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

**Fifth Quarterly Progress Report,
September 16, 1976—December 15, 1976**

December 27, 1976

Work Performed Under Contract No. NAS-7-100-954328

**Battelle Columbus Laboratories
Columbus, Ohio**

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

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FIFTH QUARTERLY PROGRESS REPORT
Covering the Period September 16, 1976, to December 15, 1976

on

**STUDIES OF ENCAPSULATION MATERIALS
FOR TERRESTRIAL PHOTOVOLTAIC ARRAYS, # #14**

JPL Contract No. 954328

Encapsulation Task
Low-Cost Silicon Solar Array Project

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

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

December 27, 1976

D. C. Carmichael
Program Manager

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

MASTER

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ABSTRACT

This Fifth Quarterly Progress Report on JPL Contract No. 954328 covers work conducted in the period from September 16, 1976 through December 15, 1976. The research is part of a five-task development project, the Low-Cost Silicon Solar Array Project (LSSA Project), being managed by the Jet Propulsion Laboratory for the Energy Research and Development Administration, Division of Solar Energy. The Encapsulation Task (Task III) of this project includes four studies assigned to Battelle's Columbus Laboratories. Two of these studies (Studies 1 and 2) have been completed; the others (Studies 3 and 4) are in progress and the efforts this quarter are discussed in this report.

The final report on Study 1 was published and distributed this quarter and is identified as follows:

Report No.: ERDA/JPL-954328-76/4

Report Title: *Review of World Experience and Properties of
Materials for Encapsulation of Terrestrial
Photovoltaic Arrays*

The final report on Study 2 is in the final editing and reproduction phase and is identified as follows:

Report No.: ERDA/JPL-954328-76/5

Report Title: *Terrestrial Service Environments for Selected
Geographic Locations*

Present efforts in Study 3, entitled "Evaluation of Test Methods and Properties of Candidate Encapsulation Materials", are concerned primarily with evaluation of the properties of candidate encapsulation materials and processes which have been identified based on the results of Study 1. Specifically, cover materials for modules, and adhesives for bonding cells to cover materials and for bonding cover materials to other encapsulation-system components, are being screened in environments including UV radiation, temperature cycling, and high relative humidity. Results of the evaluations to date are described in the report. These efforts include investigations of both polymeric and glass encapsulation materials.

Efforts this quarter in Study 4, entitled "Development of Accelerated and Abbreviated Testing Methods for Predicting Performance of Encapsulation Materials Over a 20-Year Lifetime", were concerned primarily with analyzing methods for discrimination among test methods with regard to precision, sensitivity, and cost. The background and procedures for such discrimination are discussed and examples are given.

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

F. A. Sliemers, M. C. Brockway, A. R. Bunk, G. P. Nance,
G. B. Gaines, and D. C. Carmichael

INTRODUCTION

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

The objectives of this study, therefore, are to

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

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

Results of the analysis of the world experience with existing modules (Study 1) indicate that major problems with materials interactions and interfaces have overshadowed changes in bulk properties of materials. The experience shows that many module failures have occurred, for instance, at the seals attaching the bottom cover to top cover and at those interfaces forming the seal of the electrical leads to the protective covers. Further encapsulation system developments depend significantly on finding solutions to the seal and other interface problems. Thus, a substantial portion of the current Study 3 efforts is being directed toward material properties involved in these problems. Environmental parameters of first concern are ultraviolet radiation, temperature (including temperature cycling), and relative humidity.

TECHNICAL DISCUSSION OF RESULTS THIS QUARTER

For purposes of reporting, the efforts of Study 3 are organized into studies of polymeric materials and studies of glass materials. This division is somewhat arbitrary because many of the encapsulation concepts employing glass (as the top cover) employ polymeric materials as well.

Evaluations of Polymeric Materials as Encapsulant Components

As noted in previous reports, Study 3 efforts are emphasizing those materials and materials interfaces which the world experience suggests are currently most troublesome. During this quarter, principal efforts have been directed toward screening adhesives and sealants for use with candidate encapsulants. To date, effects on bond strength of exposures to UV radiation and temperature cycling have been determined using "Teflon" FEP and weatherable Mylar films (which were the first materials received). These results are reported below. Measurements also have been made on water permeation rates of adhesive/film composites. Also reported are initial results of chemiluminescence measurements on selected specimens. Evaluations of other materials have been initiated as they have been received.

Bond-Strength Experiments

Lap-shear specimens were prepared for bond-strength measurements using 2.54 x 12.7-cm (1 x 5-in.) strips of the selected film materials. Two of these strips are used for each lap-joint. The bond area is first cleaned with a solvent wipe (differs with type of film), and then a thin film of the selected adhesive is applied with a small brush over a 6.45 cm² (1 in.²) area. The two strips are joined using a 4-1/2 lb, hard-rubber-covered roller.* Specimens are allowed to set or cure for at least 72 hours at 22.8 C (73 F) and 50 percent relative humidity before being placed on test. Bond-strength measurements are made on lap-shear specimens following exposure to a potentially degrading environment (UV radiation or temperature cycling). The specimen design is shown in Figure 1.

Temperature-cycling exposure is effected in a commercial environmental chamber with the specimens attached to aluminum sheets. Temperature is cycled in the range -40 to 90 C with a 4-hour cycle time. Relative humidity is not controlled. Bond-strength measurements are performed at 23 C on a "bench-type" Instron tester using a draw rate of 0.5 cm/min (0.2 in./min).

Exposure to UV radiation is effected by placing aluminum-backed specimens in a closed chamber in which a 6000-watt, xenon lamp is operating. Each specimen is positioned 45.7 cm (18 in.) from the lamp. The temperature is not controlled;

*Rubber-covered roller supplied by Pressure Sensitive Tape Council, 1201 Waukegan Road, Glenview, Illinois.

it can vary within the approximate range of 35 to 60 C. Radiation other than the UV component is not filtered out. Bond-strength measurements are performed as described above.

FIGURE 1. CONFIGURATION OF LAP-SHEAR SPECIMENS

Bond-strengths have been determined thus far for specimens on two types of film substrates: "Teflon" FEP and weatherable Mylar. Table 1 summarizes the results of the measurements for "Teflon" FEP specimens after UV exposure up to 1000 hours, a period which has been selected arbitrarily as a cut-off for these screening-type evaluations. For the lap-shear evaluations, the control was stored in a constant-temperature room at 23 C and 50 percent relative humidity. Note in Table 1 that in the majority of the cases film elongation rather than bond failure occurred. Generally speaking, it can be concluded that the adhesives are still stronger than the yield value of the film substrate after 1000 hours of UV exposure.

The same film-adhesive systems were examined for bond strength after exposure to temperature cycling for the periods indicated in Table 2. Adhesive bond failure occurred in all specimens in which the moisture-cured silicone adhesive RTV 118 was used. The bond-strength values were not significantly lower than those measured after UV exposure and were on an average slightly higher than those of the controls. Therefore, even though the bonds failed adhesively, the bond-strength values were still approximately the yield value of the film substrate. The moisture-cured RTV 732 failures were approximately half adhesive failures and half yield or film-substrate-elongation failures. There is little difference in stress values (in psi) between the specimens that failed and those in which the film yielded. All specimens bonded with the other three adhesives exhibited film elongation. Of the specimens bonded with the five adhesives to "Teflon" FEP and subjected to temperature cycling, none had a value lower than 6.6 psi nor more than 9.5 psi after 1133 hours' exposure before adhesive failure or film elongation occurred. The test was terminated at this exposure time.

TABLE 1. LAP-SHEAR STRENGTH OF SPECIMENS ON "TEFLON"
FEP SUBSTRATE FOLLOWING UV EXPOSURE^(a)

Specimen	Adhesive ^(b)	Exposure Time, hr	Elongation or Adhesive Bond Strength ^(c) , psi	Remarks ^(d)
5-1	RTV 118	None (control)	8.8	Adhesive failure
5-6	Ditto	122	9.2	Film elongation
5-8	"	485	9.2	Film elongation
5-10	"	1046	9.2	Film elongation
6-1	RTV 732	None (control)	8.8	Film elongation
6-6	Ditto	25	8.8	Film elongation
6-8	"	122	8.8	Film elongation
6-10	"	485	9.2	Film elongation
7-1	Silgrip SR-573 with 1-1/2% Benzoyl peroxide (cat.)	None (control)	9.0	Film elongation
7-6	Ditto	122	8.8	Film elongation
7-8	"	485	9.0	Film elongation
7-10	"	1046	9.3	Film elongation
9-1	Scotch Weld 2216 B/A (clear)	None (control)	8.8	Film elongation
9-5	Ditto	134	8.8	Film elongation
9-12	"	784	9.2	Film elongation
10-1	Cavalon 3100 S, Activator 3300 S	None (control)	8.8	Film elongation
10-5	Ditto	134	8.8	Film elongation ^(e)
10-12	"	784	9.0	Film elongation ^(e)

(a) Adhesives on "Teflon" FEP film 127 μm (0.005 in.) thick; adhesive area, 6.45 cm^2 (1 in.²). Controls stored in constant temperature room 22.8 C (73 F), 50 percent relative humidity.

(b) Silicone adhesives: RTV 118, RTV 732, and Silgrip SR-573 - supplier is G.E.; Scotch-Weld 2216 B/A (clear) - supplier is 3M; Cavalon 3100 S with activator 3300 S - supplier is DuPont.

(c) Bond strength in psi based on area of adhesive.

(d) Adhesive failure indicates bond failure between "Teflon" FEP film and adhesive; cohesive failure indicates bond failure in the adhesive itself; "film elongation" indicates that film elongation occurred in portion of film not associated with bonded area.

(e) Adhesive is brown after exposure. Starting color is yellow to amber.

TABLE 2. LAP-SHEAR STRENGTH OF SPECIMENS ON "TEFLON" FEP SUBSTRATE
FOLLOWING TEMPERATURE CYCLING (-40 to +90 C)

Specimen	Adhesive ^(b)	Exposure Time, hr	Elongation or Adhesive Bond Strength ^(c) , psi	Remarks ^(d)
5-1	RTV 118	None (control)	8.8	Adhesive failure
5-14	Ditto	598	9.35	Adhesive failure
5-21	"	1133	8.8	Adhesive failure
6-1	RTV 732	None (control)	8.8	Film elongation
6-14	Ditto	598	9.4	Adhesive failure
6-21	"	1133	9.0	Adhesive failure
7-1	Silgrip SR-573 with 1-1/2% Benzoyl peroxide (cat.)	None (control)	9.0	Film elongation
7-14	Ditto	598	9.2	Film elongation
7-21	"	1133	9.2	Film elongation
9-1	Scotch Weld 2216 B/A (clear)	None (control)	8.8	Film elongation
9-13	Ditto	500	9.4	Film elongation
9-21	"	1034	9.1	Film elongation
10-1	Cavalon 3100 S, Activator 3300 S	None (control)	8.8	Film elongation
10-13	Ditto	500	9.4	Film elongation ^(e)
10-21	"	1034	9.2	Film elongation ^(e)

- (a) Adhesives on "Teflon" FEP film, 127 μm (0.005 in.) thick; adhesive area, 6.45 cm^2 (1 in.²). Controls stored in constant temperature room 22.8 C (73 F), 50 percent relative humidity.
- (b) Silicone adhesives: RTV 118, RTV 732, and Silgrip SR-573 - supplier is G.E.; Scotch-Weld 2216 B/A (clear) - supplier is 3M; Cavalon 3100 S with activator 3300 S - supplier is DuPont.
- (c) Bond strength in psi based on area of adhesive.
- (d) Adhesive failure indicates bond failure between FEP-Teflon film and adhesive; cohesive failure indicates bond failure in the adhesive itself; "film elongation" indicates that film elongation occurred in portion of film not associated with bonded area.
- (e) Adhesive is dark brown after exposure. Starting color is yellow to amber.

Evaluations of adhesives for bond strength on weatherable Mylar film, 0.178-mm (0.007-in.) thick have given values which are more indicative of the strength of the adhesives themselves, because the yield value for Mylar for the thickness being used is higher than most bond strengths. Table 3 summarizes the results of the UV-exposed specimens after 329 hours. For the specimens exposed to UV radiations, two types of failure are noted. These failures are either adhesive or cohesive. (See note at bottom of Table 3 for definitions.) The specimens with structural-type adhesives, namely the epoxy Scotch Weld 3520 and the acrylic Cavalon 3100 S, had "adhesive" failures. For the nonstructural-adhesive specimens, namely Scotch Grip 4693 (plastic contact adhesive), moisture-cured silicone elastomeric adhesive RTV 118, and silicone resin adhesive Silgrip SR-573 (with catalyst), the failure was "cohesive". Specimens bonded with the structural adhesive Cavalon 3100 S, after 239 hours' exposure, had an average bond-strength value higher than any other adhesive listed in Table 3. However, the catalyst used to cure with acrylic adhesive discolors and darkens sufficiently that it would not be practical to use it where sunlight has to pass through the adhesive layer.

Table 4 summarizes the data for bond-strength measurements on weatherable Mylar, 0.178-mm (0.007-in.) thick after exposure to temperature cycling for 508 hours (127 cycles). In this table, it can be seen that some specimens had sufficient bond strength to cause film elongation to occur before the bond failed cohesively. There is no significant difference in bond-strength values between the structural and nonstructural adhesive specimens after 508 hours' exposure to temperature cycling. Specimens bonded with Scotch Grip 4693 exhibited the highest average bond-strength value (102 psi) of any of the adhesives studied. The unknown factor with this adhesive is its UV stability. The 1000-hour, UV-exposed specimens will provide important data in determining the value of this material for proposed encapsulant applications.

Water-Vapor Transmission Experiments (WVTR)

Experience to date with encapsulation of photovoltaic modules with polymeric materials indicates that water vapor is one of the important "contaminants" affecting the service life of the enclosed solar cells. Combinations of films (and sheets) with various adhesives are being screened so as to select a candidate list of preferred materials. The initial results have been obtained for Mylar and FEP films bonded with several adhesives (sealants).

The rate of water vapor transmission through films/adhesives is being studied through the use of a film pouch (or "pillow pack"). Figure 2 is a schematic of the pouch. As indicated, two square films, 8.9 cm (3.5 in.) on a side, are bonded together along the outside edges of the films. The bond area is 1.27 cm (0.50 in.) wide; the total bonded area is thus 38.7 cm² (6.0 in.²). Water-permeation-rate calculations are based on the total film area containing the desiccant (0.08 m²).

Pouches were prepared for measurement of WVTR before and after temperature cycling (-40 C to 90 C) and after UV exposure for 500 and 1000 hours.

TABLE 3. LAP-SHEAR STRENGTH OF SPECIMENS ON WEATHERABLE
MYLAR SUBSTRATE FOLLOWING UV EXPOSURE^(a)

Specimen	Adhesive ^(b)	Exposure Time, hr	Adhesive Bond Strength ^(c) , psi	Remarks ^(d)
13-3	Scotch Grip 4693	None (control)	79.5	Cohesive failure
13-4	Ditto	239	88	Cohesive failure
13-11	"	239	76	Cohesive failure
13-12	"	239	71	Cohesive failure
14-3	RTV 118	None (control)	36	Adhesive failure
14-4	Ditto	239	45.5	Cohesive failure
14-11	"	239	97	Cohesive failure
14-12	"	239	94	Cohesive failure
15-3	Scotch-Weld 3520 B/A	None (control)	70	Adhesive failure
15-4	Ditto	239	78	Adhesive failure
15-12	"	239	59.5	Adhesive failure
16-3	Cavalon 3100 S, Activator 3303 S	None (control)	69.5	Adhesive failure
16-4	Ditto	239	96	Adhesive failure
16-5	"	239	85	Adhesive failure
16-6	"	239	99	Adhesive failure
17-3	Silgrip SR-573 with 1-1/2% Benzoyl peroxide (cat.)	None (control)	66	Adhesive failure
17-4	Ditto	239	65	Cohesive failure
17-5	"	239	49	Cohesive failure
17-6	"	239	53	Cohesive failure

(a) Adhesives on weatherable Mylar film 178 μm (0.007 in.) thick; adhesive area, 6.45 cm^2 (1 in.²). Controls stored in constant temperature room 22.8 C (73 F), 50 percent relative humidity.

(b) Scotch Grip 4693 and Scotch-Weld 3520 B/A supplied by 3M; RTV 118 and Silgrip SR-573 supplied by G.E.; Cavalon 3100 S, Activator 3303 S supplied by DuPont.

(c) Bond strength in psi based on area of adhesive.

(d) Adhesive failure indicates bond failure between weatherable Mylar film and adhesive; cohesive failure indicates bond failure in the adhesive itself.

TABLE 4. LAP-SHEAR STRENGTH OF SPECIMENS ON WEATHERABLE MYLAR SUBSTRATE
FOLLOWING TEMPERATURE CYCLING (-40 to +90 C)^(a)

Specimen	Adhesives ^(b)	Exposure Time, hr	Adhesive Bond Strength ^(c) , psi	Remarks ^(d)
13-1	Scotch Grip 4693	None (control)	68.5	Cohesive failure
13-13	Ditto	508	97	Film elongation, then cohesive failure
13-14	"	Ditto	108	Ditto
13-15	"	"	100	"
13-16	"	"	105	"
14-1	RTV-118	None (control)	66.5	Cohesive failure
14-13	Ditto	508	88	Cohesive failure
14-14	"	Ditto	38	Adhesive failure
14-15	"	"	47.5	Adhesive failure
14-16	"	"	94	Cohesive failure
15-1	Scotch Weld 3520 B/A	None (control)	66	Adhesive failure
15-13	Ditto	508	107	Film elongation, then cohesive failure
15-14	"	Ditto	86	Film broke
15-15	"	"	92	Film broke
15-16	"	"	56	Adhesive failure
16-1	Cavalon 3100 S, Activator 3303 S	None (control)	98.5	Adhesive failure
16-13	Ditto	508	86	Adhesive failure ^(e)
16-14	"	Ditto	98	Adhesive failure ^(e)
16-15	"	"	53	Adhesive failure ^(e)
16-16	"	"	99	Adhesive failure ^(e)
17-1	Silgrip SR-573 plus 1-1/2% Benzoyl peroxide	None (control)	57	Adhesive failure
17-13	Ditto	508	109	Film elongation, then cohesive failure
17-14	"	Ditto	110	Film elongation, then cohesive failure
17-15	"	"	76	Cohesive failure
17-16	"	"	95	Cohesive failure

(a) Adhesives on weatherable Mylar film 178 μm (0.007 inch) thick; adhesive area, 6.45 cm^2 (1 in.²). Controls stored in constant temperature room 22.8 C (73 F), 50 percent relative humidity.

(b) Scotch Grip 4693 and Scotch Weld 3520 B/A supplied by 3M Company; RTV 118 and Silgrip SR-573 supplied by GE; Cavalon 3100 S, Activator 3303 S supplied by DuPont.

(c) Bond strength in psi based on area of adhesive.

(d) Adhesive failure indicates bond failure between weatherable Mylar film and adhesive; cohesive failure indicates bond failure in the adhesive itself; "film elongation" indicates that film elongation occurred in portion of film not associated with bonded area.

(e) Adhesive is yellow to brown (spotty) in color after exposure. Starting color is light yellow to yellow.

FIGURE 2. FILM POUCH (PILLOW PACK) USED IN DETERMINING WATER VAPOR TRANSMISSION THROUGH FILM/ADHESIVE SUBSYSTEM

(Drawing shows one-half of square pouch.)

Pouches are prepared by bonding three sides, inserting the desiccant (10 grams of Drierite®), and sealing the fourth side. Temperature cycling and UV exposures of the test pouches were carried out prior to adding the desiccant and sealing the fourth side. Following preparation, the pouches are inserted in a closed environment in which the relative humidity is controlled at 95 percent and the temperature is 23 C. Periodically, the pouches are removed from the environment and weighed. The weight increase is recorded; in all experiments to date, the weight increase has been a linear function of exposure time. Thus, the slope of the weight-time relationship is proportional to the water-vapor transmission rate.

Results to date are summarized in Table 5 for Mylar and FEP films. Each result represents the average of two separate measurements (two pouches). For 0.051-mm (2-mil) thick Mylar pouches, the WVTR is approximately constant for all adhesives used. Values for the 0.051-mm (2-mil) Mylar are approximately 2-1/2 times those of the 0.178-mm (7-mil) material. The difference in the extreme values is approximately 10 percent. WVTR values for the FEP pouches are lower. The difference in the extreme values is approximately 138 percent. A tentative conclusion is that the data for the Mylar experiments represent the permeation rate through the Mylar and are little affected by the selection of adhesive. The WVTR value for the FEP film is $\leq 0.146 \text{ g (24 hr)}^{-1}\text{m}^{-2}$, judging from the results of the heat-sealed pouch. Considerable differentiation, then, is obtained among the several adhesives. From the data shown, Silgrip SR-574 gives the highest WVTR value; the other adhesives lead to values grouped in a much lower range. Of these, Cavalon 3100 S gives the lowest value.

TABLE 5. WATER VAPOR TRANSMISSION RATE OF ADHESIVE-FILM SUBSYSTEMS

Adhesive	Type	WVTR, g/24 hr/m ² at 23 C, 95% R. H. (a)			
		Nonweatherable Mylar 0.051 mm, 2 mil	Weatherable Mylar ^(b) 0.178 mm, 7 mil	"Teflon" FEP, 0.127 mm, 5 mil	
				Unexposed	228.5 hr UV Exposure
Silgrip SR-573	Heat-sealable silicone	5.63	1.85	0.204	0.280
Silgrip SR-574	Pressure-sensitive silicone	5.26	—	0.250 ^(c)	0.217
Silicone RTV-118	Room temperature curing silicone	5.41	—	0.224	0.249
Silastic 732 RTV	Room temperature curing silicone	5.18	1.79	0.282	0.303
Scotch-Weld 2216 B/A	Room temperature curing epoxy	5.30	1.83	0.201	0.237
Acryloid B-7	Thermoplastic acrylic	5.72	2.25	0.273	0.218
Cavalon 3100 S	Room temperature curing acrylic-accelerator 3300 S	5.37	1.79	0.167	0.356
None (Heat sealed)	—	—	—	0.154	—

(a) Film pouches, 8.9 cm x 8.9 cm (3.5 inch by 3.5 inch) overall, were prepared with a 1.27-cm (0.50-inch) adhesive bond around the edges. Ten grams of Drierite[®] were contained within each pouch. Values are the average of two samples.

(b) These values are preliminary. They are based on three data points.

(c) Single determination. One sample failed after 20 days (WVTR = 1.354 g/24 hr/m²).

After 228.5 hours' exposure to UV, the WVTR rate increased very slightly for all the adhesives examined except for the Silgrip SR-574 and the Acryloid B-7. The pressure-sensitive silicone (Silgrip SR-574) may be "hardening" and the acrylic (Acryloid B-7) could be cross-linking actions which could lower the WVTR. The Cavalon 3100 S, which exhibited the lowest WVTR before UV exposure ($0.167 \text{ g/24 hr/m}^2$), had the highest WVTR after exposure ($0.356 \text{ g/24 hr/m}^2$).

Chemiluminescence Experiments

Measurements of the photon emission from materials owing to oxidation reactions (chemiluminescence) have been made to determine if such measurements can be used as a diagnostic tool to evaluate degradation rates. Only preliminary results are available to date. Initial measurements have been made on "sandwich" specimens of the type shown in Figure 3. Mylar and FEP films were used as the sandwich material; RTV-118 and Scotch Weld 2216 B/A were the adhesives. Exposures have included UV radiation and temperature cycling of the type described previously. Actual measurements (photon counting) were made in an air enclosure at 26 C.

FIGURE 3. CONFIGURATION OF SPECIMEN USED IN CHEMILUMINESCENCE EXPERIMENTS

The results to date are given in Table 6. Note that the emission (net counts per second) is a function of the volume of the film and adhesive used. Differences in volume of the film present no problems. The volumes of the adhesives are unknown and subject to sizable variability. Moreover, the bonded area was not defined well due to smearing along the edges of the bond. With this reservation, it can be noted that the emission rates for FEP specimens alone (no adhesive) are very small for all conditions; Mylar films with no adhesives lead to slightly higher values. With some exceptions, the emission rates from the epoxy adhesives

TABLE 6. CHEMILUMINESCENCE MEASUREMENTS ON
UV- AND TEMPERATURE-CYCLED SAMPLES

Specimen	Film	Adhesive	Test	Exposure, hr	Emission net counts/ sec ^(a)
2-1	Mylar	None	Control	None	53
2-3	Mylar	None	UV	25	13
2-5	Mylar	None	Temp cycling	598	18
2-6	Mylar	None	Temp cycling	598	24
2-11	FEP	None	Control	None	4
2-13	FEP	None	UV	25	7
2-15	FEP	None	Temp cycling	598	1
2-16	FEP	None	Temp cycling	598	9
3-1	Mylar	2216 B/A	Control	None	744
3-3	Mylar	2216 B/A	UV	25	1006
3-5	Mylar	2216 B/A	Temp cycling	598	95
3-6	Mylar	2216 B/A	Temp cycling	598	25
3-11	FEP	2216 B/A	Control	None	585
3-13	FEP	2216 B/A	UV	25	555
3-15	FEP	2216 B/A	Temp cycling	598	58
3-16	FEP	2216 B/A	Temp cycling	598	41
4-1	Mylar	RTV-118	Control	None	85
4-3	Mylar	RTV-118	UV	25	10
4-5	Mylar	RTV-118	Temp cycling	598	13
4-6	Mylar	RTV-118	Temp cycling	598	11
4-12	FEP	RTV-118	Control	None	1
4-13	FEP	RTV-118	UV	25	5
4-15	FEP	RTV-118	Temp cycling	598	22
4-16	FEP	RTV-118	Temp cycling	598	0

(a) Samples were placed in a closed chamber in air at 26 C for measurements of unfiltered chemiluminescence emission. Background counting rates were subtracted from observed emissions.

(2216 B/A) are higher than those from the silicone (RTV-118). Unexposed specimens of Mylar/2216 B/A gave a rather high count rate, and, under UV exposure, the count rate was even higher. It was also noted that exposure to temperature cycling decreased the rate substantially. Whether further curing was the cause of this decrease is not yet known. Temperature cycling gave the same trend for FEP/2216 B/A specimens. FEP/RTV-118 specimens gave low count rates for all conditions. Further analysis must await the accumulation of considerably more data on these and other systems.

Evaluations of Glass Encapsulant Components

Study 1 identified three areas of primary importance in long-life performance of encapsulation systems incorporating glass covers: (1) the cover glass/solar-cell organic bond, (2) the "hermetic" sealing of the array, and (3) the corrosion of electrical conductors (metallization, interconnects, and leads) at the interfaces with either adhesives or sealants. Thus, the material properties of prime importance to long life are those bearing on the interactions and behavior at these interfaces; and the methods evolved for life testing must reflect changes in properties which are critical to interface-degradation problems.

Glass-to-Cell Adhesive Bonding

The organic adhesive layer between a cover glass and a silicon solar cell, being investigated in this study, should serve several functions. First, it should provide optical coupling with maximum transmission over the wavelength range of 280 to 1100 nm. Second, it should maintain its mechanical integrity plus the bond integrities at both the glass-adhesive and cell-adhesive interfaces. Third, it should avoid thermal stress levels which would damage the cell, cell metallization, or interconnects. Finally, the adhesive should be noncorrosive.

Large thermal mismatches among organic adhesives, silicon cells, and soda-lime glass (preferred over borosilicate for its low cost) provide the potential for severe thermal stress over the specified temperature cycle between -40 and +90 C. The most promising solution to this thermal stress problem appears to be the use of low-modulus adhesives.

The experimental studies being implemented include two subject areas: (1) screening-type tests of cell-adhesive-glass interface samples and (2) adhesive-property measurements.

Screening tests are being performed on sandwich-type samples consisting of a single cell, adhesive, and glass. A portion of the samples contain leads to permit pre- and posttest electrical measurements on the cell. Sample sandwiches utilize either soda-lime float glass or 7740 borosilicate glass plates. Adhesives have been selected on the basis of Study 1 information and discussions with adhesive manufactures, and additional candidates are expected to be identified for screening evaluations.

TABLE 7. IMPORTANT PROPERTIES OF CANDIDATE

Polymer Type	Adhesive(a)		Mechanical					Property
	Commercial Product		Young's Modulus (10 ⁻⁵ psi)	Hardness Shore A Durometer	Tensile Strength, N/m ²	Peel Strength	Lap Shear Strength	Ultimate Elongation, %
	Designation	Supplier						
-----Ideal adhesive-----			Low	Low	High	High	High	High
Dimethyl silicone	RTV-602	GE	--	15	6.9x10 ⁵	--	--	200
Dimethyl silicone	RTV-615	GE	--	35	6.4x10 ⁶	--	--	150
--	RTV-121	--	--	--	--	--	--	--
Dimethyl silicone	Sylgard-184	Dow Corning	--	35	6.2x10 ⁶	--	--	100
Silicone adhesive	Silgrip-573	GE	--	--	--	--	--	--
Silicone rubber	RTV3140	Dow Corning	--	25	2.1x10 ⁶	--	--	450
Silicone adhesive	282	Dow Corning	--	--	--	--	--	--

(a) Yasui, R. K., and Goldsmith, J. V., "Status of JPL Solar Powered Experiments for Terrestrial Applications", Presented at Ninth Intersociety Energy Conversion Conference, San Francisco, August 26-30, 1974.

(b) Yasui, R. K., and Patterson, R. E., "Utilization of Space Technology for Terrestrial Solar Power Applications", Conference Record of Tenth IEEE Photovoltaic Specialists Conference, November 13-15, 1973, Palo Alto, California (1974).

(c) Jet Propulsion Laboratory, California Institute of Technology, Private Communications (1976).

(d) U. S. Coast Guard Station (Groton, Connecticut), Private Communication (1976).

(e) Salles, Y., "Solar Arrays for Terrestrial Applications and Sounding Balloons", Presented at the Ninth IEEE Photovoltaic Specialists Conference, May 2-4, 1972, Silver Spring, Maryland.

(f) Salles, Y., "Industrial Development of Silicon Solar Cells", *Acta Electronica*, 18 (4), 339-343 (1975).

(g) RTC La Radiotechnique-Compelec (France), Private Communication (1976).

ADHESIVES FOR BONDING SILICON SOLAR CELLS TO COVER GLASS

Characteristics							
Thermal		Optical			Potentially Corrosive to Electrical Conductors	Reason for Inclusion in Tabular Comparison	
Co-efficient of Expansion, 10^{-5} C	Brittle Point, C	Percent Transmission (280-2000 nm)	Index of Refraction	Stability to UV		Reported in Study 1 References	Considered for Study 3 Screening Evaluations
(0.3-0.9)	<-40	100	--	20-year stability	Noncorrosive	--	--
(-18 to 177 C) 29	<-59	--	--	--	--	(a, b, c)	Yes
(-18 to 177 C) 27	<-59	(350-800 nm) 81 ^(b)	--	--	--	(d)	Yes
--	--	--	--	--	--	(e, f, g)	Yes
(-55 to 150 C) 30	-65	(350-800 nm) 75 ^(b)	1.43	--	--	--	No
--	--	--	--	--	--	--	Yes
--	-60	--	--	--	Noncorrosive	--	Yes
--	--	--	--	--	--	--	Yes

The ideal adhesive for bonding silicon solar cells to glass covers might be specified qualitatively to have the following property characteristics: 100 percent light transmission over the 280 to 1100-nm wavelength range, 20-year stability to UV, a coefficient of thermal expansion between the values for silicon, and the cover glass, brittle point (glass transition) below -40 C, high ultimate elongation, high strength (lap shear, peel, and tensile), low Young's modulus, low harness, and to be noncorrosive. Such a hypothetical "ideal" combination of properties appears to be most closely approached by silicone polymers. However, as-yet-unidentified candidates of other polymer types may be included in screening tests. Table 7 indicates the properties considered most important and lists candidate materials and available data.

The screening tests being initiated subject sandwich samples to sequential thermal cycling and UV exposure for alternate periods of a week. After each week or multiple thereof, the samples will be removed from test and visually/microscopically examined for evidence of delamination or other degradation. Samples with electrical leads will be checked periodically for electrical degradation of the cell. When relevant nondestructive diagnostic techniques are evolved, they can be used for initial sample characterization and to monitor evidence of degradation. The test program is shown schematically in Figure 4.

Selective property measurements on adhesives will be made as needed to supplement available information and to assess affects of primers and/or process variables. Later the promising materials and processes from the screening tests will be used to prepare encapsulation samples for aging tests and to prepare simple modules representative of proposed encapsulation-system design concepts.

Organic Sealing of Glass Encapsulation Systems

At present it is assumed that any glass-encapsulated array must be sealed "hermetically" to achieve a 20-year performance goal. The scope of this part of the study is to investigate achieving adequate "hermeticity" with organic sealants.

For the simple glass-encapsulation concept of two glass panes having cells between them, the sealing problem is very similar geometrically to that for insulated glass units. Thus, the established sealing materials and procedures used for insulated-glass manufacture could serve as a starting point for materials selection and processing for glass encapsulated solar arrays. In fact, the sealing materials may have utility for solar arrays of geometrical design differing greatly from insulated-glass windows.

To achieve maximum "hermeticity" and lifetime of insulated-glass products, a dual seal is employed. An inner seal of butyl or butyl-polyisobutylene is employed as the primary barrier to water vapor. A second backup or edge seal serves as an adhesive-mechanical seal. This edge seal is commonly a polysulfide; however, for higher temperature service silicones are now being used. Insulated-glass units also incorporate desiccants to prolong the lifetime for which low internal-water-vapor levels may be maintained.

FIGURE 4. SCREENING TEST PROGRAM ON ADHESIVES FOR GLASS ENCAPSULATION SYSTEMS

It is not intended to imply that only the seal materials of the insulated-glass industry are viable seal candidates for sealing solar arrays. The best seal material may obviously vary with the array design and other factors. Nevertheless, the sealants from insulated-glass technology provide some candidate materials of demonstrated performance and reasonable cost.

Table 8 identifies two representative materials for inner vapor seals and two examples of edge seals used for insulated glass. Selections from these materials and other candidates are being employed to seal simple-geometry samples such as two flat-glass sheets sealed around the perimeter. Their "hermeticity" can then be assessed by subjecting the samples to high humidity and alternately to thermal cycling.

PLANS FOR NEXT QUARTER

The lap-shear specimens on test which were prepared of weatherable Mylar and of polycarbonate film (51-mm Lexan) will be evaluated at 500 and 1000 hours' exposure to UV and to temperature cycling for lap-shear bond strengths. Additional specimens will be prepared of Korad A (acrylic film) and Tedlar (fluorocarbon film). (The evaluations of lap-shear specimens evaluated after exposure to UV and temperature cycling are complete for "Teflon" FEP.)

A third test will be initiated in which the lap-shear specimens will be subjected to 95 to 100 percent relative humidity at 49 C (120 F), since high humidity can be very detrimental to an adhesive bond with some types of adhesives. Test conditions selected are expected to accelerate failures of such bonds.

Work will continue on current exposure studies involving "Teflon" FEP and weatherable Mylar. Test specimens also will be prepared and put on test for other film materials, e.g., Tedlar and Korad A, and for certain sheet materials, principally acrylic, polycarbonate, and glass-reinforced polyester.

To determine the feasibility of silicon-cell encapsulation by film lamination, several types of film materials in combination with various adhesives will be screened for this application. Bonding to silicon cells, lead wires, and to the film itself will be evaluated. In addition to bonding, conditions for assembly (temperature, pressure, and time in press) will require study. Types of laminate-forming techniques (pressure lamination, vacuum forming) will also need investigation.

An evaluation of existing information on methods of fluorinating film materials and a study of selected commercial coatings will also be conducted. The feasibility of fluorinating film materials to provide specific properties (e.g., improved WVTR properties) will receive first attention. Selected commercial coatings also will be screened for application on film substrates. Selected coatings will be evaluated to determine if improved UV resistance and/or resistance to water permeation result, and, if so, to what extent.

TABLE 8. PROPERTIES OF CANDIDATE SEALANTS FOR GLASS ENCAPSULATION

Polymer Type	Sealant		Moisture Vapor Transmission Rate	Adhesion to Glass		Tensile Strength, N/m ²	Hardness, Shore A	Brittle Temp., C	Relative UV Resistance	Percent Elongation	Service Temperature Range
	Commercial Example	Primary Function		Peel N/m	Tensile N/m ²						
Butyl-Polyisobutylene	Tremco JS-78 ^(a)	Moisture vapor barrier	.16 g/m ² /24 hr (Honeywell tester)	(excellent adhesion to glass)			--	-40	Excellent	--	-46 to 120 C
Butyl Cross-link, hot-melt	Novagard N-415 ^(b)	Moisture vapor barrier	0.2 g/m ² /24 hr for 20-mil film ASTM E96-53T	(25-27)	1.3x10 ⁵		53	--	Excellent	>300	-46 to 116 C
Two-part Polysulfide	Tremco JS-703 ^(a)	"edge" seal	3 g/m ² /24 hr (Honeywell tester)	(cohesive failure)		≈9.5x10 ⁵	50-60 (after aging)	--	Good	>250	--
Silicone (one-part)	Rhodon-Therm 542 ^(c)	"edge" seal	--	(cohesive failure)		2.9x10 ⁶	26		Excellent	600	-62 to 204 C

(a) Product of the Tremco Manufacturing Co., Cleveland, Ohio.

(b) Product of the Novagard Corporation, Trenton, N. J.

(c) Product of Rhodia, Inc., Chemicals Division, Monmouth Junction, N. J.

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

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

INTRODUCTION

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

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

- (1) Develop a suitable methodology for designing the statistical and experimental techniques for such a test
- (2) Illustrate this methodology by developing an experimental test design for an aging test on specific materials and material interfaces which are representative of candidate encapsulation systems.

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

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

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

TECHNICAL DISCUSSION OF RESULTS THIS QUARTER

In previous reports on Study 4, several aspects relative to developing a methodology for aging tests have been treated; among these topics are aging mechanisms in polymers and in glasses, sensitivity analyses required to give detectable property changes with statistical validity, and discrimination among mathematical models of aging data during the acquisition of such data. This quarter, investigations were conducted on the discrimination among test methods used in acquiring aging data on the basis of precision and cost; this report is concerned with these investigations.

In these investigations, considerable attention is being given to "abbreviated" testing. In such testing, samples are exposed under "normal" terrestrial conditions for some period of time, t_i . Using data collected in this time interval, properties of the material or system are forecasted for a future time, t_f . Guideline values for t_i and t_f in Study 4 are 2 and 20 years, respectively. For successful prediction over such a long period, properties measured in the initial 2-year interval have to be measured with high precision. One, therefore, requires a means of discriminating among various test methods on the basis of precision as well as cost and other factors.

Prior to discussing precision, it will be useful to differentiate between "precision" and "accuracy", since the two concepts are sometimes confused. In short, precision is a measure of closeness of repeated measurements of a property whereas accuracy is a measure of how close a test measurement is to some known reference value. These concepts are illustrated in Figure 5. Here, the two bell-shaped curves represent the spread of test values for Testing Methods 1 and 2 with means and standard deviations μ_1 , μ_2 , σ_1 , and σ_2 , respectively.

The true reference value is indicated on the abscissa. In this example, Test Method 2 has a smaller standard deviation than Test Method 1 and is therefore more precise. On the other hand, the population mean μ_2 for Method 2 is farther from true value than the mean of Test 1, μ_1 . Therefore, one says that Method 1 is more accurate than Method 2. Thus, accuracy and precision are two independent concepts. In this Study, precision, not accuracy, is of primary concern since the interest is in property changes. To illustrate this, suppose that a test is inaccurate by a factor δ , i. e., instead of getting the true value the measuring instrument gives $\eta + \delta$. Then for two η measurements, at times t_1 and t_2 , the rate of property change would be $[(\eta_2 + \delta) - (\eta_1 + \delta)] / (t_2 - t_1) = (\eta_2 - \eta_1) / (t_2 - t_1)$. The inaccuracies cancel out in measuring the rate of change.

FIGURE 5. ILLUSTRATION OF ACCURACY AND PRECISION

Measures of Precision

Precision is a measure of the spread (or dispersion) of data values around their mean value. An obvious measure of dispersion is the mean deviation M , where

$$M = \frac{\sum_{i=1}^N |x_i - \bar{x}|}{N} \quad (1)$$

N is the number of data points, $\bar{x}$ is the data mean, and x_i is the value of an individual measurement. Although this measure is sometimes used, it is difficult to manipulate mathematically and is, therefore, seldom used in statistical computations. A better measure of dispersion is the standard deviation, S , where

$$S = \left[\frac{\sum_{i=1}^N (X_i - \bar{x})^2}{N - 1} \right]^{1/2} \quad (2)$$

This statistic is the most common measure of dispersion. Inspection of Equation (2) reveals that the standard deviation carries the same units as the data. This is usually a desirable property for any measure of dispersion. For comparing different testing methods, however, the standard deviation is unsatisfactory. For example, suppose one is using two tests with modulus expressed in psi and elongation at break expressed in percent to determine the degree of vulcanization of an elastomeric compound. The modulus shows a standard deviation of roughly 70 psi, and elongation, approximately 20 percent. Clearly, knowledge of the standard deviations is not enough information to favor one test over the other because one cannot compare usefully psi and percentage units.

One logical alternative would be the use of the coefficient of variation, CV, where

$$CV = \frac{S}{\bar{x}} . \quad (3)$$

Clearly, the coefficient of variation is unitless, and as such would be expected to allow comparison of different test precisions. This is true in some cases but is not true generally.

Review of Published Information on Test Precision

Published information was reviewed to find information on precision, accuracy, repeatability, reproducibility, etc., as applied to polymer testing. In this effort the Engineering Index, Chemical Abstracts and NTIS files were interrogated. Out of a total of 249 hits only 21 documents appeared relevant to the problem of test comparison. Most of the 21 have been received and were found to be of little value with regard to test discrimination.

Perhaps the largest repository of information on test accuracy and precision is the American Society for Testing and Materials published test methods. Accordingly, the 1975 Annual Book of ASTM Standards, Part 35 for General Test Methods for Plastics, was scrutinized for precision information. The methods for which the coefficient of variation was given or was calculatable from the given data are shown in Table 9 along with their respective coefficients of variation. This table reveals a wide range of precision, and underscores the need for a systematic methodology for test discrimination. As noted previously, comparison of coefficients of variation is usually invalid for comparing different tests, and such statistics are of limited value. The problem of test discrimination, however, has not gone unattended. Mandel^(1,2) recognized the problem and defined a relatively sensitive statistic for test discrimination.

TABLE 9. COEFFICIENT OF VARIATION FOR VARIOUS
ASTM TESTS ON PLASTIC MATERIALS

Test	Coefficient of Variation ^(a) , percent
Density	<1
Linear Dimensional Change	<1
Dilute Solution Viscosity	1
IR Absorbance of CH ₃ on Polyethylene Type II	2
Coefficient of Linear Thermal Expansion	2
Water Vapor Transmission	2.5
Barcol Hardness	1-3
IR Absorbance of CH ₃ on Polyethylene Type III	7
High-Speed Tensile at Break	4-8
Tensile Impact Energy	6-12
IR Absorbance of CH ₃ on Polyethylene Type I	15
High-Speed Elongation at Break	15-18

(a) Coefficient of variation is standard deviation expressed as percent of mean.

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

$$RS(M/N) = \frac{|dM/dN|}{\sigma_M/\sigma_N} \quad (4)$$

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 6 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 where dM/dN , σ_M , and σ_N are constant, the relative sensitivity will, of course, also be a constant.

FIGURE 6. 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,

$$P_1(t) = P_{10} + b_1 t + b_{11} t^2 \quad (5)$$

$$P_2(t) = P_{20} + b_2 t, \quad (6)$$

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 (6) for t and substituting in Equation (5), one gets

$$P_1(t) = P_{10} + b_1 \left[\frac{P_2(t) - P_{20}}{b_2} \right] + b_{11} \left[\frac{P_2 - P_{20}}{b_2} \right]^2 \quad (7)$$

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

$$RS(P_1/P_2) = \frac{dP_1}{dP_2} = \gamma_0 + \gamma_1 P_2(t) \quad (8)$$

where
$$\gamma_0 = \frac{b_1}{b_2} - 2P_{20} \left(\frac{b_{11}}{b_2^2} \right) \quad (9)$$

and
$$\gamma_1 = 2 \left(\frac{b_{11}}{b_2^2} \right) \quad (10)$$

As a specific example, suppose one has

$$P_1(t) = 100 - 5t - 0.5t^2 \quad 0 \leq t \leq 10 \quad (11)$$

and

$$P_2(t) = 100 - 10t \quad 0 \leq t \leq 10 \quad (12)$$

These relationships are shown in Figure 7.

Then $\gamma_0 = 1.5$ and $\gamma_1 = -0.01$, and one has

$$RS(P_1/P_2) = 1.5 - 0.01 P_2 \quad (13)$$

This relationship is shown in Figure 8, and indicates that at $P_2 = 50$ (or $t = 5$) the two tests are equally sensitive. At $P_2 < 50$ ($t < 5$), P_1 is more sensitive, and at $P_2 > 50$ ($t > 5$), P_2 is more sensitive. The results are similar if $\sigma_1 \neq \sigma_2$, in which case γ_0 and γ_1 are both multiplied by the constant σ_2/σ_1 .

FIGURE 7. PLOT OF PROPERTIES P_1 AND P_2 AS FUNCTIONS OF TIME

FIGURE 8. RELATIVE SENSITIVITY AS A FUNCTION OF TEST P_2 FOR HYPOTHETICAL EXAMPLES

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. This result is important enough to repeat its deviation here.

For tests M and N, the relative sensitivity is given by (4). Now suppose that one transforms the scale of M as follows:

$$M^* = f(M) \quad (14)$$

where M^* is the transformed version of M. Then the relative sensitivity of M with respect to N is

$$RS(M^*/N) = \frac{|dM^*/dN|}{\sigma_{M^*}/\sigma_N} \quad (15)$$

Now since M is a function of N, then so is M^* . Then by differentiating (14) with respect to N one obtains

$$\frac{dM^*}{dN} = \frac{df(M)}{dN} = \frac{df(M)}{dM} = \frac{dM}{dN} \quad (16)$$

Now by the law of propagation of errors, one can write

$$\sigma_{M^*} = \left| \frac{df(M)}{dM} \right| \sigma_M \quad (17)$$

Then by substituting Equations (16) and (17) into Equation (15), one gets

$$RS(M^*/N) = \frac{\frac{df(M)}{dM} |dM/dN|}{\frac{df(M)}{dM} (\sigma_M/\sigma_N)} = \frac{|dM/dN|}{\sigma_M/\sigma_N} = RS(M/N)$$

Thus, changing the scale of M does not change the relative sensitivity.

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 if 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, say, K , 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 only of 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 limit 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.

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 incorporated 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 measurement 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

$$C(M/N) = \frac{C_M}{k^2 C_N} \quad \text{or} \quad \frac{C_M}{[RS(M/N)]^2 C_N} \quad (18)$$

Some examples are given in Table 10. 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 8 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 10. 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

Example Sensitivity Analysis

As part of a study of the adhesion of tire cord to tire-carcass compound, the wire adhesion test (ASTM D2229) was evaluated with two different types of testing. One was a jig with a hole through which the wires were pulled out of the vulcanized rubber compound. In the other, the standard jig had only a slot, and it was feared that the slot was interfering with rubber chunks stuck on the wire as the wire was pulled through. Accordingly, a sensitivity study was run on the two methods. The raw data and data means and standard deviations are given in Table 11 for four compounds selected so that the full practical range of adhesion levels would be covered.

The first step in the analysis was the regression of the data means for Test M onto those of Test N. The resulting equation was $M = 8.52 + 1.02 N$. The derivative, dM/dN , was then 1.02. The pooled standard deviations were $S_M = 3.798$ and $S_N = 3.379$. The sensitivity of Test M with respect to Test N, $RS(M/N)$ was therefore $1.02/(3.798/3.379) = 0.907$. The quantity $RS(N/M)$ was also calculated and resulted in a sensitivity of 1.04. Since the sensitivities could not be judged statistically different from 1.0, it was concluded that the type of test jig was not an important variable.

TABLE 11. RAW DATA, MEANS AND STANDARD DEVIATIONS FOR CALCULATION OF SENSITIVITY FOR THE WIRE-ADHESION EXAMPLE

Wire Adhesion, lb/in.				
Compound	A	B	C	D
<u>Hole Jig -- Test M</u>				
Raw Data	66.93	58.73	45.47	89.33
	68.33	55.33	37.73	92.0
	72.8	55.73	50.73	91.6
Mean	69.35	56.60	44.64	90.98
Std. Dev.	3.066	1.858	6.539	1.440
<u>Slot Jig -- Test N</u>				
Raw Data	49.67	46.67	39.47	79.27
	52.6	53.53	38.53	81.27
	56.6	51.93	33.40	85.47
Mean	52.96	50.71	37.13	82.00
Std. Dev.	3.479	4.996	3.267	3.164

Statistical Experimental Design for Determining
Sensitivity Ratio for Two Test Methods
Both of Which Measure Property Degradation

The goal of an experiment to determine sensitivity ratio for two tests is the determination of the regression equation of test M results on those of test N, as well as the standard deviations of each test with as much precision as possible and at a reasonable cost. Without prior knowledge of the form of the mathematical relationship between the two tests, at least four levels of the property being measured should be evaluated, preferably five or six. These points should be spread over as wide a property range as possible so that comparisons will be valid at any test level(s) likely to be found in the future.

In Study 4 we want to discriminate among tests which can follow rate of degradation. A reasonable design would be the following in which degradation of a plastic sheet is used as an example, along with measurements from two nondestructive tests. Suppose one desires six levels at which to evaluate the two tests. At each level a minimum of three replicates are required; so one requires a minimum of $3 \times 6 = 18$ samples of the plastic sheet. Preferably, these should be taken from random areas of the material to be fully representative. Three

samples are randomly selected from the 18, and the remainder are put in equivalent positions in a Weatherometer. At the end of each of five weathering periods, three of the samples are randomly withdrawn from the chamber. The total weathering period should be long enough to allow nearly complete degradation of the plastic. If this time is unknown, more samples will be required so that sample-withdrawal times can be determined in a sequential manner.

After all 15 (or more) samples have been withdrawn from the Weatherometer, they should be combined with the original three samples and tested in random order by both methods. For each sample, a coin should be flipped to determine which of the two tests to run first. This allows for possible changes in the sample due to testing.

The first step in analyzing the data is to calculate the means and standard deviations for each group of replicates for each test. Bartlett's test⁽³⁾ for homogeneity of variance is then applied. If heterogeneity is not found to be significant, the standard deviations for each test are pooled for a single estimate for each test, i.e., S_M and S_N . A regression analysis is then run for the means of test M onto those of test N. First, a linear relationship should be tried as follows:

$$M = b_0 + b_1 N \quad , \quad (19)$$

where b_0 and b_1 are fitted intercept and slope, respectively. If fit is not adequate as judged by calculation of an F ratio for lack of fit⁽⁴⁾, a quadratic equation should be fitted as follows:

$$M = h_0 + h_1 N + h_{11} N^2 \quad (20)$$

and evaluated for lack of fit. The process is continued until adequate fit is found. Once an adequate equation is obtained, the derivative of M with respect to N is taken, and the relative sensitivity calculated from Equation (4). If Equation (19) gave an adequate fit, $RS(M/N)$ will be a constant, otherwise it will be a function of N. The design and analysis are easily extended to cover any number of tests if the RS values are all constant. If they are not, linear and nonlinear programming methods are indicated.

Concluding Remarks

The relative sensitivity appears to be an excellent criterion for discriminating among various test methods. Mandel's results indicate that such discrimination can be made not only on the basis of precision, but also with testing costs taken into consideration. This methodology appears to be well suited to the goals of Study 4 and will be incorporated into the overall methodology for designing abbreviated and accelerated tests.

PLANS FOR NEXT QUARTER

Two principal tasks remain on Study 4: (1) finish the development of the methodology by treating sample selection, testing sequence, and selection of stresses related to specific environments, and (2) relating the methodology to a specific example of the design of an aging test. Following these tasks, the draft of the final report on Study 4 will be prepared.

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- (3) Dixon, N. J., and Massey, F. J., "Introduction to Statistical Analysis", Third Edition, McGraw Hill, p 308 (1967).
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NEW TECHNOLOGY

No items of new technology have been reported thus far in Studies 3 and 4.