method for obtaining T_g is dynamic mechanical measurements. In addition to providing a measure of T_g, this family of techniques yields potentially valuable information on the mechanical behavior of the materials. If these measurements are undertaken, the measurements by DTA or DSC will probably be unnecessary. Dynamic mechanical measurements would thus be recommended over DTA or DSC. Since temperature is a more important variable than frequency for dynamic mechanical measurements, any of the previously described techniques may be used, depending upon availability and ease of measurement.

- The applicability of infrared thermovision in diagnosing degradation in solar-cell modules requires and merits further characterization. The infrared transmission of the various cover and adhesive materials needs to be examined over the wavelength range to which the instrument is sensitive. Also evaluations need to be made of the spectral emittance of opaque materials and of the possibility of radiation from these materials being propagated through the cover and adhesive materials. Infrared thermovision has already been demonstrated as being of value in detecting the presence of defects as evidenced by certain areas of modules being hotter or colder than surrounding regions. Further testing will be required to establish quantitative relationships, such as apparent temperature differences versus a quantitative measure of the degree of the defect.

- The applicability of ultrasonic techniques also requires and merits further testing and evaluation. A theoretical analysis appears to be necessary in order to interpret the various echo signals which may be received. Some experimental testing will be needed in order to select optimum transducers and locations. It is considered that ultrasonic methods have a great potential for applicability in this area, and thus tests should be conducted on cells with and without defects in order to establish the potential magnitudes of changes in ultrasonic signals that may be experienced.

F. OTHER "PHYSICAL" TECHNIQUES

1. Background

This measurement category includes those techniques which are considered to fall outside of the scope of the efforts in the other categories either for technical reasons or for the convenience of the overall effort. Three primary candidates of interest are investigated in detail in this category – profilometry, photoacoustic spectroscopy, and water vapor/gas permeability. These are discussed below.

2. Profilometry

The stylus profilometer has been a major engineering tool for measuring surface topography and surface roughness for many years. Profilometry was developed in the late 1930's as a result of the need to characterize the engineering surfaces used in the new (at that time) high-performance aircraft engines. The instrument consists basically of a diamond stylus that moves horizontally relative to the surface of the test sample. The vertical displacements of the stylus are detected and converted to analog or digital signals that can be recorded on strip charts or displayed on appropriate meters. In some cases, the sample is moved and the sensing head is stationary, while in others, the stylus is moved across a stationary sample. The technique displays an accuracy comparable to that of the X-ray and optical interference techniques used in the measurement of film thicknesses and profiles.(IV-95) Vertical resolution for standard stylus-type measurements is limited to about 20 Å by the electrical and mechanical noise associated with the measuring instrument. The horizontal resolution depends on the contour of the stylus tip, although it is not limited to lateral geometries larger than the stylus-tip diameter. Reference (IV-95) gives an excellent example of a high-resolution profile in a series of strips 3 5 μm wide and 450 Å thick made by using a 0.0005-inch (~13 μm)-radius stylus

The combining or direct interfacing of profilometers with digital computers over the past few years(IV-96,IV-97) has had a major impact on the accuracy and effectiveness of the technique The use of the computer greatly simplifies the task of analyzing and evaluating the data to determine average and rms surface roughness and eliminates the element of individual interpretation present in the graphical analysis techniques previously used. In addition, computer processing of the data can include elimination of the contributions of electrical noise and instrument drift. Limit sensitivities of the order of 5 Å (signal/noise = 1) are reported for configurations of this type.

In selecting instruments for characterizing the surfaces of encapsulation materials, and particularly degradative changes of these surfaces associated with abrasive or chemical attack, it should be kept in mind that it will probably be desirable to look at those surfaces at several different levels of magnification. Certain types of chemical attack (e.g., certain leaching or etching reactions) may result in a high density of relatively small pits or defects that might appropriately be evaluated by SEM studies. Other types of chemical and abrasive attack could have a more gross effect on surface roughness which might, for example, ultimately result in increasing the dirt accumulation rate. Some of these types of effects might better be studied, particularly where quantitative assessments over large areas are desired, by profilometry. Profilometry provides a quantitative measure of surface roughness in its range of sensitivity, and evaluation of the data,

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especially when coupled with a computer, is reasonably straightforward. It should also be pointed out that it is not essential that the computer interface directly with the profilometer The data can be recorded in digital form (e.g., on tape) at the measurement site and transported to the computer for processing in cases where no on-site computer is available.

In view of the sensitivity and accuracy of present-day surface profiling instruments, and particularly considering the quantitative nature of the information it supplies, it is felt that profilometry can be a useful tool in degradation and life-testing studies, particularly in environmental situations where abrasive or other forms of relatively gross attack are potentially significant factors. Profilometers are available from Taylor Hobson, Inc., of Leicester, England (Talysurf); and Sloan Instruments (DekTak), among others, at a cost of about $10 K and up.

3. Photoacoustic Spectroscopy

Photoacoustic spectroscopy (PAS) is a technique which has only recently found application in the study of solids, although its origin can be traced to early studies of the "opto-acoustic effect" in gases by Alexander Graham Bell and others in the 1880's.(IV-98) The technique consists of illuminating a sample with a modulated, high-intensity, monochromatic light beam (UV-visible-near IR) while it is enclosed in a sealed, small-volume cell which also contains a sensitive microphone. The incident light is absorbed by the sample, resulting in the excitation of electrons to higher energy states. These electrons then decay back to the lower energy states through primarily nonradiative processes, thereby creating a periodically varying (due to the modulation) heat distribution in the vicinity of the point of absorption This heat diffuses to the surface of the sample where it creates periodic pressure waves in the gas-boundary layer. These are propagated through the bulk of the gas to drive the microphone and produce the output signal. Both the amplitude and the phase of the signal contribute useful information. These signal properties depend upon a number of factors, including the optical absorption and thermal diffusion properties of the sample, the modulation or chopping frequency, and the cell/sample geometry. A block diagram of a commercially available unit (Guilford Instrument Lab Model R-1500) is shown in Figure IV-52.(IV-99) The basic instrument consists of a light source with either an electrical or a mechanical modulation capability (the illustrated unit incorporates both), a monochromater, the sealed sample cell (the illustrated unit incorporates two cells to allow comparisons with reference cells or the production of difference spectra), and suitable electronics for determining and displaying the amplitude and phase of the output. Figure IV-53 shows the elements of one type of PAS cell design.(IV-100) The cell is basically a sealed unit with a transparent window for light admittance containing some means of sample support and the sensing microphone The physical dimensions of the cell and the thermal properties of the gas are important factors in determining the sensitivity of the photoacoustic spectrometer.(IV-101)

PAS can be used to study both the optical absorption properties and the thermal diffusivity/thermal conductivity properties of a material. A principal advantage of the technique is its ability to obtain spectra directly from various types of solids such as crystals, powders, gels, and other forms and types of materials where scattered light or opaqueness might present a significant problem for more conventional spectroscopies. The technique has been used advantageously in studies of biological materials (PA-Z), organometallic compounds(IV-102), and nonradiative processes in luminescent solids(IV-103), and in the separate determination of bulk- and surface-absorption coefficients in weakly absorbing materials(IV-104)

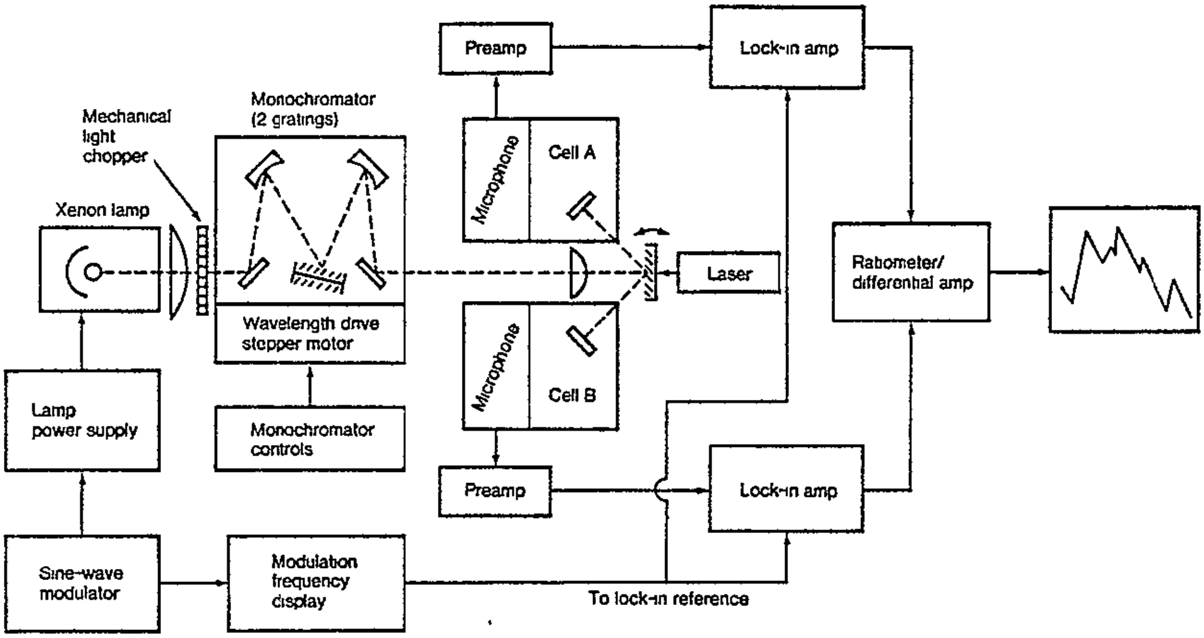

FIGURE IV-52. BLOCK DIAGRAM OF GILFORD R-1500 SHOWING THAT EITHER ELECTRONIC MODULATION OF LAMP POWER SUPPLY OR MECHANICAL MODULATION CAN BE USED

Position of mirror can be changed to direct output from a laser excitation source to the cell.

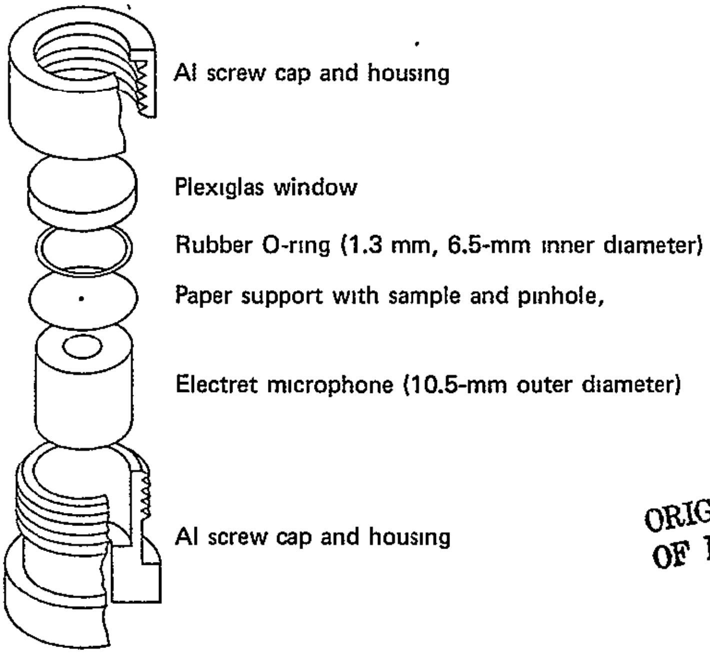

FIGURE IV-53. SMALL-VOLUME PHOTOACOUSTIC CELL (40 MM^3)

In the study of the degradation of encapsulant materials and encapsulant systems for photovoltaic applications, PAS offers several potential advantages as a laboratory tool.

- PAS provides detailed information on changes in both the optical and thermal properties of materials.
- PAS has the capability of measuring changes in bulk optical properties in cases where unrelated degradation of surface properties (e.g., abrasive attack) might make characterization by more conventional techniques extremely difficult
- With PAS, by varying the region in which the photon energy is deposited (i.e., by varying the wavelength of the incident radiation), it may be possible to obtain information that allows discrimination between several degradation modes/ mechanisms occurring simultaneously.
- With PAS, with proper choice of photon wavelength and modulation frequency, changes in the properties of bonds at material interfaces might be detected, thereby providing a means of predicting delamination.(IV-102)

The ultimate usefulness of this technique, including its sensitivity, accuracy and precision for specific applications in this area cannot be fully determined from information presently available. A program to experimentally investigate the usefulness of the technique for these studies is currently under way at the Jet Propulsion Laboratories and should soon provide some insight. The potential advantages of the technique clearly warrant a careful investigation of possible evaluative areas in which it might be used.

4. Water Vapor and Gas Permeability

The permeability of materials used in photovoltaic modules to gases and water vapor is of interest in degradation studies from two points of view. On the one hand, it controls the level of exposure of those elements of the module that are vulnerable to attack by water vapor, oxygen, and other corrosive agents, hence, increases in permeability to these agents could be precursive of increased rates of attack by them. On the other hand, changes in the permeability of polymers are generally the result of structural, morphological, and chemical changes that could lead to failure because of noncorrosive effects such as embrittlement, weakening of bonds, etc., in which case, the permeability is a potential diagnostic tool for detecting and measuring such changes. The permeability (P) of a material to a gas or vapor is the product of the solubility (S) of the gas or vapor in the barrier material and its diffusivity (D) in and through the material: $P = S \cdot D$. This quantity (P) can be directly measured and is normally expressed as the rate of transfer of the penetrant (e.g , cm^3/sec) per unit area, per unit pressure differential, and per unit thickness of the barrier material. The diffusivity is basically related to the physical limitations of diffusion, such as the size and shape of the penetrant molecule and the size and shape of the spaces or passages in the solid material through which the molecule must pass. The solubility is influenced by interactions between the penetrant molecule and the surrounding medium due to molecular forces such as those associated with the degree of the molecule's polarity and the medium. There are a number of ways to determine S and D from permeability data when that is desired. In some cases, independent data on solubility can be obtained without great difficulty (e.g., from immersion tests in the case of water vapor), thereby permitting calculation of D. This approach can, however, be difficult for species exhibiting low solubility. Alternatively, diffusion coefficients and diffusivities can be deduced from studies of the kinetics of sorption and transmission processes in the transient (nonequilibrium) stage.(IV-105)

Permeability measurements are generally made by impressing a pressure or partial pressure gradient of the gas or vapor across a sheet of the material and measuring the rate at which it is transmitted to the low pressure side. The means of measuring the transmission rate varies with the penetrant species and the level of sensitivity desired. In the ASTM methods (E-96-66 and C355-64) for measuring water-vapor transmission, the film materials are sealed over a dish or container in which desiccant (or water) has been placed. The change in weight due to the absorption (or escape) of water is measured to determine the transmission rate. Some of the more advanced systems use IR detection systems to measure water vapor and carbon dioxide transmission rates(IV-106), and one manufacturer uses a "coulometric" fuel-cell-type detector to measure oxygen transmission rates(IV-107). These techniques offer advantages in speed and sensitivity.

The permeability of polymeric films to water vapor, carbon dioxide, and oxygen has been of concern to the packaging industry for many years and considerable information has been developed and published in this area. The importance of water vapor permeability in photovoltaic module construction materials was recognized early in the terrestrial photovoltaic module development program, and studies of this property for a number of candidate materials have been conducted.(IV-108) These studies have used variations on the desiccant absorption technique, for the most part, to measure transmission rates, although one interesting current study involves the use of humidity sensors imbedded at various positions in the encapsulant (IV-109) Studies on the barrier properties of encapsulation materials are already a well-established part of the LSSA encapsulation program so that recommendations on the use of permeability measurements for such studies are not needed. It is worthwhile to emphasize that such studies should include a careful examination of the conditions which will exist in operating modules (e.g., temperature gradients, interfaces) in order to determine the actual impact of differences in barrier properties.

The potential of permeability as a diagnostic tool for studying changes in polymers has been indicated in recently reported studies by Professor C. Rogers of Case Western Reserve University.(IV-10) His investigations of the effect of UV exposure on the permeability of polymers to water vapor and nitrogen have shown clear correlations between the degree of oxidation (carbonyl concentration) of the polymer, as determined by FTIR measurements, and changes in the permeability properties. Detailed examinations of the solubility and diffusivity have permitted deductions concerning the nature of some of the changes occurring (i.e., structural densification, increases in polarity). The potential applicability of permeability measurements as a laboratory technique for studying degradation associated with structural and chemical changes in polymers is apparent from these studies. One might ultimately envision a diagnostic test in which the permeabilities of a series of gases or vapors of various molecular sizes and polar characteristics are used to characterize degradative changes in polymers. The question of the advantages of permeability measurements as compared with competing techniques that might characterize strucural and chemical changes is addressed in Section V of this report.

Water-vapor-transmission measurement equipment is commercially available from several sources, including the Thwing-Albert Instrument Company of Philadelphia, Pennsylvania; and Modern Controls, Inc., of Minneapolis, Minnesota, at costs in the range of \$2000 to \$22,000. Sensitivities of 0.01 $g/100\ in.^2/24$ hr and better are achievable, and accuracies of 2 to 5 percent are quoted (perturbed by thickness and/or transmission rate). Repeatability ranges from ±2 to ±30 percent, also depending upon transmission rate.

Modern Controls also produces instrumentation for measuring transmission rates of gases (O_2 and CO_2) at costs of $7000 to $22,000. Sensitivities of these units, which use IR radiation at specific wavelengths as the sensing mechanism, are of the order of 0.002 cc/100 in.^{2}/24 hr for films. Accuracies and repeatabilities are similar to those quoted for WVTR measurements above.

5. Summary – Other "Physical" Techniques

- Profilometry, when combined with computer processing of the data, could be a powerful tool for quantitative assessment of changes in surface roughness over large areas, such as that which might occur due to abrasive attack of photovoltaic module covers.
- Photoacoustic spectroscopy (PAS) offers some potentially unique capabilities in studying optical, thermal, and possibly bonding characteristics of polymers. Experimental evaluations that are needed to demonstrate its capabilities in the context of studies of photovoltaic module degradation have been initiated at JPL.
- Permeability measurements of polymeric materials are important for establishing their barrier properties against potential corrosive agents; however, these measurements could also be useful in diagnosing chemical and structural changes associated with degradation modes that are not related to corrosion. As with PAS, experimental evaluations and developmental work are required to demonstrate these capabilities, and such an investigation is under way at Case Western Reserve University.

V. SELECTION CRITERIA AND COMPARATIVE ANALYSIS OF TECHNIQUES/INSTRUMENTS

V. SELECTION CRITERIA AND COMPARATIVE ANALYSIS OF TECHNIQUES/INSTRUMENTS

A. SELECTION CRITERIA*

A key requirement of an accelerated/abbreviated test for photovoltaic modules is the early detection of change in any module component. The need for measuring very small changes is emphasized throughout this report. Analytical instruments with precision adequate for detecting and characterizing these small degradative changes are required. To develop an idea of the magnitude of the problem, let us assume that the component of interest degrades by a first-order process. In this case, the following relationship is applicable

$$P_t = P_o e^{-kt} \tag{1}$$

where P_t is the property level at time t, P_o is the property level prior to the onset of degradation, t is time in days, and k is the first-order rate constant for the degradative process. Now, if we assume a specific amount of degradation by the end of the twentieth year, the rate constant, k, and the fractional degradation for any time period can be calculated Some representative calculations are shown in Table V-1. Of course, without defining a specific application and its requirements, one cannot determine the limit of power output degradation which represents array failure However, it is obvious from Table V-1 that very sensitive instruments are required for early detection of change.

TABLE V-1. FRACTIONAL DEGRADATION FOR VARIOUS ELAPSED TIMES BASED ON VARIOUS AMOUNTS OF TOTAL 20-YEAR DEGRADATION

Assumed 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

Before discussing instrument requirements further it is necessary to define some terms used in describing these requirements: precision, accuracy, sensitivity, and selectivity. Precision and accuracy are often used interchangeably although they are two different entities. The difference is discussed in detail in Reference (III-3) In brief, precision refers to the closeness of repeated measurements to one another and thus to the mean value, while accuracy refers to the closeness of test measurements to some reference value

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*The selection criteria used in evaluating measurement techniques/instruments in this study are listed in Table IV-2

As discussed in Reference (III-3), precision, being a measure of the spread or dispersion of data points around their mean value, can be described in terms of several different quantities, including the mean deviation, M,

$$M = \frac{\sum_{i=1}^{N} |X_i - \overline{X}|}{N} \tag{2}$$

or the more commonly used standard deviation, σ,

$$\sigma = \left[\frac{\sum_{i=1}^{N} (X_i - \overline{X})^2}{N - 1} \right]^{1/2} , \tag{3}$$

and, alternatively, the coefficient of variation, CV,

$$CV = \frac{\sigma}{\overline{X}} , \tag{4}$$

where N is the number of data points, $\overline{X}$ is the mean value, and X_i is the value of an individual measurement or data point.

Sensitivity, a sometimes misused word, refers to the smallest quantity or concentration of a substance that can be detected. Preferably, the less ambiguous term, "lower limit of detection" should be used.(V-1) The magnitude of the lower limit of detection is based on the ability to differentiate between a signal representative of the substance sought and the absence of that signal Finally, selectivity is a measure of the degree to which extraneous substances interfere with the signal from the substance of interest.

1. Estimation of Necessary Precision

If several simplifying assumptions are made, one can roughly estimate the coefficient of variation required to detect fractional changes of the size indicated in Table V-1. First, let a generalized value in the table be denoted γ, where

$$\gamma = \frac{P_t - P_o}{P_o} \tag{5}$$

and P_t and P_o are as defined earlier. Furthermore, assume that $\overline{P}_o$ is known without error and that measured values of P_o are normally distributed with mean $\overline{P}_o$ and standard deviation σ. Now assume that after a time t (very small in relation to the time required for total degradation), a property measurement P_t is made and it is desired to know the minimum property change, $P_o - P_t$, that can be detected with 95 percent confidence. Using a one-tailed test, one can write

$$\frac{P_o - P_t}{\sigma} \geqslant 1.64 . \tag{6}$$

Now since t was selected to give little if any degradation, one can see that P is relatively constant over the given interval so that one can write

$$\frac{P_o - P_t}{CV(\bar{P})} \geqslant 1.64 \quad , \tag{7}$$

where CV is the population coefficient of variation, $\frac{\sigma}{\bar{P}}$, and $\bar{P}$ is the property mean over the time interval Since $P_o - P_t \approx 0$, one can write $\bar{P} \approx P_o$ so that

$$\frac{P_o - P_t}{P_o} \geqslant 1.64\ (CV) \quad , \tag{8}$$

or

$$\gamma \geqslant 1.64\ (CV) \quad , \tag{9}$$

or

$$CV \leqslant \frac{\gamma}{1.64} \tag{10}$$

Thus to detect a fractional change γ, the coefficient of variation must be no larger than approximately $\gamma/2$, where again γ represents any general entry in Table V-1. Therefore, even if the assumptions would change this result by a factor of 2 in the direction favorable to the experiments, the coefficient of variation should then be about the size of the table entries. Thus, for example, if one expects to detect degradation after 90 days (again using the assumed first-order degradation kinetics), the test coefficient of variation required would be roughly 0 3 percent to 2 percent for 20-year degradation levels of 20 and 80 percent, respectively. Although admittedly very rough, Equation (6) will give an approximation to the precision levels required for a candidate test.

2. Test Stability Over Time

Measurements of property changes of photovoltaic array components will be made over relatively long periods of time. In addition to a high level of precision, sensitivity, and selectivity, the ideal measuring instrument must be stable over time. This implies that it must be insensitive to or capable of being calibrated to negate effects of factors such as temperature and humidity changes and operator technique, which may fluctuate from day to day even in a well-controlled laboratory experiment Unfortunately, few if any analytical instruments are completely stable with such changes. The degree and nature of the instabilities and the possibility of compensating for them must be considered in determining which instruments are selected for monitoring array degradation and what precautions have to be taken in designing the testing program. For example, if an instrument exhibits wide variability from laboratory to laboratory, it may be advisable either to find an equivalent stable instrument/test or, alternatively, to do all such testing at a single laboratory. Likewise, if instabilities exist over time for any reason, it may be desirable to accumulate a large number of specimens and test them all at once. It is desirable then, for any analytical test considered for array-component-degradation testing, that as much as possible be known about the test's stability. It is not possible to make a general statement as to the level of instability which will disqualify a test from consideration. However, for two similar tests, all other considerations being equal, the one less sensitive to extraneous factors will be most useful.

One way to deal with the kinds of measuring-instrument instabilities discussed above is to use standard samples, if available. For example, suppose that two different laboratories measure supposedly identical samples of an aged polymer film and get different values, say 40 and 45, due to the existence of one or more instabilities in the measuring instrument If a reference standard were available, it would allow determination of whether or not the test values of 40 and 45 represented real material differences. In the example, if the two laboratories measured nearly identical values for the reference sample, it would be an indication that the two polymer films did actually differ. If, on the other hand, the two laboratories differed by about five units for the reference sample, it would be concluded that the two film samples were the same. Standard reference samples such as those supplied by the National Bureau of Standards are therefore quite useful. For many applications, however, good reference standards do not exist. For example, no applicable reference standard exists for measurements of the degree of carbonyl formation on the surface of an acrylic array cover.

3. Sources of Information for Test Stability

Information on test stability is generally found by running interlaboratory or round-robin tests. Typically, such a test involves random selection (if possible) of several laboratories equipped to run the test. Each laboratory is then sent a set of nominally identical samples along with instructions for running the test. The test is then run at different times, with different operators, etc., depending upon which components of variance (i.e., sources of test instability) are suspected as being significant. A typical experimental design for such a program is shown in Figure V-1. Here each laboratory is to test four samples on each of three different randomly selected (to the

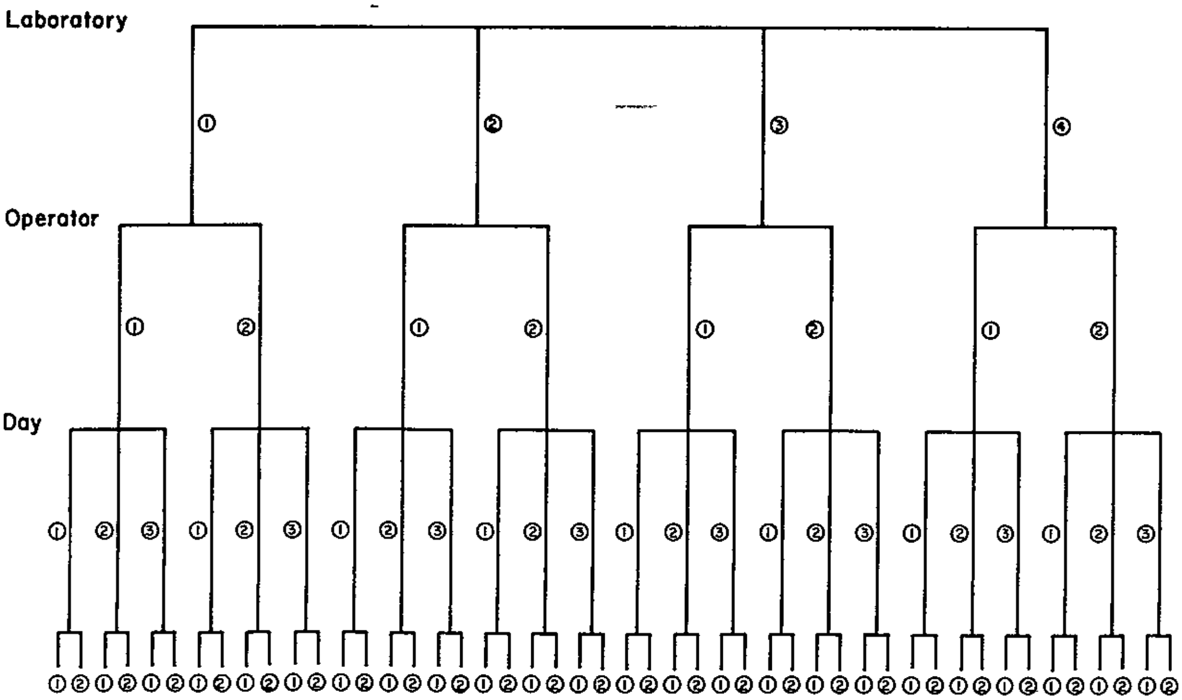

FIGURE V-1. EXPERIMENTAL DESIGN FOR INTERLABORATORY TEST

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extent reasonable) days On each of these days, two different operators will test two duplicate samples each. Analysis of the data from such a design allows the variance due to each source of variation to be estimated. The ideal outcome, of course, is to have none of the sources exhibit significant variability aside from that due to replication error. In such a case, the test can be run in any laboratory with any qualified operator on any day with reasonable assurance of stable test results. On the other hand, significant variance of laboratory, operator, or day sources would necessitate a more rigid experimental design, as discussed earlier.

Interlaboratory test data could be extremely useful in a meaningful experimental program for measurement of array-component degradation. Once the candidate tests have been identified, a search should be made for such information The American Society for Testing and Materials and the National Bureau of Standards are two organizations concerned with such testing and should be contacted in an effort to obtain available test results If such results are not available, it will be desirable, if not necessary, to set up such a test The test need not be an interlaboratory test. If it is determined that only one laboratory is sufficient, a similar test plan can be set up to evaluate only operator, day, and replicate variability. The first 12 tests in Figure V-1 would then represent one such design.

4. Comparison of Tests Which Measure the Same Phenomenon

When two tests which measure the same underlying phenomenon are compared, knowledge of lower detection limit, precision, accuracy, and selectivity for each test is not always sufficient to determine which is best capable of sensitively measuring small amounts of degradation. For example, Tests M and N may have standard deviations of 1 and 2, respectively. Suppose that during the course of material degradation property M changes from 90 to 80, whereas property N changes from 140 to 110 Clearly Test M is preferred over Test N only if the range of test values is the same for both tests. In this example, this is not the case. Mandel$^{(V-2)}$ developed a unitless quantity, the relative sensitivity of Test M compared to Test N or RS(M/N), to make such comparisons with validity. This quantity has been discussed in an earlier report$^{(III-3)}$, but is repeated here because of its relevance to the task at hand, i.e., comparison of techniques

Mandel's Sensitivity Ratio

Suppose that two test methods, M and N, both measure the same property – say Q. If M is a function of Q and N is a function of Q, it follows that M is functionally related to N. Suppose that the standard deviation of Test M is σ_M and that of Test N is σ_N. Mandel has shown that the two tests can be compared by a quantity called the relative sensitivity of Test M with respect to Test N, RS(M/N), where

$$\mathrm{RS(M/N)} = \frac{dM/dN}{\sigma_M/\sigma_N} \quad . \tag{11}$$

Note that the relative sensitivity is unitless and favors Test M when RS(M/N) > 1 and Test N when RS(M/N) < 1. This concept is illustrated in Figure V-2 where the differentials are shown as ΔM and ΔN. Careful inspection of this figure will indicate that RS(M/N) is not necessarily constant, but will vary from point to point depending upon the shape of the sensitivity curve and whether or not the standard deviations are constant. Thus, one cannot say that Test M is "better" than Test N unless RS(M/N) > 1 for all values of M and N. In the special case when dm/dn, σ_M, and σ_N are constant, the relative sensitivity will, of course, also be a constant

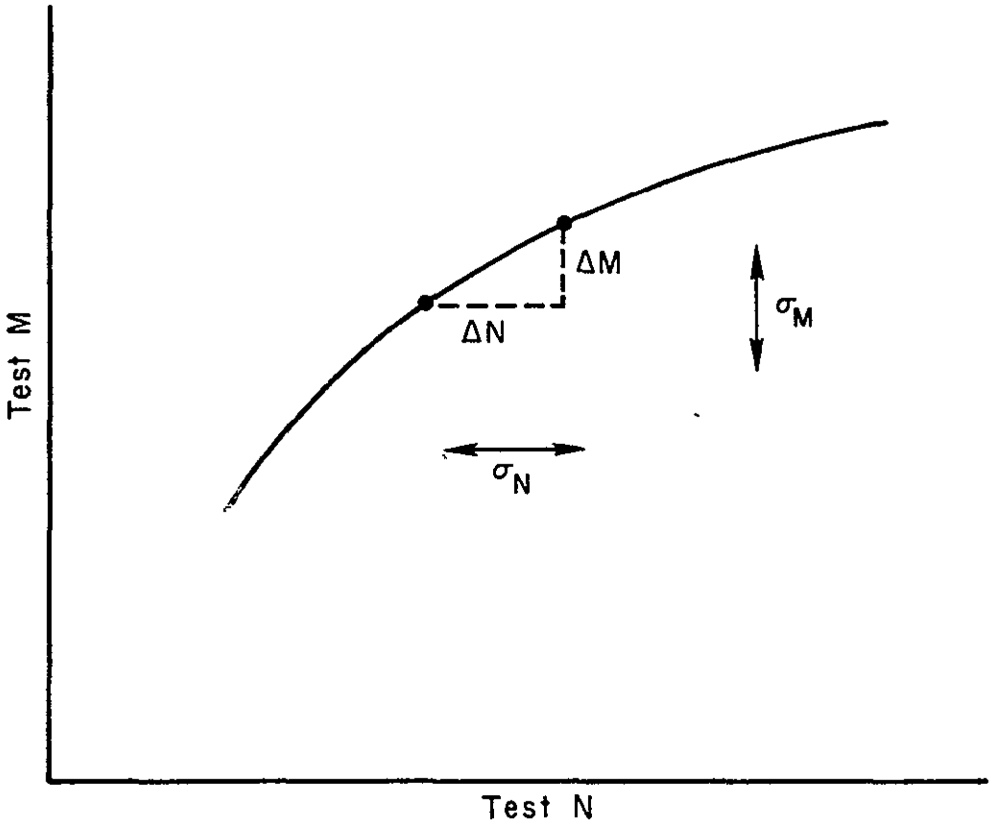

FIGURE V-2. ILLUSTRATION OF RELATIVE SENSITIVITY OF TWO TESTS, M AND N

As an example, suppose that one has the properties, P_1 and P_2, from two different test methods, each of which can follow the degradation of, say, a polymer film as a function of exposure time, t. Furthermore, suppose that P_1 and P_2 have equal standard deviations and decrease with exposure time, t, according to the following relationships:

$$P_1(t) = P_{10} + b_1 t + b_{11} t^2 \tag{12}$$

$$P_2(t) = P_{20} + b_2 t \ , \tag{13}$$

where P_{10} and P_{20} are initial property levels for tests P_1 and P_2, respectively, $P_1(t)$ and $P_2(t)$ are property levels at time t for tests P_1 and P_2, and b_1, b_{11}, and b_2 are constants Solving Equation (13) for t and substituting in Equation (12) yields

$$P_1(t) = P_{10} + b_1 \left[\frac{P_2(t) - P_{20}}{b_2}\right] + b_{11}\left[\frac{P_2(t) - P_{20}}{b_2}\right]^2 \ . \tag{14}$$

Then the relative sensitivity of test P_1 with respect to test P_2, $RS(P_1/P_2)$, is as follows

$$RS(P_1/P_2) = \frac{dP_1}{dP_2} = \gamma_o + \gamma_1 \ P_2(t) \ , \tag{15}$$

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where

$$\gamma_o = \frac{b_1}{b_2} - 2P_{20}\left(\frac{b_{11}}{b_2^2}\right) \tag{16}$$

and

$$\gamma_1 = 2\left(\frac{b_{11}}{b_2^2}\right) . \tag{17}$$

As a specific example, suppose one has

$$P_1(t) = 100 - 5t - 0.5t^2 \qquad 0 \leqslant t \leqslant 10 \tag{18}$$

and

$$P_2(t) = 100 - 10t \qquad 0 \leqslant t \leqslant 10 . \tag{19}$$

These relationships are shown in Figure V-3.

Then $\gamma_o = 1.5$ and $\gamma_1 = -0\ 01$, and one has

$$RS(P_1/P_2) = 1\ 5 - 0\ 01\ P_2 . \tag{20}$$

This relationship, shown in Figure V-4, indicates that at $P_2 = 50$ (or $t = 5$) the two tests are equally sensitive At $P_2 < 50$ (i.e., $t < 5$), P_1 is more sensitive, and at $P_2 > 50$ (i.e., $t > 5$), P_2 is more sensitive. The results are similar if $\sigma_1 \neq \sigma_2$, in which case γ_o and γ_1 are both multiplied by the constant σ_2/σ_1.

It might appear that the relative sensitivity is equivalent to the rates of the two coefficients of variation Mandel has shown that this is the case only when the two tests are proportional or reciprocal to each other. That is, one of the following equations must hold.

$$M = kN \tag{21}$$

$$M = k/N , \tag{22}$$

where k is a constant

Transformations of Scale

For any scheme for test-method discrimination to be completely valid, transformations of scale should not affect the discrimination results. For example, suppose one has determined that elongation at break is twice as sensitive a measure of the degree of vulcanization of rubber as tensile strength. If one modifies the tensile test to give results on a logarithmic scale, is the sensitivity ratio still 2 to 1? Mandel has shown that the relative sensitivity is unchanged by a transformation of scale for one or both tests.(V-2)

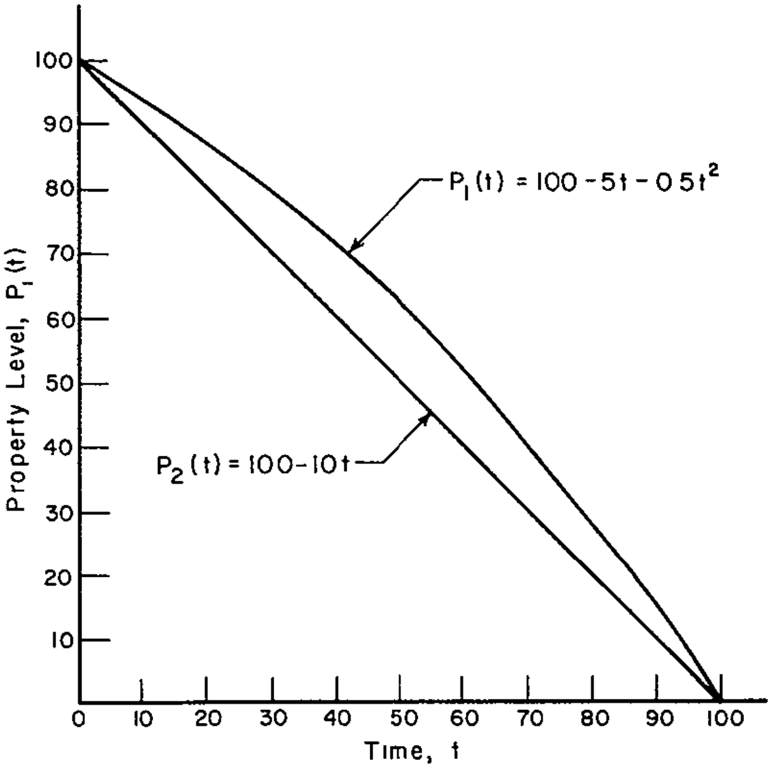

FIGURE V-3. PLOT OF PROPERTIES P_1 AND P_2 AS FUNCTIONS OF TIME

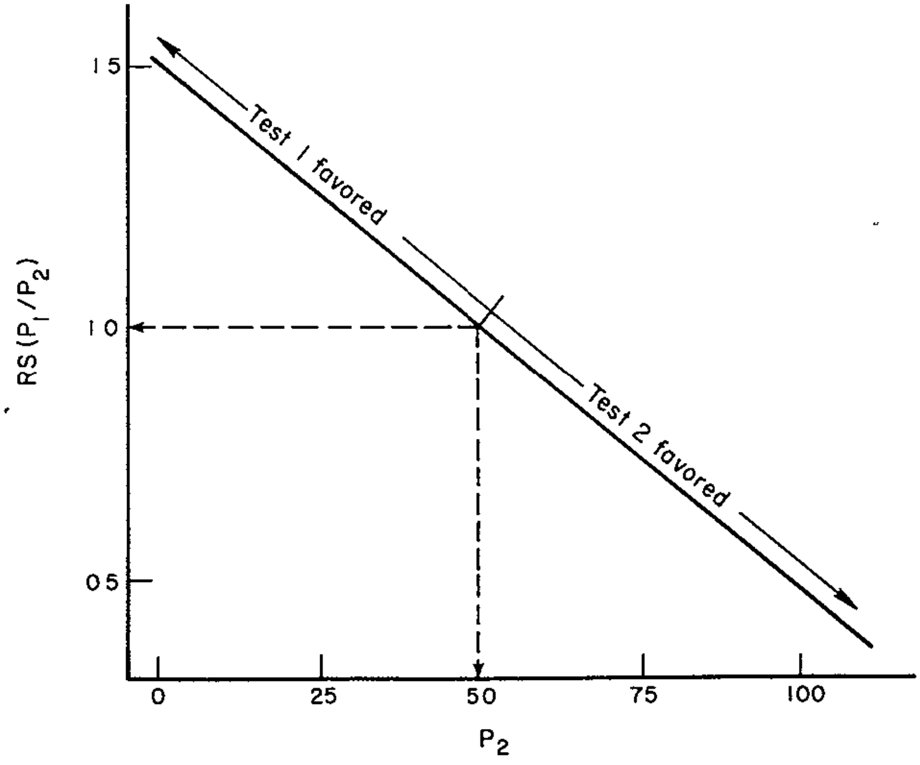

FIGURE V-4. RELATIVE SENSITIVITY AS A FUNCTION OF TEST P_2 FOR HYPOTHETICAL EXAMPLES

Inferences Concerning the Sensitivity Ratio

The discussion of the sensitivity ratio thus far has dealt with population parameters, σ_M/σ_N, and slope, dM/dN. All of these parameters must be estimated from actual data and are therefore subject to random fluctuations. A means is required to determine whether a calculated sensitivity ratio is significantly greater than unity Unfortunately, an exact solution is not possible, and it is necessary to resort to an approximation First, it is assumed that the slope dM/dN, estimated by K for example, is sufficiently precise that it can be ignored as a source of variation for the sensitivity ratio This is often a reasonable assumption. Since the sensitivity ratio would normally be estimated from data from a well-designed experiment, the experimenter can usually minimize the variability of K The variation in the sensitivity ratio is then assumed to be a result of only the variation in estimates of σ_N and σ_M, denoted S_N and S_M. It is known that the quantity $(S_N^2/\sigma_N^2)/(S_M^2/\sigma_M^2)$ follows an $F_{i,j}$ distribution, where i and j are the number of degrees of freedom associated with S_M and S_N, respectively. Now it can be shown that the quantity $[\,|K|\,(S_N/S_M)]\,\sqrt{F}$ represents a lower confidence limit for the sensitivity ratio $|K|\,(\sigma_N/\sigma_M)$. If this lower limits exceeds unity, it is concluded that at the confidence level chosen M is more sensitive than N If it does not exceed unity, it must be concluded that the data are consonant with the hypothesis of equal sensitivities. In most instances, however, a choice has to be made between two tests, and it would be sensible to select the one with the higher calculated sensitivity, regardless of the lack of statistical confidence at the desired level.

5. Sensitivity, Sample Size, and Cost

In discriminating among candidate test methods, cost as well as precision must be considered. For example, if σ_i is the standard deviation for a single measurement from test i, the standard deviation for a *mean* of N observations is $\sigma_i \sqrt{N}$. This illustrates that the precision of any test method can be increased to any level desired simply by increasing the number of replicates, N. It is therefore necessary to consider testing costs and sample size in any test-discrimination methodology. These factors can be easily incroporated into the relative sensitivity concept.

Mandel has shown that if RS(M/N) = k, a single measurement by Method M has the same precision as the mean of k^2 measurements by Method N Furthermore, he has shown that if C_M is the cost of a single measurement for Method M, and C_N is the cost for Method N, then the ratio of costs, C(M/N), to achieve equal precision is

$$C(M/N) = \frac{C_M}{k^2 C_N} \text{ or } \frac{C_M}{[RS(M/N)]^2 C_N} \qquad (23)$$

Some examples are given in Table V-2. In Example 1, for equal costs and a sensitivity ratio of 1, the cost ratio is 1. If the cost of Test M is doubled with no change in sensitivity ratio, the cost ratio is also doubled In Example 5, if Test N costs twice as much as Test M, but Test M is twice as sensitive as Test N, then one would have to spend eight times as much for Test N to get the same precision as in Test M. One is therefore able to evaluate various testing methods not only on the basis of precision but also on the basis of cost.

TABLE V-2. EXAMPLE OF COST RATIO AT EQUAL PRECISION AS A FUNCTION OF TESTING COSTS AND SENSITIVITY RATIO

	Examples				
	1	2	3	4	5
C_M	1	2	1	2	1
C_N	1	1	1	1	2
RS(M/N)	1	1	2	2	2
C(M/N)	1	2	1/4	1/2	1/8

6. Summary

Exact precision requirements cannot be specified at this time because of many remaining unknown quantities such as the level of degradation which will be considered failure. However, using the results presented in this section one can judge tests with coefficients of variation greater than 5 percent to be too imprecise for useful monitoring of degradation. Tests ranging between 2 and 5 percent can be tentatively considered, whereas tests under 2 percent can be accepted, all on the basis of precision. These divisions are admittedly rather arbitrary but should serve as a useful rule of thumb.

Accuracy involves comparison with a standard reference value of some kind and is not considered necessary for following degradation of most if not all array components For example, suppose a test measurement is biased (or inaccurate) by an amount 8. If Q_1 refers to the actual property level one is trying to determine, $M_1 = Q_i + 8$ will then be the measured value. To measure rate of change of Q with time over the interval (t_1, t_2) one has

$$\text{Rate of change} = \frac{Q_2 - Q_1}{t_2 - t_1} = \frac{M_2 - 8 - M_1 + 8}{t_2 - t_1} ,$$

or

$$\frac{Q_2 - Q_1}{t_2 - t_1} = \frac{M_2 - M_1}{t_2 - t_1} .$$

Thus, accurate rates can be determined even with an inaccurate test instrument.

All that can be said about detection limit is that given two tests, both measuring the same underlying degradation phenomenon and with relative sensitivity not significantly different than 1, the test with the lowest detection limit is preferred.

Selectivity on the other hand deals with interfering substances and must be considered separately for each testing situation.

Given that more than one test is applicable to measurement of a given degradation phenomenon (i.e., ATR-FTIR and ESCA for surface carbonyl formation), the *only* way to compare them sensibly is with Mandel's relative sensitivity [if Equations (21) or (22) are not known to hold]. Although this method is discussed for only two candidate tests, the results are readily extendable to a larger number of tests. If Equation (21) or Equation (22) is valid, then and only then can two equivalent tests be compared using ratios of their coefficients of variation.

B. COMPARATIVE ASSESSMENTS OF TECHNIQUES AND INSTRUMENTS

In attempting to make comparative assessments and selections among different types of techniques which might measure the same property, it is desirable to divide them into those which, from the point of view of applicability to the goals of this specific study, are developmental in nature and those which are more or less fully developed (albeit not necessarily proven adequate). In making this division, it is recognized that there is no clear-cut dividing line between the two and, hence, a certain amount of subjectivity is involved. In general, developmental techniques cannot be adequately assessed on a comparative basis except in those cases where first principles can be shown to lead to fundamental limitations (sensitivity, precision, etc.), such that one technique clearly compares unfavorably with competing techniques, such is seldom the case.

1. Recommended Techniques Which are Fully Developed

Table V-3 identifies those recommended techniques which are felt to be fully developed from the point of view of applicability to the quantitative study of degradation-related property changes in photovoltaic module materials and structures "Fully developed" implies that they

TABLE V-3. RECOMMENDED TECHNIQUES WHICH ARE CONSIDERED FULLY DEVELOPED

(1) Chemical Measurement Techniques
  - FTIR (Including ATR)
  - Gel Permeation Chromatography (GPC)
  - Gas Chromatography/Mass Spectrometry (GC/MS)
  - ESCA

(2) Electrical Measurement Techniques
  - Cell I-V (Including Dark, Illuminated, and Spectral Response)

(3) Optical Measurement Techniques
  - Microscopy
  - Spectral Transmission

(4) Thermal
  - Differential Scanning Calorimetry (DSC)

(5) Mechanical
  - Dynamic Mechanical Analysis

(6) Other
  - Profilometry

have been or are being used in studies of these or similar materials and/or structures and that their capability of supplying quantitative information on changes which are considered to be degradation related is established The term does not imply, however, that they have demonstrated adequate sensitivity and precision to establish their capability for providing data that would allow reliable lifetime prediction for arrays which might approach the LSSA operational lifetime goal of 20 years or more. In fact, it can be stated that such is not the case. That is, none of the techniques (alone) that have been investigated has *demonstrated* characteristics adequate to allow such predictions. Further, an examination of the data given in Section IV (see tables in Section VI for a summary) reveals that reliable information on key characteristics, such as precision, is not available for a significant number of the techniques. Without such data, the limits of the techniques in characterizing small property changes cannot be fully evaluated. It is clear that this lack of data makes it difficult if not impossible to make comparisons and selections. As an example, as discussed in Section IV, FTIR and ESCA have overlapping applicabilities in characterizing surface oxidation in polymers. However, precision data to allow a comparative assessment of their capabilities are not available and will have to be developed to determine the preferred technique. Similar statements apply for comparisons of differential scanning calorimetry and the dynamic mechanical tests, in determining T_g. Comparative assessments of these techniques cannot, then, be made on the basis of the existing data base; additional data will have to be developed using the procedures discussed and cited in V.A. to establish both the minimum property change which can be characterized by each technique and, given the choice, the preferred technique for measuring a given property change

Unfortunately, the above procedure does not completely solve the problem of determining how accurately one can expect to predict the lifetime of a photovoltaic module/array using such diagnostic techniques. Assuming, for example, that the precision with which T_g and its changes can be determined by a given technique is known, the question of the uncertainty of the derived values of quantities such as molecular weight or percentage of crystallinity still remains. Further, the certainty with which one can extrapolate from these primary derived quantities to secondary derived quantities which are more directly relatable to power degradation mechanisms (e.g., optical absorption) or even protective function degradation mechanisms (e.g., embrittlement, delamination) adds another level of potential error in this case. These uncertainties can be resolved only through experimental evaluation, and thus, to a certain extent, even the more advanced techniques listed in Table V-3 might be considered somewhat developmental *for this application.*

The major area of overlap in the techniques listed in Table V-3 is in the measure of bulk polymer properties. FTIR, GPC, GC/MS, DSC, and the dynamic mechanical techniques all measure bulk-property-related changes, although in most cases somewhat different primary-property changes (e.g., volatile fragments, nonvolatile fragments, T_g, modulus, molecular species). A determination of the relative certainty with which each of these property changes can be related to actual failure modes and lifetimes and even the overlap (or lack thereof) of failure modes to which each can be related cannot be made at present.

Both microscopy and profilometry are applicable to studies of first surface damage However, it is felt that no conflict in the choice of technique exists here, in that profilometry offers clear-cut advantages in its range of sensitivity in a laboratory situation, whereas high resolution SEM is more suited where finer sensitivity is required. More conventional microscopic techniques are better suited to field situations than either of these two Both microscopy and profilometry are considered to have a place in array-lifetime studies

Measurements of current-voltage characteristics, including spectral response, are directly applicable to quantitative characterization of power degradation changes; however, their limitations (discussed in Section IV), as presently applied, are considerable for this application. It is, however, the primary in-situ measurement technique at present and, as such, considerable attention should be directed to refinement of measurement and diagnostic aspects of the technique.

2. Recommended Techniques Which are Developmental

Table V-4 identifies the developmental techniques which are being recommended. While the experimental problems involved in their evaluation may not be any more formidable than those associated with needed evaluations of the more developed techniques in Table V-3, it is felt that more fundamental questions as to the applicability and suitability of these techniques exist at the present state of their development. Since some of the techniques listed here are fairly well established in the field of experimental physics (e.g., ellipsometry, reflectometry) it should be reemphasized that the primary consideration here is the capability of providing high-precision, quantitative measurements of low-level property changes which are relatable to the degradation of photovoltaic modules

TABLE V-4. RECOMMENDED DEVELOPMENTAL TECHNIQUES

- (1) Chemical Measurement Techniques
    - Chemiluminescence
    - Surface Energy Analysis
- (2) Electrical Measurement Techniques
    - Electrical Noise
    - Electrical Conductivity
    - Dielectrometry
    - Special Detectors
- (3) Optical Measurement Techniques
    - Ellipsometry
    - Holographic Interferometry
    - Light Scattering
    - Reflectometry
- (4) Thermal Measurement Techniques
    - Infrared Thermovision
- (5) Mechanical Measurement Techniques
    - Ultrasonic Pulse-Echo
- (6) Other Measurement Techniques
    - Permeability (Gas and Water Vapor)
    - Photoacoustic Spectroscopy

In summary, adequate data for making comparative assessments of techniques having potentially overlapping capabilities, on the basis of precision, have not been found. This, of course, does not exclude interim selections on the basis of other criteria (e g., availability, field-use capability) as listed in Table IV-2, but does preclude the recommendation of *the preferred technique* for measurement, for example, of bulk polymer properties. Recommendations for developing the needed information and a discussion on how well existing techniques might cover the total needs of an array-lifetime-prediction effort are given in the following section

VI. CONCLUSIONS AND RECOMMENDATIONS

VI. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

The discussions of Section IV are summarized in Tables VI-1 through VI-5. These tables identify the recommended techniques in each of the categories, along with values and comments regarding some of the key selection criteria and other attributes.

In identifying and evaluating a set of techniques for use in photovoltaic module lifetime testing, it is necessary to identify those properties which need to be monitored in order to ensure that any degradative change which does occur can be detected and measured. This problem was addressed in Sections II and III which distinguished (1) degradation that directly affects power output and (2) degradation of the protective function of the encapsulation system, and which noted the correlation of power degradation factors with components of the lumped-constant model of the photovoltaic device. From these discussions it is clear that, from the point of view of degradation mechanisms directly affecting power output, one needs to measure (a) changes in the light reaching the cell or related precursors thereto, and (b) changes in internal (to the module) power dissipation due to series-resistance and shunt-conductance effects or related precursors thereto. For characterizing degradation of the protective capabilities of encapsulation systems, the major areas of concern are (a) interface separation or debonding, (b) permeability changes relative to corrosive agents, and (c) mechanical property changes such as strength.

Table VI-6 identifies recommended techniques considered to be relatively well developed for application to array encapsulation degradation studies; these techniques are listed according to the degradation-related properties or areas to which they are applicable. As was noted in Section V.B. (and as Tables VI-1 through VI-5 show), there is a considerable lack of reliable information on the precision of many of these techniques, a fact which hampers comparisons of competing techniques. There is also a need for accelerated-test-type experiments for those advanced techniques that measure property changes indirectly related to power degradation (i.e., carbonyl formation, T_g, etc.) in order to establish the degree of correlation and the magnitude of the errors involved in projecting from those measured properties to power degradation rates and failure modes Specifically, FTIR, GC/MS, DSC, ESCA, and the dynamic mechanical tests all require determination or verification of precision for properties measured, and all of the tests listed under (1), (2), and (3) in Table VI-6, require studies to establish confidence in projections to power degradation rates. It is also significant that none of these developed techniques are directly applicable to studies of interface changes (delamination)

I-V characteristic measurements (including spectral response) are the most universally used technique in studying degradation of solar cells and arrays. The technique is capable in principle of measuring any change which degrades power output. The shortcomings of present practice in this area are discussed in Section IV. It must be emphasized that the requirements imposed on diagnostic measurements in array lifetime prediction studies are more stringent than those on conventional measurements or even those on qualification and acceptance testing. For the purposes of life-test studies, there is a need to bring the I-V characteristic measurement technique to the highest state of refinement possible in order to make maximum use of its capabilities, particularly in in-situ situations. Long-term stability of instrumentation is a major concern with this and other measurement techniques.

TABLE VI-1. RECOMMENDED CHEMICAL TECHNIQUES

Instrument/Technique	Properties Measured-Applicable Degradation Modes	Sensitivity	Accuracy	Precision	Specimen Form	Effect on Specimen	In-Situ Suitability	Cost	Set up/ Run Time	Availability for test	Comments
Fourier Transform Infrared Spectroscopy including ATR	Surface and bulk carbonylization of polymers	100 ppm range?	$<0\ 1\ cm^{-1}$	$<0\ 1\ cm^{-1}$**	Various and as little as 25 nanograms	none	No	$120,000	1/2 to 1 hr per specimen	Yes - BCL	--
ESCA	Surface carbonylization of polymers, Depletion of surface species on glass plate, i e , Na^+ Interface evaluation after teardown analysis	01 - 02 atomic fraction	*	*	Small flat sheet	Negligible	No	$200,000	5 t 10 specimens per day	Yes	Depth profiling possible in conjunction with ion sputtering
Gel Permeation Chromatography	Changes in polymer molecular wt due to chain scission and crosslinking Detection of low MW species such as residual monomers, plasticers, etc	*	20% at worst	5-7% for Mn or Mw 1-2% for Mw/Mn	Powder or sheet Small amount	Destructive	No	*	-	Yes	--
Chemiluminescence	Photon emission from degradative reactions	10^{-15} moles/yr degradation rate	*	*	Sheet 3-in dia or less	none	Possible with specially built apparatus	$6,000 built from individual components	< 30 min.	Yes - BCL	--
Gas Chromatography/ Mass Spectrometry	Volatile polymeric fragments - Photolytic breakdown of polymers	10 mg/mil	10% at worst	*	Any form, down to 10 mg of material	Destructive ‡	No	$30,000 to $150,000	ca 30 min	Yes	--
Surface Energy	Surface properties	*	*	*	Sheet	none	Yes	$1,000	5-10 min per liquid		Currently being evaluated.

* Could not be found

** Repeatability.

‡ Not destructive if used as described in the text

TABLE VI-2. RECOMMENDED ELECTRICAL TECHNIQUES

Instrument/ Technique	Properties Measured- Applicable Degradation Modes	Sensitivity	Accuracy	Precision	Specimen Form	Effect on Specimen	In-Situ Suitability	Cost	Setup/ Run Time	Availability for Test	Comments
Illuminated I-V Characteristics	I_{sc}, P_{max}, V_{oc}, R_s, R_{sh}- any output degradation	Potentially high	I_{sc}- ± 2%	I_{sc}- ± 1%	cell/module/ array	none	yes	$3K to >$50K	Setup-few min , Run-seconds or less	Yes - BCL	See Section IV
Dark I-V Characteristics	R_s, R_{sh}, Diode Parameters-cell/ module power dissipation	Potentially high	± 0 03% to ± 0 1%	Potentially high	cell/module/ array	none	Need light tight cell cover	~$1K up	Setup-run 5 to 15 min	Yes	See Section IV
Spectral response	I_L vs λ - optical transmission degradation	Potentially high	± 5% to ± 20%	± 1% at best	cell/module?/ array?	none	crude with filters possible	--	Run- 5 to 30 min	Yes - BCL	See Section IV
Electrical noise	Current noise - contact corrosion interconnect corrosion	--	± 0 5 dB (-40 to + 60 dB)	± 1 dB	cell/module?/ array?	none	yes	$3K to $15K	Setup- Run-nominal	Yes	Requires experimental evaluation
Conductivity	Electrical conductivity- ionic impurities moisture content breakdown	Potentially high	± 0 03% to ± 4 0%	Potentially high	Various, known geometry	None, unless excessive temperature excursion	Could be with special custom design	$0 3K to $10K	Setup- Run-min	Yes	Accuracy varies with magnitude, worse for very low conductivities
Dielectrometry	Permittivity, Loss factor- polar groups moisture ions	--	Temp ± 1% C ± 0 02% loss ± 1%	Temp ± 0 25°C	Various, known geometry	None, unless excessive temperature excursion	Conventional-No Special designs conceivable	~$10K to $15K	Setup-5 to 10 min Run-min to hrs	Yes - BCL	Requires experimental evaluation
Special detectors	Detector Electrical Properties- presence of alien species	Potentially high	Potentially high	Potentially high	module/array	none	yes	--	Built in to module/array Normal run time	Could design test	—

TABLE VI-3. RECOMMENDED OPTICAL TECHNIQUES

Instrument/Technique	Properties Measured-Applicable Degradation Modes	Sensitivity (OPD detectable)	Accuracy[a]	Precision[a]	Specimen Form	Effect on Specimen	In-Situ Suitability	Cost	Set up/Run Time	Availability for test	Comments
Reflectometry	Reflectance-1st surface degradation, interface changes	200-500 Å	0 1%	1% (long term)	Reasonably flat	None	Possibly, with lower accuracy, precision, etc	$5,000	Initial setup and cost 1-2 days, other times nominal	Yes-could set up at BCL	Scattering angle, not optical path difference (OPD), used in actual measurement
Ellipsometry	Ellipticity of reflected light-delamination, other changes in optical path	5-10 Å (frequently)	0 01%	0 01%	Reasonably flat, can be relatively large	None	No	$10,000 to $50 000	Setup nominal Measure-a few minutes per point	Currently under investigation	--
Holographic Interferometry	Phase change at points in light path-incipient delamination	50-3000 Å	Variable	low long-term with available instruments	Few restrictions	None	No	$30,000	Few minutes to 1 hour per shot	Yes - BCL	High risk, high payoff technique
Light Scattering	Small angle forward scattering of light-delamination, bubble formation, surface damage	high	high	high	Fairly transparent	None	No	$15,000 to $30,000	Nominal	Yes - BCL	Whether delamination occurs in such a way as to cause scattering is not known
Microscopy	Surface structure-first surface damage	50-100 Å resolution for SEM	--	--	Various	None	Yes, with special mounting	> $60,000 for SEM, others vary considerably	Varies with type	Currently in use	--
Spectral Transmission	Transmitted light-optical transmission degradation, UV damage	high	high	± 1% - ± 2% over 6 months	Various, transparent	None	Possibly with special arrangements	$5,000 - $25,000 for commercial instruments	Minutes to 1 hour	Yes - BCL	Development of suitable field use setup needed

(a) Precision and accuracy are for the quantity measured and not for any derived quantities

TABLE VI-4. RECOMMENDED THERMAL AND MECHANICAL TECHNIQUES

Instrument/ Technique	Property Measured	Sensitivity	Accuracy	Precision	Form of Specimen	Effect of Measurement on Specimen	Suitable for In-Situ Meas ?	Cost	Set up/Run Time	Availability for test	Comments
Differential thermal analysis	Temperature differential/ due to "heat effects"	0 002°C Temp difference	± 4 0°C for Tg, ~± 2 0°C for T_{melt}	± 2 5°C for Tg, ~± 1 5°C for T_{melt}	Various forms, 0 1 to 100 mg	May or may not be destructive	No	~$20,000 to $25,000	Set up time nominal, run time 10 min to 2 hrs	Yes - BCL	
Differential scanning calorimetry	Differential heat input	3 μcal/sec	± 0 2% on Q ~± 1°C on T	± 1% on Q	Various forms, 0 1 to 100 mg	May or may not be destructive	No	~$20,000	Set up time nominal, run time 10 min to 2 hrs	Yes - BCL	
			± 4 0°C for Tg, ± 2 0°C for T_{melt}	± 2 5°C for Tg, ± 1 5°C for T_{melt}							
Torsion Pendulum	Dynamic modulus and damping (G' and G")	*	G' for T<Tg 7% G' for T~Tg: 30% G" for T>Tg 20% G" for T<Tg 10% ± 3 0°C for Tg	G' for T<Tg: 3 5% G' for T~Tg 15% G" for T>Tg: 10% G" for T<Tg 5%	Rectangular 0 015-0 10 in by 0 10-0 60 in , 1 to 6 in long or circular 0 30 in radius, 1 to 6 in long	Nondestructive	No	~$40,000 for automated system	10 min to few hrs	Yes - BCL	
Forced vibration Viscoelastometer	Dynamic modulus and damping	*	5-10%	3%	Solid bar 2mm x 2mm x 2cm	Nondestructive	No	$25,000 to $50,000	Set up 15 min to few hr Run time 1 hr for several frequencies at a given temperature	Yes-BCL(Weissenberg Rheogoniometer)	
Ultrasonic Pulse-echo	Flow detection	*	*	*	--	Nondestructive	Yes	~$ 5,000	Several minutes	Yes - BCL	Needs further theoretical and experimental evaluation, currently under investigation.
Infrared Thermo-vision	Temperature differences at flaws	0 2°C	*	*	--	No effect	Yes	~$45,000	Several minutes	Yes - BCL	Needs further evaluation to account for non-blackbody radiation and transparency in sensitive wave-length range

TABLE VI-5. OTHER RECOMMENDED TECHNIQUES

Instrument/Technique	Properties Measured-Applicable Degradation Modes	Sensitivity	Accuracy	Precision	Specimen Form	Effect on Specimen	In-Situ Suitability	Cost	Set up/ Run Time	Availability for test	Comments
Profilometry	Surface roughness - surface etch/leach abrasion	CLA ± 2% (2-400 μin) H± 1 to 200 μin (20-4000 μin)	—	± 2%	Flat or circular curvature	0 1 gm force on 1-10μ radius tip	Conventional is lab only, special design conceivable	\$10K +	Tedius adjustment/ 0 2 - 180 mm/min	Yes - BCL	Roughness sensitivity of 5 Å claimed for Dektak unit coupled with computer
Water Vapor & Gas Permeability	Flow rate of Gas/ WV through material-molecular wt, crystallinity cross linking, density	WVTR-0 01 gm/100 in^2/24 hr	Temp ± 0 5°F WVTR- ± 2%	± 10%	Generally sheet	none	Conventional no	\$1K - \$14K	~1 hr/ 30 min to days	Currently under investigation	none
Photoacoustic Spectroscopy	Optical Absorption, Thermal Diffusion-optical properties	11 mV/mW	*	*	Various	none	no	\$25K - \$30K	-	Currently under investigation	none

TABLE VI-6. DEVELOPED TECHNIQUES ACCORDING TO APPLICATION AREA

(1) First Surface Damage (Including Dirt)
    - Microscopy
    - Profilometry

(2) Polymer Surface Chemical Change
    - ATR-FTIR
    - ESCA

(3) Bulk Polymer Properties
    - FTIR
    - GPC
    - GC/MS
    - DSC
    - Dynamic Mechanical Analysis

(4) Interface Properties
    - None

(5) General Optical Properties
    - Spectral Transmission
    - I-V Characteristics (Illuminated)

(6) Contact/Interconnect Damage (Corrosion, Fracture)
    - I-V Characteristics

(7) Shunting
    - I-V Characteristics

The adequacy of the techniques shown in Table VI-6 for measuring naturally produced (i.e., not accelerated) changes compatible with an array lifetime of greater than 20 years has not been demonstrated, and the degree to which they are adequate for accelerated-aging-test measurements is also not clear. It is recommended that steps be taken to clarify this situation (see VI.B. below).

Table VI-7 lists recommended techniques considered to be developmental for this application, they are listed according to their areas of application These techniques are felt to offer significant potential advantages in their categories through convenience or increased sensitivity, however, research and developmental work is required to firmly establish their applicability, usefulness, and capabilities. Several of these are currently under investigation at various laboratories under DOE/JPL or other sponsorship, while others have yet to be explored A number of these recommended developmental techniques are applicable to areas not adequately covered by the more developed techniques listed in Table VI-6. Preliminary evaluations of some of the techniques in Table VI-7 are recommended for Phase II of this program (see VI.B. below), while the evaluation of others (e.g., holographic interferometry, ultrasonic pulse-echo, and infrared thermovision) is beyond the level of effort of Phase II and consideration of more long-term studies is warranted.

TABLE VI-7. DEVELOPMENTAL TECHNIQUES ACCORDING TO APPLICATION AREA

(1) First Surface Damage (Including Dirt)
- Light Scattering
- Reflectometry
- Surface Energy Analysis

(2) Polymer Surface Chemical Change
- Electrical Conductivity
- Photoacoustic Spectroscopy
- Reflectometry
- Surface Energy Analysis

(3) Bulk Polymer Properties
- Chemiluminescence
- Dielectrometry
- Electrical Conductivity
- Light Scattering
- Permeability
- Photoacoustic Spectrometry
- Special Detectors

(4) Interface Properties
- Ellipsometry
- Holographic Interferometry
- Light Scattering
- Photoacoustic Spectroscopy
- Reflectometry
- Ultrasonic Pulse-Echo

(5) General Optical Properties
- Light Scattering
- Reflectometry
- Special Optical Detectors

(6) Contact/Interconnect Damage (Corrosion, Fracture)
- Electrical Noise
- Infrared Thermovision
- Reflectometry
- Special Electrical Detectors

(7) Shunting
- Dielectrometry
- Electrical Conductivity

It is also useful to examine the recommended techniques according to their suitability for field-installation-type measurements. The situation is summarized in Table VI-8. Of the more developed techniques, only I-V characteristic measurements, spectral transmission, and some forms of microscopy are suitable, on a routine basis, for in-situ measurements, while a considerable number of the developmental techniques are potentially adaptable to such measurements (although special arrangements would be required in most cases). There is a serious need to develop techniques for in-situ measurements of various properties of photovoltaic modules to provide needed supplemental data in accelerated-test experiments.

TABLE VI-8. TECHNIQUES ACCORDING TO USE LOCATION

Developed Techniques	Developmental Techniques
(1) In-Situ	(1) In-Situ
Cell I-V Characteristics	Electrical Noise
Spectral Transmission	Dielectrometry
Microscopy	Electrical Conductivity
	Special Detectors
	Light Scattering
	Reflectometry
	Infrared Thermovision
	Ultrasonic Pulse-Echo
	Surface Energy Analysis
(2) Laboratory	(2) Laboratory
FTIR	Chemiluminescence
Gel Permeation Chrom.	Holographic Interferometry
Gas Chrom./Mass Spec.	Ellipsometry
Diff. Scanning Calorimetry	Gas and Vapor Permeability
Dynamic Mechanical Analysis	Photoacoustic Spectroscopy

B. RECOMMENDATIONS

1. Scope of the Recommendations

The recommendations presented in this section are tendered as general recommendations for the consideration of the community of those concerned with array degradation and lifetime-prediction studies. A limited number of the techniques listed in this section will be selected for preliminary experimental evaluation in Phase II of this program. While the other techniques are felt to be equally meritorious, they cannot all be pursued within the level of effort of Phase II. It is hoped that other studies will be initiated by researchers within the community to develop the experimental data needed to fully evaluate the potential usefulness of those techniques.

2. Establishment of the Adequacy of Existing (Developed) Techniques

As elaborated previously, none of the developed techniques has been appropriately evaluated to determine whether it has adequate precision for determining degradation rates that might be encountered in long-life arrays. It is therefore recommended that steps be taken to establish the limits of these techniques for this application. Specific recommendations are

- It is recommended that a determination of the precision for measured properties be made for ESCA, FTIR, and the gas chromatography/mass spectroscopy combination and that ESCA and FTIR be compared for measuring surface carbonyl concentration using the Mandel sensitivity ratio criterion. Basic instrument precision determinations could be performed in the context of Phase II of this study, while broader questions of interlaboratory variability are probably outside the scope of this phase.

- It is also recommended that a major effort be directed toward establishing quantitative correlations between key measurable properties, such as carbonyl formation, T_g, and molecular weight changes, and degradation/failure modes. This should include consideration of the accuracy and precision associated with extrapolation from a change in value of a given measured property to a derived degradative change. This is considered to be a task beyond the time and effort of the Phase II evaluations, but is very important. Without this information, one is forced to rely primarily on techniques that directly measure degradative changes, these techniques are not necessarily the most sensitive for early detection.

- It is recommended that a set of experiments be conducted to determine the relative precision of DSC, DTA, torsion pendulum, and the forced vibration viscoelastometer for measuring T_g. Such tests could reasonably be included in Phase II of this program.

- It is recommended that a study be made of cell characteristic (I-V, spectral response) measurement techniques from the point of view of the special needs of lifetime prediction and degradation studies. These should have the aim of instituting refinements which will result in optimizing the sensitivity, precision, and accuracy of such measurements. Long-term stability of illumination sources and other instrumentation is one of the major concerns here. The Fourier transform spectrophotometric approach to spectral response measurements, using an interferometer rather than dispersive optics to accomplish spectral discrimination, is a specific technique warranting further investigation in this area

3. Evaluations of Potentially Useful Developmental Techniques

Some of the potentially useful developmental techniques are currently being investigated in various laboratories under JPL sponsorship and hence require no further recommendation other than that they be focused on *combinations* of materials and structures related to photovoltaic modules. These include photoacoustic spectroscopy, gas and vapor permeability, ellipsometry, ultrasonic measurements, and surface energy analysis. For the remainder, the following recommendations are offered. The priorities reflected in these recommendations are in part related to the finding that to meet the immediate needs of lifetime testing, it is necessary to focus on techniques which measure properties having direct relation to power degradation. As reliable quantitative correlations between other measured property changes and power degradation mechanisms are established, techniques sensitive to those changes can be brought more directly to bear With this in mind then,

- It is recommended that electrical noise measurements, polymer electrical conductivity measurements, reflectometry and light-scattering measurements, and the use of special electrical and optical detectors for in-situ measurements be subjected to preliminary experimental evaluations such as those planned in Phase II.
- It is also recommended that chemiluminescence and dielectrometry be considered for similar evaluations, but on a secondary priority basis
- Holographic interferometry and infrared thermovision will probably require considerably more effort to bring them to a state of providing useful quantitative information for lifetime studies, although, if developed, they offer significant advantages. It is suggested that they be considered for investigation on a high-risk, high-return basis.

4. Measurement Needs Not Presently Satisfied

- Adequate means do not appear to be available to measure changes in the breaking strength or static fatigue of glasses. The destructive nature of the usual tests and the large statistical variations in strength are definite limitations in this respect. A knowledge of the fracture toughness of the material and a test which monitors surface flaw sizes might provide an approach to this problem.
- A technique for in-situ determination of changes in mechanical strength of encapsulation materials could be a useful tool in degradation studies. A suitable technique has not been identified in this study.
- Another need is for a reliable, reasonably inexpensive method for making in-situ spectrophotometric measurements with relatively high precision (preferably to within about 0.1 percent) over relatively long periods of time (up to a year). Since a satisfactory instrument does not exist, the best course may be to initiate discussions with designers of opto-electronic equipment and other photometry experts in order to instigate new idea generation and to obtain a sample of expert opinion on what might ultimately be obtainable.

5. Recommendations for Phase II of Study

Because the size (time-funds) of the Phase II effort will be limited, it will be necessary to select from the recommended techniques those which offer the most promise in terms of contributing a new element or advantage in life-test studies and which are amenable to evaluation within the effort allotted. On this basis, appropriate techniques from those recommended in this section are being selected for Phase II experimental evaluations, these selections will be reviewed with JPL and specific experimental plans will then be prepared.

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VIII. APPENDIX

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This section presents brief descriptions of some of the techniques which were considered but are not at present recommended for use in studies of failure-related degradation in terrestrial photovoltaic modules. The descriptions include an identification of considerations which resulted in the exclusion of the technique from the present recommendations. The techniques discussed in this appendix are.

1. Low Energy Electron Diffraction (LEED)
2. Secondary Ion Mass Spectrometry (SIMS)
3. Ion Scattering Spectrometry (ISS)
4. Electron Microprobe
5. Raman Spectrometry
6. Mass Spectrometry
7. Optical Emission Spectrography
8. Electron Paramagnetic Resonance (EPR or ESR)
9. Nuclear Magnetic Resonance (NMR)
10. Mossbauer Spectroscopy
11. Chromatography
    - Gas Chromatography (GC)
    - High Performance Liquid Chromatography (HPLC)
    - Thin Layer Chromatography (TLC)
12. Neutron Diffraction
13. Acoustic Emission
14. Thermal Conductivity
15. Mechanical Strength
16. Inelastic Electron Tunneling Spectroscopy (IETS)

1. Low-Energy Electron Diffraction(VIII-1,VIII-2,VIII-3)

Low-energy electron diffraction is a tool for studying the crystal structure of solid surfaces It involves the impinging of low-energy electrons (<5 kV) on the sample surface and detection of those electrons which are scattered back from the surface. These electrons are diffracted by the first several atomic layers of the sample. Only the elastically diffracted electrons pass through suppressor grids and impinge on the fluorescent display screen producing an array of bright spots – the diffraction pattern. This instrument is basically qualitative and thus is not expected to be useful in measuring rates of degradation of photovoltaic array components

2. Secondary Ion Mass Spectroscopy (SIMS)(VIII-4)

Secondary ion mass spectroscopy is an ultrahigh-vacuum surface technique which involves the bombardment of a surface with ions such as O_2 ions created in a plasma. It is a sputtering technique capable of measuring elemental composition versus depth (i.e., depth profile) to a depth of 2 microns. Since some molecular species are observed in the SIMS spectrum, it is also possible to derive some chemical bonding information about surface species. In general, SIMS detection limits are in the parts per million area with little dependence on atomic number The technique provides isotopic resolution and is fast. Its limitations are the difficulty in quantification and interference of various matrix effects. One of the major quantification difficulties is the fact that different sputtered species are typified by escape probabilities which are difficult to determine. For this reason its use as a quantitative tool in measuring array-component degradation will be quite limited.

3. Ion Scattering Spectrometry (ISS)

In ion scattering spectrometry a surface is bombarded with a beam of noble or inert gas ions ($^3He^+$, $^4He^+$, $^{20}Ne^+$, or $^{40}A^+$). A fraction of these ions (~ 1 in 10^5) experiences a single binary collision with a surface atom. This interaction changes the energy and momentum of these primary ions and scatters them. Analysis of the energies of the scattered ions provides information on the elemental composition of the outermost atomic monolayer of the surface.

If the source ion penetrates the first monolayer, it has a very low probability of escaping from the surface without undergoing multiple collisions. As a result, the surface atoms found by ISS must reside almost exclusively in the first average atomic layer. This sensitivity to the surface monolayer is unique to ion scattering spectroscopy.

ISS can be used to estimate elemental composition as a function of depth through sputtering, which is done at the rate of 3 to 50 monolayers per hour.

Because ISS is only a semiquantitative method, it is not suitable for the goals of the LSSA project which requires monitoring of extremely small degradative changes. It, of course, may be useful for the postmortem type of analyses required for determining degradative failure modes.

4. Electron Microprobe

The electron microprobe technique involves the interaction of a monoenergetic electron beam in the 5 to 50-keV energy range with a solid sample. Heat, X-radiation, light, and a complex spectrum of electrons are generated (see Figure VIII-1). This method is used mainly for elemental analysis of metals as it requires a conductive material with high melting point. Because of the high temperature and conductivity requirements, this technique is not useful for following polymer or glass degradation.

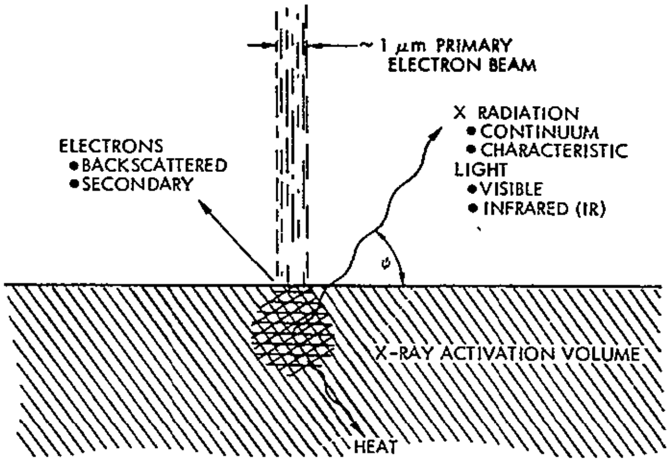


FIGURE VIII-1. SCHEMATIC OF ELECTRON MICROPROBE

5. Raman Spectroscopy

Raman spectra are due to changes in electron cloud (dispersion) symmetry and are obtained with visible or UV light by observing the change in frequency produced when the molecule is irradiated. In many cases Raman and IR spectroscopy are measures of the same vibration. However, for highly symmetric molecules such as benzene, vibrations active in the Raman spectra are absent in the infrared and vice versa. Consequently, as Painter and Koenig(VIII-5) have pointed out, both IR and Raman spectroscopy are necessary for complete characterization of molecular species.

Raman spectroscopy has become a much more powerful tool, over the last few years with the advent of the laser. Today all commercial Raman spectroscopes have a layer source. This creates problems if the material being analyzed fluoresces, as is often the case in measurements related to polymer degradation. In such cases the fluorescence overshadows the Raman spectrum.(VIII-2,VIII-3) This can be overcome in many cases by changing the wavelength of the exciting radiation.

Raman spectroscopy is much more sensitive to the stretching of homonuclear bonds such as C–C, S–S, N–N, C=C, and C≡C than is infrared. The degradative changes involved in the glass and polymeric materials of photovoltaic arrays, however, usually involve polar groups such as C=O, SiOH, and OH. Since these are most easily detectable with infrared, Raman spectroscopy does not appear to be particularly useful for the weathering changes of interest in the photovoltaic area.

6. Mass Spectroscopy

In mass spectrometry, samples are vaporized and introduced into an electron beam which ionizes and fragments the molecules. These charged particles are accelerated in an electric field and then spread out by a magnetic field so that each individual mass is isolated and detected in a scan of the ratio of mass to charge (m/e) for all components. The intensity of the sharp peaks obtained is related to the concentration of each fragment. In polymer work, mass spectroscopy is often used in conjunction with gas chromatography for detection of pyrolysis products given off when the polymer is decomposed. Sensitivity is very high, with as little as 10^{-12} grams being detectable. Precision however is approximately 10 percent and therefore mass spectroscopy is not immediately applicable for following minute degradation changes in polymers.

7. Optical Emission Spectrography

Optical emission spectrography is used for detection, identification, and semiquantitative analysis for elements in the range of 1 to 100 ppm. The main components of this instrument are an arc or spark chamber, a diffraction grating of known spacing (1.5 meter, 25,000 line/inch), and a photographic film. The specimen is first burned in the spark chamber, and the light emitted from the specimen then goes through a slit, is diffracted from the grating, and is recorded on photographic film. The emission spectrum is analyzed by comparison with a known standard spectrum. This is basically a qualitative technique and as such is not applicable to following minute degradative changes.

8. Electron Paramagnetic Resonance Spectrometry (EPR)

Electron paramagnetic resonance is based on the splitting of Kramer's degenerate electronic levels by a magnetic field and promotion of unpaired electrons from lower to upper levels by resonance absorption of electromagnetic radiation. Although it is analogous to NMR, they differ in many respects. EPR spectra must usually be thoroughly interpreted before an assignment can be made, whereas in NMR, identification of functional groups is relatively straightforward. EPR is limited to the existence of unpaired electrons and is orders of magnitude higher than NMR with respect to sensitivity because the electron magnetic moment is much larger than the nuclear one.

McMillan(VIII-8) indicated that the absolute number of unpaired spins present in the sample can be determined by double integration of the first derivative curve. However, such a procedure is one of the most difficult in EPR spectroscopy because of the great difficulty in eliminating systematic error from the EPR measurement; therefore this procedure is not recommended. Relative determinations by comparison with standards of known concentration are preferred but even here, accuracies better than 10 percent are hard to attain. In view of this and the absence of any unique capabilities of EPR for the LSSA program, EPR is not recommended as a means of following photovoltaic-array degradation. Of course, this tool may still be useful for the post-mortem type of qualitative analysis which will be required in studying failure modes.

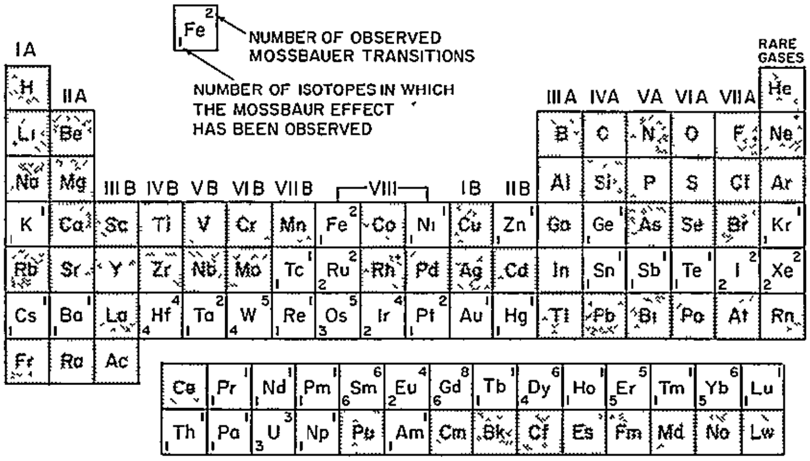
9. Nuclear Magnetic Resonance (NMR)

Most nuclei possess angular momentum due to nuclear spin. In nuclear magnetic resonance (NMR) spectroscopy, the energy required to raise nuclear spin to higher energy states is measured. Since the amount of energy required is dependent on the kind of nuclear species present it can be used for compound identification. Nuclear magnetic resonance has found wide use in polymer characterization for elucidation of structure, stereoregularity orientation, and relaxation. Because NMR is only a semiquantitative tool, it is not expected to be particularly useful for measuring the minute degradation changes of concern in the LSSA program. It may, however, be useful in tear-down analyses to study failure modes.

10. Mössbauer Spectroscopy(VIII-9)

Mössbauer spectroscopy is a nuclear resonance technique which uses gamma photons of an appropriate frequency from a radioactive source to populate low-lying nuclear energy levels in the sample. Nuclear resonance absorption (or scattering) is exhibited in nuclides with excited state energies typically less than 150 keV, with lifetimes between 10^{-10} to 10^{-7} seconds. The energy width of the gamma photons is small enough so that no nuclei other than those of the Mössbauer nuclide can be resonantly excited in the sample. For example, a commonly studied Mössbauer isotope is ^{57}Fe. If a radioactive source which populates the Fe-14.4 keV excited state, e.g., ^{57}Co in palladium metal, is used then, regardless of which other elements are present in the sample, only the ^{57}Fe can be resonantly excited. Hence, in this respect this method is completely specific, and thus is limited to the Mössbauer isotopes shown in Table VIII-1. Because of this limitation, Mössbauer spectroscopy will be of limited value. It may be useful in following the darkening of glass due to change in the valence state of iron in glass The only photovoltaic-module metallization material to which Mössbauer is sensitive is gold, which is not

TABLE VIII-1. MÖSSBAUER ISOTOPES(a)



(a) Periodic table of the Mössbauer isotopes, showing the number of isotopes (lower left corner) and nuclear transitions (upper right corner) for each element exhibiting the Mossbauer effect (nonshaded). [From J G. Stevens and V. E. Stevens, 1972. "Mossbauer Effect Data Index Covering the 1970 Literature." Plenum Press, New York.]

expected to cause corrosion. Mössbauer spectroscopy has been used on organotin stabilizers of polyethylene and other polymers. In this respect it may possibly be of some use in measurement of polymer degradation rates, but further study would be needed before a definite recommendation could be made.

11. Chromatography

Chromatography covers a variety of analytical techniques for separation and identification of components from a complex mixture. The main components of these techniques are (1) the mobile phase, which is a flow system for carrying the specimen to be analyzed, (2) the stationary phase or the column; (3) a detector; and (4) a strip-chart recorder. In some techniques, a piece of paper or a plate will serve for the last three items. The separation processes are based on differential migration of the mobile sample components through the stationary column. Once each component has gone through the column, the detector and strip-chart recorder record the concentration and the time it takes to reach the peak maximum which is called "retention time". A plot of this detector output on the ordinate verse time on the abscissa is called a "chromatogram" which is characteristic of a given compound on a specific column under a given set of conditions, i.e., flow rate, temperature, and pressure. Chromatograms can be used for analysis by comparing with known standard references.

Various chromatographic techniques have different forms of mobile and stationary phases Chromatography with a gas mobile phase is called gas chromatography; with a liquid or solution mobile phase it is called liquid chromatography. There are also a large number of stationary phases which can be solid or liquid in form. The choice depends on the mode of separation, i.e., separation by molecular size, solubility, or polarity. Therefore, chromatography can also be classified as absorption, partition, and ion-exchange chromatography. Several chromatigraphic techniques are discussed below.

Gas Chromatography (GC)

GC is used to separate volatile compounds and has both qualitative and quantitative application. The mobile phase is a gas, usually helium, that transports the compound through the column. The stationary phase can be solid or liquid; in most cases it is a liquid of low volatility. Actually the liquid is impregnated on a solid support, generally diatomaceous earth particles, that retain the liquid and allow gas flow. A flame ionization detector is used for routine analysis of a compound in the nanogram (10^{-9} g) range. GC has been applied in the polymer field for identification of residues, monomers, and volatile additives in polymers. It is however a qualitative technique and as such is not expected to be useful for measuring minute degradation rates

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High-Performance Liquid Chromatography (HPLC)

HPLC is a high-resolution, high-speed, and high-sensitivity liquid-chromatographic technique. The mobile phase is a liquid which carries the compound to be analyzed through the column or the stationary phase, which can be solid (rigid gel) or liquid coated on a support material Potentially, liquid-liquid chromatography has greater versatility than liquid-solid chromatography, since the pairs of liquid which can be used are numerous. In order to avoid phase miscibility, the stationary phase should be a good solvent to the sample, but a poor solvent for the mobile phase.

To obtain high speed, a narrow, long, high-resolution column operated at high pressure is required. High-sensitivity detectors such as UV and IR photometers are used, which permit measurement of nanogram (10^{-9} g) quantities of the compound. HPLC, however, is a qualitative tool and as such is not expected to be useful for measurement of degradation rates.

Thin Layer Chromatography (TLC)

Thin layer chromatography is considered a complementary technique to paper chromatography and is most valuable when the materials to be analyzed are available only in minute quantities. The stationary phase of TLC is an absorption plate about 250 μ thick, on which separation is carried out. This chromatoplate is prepared by spreading a thin and uniform layer of absorbent such as silica gel or alumina, together with a suitable binding agent, on a glass plate. A small drop of sample solution is placed on one end of the plate, and is allowed to air dry. The plate is then dipped in a container with a suitable developing agent such as phenol The developing agent ascends along the plate by capillary action and causes the components in the sample mixture to migrate at differential speeds behind it. The separated components can be identified readily by treatment of the plate with suitable color-forming reagents. Each component then appears as a smeared spot located at a rather well defined relative distance from the starting position and bearing a characteristic color.

TLC is not a quantitative method and therefore is not expected to be useful for measuring the minute degradation rates of interest in the LSSA program.

12. Neutron Diffraction

Since the wavelengths of neutrons and X-rays are of the same order (about 1 0 Å), the theory and mechanism of X-ray diffraction can also be applied to neutron diffraction. These techniques are useful for studying the atomic and molecular structure of crystalline materials. Neutron diffraction is more accurate and sensitive then X-ray diffraction for examination of extremely heavy and light atoms. X-rays are diffracted from the electrons of atoms and produce a picture of electron density. It follows that, heavy atoms such as lead and uranium will dominate in these pictures, and that a one-electron atom, i e., hydrogen, can be located and detailed with less accuracy. Neutrons are scattered by the neutrons of an atom. The scattering power depends on both the cube root of the atomic weight and the structure of the nucleus.

The neutron diffraction technique is still at the university-laboratory level of development, since a nuclear reactor is needed to produce a neutron beam. It is therefore deemed not applicable to the goals of the LSSA project.

13. Acoustic Emission

Acoustic emission or stress-wave emission is a relatively new NDT technique.(VIII-10,VIII-11) A schematic of the use of this technique is presented in Figure VIII-2.(VIII-11) Stress waves are emitted by a material when plastic deformation occurs or when a microcrack propagates These stress waves may then be sensed with piezoelectric transducers. This technique has the drawback

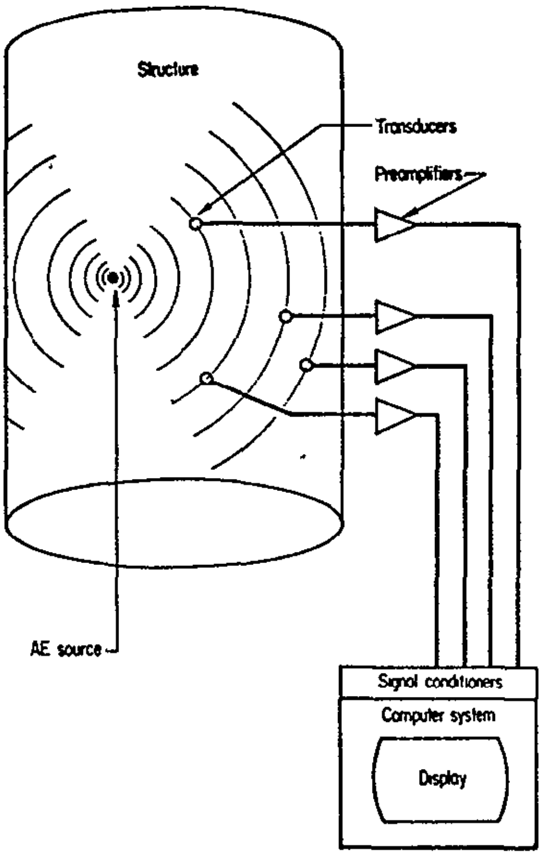


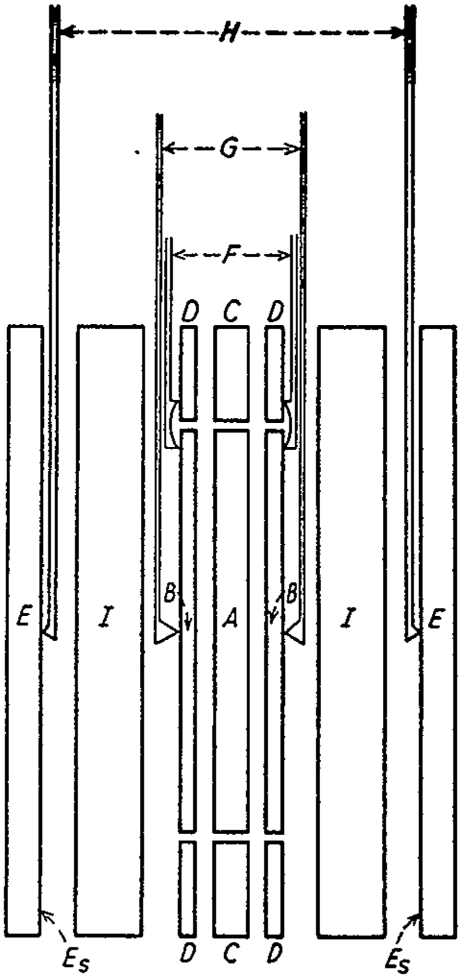
FIGURE VIII-2. SCHEMATIC OF ACOUSTIC EMISSION NDT TECHNIQUE

that it can be employed only while defects are growing under mechanical or thermal stress. Also, at the present time, it is difficult to interpret quantitatively the signals which are detected. For these reasons, this technique was not selected for further analysis.

14. Thermal Conductivity

Many techniques are available for measuring the thermal conductivity of solids. For low-conductivity materials such as glasses and polymers, the standard technique is the guarded hot plate, which is covered by ASTM Designation C-177.(VIII-12) A schematic of the test section of a guarded hot plate apparatus is presented in Figure VIII-3. The test stack is composed of a guarded electrical heater (or hot plate) sandwiched between two identical flat-plate specimens which are further bounded by cooling plates. At steady-state conditions, the electrical energy supplied to the central heater of the hot plate is measured and is used in conjunction with measured temperature differences and specimen dimensions to obtain thermal-conductivity values.

The difficulties encountered in making thermal-conductivity measurements are well documented.(VIII-13,VIII-14) Because of the many pitfalls which may be encountered, normal thermal-conductivity-measurement techniques were not considered in detail. Special techniques for use with modules may have some merit. A possible special technique is to instrument the cells and other parts of the module with very small thermocouples and then supply heat by passing a current through the cells in a reverse direction. This technique might prove to be useful in following the development of delaminations It is likely, however, that the initial occurrence and growth of delaminations might be more easily detected by ultrasonic or optical techniques.



Heating Unit

Central Section of Heating Unit

Guard Section of Heating Unit

A–Central Heater
B–Central Surface Plates
C–Guard Heater
D–Guard Heater
E–Cooling Units
F–Differential Thermocouples
G–Heating Unit Surface Thermocouples
H–Cooling Unit Surface Thermocouples
I–Test Specimens

FIGURE VIII-3 SCHEMATIC OF GUARDED HOT PLATE THERMAL CONDUCTIVITY APPARATUS

15. Mechanical Strength

Numerous methods are used for measuring the mechanical strength and other related properties. These methods usually involve the application of a load to a specimen of a given geometry and a measurement of the resulting deformation (elongation, deflection, etc.). The most familiar test is the tensile test illustrated in Figure VIII-4.(VIII-15) Here the specimen is elongated at a uniform rate and a plot of load versus elongation (or equivalently, engineering stress versus strain) is obtained, as shown in Figure VIII-5.(VIII-16) Various important features which may be read off a tensile stress-strain curve are: modulus of elasticity (initial slope of stress-strain curve), the yield stress (σ_y), tensile strength (σ_B), and elongation at break (ϵ_B). Tests similar to this may also be run in compression. The typical test for measuring the strength of brittle materials such as glass is the four-point bending test, in which a beam is supported at both ends and loads are applied symmetrically at two points in the center section. The load is then increased until the specimen breaks.

Another type of test is the impact test, shown schematically in Figure VIII-6.(VIII-15) Here, the sample in the form of a notched bar is placed across the jaws of the testing mechanism. A heavy pendulum, released from a known height, strikes and breaks the sample before its upward swing. The energy absorbed in the fracture is then calculated from a knowledge of the initial and final potential energies of the pendulum.

Since strength tests are usually destructive and may require numerous replicate samples (as in the case of glass), these tests were not considered for detailed evaluation for use in an accelerated testing program. Further information on mechanical-property tests can be found in the ASTM Standards.(VIII-17,VIII-18) Many tests for the strength of adhesive bonds can be found in the book by Anderson, et al.(VIII-19)

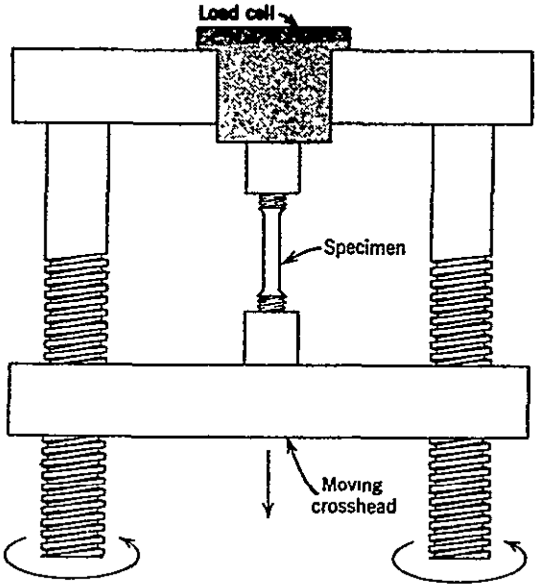


FIGURE VIII-4. SCHEMATIC OF A TENSILE-TESTING APPARATUS

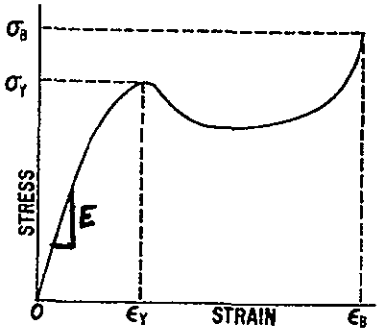


FIGURE VIII-5. STRESS-STRAIN NOTATION

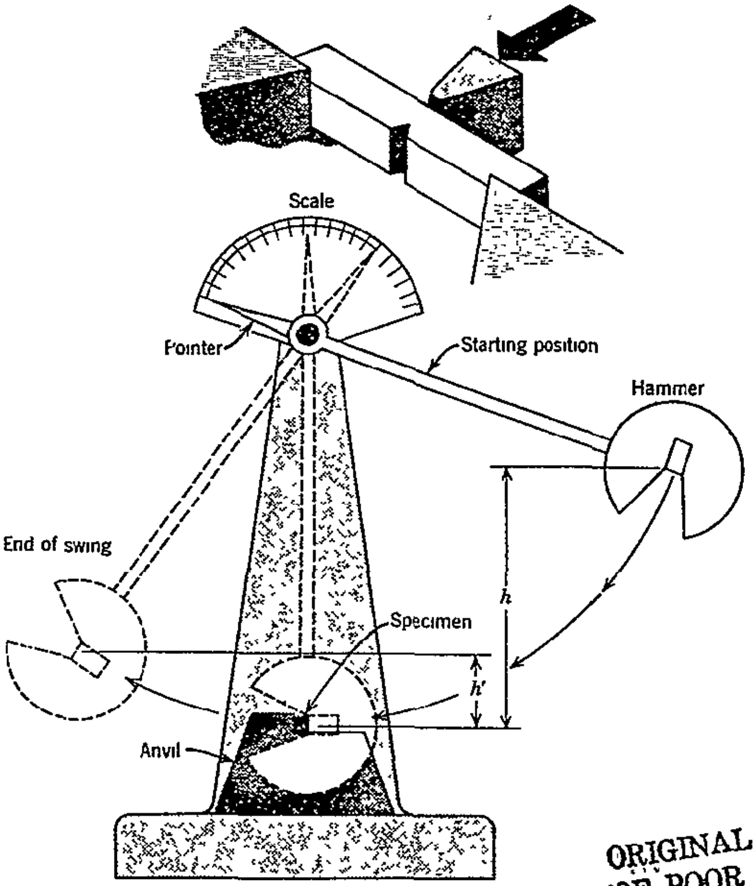


FIGURE VIII-6. SCHEMATIC OF A STANDARD IMPACT-TESTING APPARATUS

16. Inelastic Electron Tunneling Spectroscopy (IETS)

Inelastic tunneling spectroscopy is a technique which is currently employed to investigate the vibrational-rotational energy levels of organic materials and of bonds between thin layers of organic materials and metal oxide surfaces. The technique consists of measuring the bias dependence of changes in the electron tunneling current through a tunneling structure which incorporates, as a dopant, the material to be studied and correlating these changes with known molecular transitions to effect an identification of the chemical species present.

The tunneling structure used in these studies consists of two metal layers (each ~500 to 3000 Å thick) separated by a thin (~30 Å) insulating layer in a sandwich-type structure. The metal layers are generally vacuum deposited. The insulating layer is usually formed by oxidation of the first metal layer. The oxide surface is then "doped" with the organic material to be studied – either by vacuum evaporation, dipping, or spin coating – to provide a thin (generally estimated to be a monolayer or less) layer. Finally, the second metal layer is deposited on top of the metal-oxide-dopant structure to complete the tunnel device. A commonly used structure consists of a 2000 Å layer of aluminum, a 30 Å layer of aluminum oxide, the "dopant", and a 2000 Å layer of lead. Lead is preferred as the top metal layer in most experiments because it appears to have a smaller effect on the dopant's vibrational spectra than other candidates (VIII-20)

Electron tunneling is a quantum mechanical effect whereby an electron can penetrate through a potential barrier whose height is greater than the maximum energy of the electron. Figure VIII-7 is a simplified electron-energy-level diagram of a metal-insulator-metal junction across which a bias voltage V has been applied (Metal A is biased negatively with respect to Metal B). This bias results in a separation of the Fermi levels of the two metals by an amount eV. Elastic tunneling (i.e., tunneling without energy loss) is represented by the horizontal motion of electrons (dashed line) near the Fermi level in Metal A through the insulator (I) to adjacent *vacant* energy states above the Fermi level in Metal B. Elastic tunnel currents increase approximately linearly with bias voltage and typically constitute ~99 percent of the total tunnel current. Under certain conditions, a tunneling electron can excite a vibrational mode ν_η (resulting in a transfer of energy, $h\nu_\eta$) of a dopant molecule on or within the insulating layer and still reach an empty state above the Fermi level in Metal B This can occur when

$$eV > h\nu_\eta$$

and results in inelastic tunneling currents which are of the order of 0.5 to 1 percent of the total tunnel current. The diagram in Figure VIII-8 shows tunneling between two normal metals. In actuality, most inelastic electron tunneling experiments employ one superconducting metal electrode and are performed at temperatures less than 10°K. This mode of operation results in increased resolution and affords a means of testing the junction to ensure that tunneling is the principal means of current flow.(VIII-21)

Figure VIII-9 illustrates the sample construction and a simplified measurement circuit. Since the change in the current (I) and the conductance (dI/dv) associated with the onset of an inelastic tunnel current is so small the second derivative, d^2I/dV^2 (or more typically d^2V/dI^2 which is reasonably linearly related over the voltage range of interest), is measured to accentuate the small change. The step in the plot of dI/dv versus V becomes a peak in the plot of d^2I/dv^2 versus V, as illustrated in Figure VIII-8. Figure VIII-10 is a schematic of a typical instrumentation arrangement for measurements with inelastic electron tunneling spectroscopy. Details of such

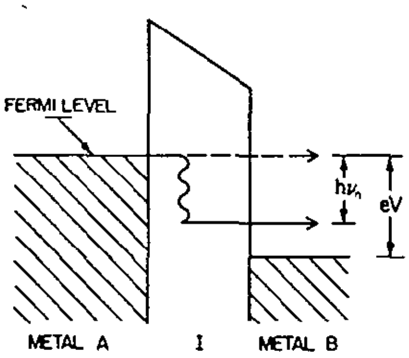


FIGURE VIII-7. ELECTRON-ENERGY-LEVEL DIAGRAM OF A METAL-INSULATOR-METAL JUNCTION

For $eV > h\nu_\eta$, tunneling electrons can excite a molecular vibration of energy $h\nu_\eta$. If $eV < h\nu_\eta$, there are no available vacant states to which the electron can tunnel

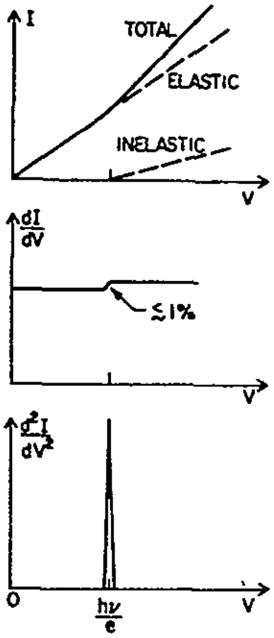


FIGURE VIII-8. IDEALIZED INELASTIC ELECTRON TUNNELING SPECTRA

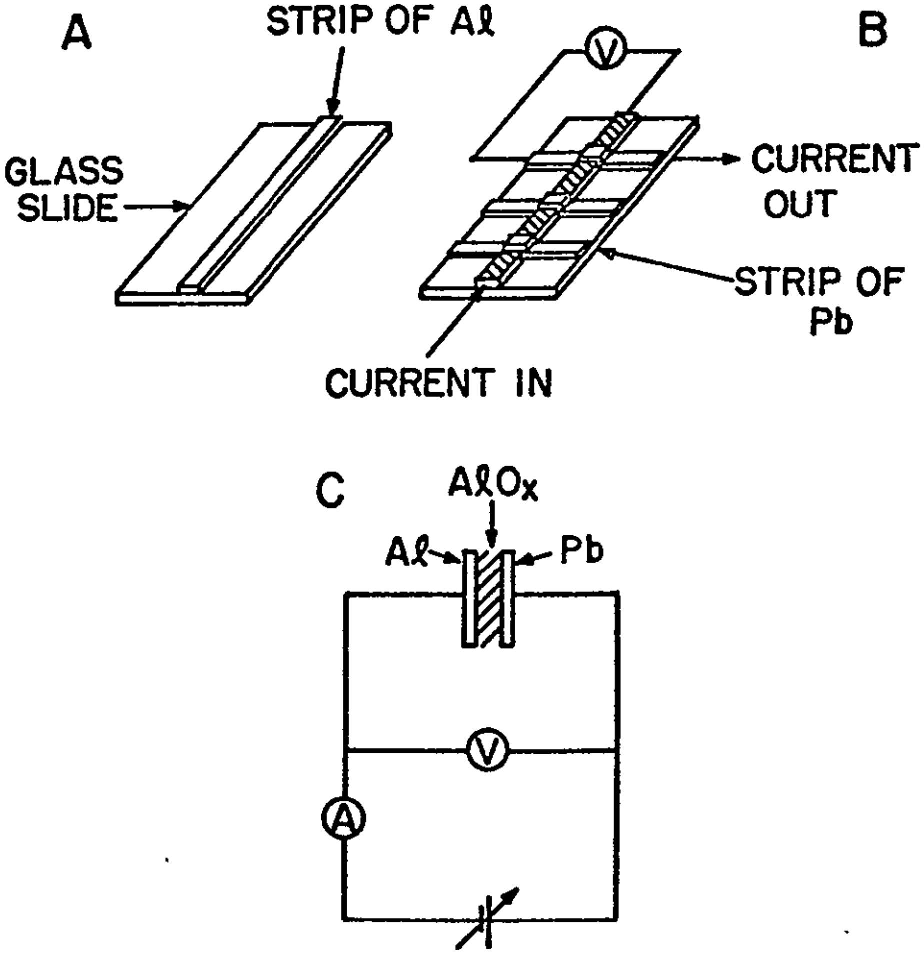


FIGURE VIII-9. SAMPLE CONSTRUCTION AND SIMPLIFIED MEASUREMENT CIRCUIT

Note that multiple junctions are generally formed on a single substrate (glass slide).

C-3

measurements and extensive discussions of the history theory are given in the references cited in this section (and in references cited therein).

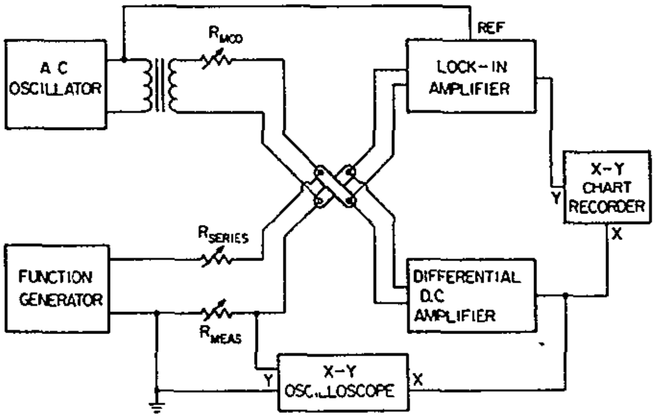


FIGURE VIII-10. SCHEMATIC OF TYPICAL INSTRUMENTATION ARRANGEMENT FOR MEASUREMENTS WITH INELASTIC ELECTRON TUNNELING SPECTROSCOPY(VIII-20)

Standard electronics for tunneling spectroscopy includes an x–y chart recorder for recording tunneling spectra, d^2V/dI^2 versus V, and an oscilloscope for measuring I versus V as a check on junction quality

Tunneling electrons can produce both IR-type (i.e., intrinsic dipole moment) and Raman-type (i e., polarizability) interactions and, hence, the IETS spectra include both of these modes, although there is no direct correlation between the relative intensities of observed infrared or Raman lines and the corresponding tunneling peaks.(VIII-22) The IETS technique is considered to be more sensitive than IR and Raman techniques and has been shown to exhibit sensitivities in the parts per million range in some cases. The methods used to fabricate the test units could, however, result in breakdown or alteration of the organic test material in such a way as to confuse degradation studies. The fact that materials must be volatile enough for vacuum deposition or dissolved for spin/spray deposition is also restrictive. In addition, interaction of the dopant with the host insulator material and the possible presence of O–H bonds within the insulator could further confound the interpretation of spectra for the purposes of degradation studies. Finally, while the IETS technique is a sensitive means of establishing the identity of chemical species present, the quantitative interpretation of IETS data to determine percentages or number of a given species present would be extremely difficult for the present state of the art. For these reasons IETS is felt to be not applicable for present or near-future degradation diagnostics and is not recommended for further investigation in this regard at this time.

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