Aging of FSA Polymeric Encapsulation Materials

By

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The goal of this program is to identify, develop and evaluate materials and processes for the low cost encapsulation of silicon photovoltaic cells consistant with the FSA objective of achieving a solar array at a manufactured cost of $0.70 per peak watt ($70/m^2) (1980 dollars).

Phase I at Springborn Laboratories has been concerned with the identification and/or development of materials and classes of materials to provide specific functions in the construction of PV modules. This includes pottants, outer cover films, substrates, ultraviolet stabilizers, back covers and adhesive systems. Phase II activities have now been started in which these materials are being technically optimized and evaluated by accelerated aging studies and lifetime estimations.

To date, aging studies have emphasized pottant materials due to their critical importance in module function. Four pottants were developed in this program; EVA and EMA for lamination, butyl acrylate and aliphatic urethane for the casting process. Work is continuing on the "technology readiness" phase of these materials, which includes extended studies of antioxidants, ultraviolet absorbers, metal deactivators, crosslinking agents and test methodologies.

Four major properties are considered to be relevant for determining module service life: (A) mechanical; creep resistance, modulus, tensile strength, (B) optical; integrated transmission 0.4 to 1.1 microns, (C) chemical; inertness with respect to metals and other components, retention of stabilizers, etc. and (D) electrical; maintaining effective isolation of conductive components. These properties were all measured after exposing polymer (pottant) specimens to three types of accelerated stress; thermal, ultraviolet and metal catalysis. These conditions give rise to a large number of complex interrelated free radical reactions that result in the deterioration of polymeric materials. (5) The progress of this degradation was assessed with a routine test sequence and the resulting data was then used for "empirical modeling" of material behavior and lifetime prediction. Such data may be used in mathematical schemes such as first order kinetics, Arrhenius, induction period, Weibul or some other treatment.(7)

Note: Numbers in parenthesis refer to VU graph numbers.

In all experiments the data was plotted as log % property retained versus time to yield generally useful graphs of material behavior. The first property to show change is color (yellow) and was determined quantitatively by spectroscopy as %T at 400 nm. The total optical transmission, however, (400 nm to 800 nm), retains a surprisingly high value, even with severe yellowing. Specimens retaining only 10% of the original transmission at 400 nm were still found to have 74% total integrated transmission. The mechanical properties during aging were, for the most part, unaffected. When physical deterioration was observed, the decrease in elongation at break was the first characteristic to change, followed by the decay of tensile strength. The dielectric strength (insulation breakdown) was found to be the least variable of the properties measured and retained 100% of control values in all but the most extreme cases of degradation.

Thermal aging [10-16] was conducted in the dark in atmospheres of air and nitrogen at temperatures of 60°, 85°, 105° and 130°C. The results to date show that the candidate pottants have very good thermal stability, with no life limiting degradation occurring at 105°C. Specimens of EVA have survived 7,200 hours at 90°C with virtually no change, and retain 91% integrated optical transmission.[13]

The life limits that are discernable at the 130°C condition and are: polyurethane - 250 hours, and EVA - approximately 2,000 hours. No real difference was noticed between the air and nitrogen conditions.

The ultraviolet stress condition was provided by exposure to a medium pressure mercury lamp (General Electric RS/4) at a temperature of 50°C. In terms of time integrated UV energy , 1300 hours of RS/4 is equivalent to one year of outdoor (AM-1) solar ultraviolet.[19] Reference materials, unstabilized poly(propylene) and poly(ethylene) were totally degraded by this condition in 200 and 600 hours respectively.[20] To date the following materials have survived without change: EMA - 10,000 hours, Urethane - 8,000 hours, Tedlar 100BG30UT - 25,000 hours, and EVA, an astonishing 35,000 hours.[21, 22] For EVA, this is equivalent, in UV energy, to 27 years of outdoor exposure and without the benefit of a glass (or other) covering. Unstabilized EVA base polymer (Elvax 150) degraded within 500 hours. Life limits for pottants under RS/4 exposure were found to be: Butyl acrylate - 10,000 hours , and PVB - 500 hours.[25-26]

Metal catalyzed oxidation in the presence of copper was discovered to be the most severe condition examined so far.[31-34] Pottant compounds were molded around copper screens and the color (%T-400 nm) measured after periods of thermal soak at 105°C. All pottants were found to degrade rapidly,and all reached end of life (complete deterioration) in about 400 hours. Formulations compounded with metal deactivators (ion chelators) and specimens in which the copper had been treated with silane primer both demonstrate improved performance and are still under test (out to 1,000 hours).[36-39] No metal reactions were found with aluminum or 60/40 solder.

In summary, color (yellowing) was found to be the first quantifiable property change. This and the other properties showed predominantly "induction period" type behavior during aging in which the measured values began to change rapidly at a certain point in time. Thermal stability and ultraviolet resistance of the candidate encapsulation materials was generally found to be very good, however exposure to metallic copper should be stringently avoided due to intense catalytic oxidation. Future experiments will continue with these evaluations and also include higher stress conditions to evaluate failures and material performance in shorter periods of time.

Figure 1

AGING OF FSA POLYMERIC
ENCAPSULATION MATERIALS

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Figure 2. Scope and Approaches

IDENTIFIY/DEVELOP LOW COST
MODULE CONSTRUCTION MATERIALS :

PHASE I

- POTTANTS
- OUTER COVER FILM
- SUBSTRATES
- ANTI-SOILING TREATMENTS
- ULTRAVIOLET STABILIZERS
- FABRICATION CONCEPTS
- FIELD EXPOSURES
- ADHESIVES/PRIMERS

PHASE II

(TECHNOLOGY READINESS)

- OPTIMIZED MATERIALS FORMULATION
- MATERIALS LIFETIME AND AGING STUDIES

Figure 3. Candidate Polymer Encapsulation Materials

POTTANTS: MECHANICAL STRESS RELIEF, ELECTRICAL ISOLATION, CELL POSITIONING, ENVIRONMENTAL ISOLATION, CORROSION BARRIER

- ETHYLENE/VINYL ACETATE (EVA)
- ETHYLENE/METHYL ACRYLATE (EMA)

→ LAMINATION TYPES

- ALIPHATIC POLYURETHANE (PU)
- POLY(BUTYL ACRYLATE) (BA)

→ CASTING TYPES

OUTER COVERS: PROVIDES HARD SOIL RESISTANT SURFACE, UV SCREENING, MECHANICAL BARRIER

TEDLAR 100BG30UT , TEDLAR 4462

ACRYLAR 22417 , POLYESTER EH 723 (EXPTL.)

BACK COVERS: MECHANICAL BARRIER, ELECTRICAL ISOLATION EMMISIVITY FOR COOLING MODULE

KORAD 63000 , TEDLAR 150BS30WH

SCOTCHPAR 20CP - WHITE (POLYESTER)

Figure 4. Encapsulant Properties

(MAJOR EMPHASIS ON POTTANTS)

RELEVANT MATERIAL PROPERTIES FOR MODULE SERVICE LIFE:

MECHANICAL	• CREEP RESISTANCE (GEL) • YOUNG'S MODULUS
OPTICAL	• INTEGRATED TRANSMISSION OVER 0.4 TO 1.1 MICRONS
CHEMICAL	• INERTNESS OF ENCAPSULANT TO CELL HARDWARE • DEGRADATION (WEATHERING) • INVENTORY OF ADDITIVES (STABILIZERS) IN POLYMER WITH TIME (HPLC)
DIELECTRIC	• ELECTRICAL ISOLATION OF CONDUCTIVE COMPONENTS (HI POT AND LEAK CURRENT)

Figure 5. Polymer Degradation

RESULTS IN DECREASE OF DESIRED PROPERTIES SUCH AS TENSILE STRENGTH, ELONGATION, TRANSPARENCY, DIELECTRIC STRENGTH, ETC.

OXIDATION MECHANISM[A.]

GENERAL DEGRADATION MECHANISM: INITIATED OR ACCELERATED BY HEAT, LIGHT, OXYGEN AND CERTAIN METALS

INITIATION: (SLOW)

$$RH \longrightarrow R\cdot + H\cdot$$
$$R\text{-}R \longrightarrow 2P\cdot$$

PROPAGATION: (AUTOCATALYTIC):

$$R\cdot + O_2 \longrightarrow ROO\cdot$$
$$ROO\cdot + PH \longrightarrow ROOH + R\cdot$$
$$ROOH \longrightarrow RO\cdot + HO\cdot$$
$$RO\cdot + RH \longrightarrow ROH + R\cdot$$
$$HO\cdot + RH \longrightarrow H_2O + R\cdot$$

TERMINATION:

$$R\cdot + R\cdot \longrightarrow R\text{-}R$$
$$R\cdot + ROO\cdot \longrightarrow ROOR$$
$$R\cdot + HO\cdot \longrightarrow ROH$$

A. DEGRADATION RATE VARIES WITH TEMPERATURE, UV EXPOSURE, OXYGEN DIFFUSION, CRYSTALINITY, ADDITIVES.

Figure 6. Encapsulant Degradation Studies

- EXPOSE CANDIDATE ENCAPSULANTS TO OVER - STRESS CONDITIONS: ACCUMULATE DEGRADATION DATA
- CHEMICAL MECHANISM CONSISTANT WITH DEGRADATION IN MODULE APPLICATION (?)
- CORRELATE DATA TO PREDICT LIFETIMES, ASSESS FORMULATION EFFECTIVENESS

CONDITIONS[A.]

- THERMAL STRESS (HEAT AGING)
- ULTRAVIOLET STRESS (UV EXPOSURE)
- CATALYTIC STRESS (METAL CORROSION)

A. AMBIENT HUMIDITY

Figure 7. Data Correlation

OVERALL DEGRADATION REACTION IS COMPOSITE OF MANY COMPETING CHEMICAL REACTIONS IN COMPLEX RELATIONSHIP

DATA TREATMENT

1. FIRST ORDER BEHAVIOR
   - SUMMATION OF REACTIONS APPROXIMATES FIRST ORDER BEHAVIOR
   - LOG (RETAINED PROPERTY) PLOTTED AGAINST TIME IS LINEAR. (PREDICTIVE)
   - ARRHENIUS TREATMENT: FOR CONSTANT RATE (FIRST ORDER), LOG TIME VS $1/^{o}T$ IS LINEAR. PREDICT TIME TO SPECIFIED PROPERTY VS TEMPERATURE.
2. INDUCTION PERIOD BEHAVIOR
   - REACTION KINETICS SUDDENLY CHANGE
   - PLOT OF LOG PROPERTY VS TIME SHOWS SHARP ONSET OF DEGRADATION AT END OF INDUCTION PERIOD.
   - OBSERVED WITH AUTOCATALYTIC REACTIONS, KINETIC CHAIN BRANCHING. TYPICAL OF FREE RADICAL PROPAGATION STEPS.
3. OTHERS ? (WEIBULL)

Figure 8. Data Correlation (Cont'd)

EMPIRICAL

- STRESS CONDITIONS SIMILAR TO MODULE APPLICATION
- INFORMATION USEFUL WITHOUT CORRELATION

Figure 9. Encapsulant Life-Prediction Thermal-Aging Program

DETERMINATION OF THE PEAK SERVICE TEMPERATURE:

- DETERMINE WHICH PROPERTY IS LIFE-LIMITING
- DETERMINE RATE OF CHANGE OF PROPERTY WITH INCREASING TEMPERATURE
- ASSIGN END-OF-LIFE VALUE TO PROPERTY
- EXPRESS DESIRED MODULE LIFE TIME AND RELATED PEAK SERVICE TEMPERATURE

CONDITIONS:

- AGE TEST SPECIMENS AT 60°, 80°, 105°, 130°
- INCLUDE BOTH "OPEN" AND "CLOSED" CONDITIONS TO SIMULATE HERMETIC AND NON-HERMETIC MODULE DESIGNS
- AIR AND NITROGEN

CORRELATE:

- PREPARE PLOTS OF LOG PROPERTY VS TIME; MEASURE RATE OF CHANGE OR INDUCTION PERIOD

Figure 10. Thermal Degradation

- FREE RADICAL CHAIN REACTIONS WITH OXYGEN: INITIATION, PROPAGATION, TERMINATION.
- DEGRADATION IS COMPOSITE OF MANY REACTIONS
- FREQUENTLY GIVES " INDUCTION " PERIOD TYPE CURVE

ANTIOXIDANTS (PROTECTIVE CHEMISTRY)

PRIMARY: FUNCTION AS FREE RADICAL TRAPS

$$ROO\cdot + AH \text{ —— } ROOH + A\cdot$$

$$R\cdot + AH \text{ —— } RH + A\cdot$$

$$A\cdot \text{ ———— STABLE PRODUCTS}$$

SYNERGISTS: CATALYZE DECOMPOSITION OF HYDROPEROXIDES VIA IONIC MECHANISMS: NO FREE RADICALS.

ETHYLENE VINYL ACETATE (EVA)

"THERMOLYSIS" REACTION

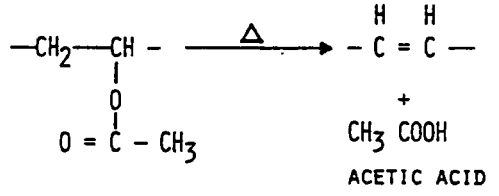
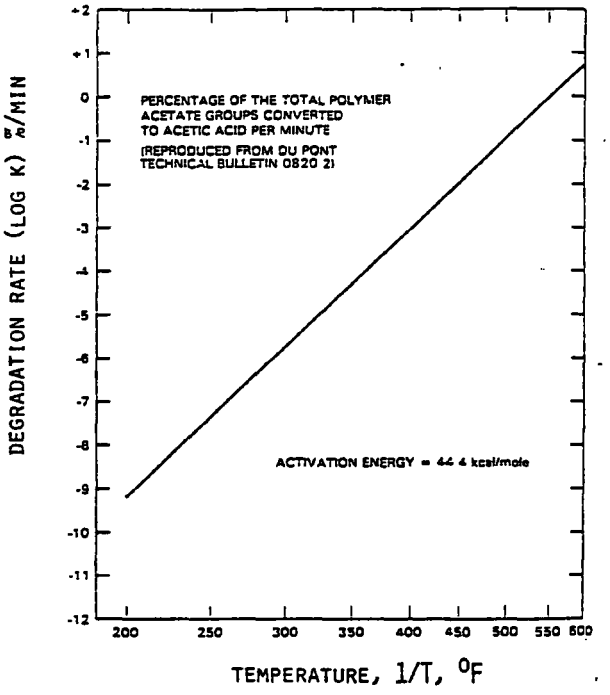


Figure 11. Thermolysis of EVA (Acetic Acid Evolution)



- AT 85°C (ROOFTOP ARRAY), RATE IS 6 X 10^{-10}% PER MINUTE
- 20 YEARS AT 85°C EQUALS 0.002 WT % DEGRADATION
- ACETIC ACID GENERATION NOT EXPECTED TO BE A PROBLEM (NOR OBSERVED EXPERIMENTALLY)

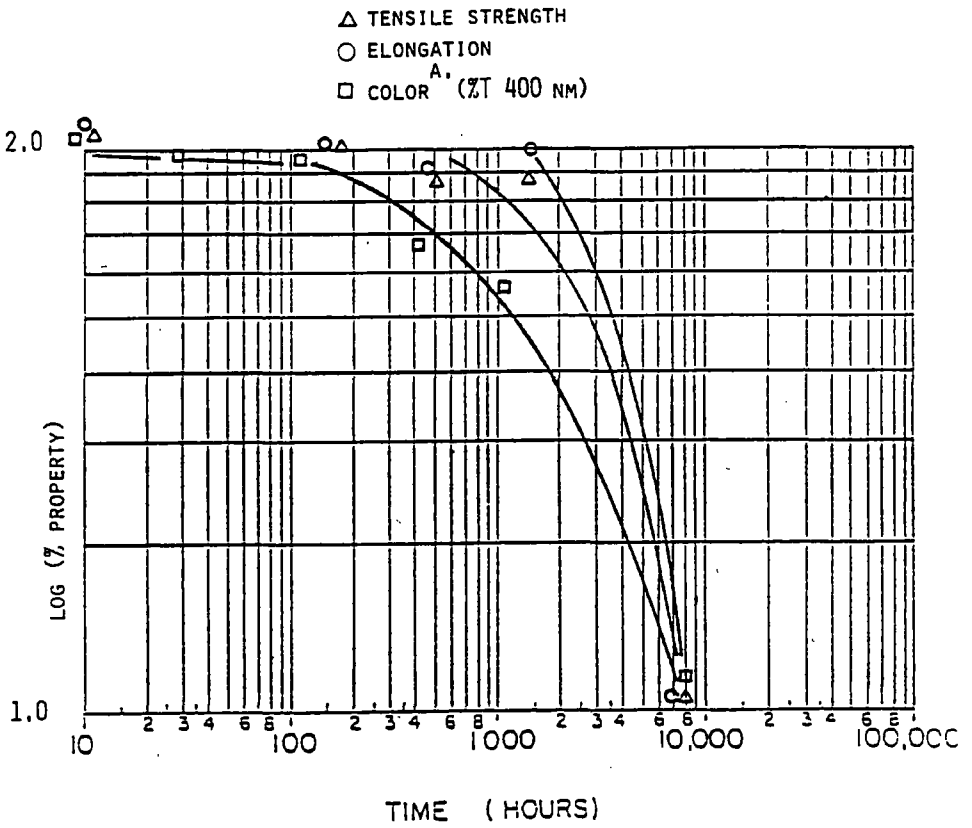
Figure 12. Differential Thermal Analysis (DTA)

DETERMINE EARLIEST TEMPERATURE OF OXIDATION EXOTHERM
OR THERMAL DEGRADATION

MATERIAL	IN AIR (°C)	IN NITROGEN (°C)
EVA (ELVAX 150) BASE RESIN	216	350
EVA (A9918) COMPOUNDED-CURED	227	310
EMA 2205 BASE RESIN	350	420
EMA (A11877) COMPOUNDED - CURED	212	400
SAFLEX - PVB	180	360

- EMA BASE RESIN MOST THERMALLY STABLE
- EMA AND EVA COMPOUNDED POTTANTS ABOUT EQUIVALENT IN AIR
- EVA AND EMA BOTH MORE STABLE THAN PVB

Figure 13. Thermal Aging: EVA A-9918, 130°C

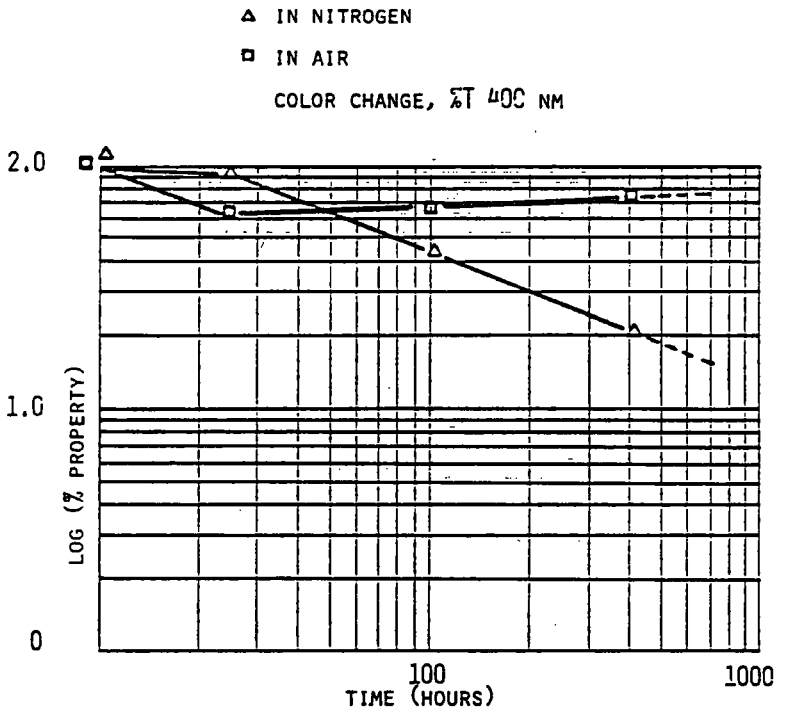


- PROPERTIES ALMOST GONE AFTER 7200 HOURS - 130°C (STILL HAS 74% T OPTICAL)
- NO CHANGE IN OPTICAL, MECHANICAL OR ELECTRICAL PROPERTIES AFTER:

  7200 HRS - 90°C
  1000 HRS - 105°C

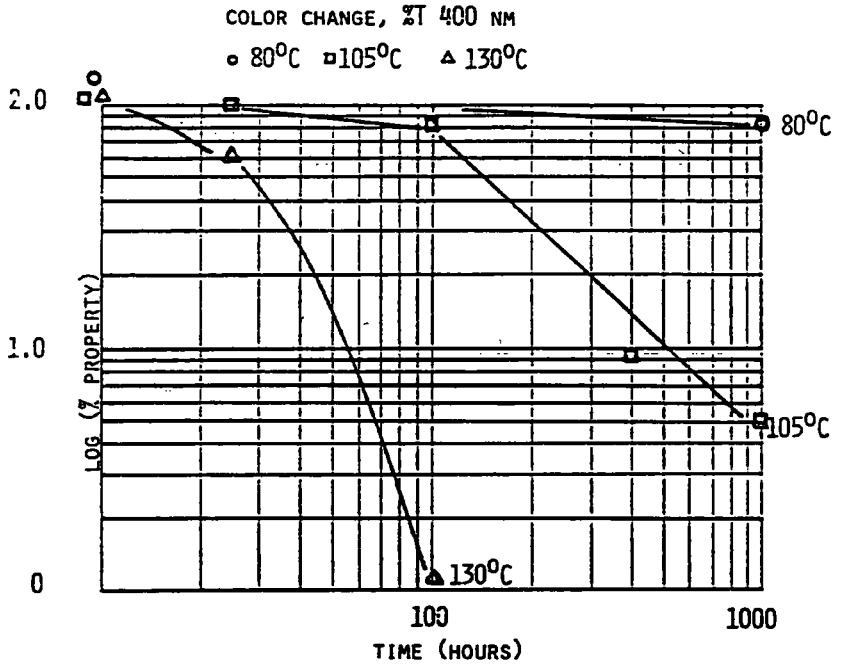
A. AIR AND NITROGEN VALUES APPROXIMATELY THE SAME.

Figure 14. Thermal Aging: EMA 13439, 130°C



- AT 80°C AND 105°C, NO CHANGES IN OPTICAL MECHANICAL OR ELECTRICAL PROPERTIES AFTER 400 HRS.
- AT 130°C, ONLY COLOR CHANGE (86% T OPTICAL)
- LESS COLOR FORMATION IN AIR THAN NITROGEN

Figure 15. Thermal Aging: Polyurethane Z-2591



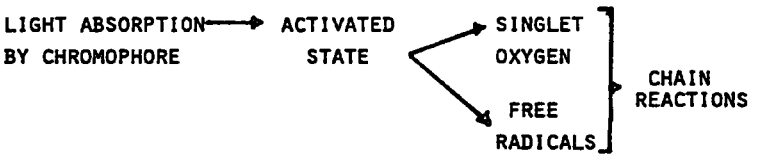
- NO CHANGE IN OPTICAL, MECHANICAL OR ELECTRICAL PROPERTIES AFTER 1000 HRS AT 80°C AND 105°C
- AT 130°C ALL PROPERTIES LOST AFTER 250 HOURS
- COLOR CHANGE APPX. SAME IN AIR AND NITROGEN
- AFTER 1,000 HOURS AT 105°C STILL HAS 82%T TOTAL OPTICAL

Figure 16. Thermal Aging: PVB (Saflex PT-10)

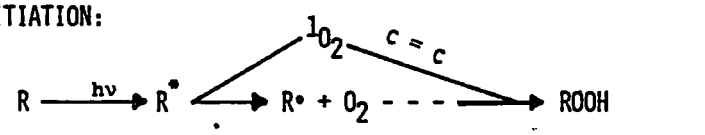
- JUST STARTED, NO CHANGE IN PROPERTIES AFTER 400 HOURS 80°C
- STRONG YELLOW AFTER 350 HOURS AT 105°C
- 130°C CONDITION NOT RUN - RESIN FLOWS

Figure 17. Polymer Photodegradation

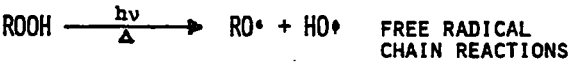
GENERAL MECHANISMS:



INITIATION:



PROPAGATION:



TERMINATION:

(MAY GENERATE PHOTOACTIVE SITES)

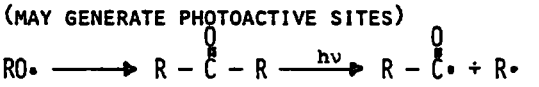


Figure 18. Polymer Photodegradation (Cont'd)

PROTECTIVE CHEMISTRY

1. ABSORBER (SCREENER) ABSORBS UV LIGHT ⟶ HEAT
2. QUENCHER (DEACTIVATES EXCITED STATE)
   DEACTIVATION ⟶ HEAT
3. CHAIN TERMINATOR (RADICAL TRAP)
   RADICALS ⟶ COVALENT BOND
4. HYDROPEROXIDE DECOMPOSERS DESTROY CHROMOPHORE

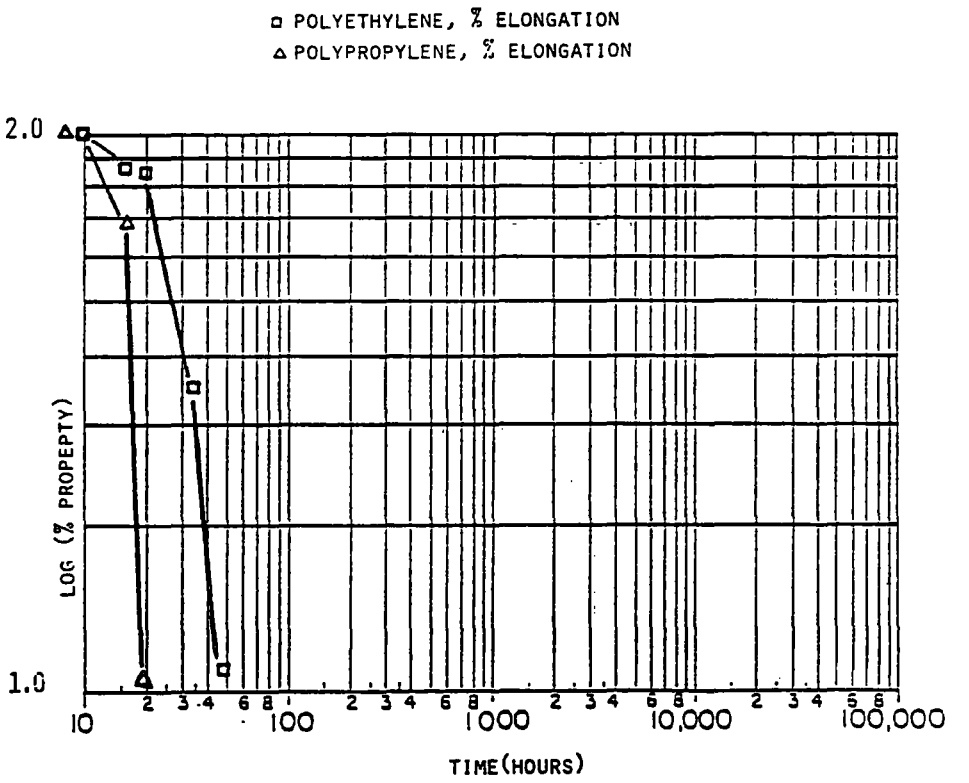
Figure 19. Photodegradation Experiments

- CARBON - CARBON BOND = 80 KCAL/MOLE
  SUNLIGHT (UV) 290 NM - 400 NM = 100 - 70 KCAL/MOLE
- FREE RADICAL REACTIONS INITIATED IN THIS WAVELENGTH RANGE, ESPECIALLY WITH PHOTOSENSITIVE GROUPS
  (HYDROPEROXIDES, KETONES, ARYL RINGS)

<u>RS/4 SUNLAMP EXPOSURE</u>

- MEDIUM PRESSURE MERCURY ARC LAMP IN GLASS ENVELOPE
- FILTERED TO REMOVE WAVELENGTHS BELOW 295 NM
- CORRELATION TO SUNLIGHT:
  LAMP OUTPUT = 1.4 SUNS AT AM 1.5
  ONE DAY OF AM 1.5 SOLAR UV = 5 HOURS/DAY
  3.6 HOURS RS/4 = ONE DAY OF AM 1.5 UV
- 1300 HOURS OF RS/4 EQUIVALENT TO ONE YEAR OUTDOOR SOLAR ULTRAVIOLET
- OPERATING TEMPERATURE, 50°C
  CLOSE TO ARRAY OPERATION TEMPERATURE

Figure 20. RS/4 Exposure: Reference Materials (Unstabilized)



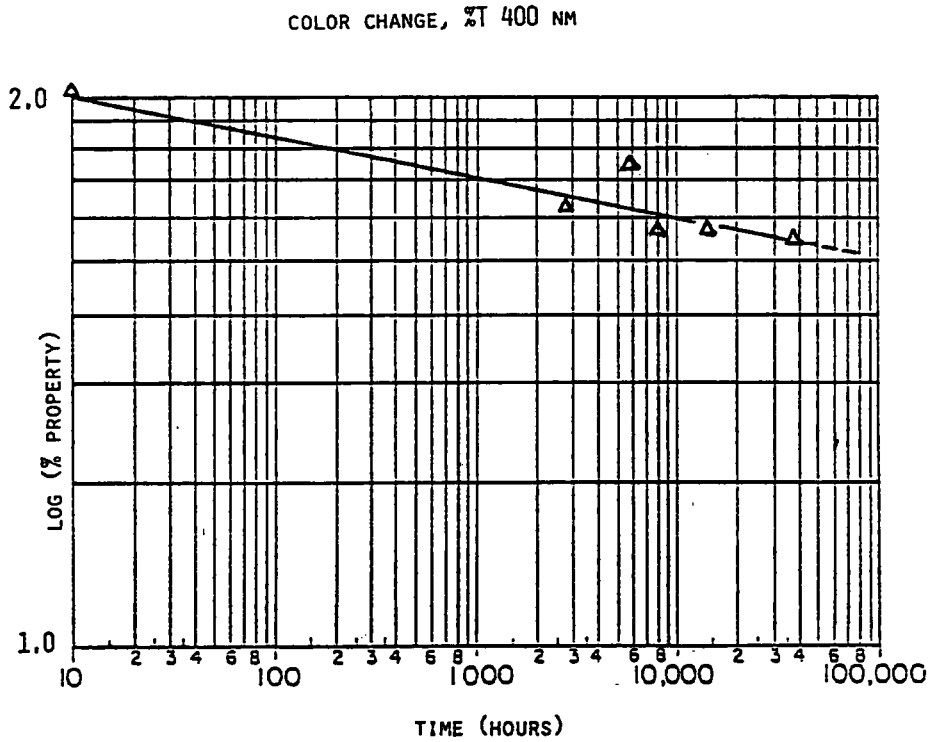
● MECHANICAL PROPERTIES TOTALLY LOST AT

200 HRS. - POLYPROPYLENE

600 HRS. - POLYETHYLENE

(UNSTABILIZED)

Figure 21. RS/4 Exposure: EVA A-9918



- NO CHANGE IN OPTICAL, MECHANICAL OR ELECTRICAL PROPERTIES AFTER 35,000 HOURS
  (SMALL CRACKS NOW APPEARING ON SURFACE)
- EQUIVALENT TO 27 YEARS OF SOLAR ULTRAVIOLET

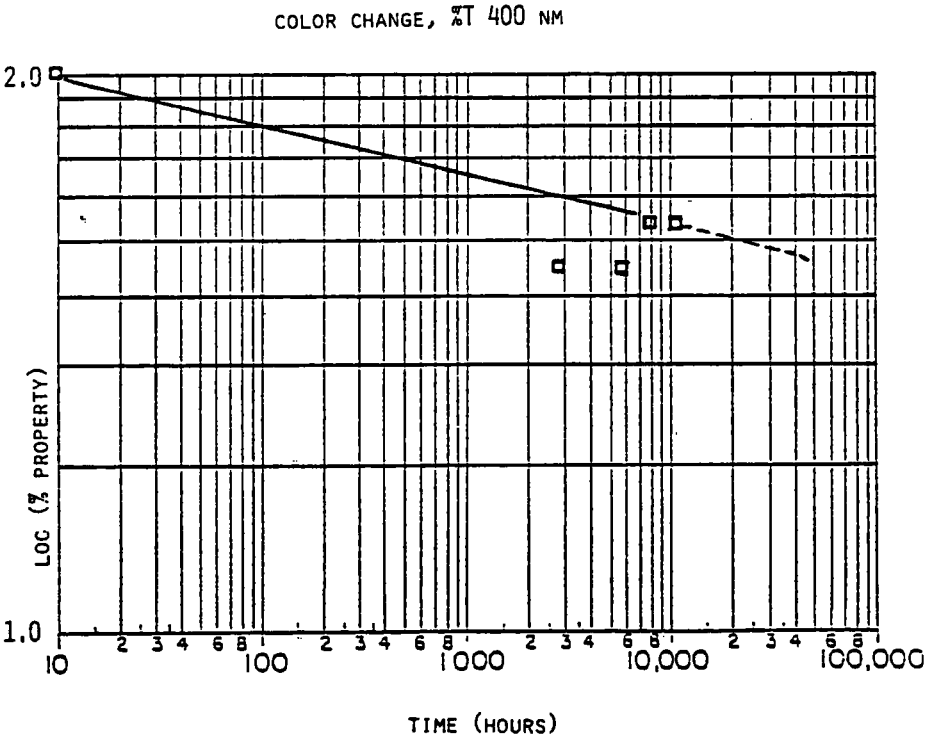
Figure 22. RS/4 Fluorescent Sunlamp Exposure: EVA A-9918 (No Cover Film)

- CLEAR STABILIZED EVA EXPOSED 35,000 HOURS, SOLAR UV EQUIVALENT, 27 YEARS

	TOTAL INTEGRATED TRANSMISSION (%)	ULTIMATE ELONGATION (%)	TENSILE STRENGTH (PSI)	COLOR (%T 400)
CONTROL	91	510	1890	75
EXPOSED 35,000 HRS.	90	480	1450	24
% CONTROL	99%	94%	77%	31%

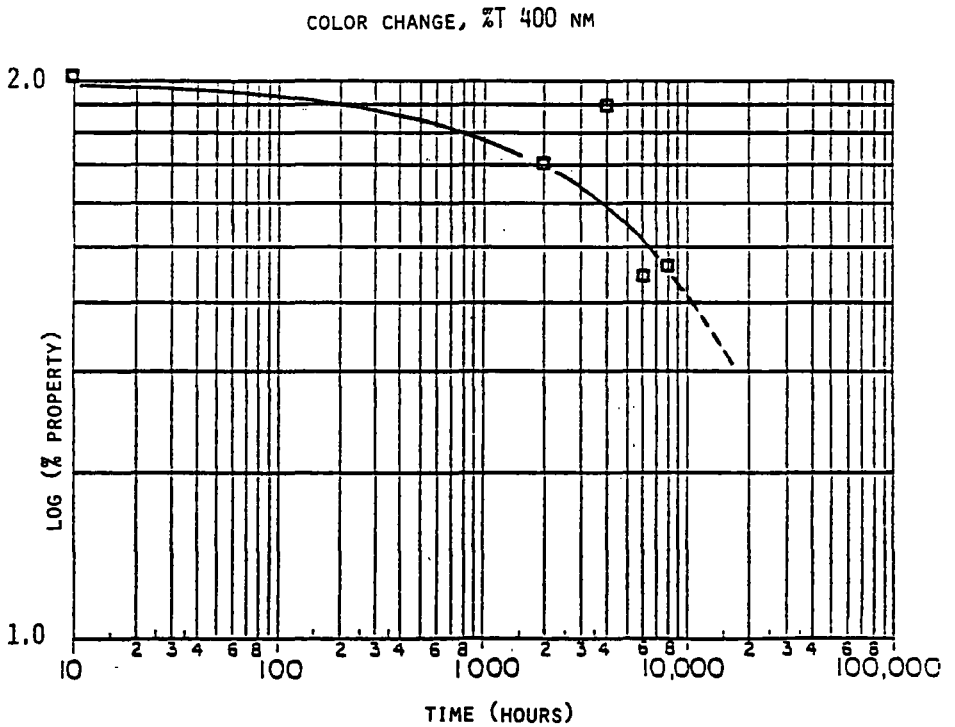
- SPECIMEN NOW SHOWING SMALL SURFACE CRACKS
- UNSTABILIZED ELVAX 150 (EVA) BECOMES SOFT, TACKY, - LOSES PHYSICAL PROPERTIES IN LESS THAN 1,000 HOURS.

Figure 23. RS/4 Exposure: EMA 13439



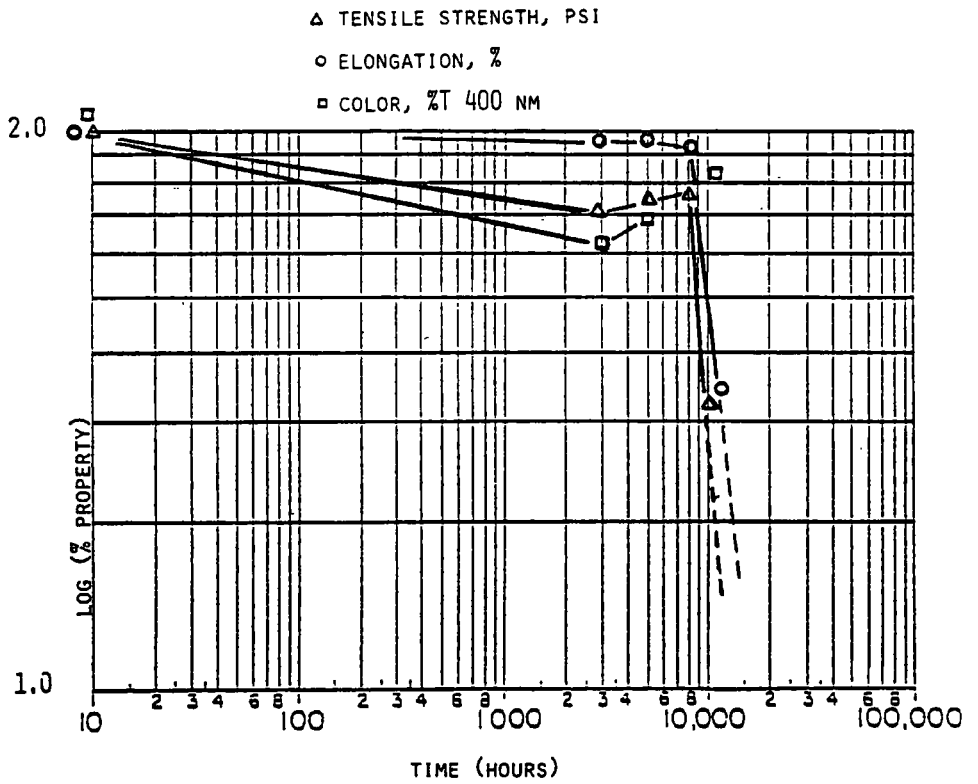
- NO CHANGE IN OPTICAL, MECHANICAL OR ELECTRICAL PROPERTIES AFTER 10,000 HOURS.
- EQUIVALENT SOLAR UV, 8 YEARS

Figure 24. RS/4 Exposure: Polyurethane Z-2591



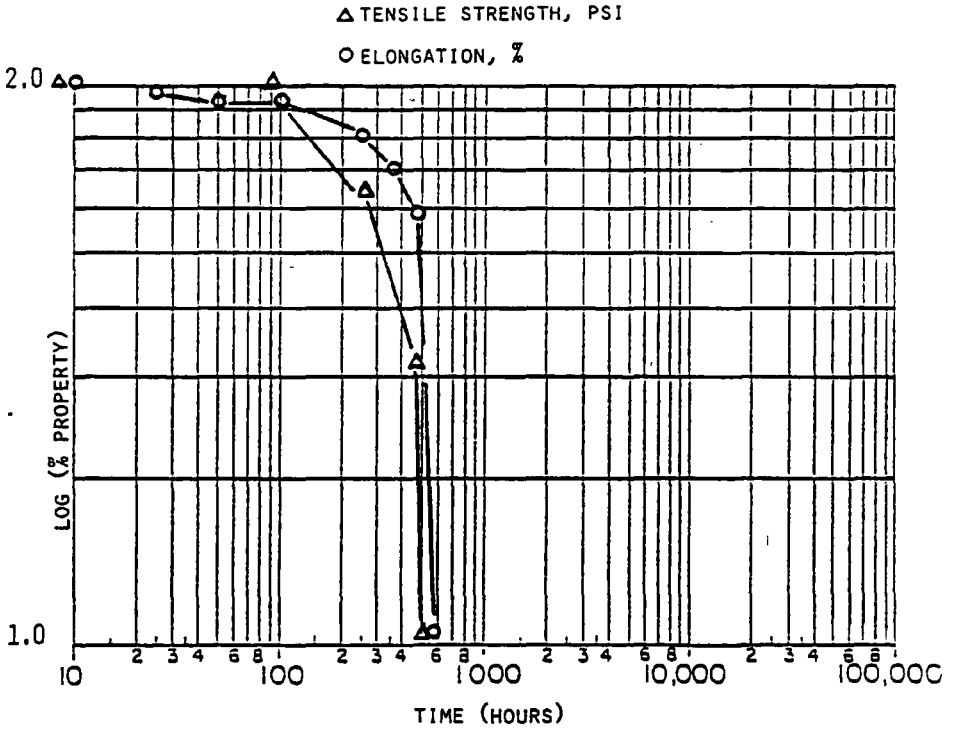
- DATA FIRST ORDER OR INDUCTION TYPE?
- NO CHANGE IN OPTICAL, MECHANICAL OR ELECTRICAL PROPERTIES AFTER 8,000 HOURS
- EQUIVALENT SOLAR UV, 6 YEARS

Figure 25. RS/4 Exposure: Butyl Acrylate 13870



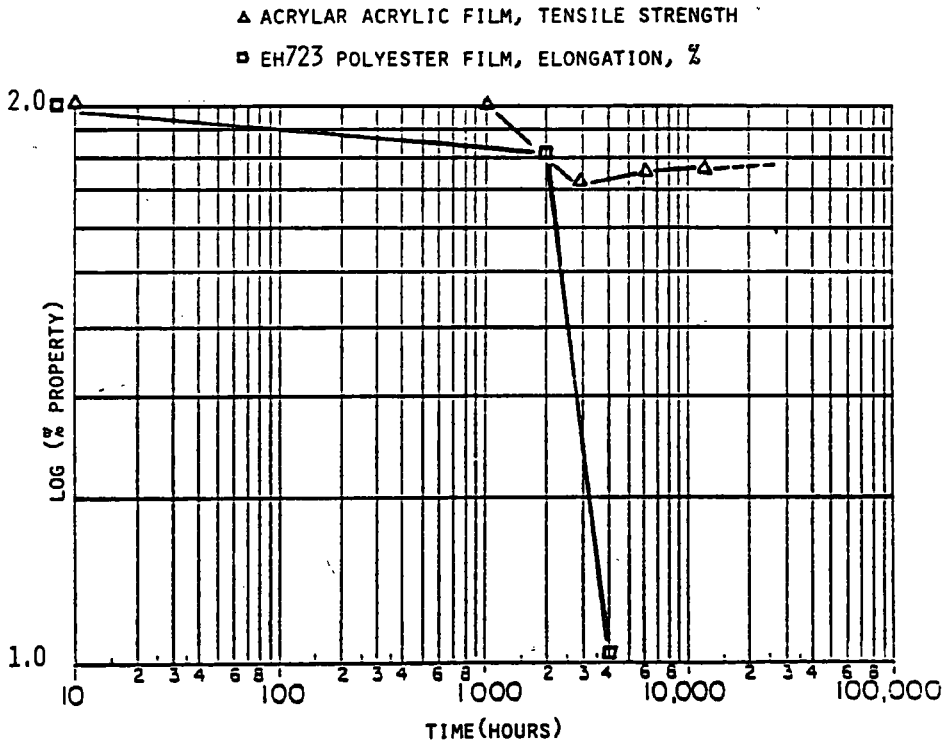
- END OF INDUCTION PERIOD AT 10,000 HOURS
- EQUIVALENT SOLAR UV, 8 YEARS

Figure 26. RS/4 Exposure: PVB (Saflex PT-10)



- INDUCTION PERIOD 500 HOURS - COMPLETE LOSS OF MECHANICAL PROPERTIES
- EQUIVALENT SOLAR UV, 5 MONTHS
- VERY DARK COLORATION AT 700 HOURS RS/4
- REQUIRES GLASS/LAMINATION FOR STABILITY

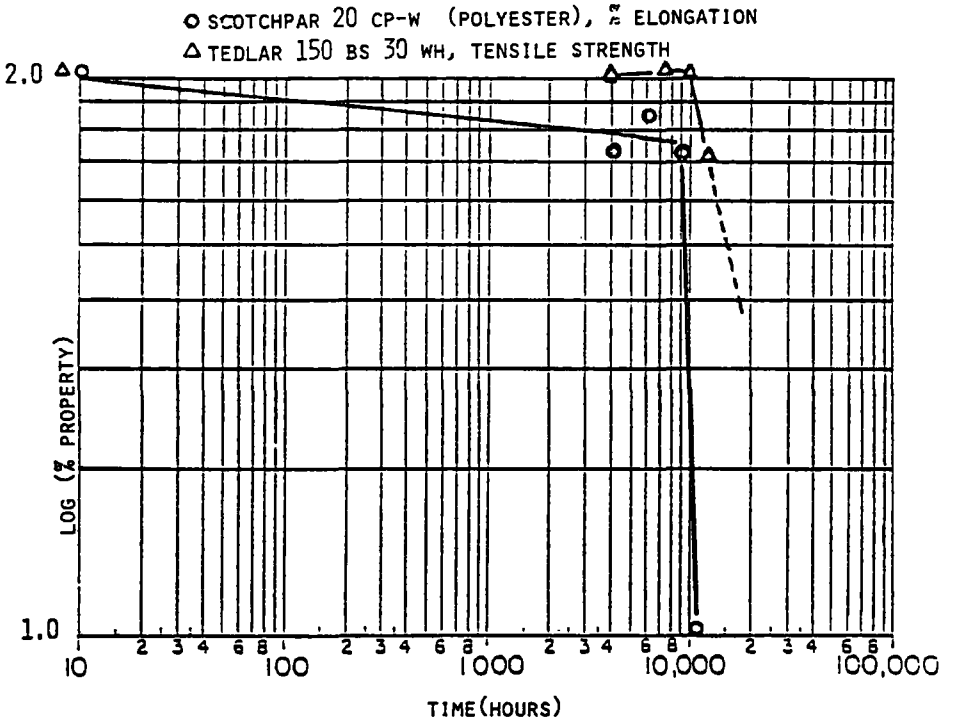
Figure 27. RS/4 Exposure: Outer-Cover Candidates



- NO CHANGE IN PROPERTIES FOR:
  TEDLAR 100BG30UT, 15,000 HRS[A.]
  TEDLAR 4462 , 11,000 HRS
- EH723 POLYESTER DEGRADES TO ~1% ELONGATION IN 4,000 HRS.
- ACRYLAR LOSES 40% TENSILE IN 3000 HRS. THEN STABILIZES. (STRESS RELAXATION AND SOME LOSS OF $\bar{M}v$)

A. EQUIVALENT SOLAR UV, 11 YEARS

Figure 28. RS/4 Exposure: Back-Cover Candidates



- END OF INDUCTION PERIOD FOR SCOTCHPAR; RETAINS 3% ELONGATION, 40% OF TENSILE AT 10,000 HOURS
- END OF INDUCTION PERIOD FOR TEDLAR?
- KORAD 6300 WHITE ACRYLIC FILM NO CHANGE AT 8,000 HOURS

THESE FILMS ARE NOT EXPOSED TO DIRECT SUNLIGHT, BACK SCATTERED LIGHT ONLY.

Figure 29. RS/4 Exposures

TWO NEW CONDITIONS STARTED

I. RS/4; 50°C, WATER SPRAY

II. RS/4; 85°C, HIGH HUMIDITY

- WORST CASE ROOFTOP MODULE CONDITION SIMULATED BY 85°C EXPOSURE
- RAIN EXTRACTION SIMULATED BY WATER SPRAY EXPOSURE
- WATER SPRAY ALSO INTRODUCES HYDROLYTIC STRESS
- CONDITIONS WILL PROVIDE HIGHER DEGREE OF ACCELERATION, SHORTER TIMES TO CHANGE OR FAILURE
- ASSESS FORMULATION EFFECTIVENESS IN SHORTER TIME

Figure 30. RS/4 Exposures (Cont'd)

- RS/4, 50°C WITH WATER SPRAY (10 MINUTES WATER EVERY 2 HOURS)
- DATA TO DATE, 4,000 HOURS
- NO CHANGE FOUND FOR:
  EVA, EMA, PU, TEDLAR 100BG30UT
- ACRYLAR FILM:
  EXTRACTION OF STABILIZER
  (UV CUTOFF: 382 NM ⟶ 315 NM)
- EH 723 POLYESTER FILM:
  - APPX. 0% ELONGATION AFTER 2,000 HOURS (HYDROLYSIS)
  - UV CUTOFF GOES UP:
    (362 NM ⟶ 379 NM)
    (GENERATING CHROMOPHORES?)

Figure 31. Metal Catalyzed Degradation

COPPER AND OTHER MULTIVALENT METALS[A.]
ACCELERATE OXIDATION REACTIONS IN POLYMERS
"PRO-OXIDANTS"

GENERAL MECHANISMS:

INITIATION: $R - R \xrightarrow{\Delta} 2\ R\cdot$

PROPAGATION: $R\cdot + O_2 \longrightarrow RO_2\cdot$

$RO_2\cdot + RH \longrightarrow R\cdot + ROOH$

METAL CATALYSIS:

- MULTIVALENT METALS COMPLEX HYDROPEROXIDES. REACT THROUGH REDOX MECHANISMS, ACCELERATES PRODUCTION OF FREE REDICALS.

  $ROOH + M^{n+} \longrightarrow M^{(n+1)} + OH^- + RO\cdot$

  $ROOH + M^{(n+1)} \longrightarrow M^{n} + H^+ + ROO\cdot$

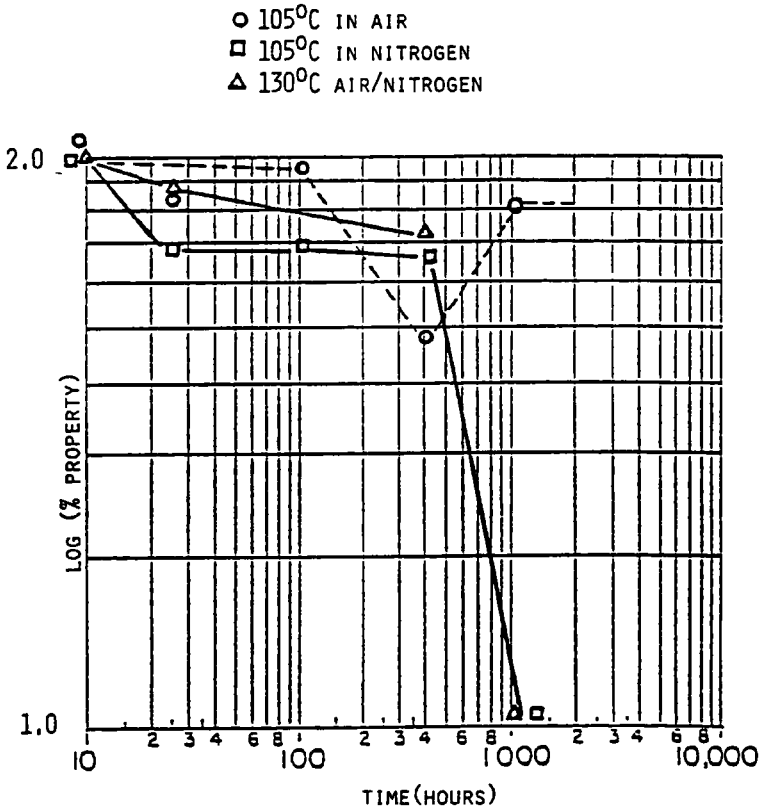
- SOLUBLE IONS ARE VERY CATALYTIC. AFFECT PROPAGATION RATE ONLY.

  SUM:

  $2\ ROOH \xrightarrow[\text{(FAST)}]{Cu^{+2}/Cu^{+3}} RO\cdot + RO_2\cdot + H_2O$

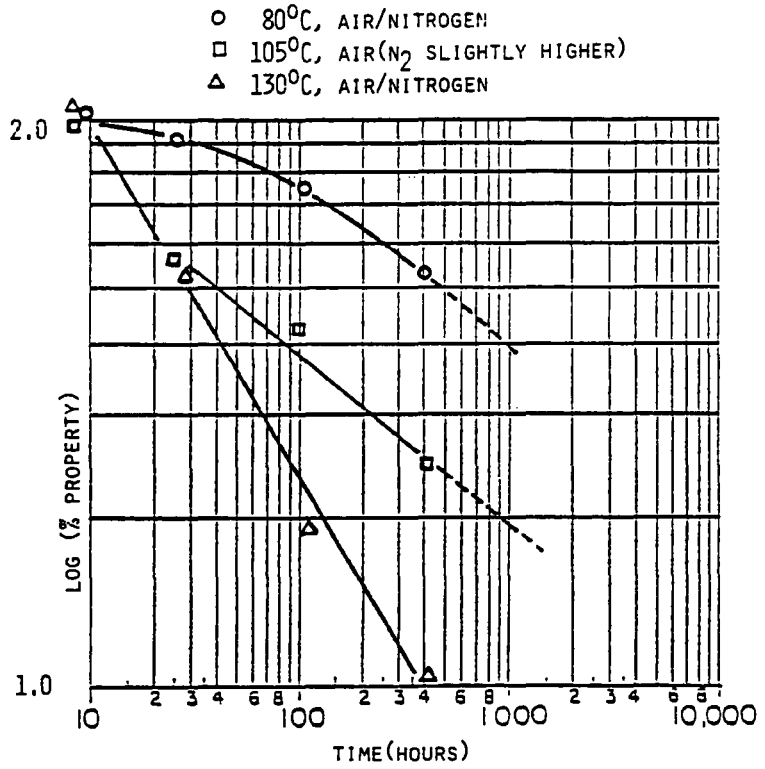
A. NO REACTION WITH ALUMINUM OR 60/40 SOLDER

Figure 32. Metal Activation (Copper Powder): Color Change, EVA A-9918



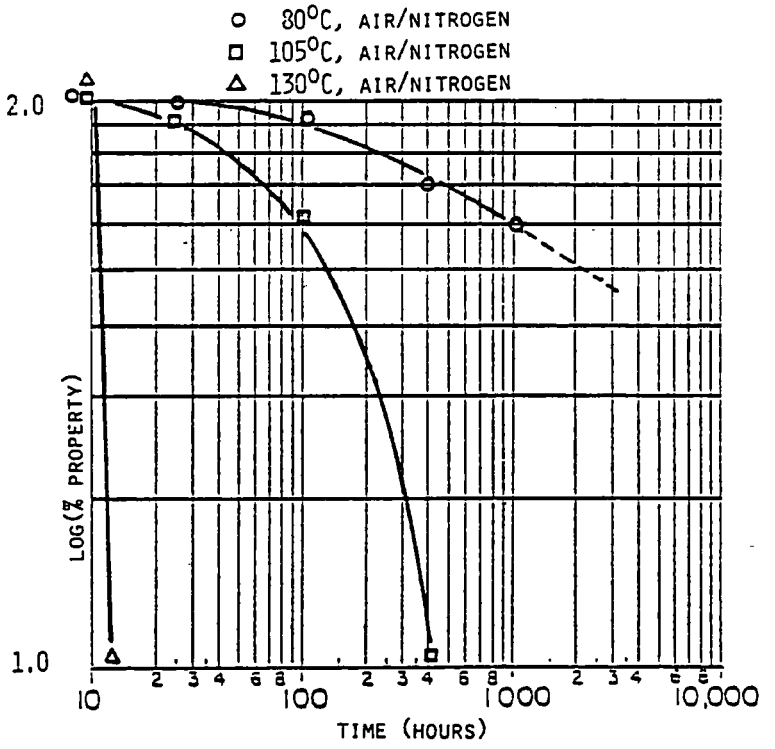
- EVA/COPPER SURVIVES BETTER IN NITROGEN THAN AIR ATMOSPHERE (AT 105°C)
- AT 130°C (AIR OR NITROGEN) ALL PROPERTIES DEGRADED BY 1,000 HOURS. INDUCTION PERIOD APPROXIMATELY 400 HOURS
- EQUIVALENT TO 2,000 HOURS WITHOUT COPPER (EST).
- ACCELERATION FACTOR 14 TO 20

Figure 33. Metal Activation (Copper Powder): Color Change, EMA 13439



- COMPLETE DEGRADATION, ALL PROPERTIES LOST AT 250 HOURS — 130°C (AIR/N_2)
- BETTER IN ABSENCE OF AIR AT THE 105°C CONDITION

Figure 34. Metal Activation (Copper Powder): Polyurethane Z-2591



- COMPLETE DEGRADATION - LOSS OF ALL PROPERTIES: 105°C - 4000 HOURS, 130°C < 20 HOURS
- RESULTS FOR AIR OR NITROGEN APPROXIMATELY EQUIVALENT
- WITHOUT COPPER, PU DEGRADES IN:
  - >1000 HRS - 105°C
  - ~ 250 HRS - 130°C

Figure 35. Metal-Catalyzed Degradation

METAL DEACTIVATION IMPORTANT IN WIRE AND CABLE INDUSTRY: COPPER CONDUCTORS

METAL DEACTIVATORS:

COMPLEXING AGENTS FUNCTION TO INSOLUBLIZE THE METAL ION

$$Cu^{++} + 2L \xrightleftharpoons{\text{BASE}} \underline{\text{COMPLEX}}\ (L_2)\ Cu^{++}$$

Cu^{++} → HIGH CATALYTIC ACTIVITY

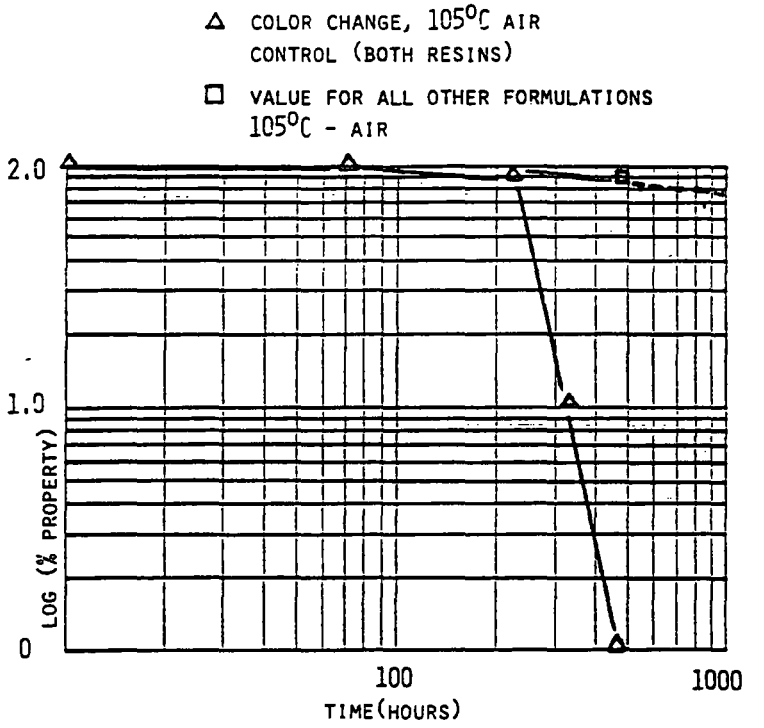
$(L_2)\ Cu^{++}$ → LOW CATALYTIC ACTIVITY (BUT NOT ZERO)

- POLYMERS <u>NOT</u> CONTAINING METALS MORE STABLE THAN POLYMERS WITH DEACTIVATORS
- DEACTIVATOR EFFECTIVENESS: POLYMER COMPATABILITY LIGAND NUMBER, SOLUBILITY, PERMANENCE, SYNERGISM WITH ANTIOXIDANTS
- EFFECTIVE:
  - POLYPROPLYLENE: CIBA GEIGY MD 1024
  - POLYETHYLENE: MD 1024/IRGANOX 1010; CYANOX 2379
- CATALYSIS FROM <u>SOLUBLE</u> IONS: REMOVE SOLDERING FLUX!

Figure 36. Metal Deactivation Experiments

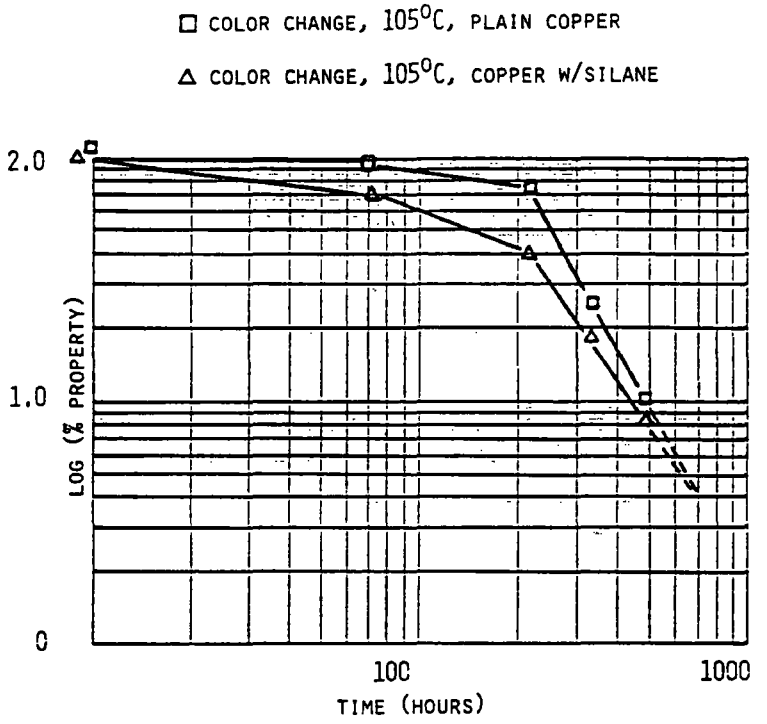
- PREPARE POLYMER FORMULATIONS 0.2 PHR DEACTIVATOR
- MOLD OVER COPPER SCREEN
- COPPER: SILANE / NO SILANE TREATMENT (Z-6030)
- THERMAL AGE, AIR AND NITROGEN
- MONITOR % T 400 NM (YELLOWING)

Figure 37. Metal Deactivation (Copper Screen): EVA A-9918, EMA 13439



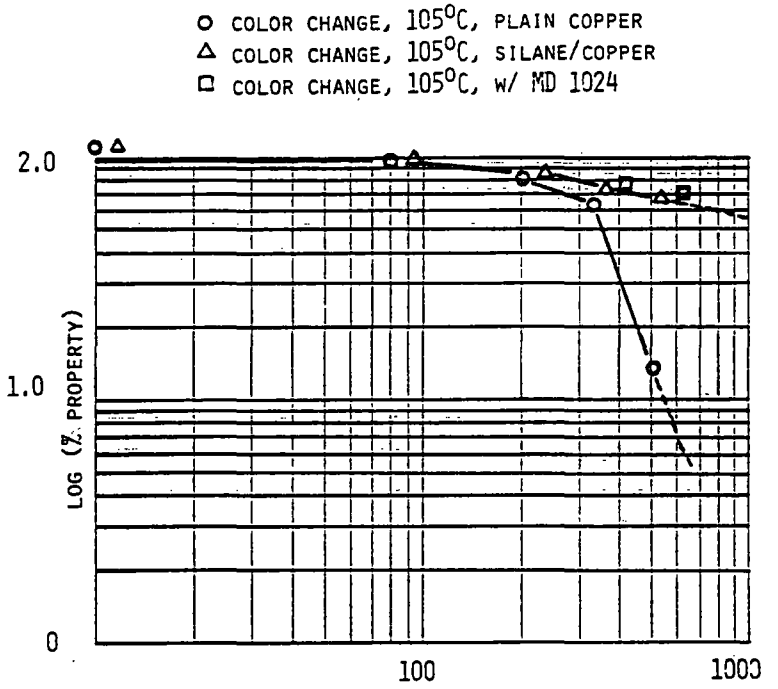
- EMA AND EVA CONTROLS DEGRADED AT 400 HOURS (COLORATION AND FLOW OF RESIN AWAY FROM COPPER SCREEN)
- LITTLE TO NO CHANGE OBSERVED FOR FORMULATIONS CONTAINING 0.2 PHR MD-1024, CYANOX 2379 OR SILANE TREATED COPPER (Z6030)
- SLIGHT DISCOLORATIONS VISIBLE ON ALL COPPER SPECIMENS WITHOUT SILANE TREATMENT
- EXTENDED INDUCTION PERIOD?

Figure 38. Metal Deactivation (Copper Screen): PVB Saflex PT-10



- STRONG YELLOW COLOR VISIBLE IN ALL SPECIMENS AT 350 HOURS (THERMAL AND METAL REACTION)
- RESULTS FOR AIR AND NITROGEN APPROXIMATELY EQUAL
- RESULTS WITH SILANE Z6030 SLIGHTLY WORSE THAN CONTROL

Figure 39. Metal Deactivation (Copper Screen): Polyethylene, TBEC-Crosslinked



- SILANE GIVES IMPROVEMENT OVER CONTROL
- MD 1024 FORMULATION - NO CHANGE

Figure 40. Conclusions (Results to Date)

THERMAL AGING

- ACETIC ACID GENERATION (EVA) NO PROBLEM
- EVA AT 90°C OUT TO 7,200 HOURS - NO CHANGE
- EMA AT 130°C OUT TO 400 HOURS - NO CHANGE
- PU AT 105°C OUT TO 1,000 HOURS - NO CHANGE

LIFE LIMITS

EVA	130°C	APPX. 2,000 HRS.
PU	130°C	250 HOURS

Figure 41. Conclusions (Results to Date, Cont'd)

GENERAL OBSERVATIONS

- SEVERITY OF CONDITION: METAL EXPOSURE, THERMAL (130°C). THEN RS/4
- PROPERTIES LEAST AFFECTED: DIELECTRIC, OPTICAL AND MECHANICAL
- FIRST PROPERTY TO CHANGE: COLOR (YELLOW)
- DEGRADATION: PREDOMINANTLY INDUCTION PERIOD TYPE, FEW FIRST ORDER
- EXPOSURE TIMES ARE LONG. NEED HIGHER ACCELERATION TO ASSESS FORMULATION CHANGES IN LESS TIME.

Figure 42. Conclusions (Results to Date, Cont'd)

RS/4 EXPOSURE

- UNSTABILIZED POLYMERS DEGRADE RAPIDLY
- EVA OUT TO 35,000 HOURS - NO CHANGE
- EMA OUT TO 10,000 HOURS - NO CHANGE
- PU OUT TO 8,000 HOURS - NO CHANGE
- TEDLAR 100BG30 - 25,000 HOURS - NO CHANGE

LIFE LIMITS

BUTYL ACRYLATE	10,000 HRS.
POLYESTER, EH 723	4,000 HRS.
SCOTCHPAR 20 CPW	10,000 HRS.
PVB	500 HRS.

Figure 43. Conclusions (Results to Date, Cont'd)

METAL ACTIVATION

- AVOID METALLIC COPPER IN CONTACT WITH POTTANT: (OTHER MULTIVALENT METALS?)
- NO REACTIONS OBSERVED WITH ALUMINUM, 60/40 SOLDER
- WASH OFF SOLDER FLUX (ACIDIC RESIDUES, SOLUBLE IONS)
- DEACTIVATORS GIVE IMPROVEMENT (EFFECTIVENESS?)
- SILANE GIVES IMPROVEMENT (EFFECTIVENESS?)

LIFE LIMITS

ALL POTTANTS 105°C
APPROXIMATELY 400 HRS.

Figure 44. Life-Limiting Factors (?)

- VOLATILE LOSS OF STABILIZERS
- EXTRACTIVE LOSS OF STABILIZERS (RAINWATER)
- ADHESIVE BOND FAILURE
- LONG PERIODS OF " HOT SPOT " HEATING UNDER VERY BACK BIASED CONDITIONS

Figure 45. Future Work

- CONTINUE CURRENT AGING STUDIES
- ACCUMULATE DATA FROM NEW CONDITIONS:
  - RS/4 AT 85°C
  - CONTROLLED ENVIRONMENT REACTORS (CER)
  - OUTDOOR PHOTOTHERMAL REACTORS (OPT) (COMBINE NATURAL SUNLIGHT EXPOSURE WITH INCREASED TEMPERATURES)
  - OUTDOOR EXPOSURE (PHOENIX, FLORIDA)
- CHEMICAL INVENTORY OF STABILIZERS REMAINING IN AGED SEPEIMENS
- EVALUATE ADHESIVE BOND DURABILITY/ LIFETIME (RS/4, THERMAL, OUTDOOR)

DISCUSSION

GARCIA: Has work been done on the interaction of silver with the pottants? That is one question. The second question is: is polyurethane used in this case--was this the latest formulation of so-called non-yellowing polyurethane or the earlier one? I will ask that of Bud (Nannig) too.

NANNIG: It is the latest.

CUDDIHY: Thank you, Bud. I can take care of the first question. We have no experience with silver. Again, as you know, the Springborn activity is supposed to be the low-cost material with so-called advanced metallization systems, which really means copper, nickel, solder, tomorrow's lower-costing systems. Industries are taking care of today's systems. So you probably know a lot more about silver interactions than I would. Bud (Nannig), you did supply Paul (Willis) with the polyurethane which has the non-yellowing additive?

NANNIG: Right. I would like to make a comment about that. We have done a lot of work with various additives--with aliphatic polyurethanes to stabilize them against UV and oxidation. We're not sure exactly what happens, but one of the things we have run into, at one time, and it may be a warning, is that we found that the UV absorber itself yellowed on thermal aging. It was a UV screener, I won't mention the product, but it was an excellent UV screener and gave us excellent surface characteristics and so forth, but we found that the screener itself yellowed, especially at high temperatures. So it wasn't the polymer itself but the additive.

COULBERT: Along that line: Ranty (Liang) showed that you can suffer losses in this yellow region or in the blue absorption region, something like 80% absorption in the 500-nanometer band, with a net effect on solar-cell performance of 5% or 10%. So it is a very exaggerated effect. When we see the yellowing visually, there may be little performance loss.

KETOLA: Do you have any speculations as to why you have the massive failures all of a sudden at 10,000 hours, and can you possibly rule out a process upset in your aging machines? We have seen the same type of results and have been able to trace those massive failures to interruptions in the aging device itself.

CUDDIHY: You have caught we me very cold on that. I don't know the answer. I saw that data trace for the first time as I was presenting it to you so I haven't had a chance to ask Paul (Willis) on that although the contractors are obligated to write us a monthly report on both good things and bad things and there has been nothing in Paul's reports to indicate any kind of system failure. It could be just in the nature of the plotting format that merely reflects an exaggeration of the induction period and just a sharp deterioration. It looks like that on a log-log format. That's my guess right now.

LEWIS: About this UV susceptibility of the back covers. Is there any intention to look at how UV gets back-scattered in a sandy area or where there's snow on the ground? You know we are trying to put these arrays in a lot of different places, and that worries me.

CUDDIHY: I appreciate your view. We don't do this, do we?

COULBERT: Not quantitatively. Some of the reflectance data, as on the mirrors at DSET, the UV reflectances fall off very rapidly, which suggests reflection from any other surface would essentially absorb UV very quickly and the back-scattering UV would be orders of magnitude less than the direct UV.

CUDDIHY: Could Ami's (Gupta) actinometer that he has on the front of modules just be placed on the back side?

COULBERT: Yes. It could be measured if somebody is interested in it.

PLUEDDEMANN: I haven't talked with Paul (Willis) about this but he mentioned that with the silanes he didn't seem to get a copper effect and suggests then that if he has adhesion to the copper, the copper doesn't corrode, and therefore you don't get copper ions. I have often wondered which comes first, corrosion or loss of adhesion, and I have always proposed that as long as you have good adhesion you can't have corrosion. It seems to bear that out a little bit, here at least. But you don't have copper ions if you have good adhesion.

CUDDIHY: Let's take a minute on that. If anything is controversial today it has to do with how to stop corrosion and tarnish of corrodible metals with silane coupling agents. I personally believe that if you have the right chemical coupling agent you chemically react with the surface. You do two things. You destroy the chemical entities at the surface, by preferential reactions that are water-attractive. You shift the physical water absorption characteristics at the surface from hydrophilic to a hydrophobic base. That means then that atmospheric water vapor, sitting outside looking through the polymeric film as though it were a membrane, the membrane may have a permeation constant but it does not have the action of permeation because you have arrested the driving force both chemically and physically. If it takes liquid water condensed on the surface of a corrodible metal to corrode and you have arrested the driving force, you have arrested the action for that moisture to permeate, get there and condense. Ed (Plueddemann) is one of our contractors and we have asked him to develop, of course not only this family of primer systems for bonding things like EVA to glass which indirectly, I should tell you if I didn't, gives us bond strengths greater by 45 pounds now per inch of width. You break glass with these things; they are enormously powerful. Combining some of the rules too with Dr. Koenig of the prehydrolysis to get rid of this superstructure, you get down to the really tight areas. But back to the metals. Ed developed for us a primer system for bonding EVA to copper, bonding EVA to stainless steel, mild steels and other things like that. With this primer system, it chemically bonds to the aluminum copper surface. I am convinced of it. It also bonds to the EVA. We took such a material, copper, EVA with that primer system, at JPL--we have not published this yet--and we put it in test chambers at 100% relative humidity established at temperatures like 50°, 60°, 70°C and they have been in there for hours and weeks and months, and I took one out on my last trip to Ed and showed it to him. Zero tarnish, nothing. Absolutely dead zero. No water got to the interface, therefore you could not induce it. But if you took the EVA and you laminated it around the copper without these silane coupling agent

systems--you can't just go buy this stuff off the shelf, it's a mixture of things--it will tarnish overnight at 50°C or 100% RH; it just comes rolling through. At Springborn Laboratories we took the primer system that Ed developed for mild steel and we encapsulated or laminated EVA around that primer system. It's been in the ASTM B117 salt-fog chamber at Springborn 4000 hours. There isn't a mark on the mild steel. The EVA is transparent and we can look right through it. It works. I am convinced it works. I may not claim to understand all of the chemistry, but I see it works.

WHITE: Am I to understand, then, that the water in the EVA does nothing to degrade the EVA itself and that photooxidation is the major component of the degradation, and therefore, if it is, then once the photooxidation occurs, does the water help increase the rate of degradation in the EVA or does it not do anything at all?

CUDDIHY: You are asking a different question now, I think. You are asking is EVA susceptible to photohydrolysis or is it susceptible to hydrolysis itself at elevated temperature?

WHITE: What I am trying to say is, does the water, if at the surface of the metal in the EVA, if there is nothing for the water to condense at, the water can still get into the EVA. Does it do anything? Does it not get into the EVA at all?

CUDDIHY: Let's call water what it is at that point. It is vapor. It is non-condensed. It is not liquid. It is just like the paper in front of you right now. It has picked up water vapor in equilibrium with the current relative humidity in this room. As the relative humidity goes up and goes down the water vapor absorbs and desorbs. The question now is, does water vapor have energetic effects in deterioration? I don't know the answer to that. One of the things that is starting up--the wet RS/4 was just beginning to answer questions like that. We don't know. However, the evidence would be, from what I have seen in actual arrays outdoors in installations where commercial modules in EVA have been--in Guam, for example, for over a year in some other locations: don't see a thing.