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Advanced Development of PV Encapsulants

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W. Holley, S. Agro, J. Galica, L. Thoma,
R. White, R. Yorgensen
Springborn Laboratories, Inc.
Enfield, Connecticut

NREL technical monitor: H. Thomas

National Renewable Energy Laboratory
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Golden, Colorado 80401-3393
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SUMMARY

EVA copolymer-based encapsulants have been widely used for more than a decade for flat plate PV modules for terrestrial application. Recently, a yellowing or browning of the EVA encapsulant has been noted in some fielded modules after a few years of service. The purpose of much of the investigation covered in this report was to better define the nature and extent of this discoloration problem.

A thorough review of the literature on thermal and photothermal degradation of EVA, plus a survey of case histories of discoloration (yellowing/browning) of EVA-based encapsulants in fielded flat-plate PV modules have solidified some significant findings regarding EVA discoloration.

The literature reveals that EVA will undergo thermolysis of the acetate groups at temperatures of 130 to 150°C and above, leading to formation of double bonds in the backbone of the copolymer. EVA copolymers, especially those such as Elvax 150 with comparatively high vinyl acetate contents, tend to contain blocks of vinyl acetate homopolymer. These blocks, when exposed to elevated temperatures, will yield conjugated unsaturation or "polyenes" that result in a yellow to brown color in the material.

The thermolysis phenomenon is also evident with combined U.V. radiation and temperature, but at moderate conditions (ie. U.V. radiation of one sun or temperature of less than 125°C), temperature or U.V. alone appear insufficient to cause the discoloration. At moderate conditions, both U.V. and temperature are required.

Also, the EVA discoloration has been found to be accelerated by metal (e.g. silver and copper) and metal oxide interfaces such as those found in cell grid lines. It is also evident, that the formation of polyenes in the EVA is but an intermediate step in the overall photooxidative degradation process, which leads to chain scissioning and crosslinking and loss of ultimate tensile elongation, but does not seem to affect the elasticity of the EVA at low elongations. Further oxidation or photooxidation of the polyenes can also lead to apparent "bleaching" of the yellow-brown color.

A survey of case histories of EVA-based encapsulant discoloration in fielded modules in the U.S. reveals that the problem is limited to those areas of the West and Southwest that have comparatively high solar insolation and ambient temperature. We have seen no reported cases of discolored EVA-based encapsulant from modules fielded in Northeast and Central U.S. or Western Europe.

The absence of reliable data regarding module operating temperatures, solar insolation, the onset of discoloration, and quantitative information regarding the degree of discoloration has made any correlations between various fabrication, placement, and operating conditions and incidence of discoloration difficult if not impossible. However, the degree of discoloration does appear to correlate approximately with increasing average daily direct normal solar radiation and approximate maximum module operating temperature, as estimated from maximum ambient temperatures.

It is clear that the discoloration problem is not limited to the modules of any one PV module manufacturer. Discoloration in the EVA encapsulant has been experienced in fielded modules from all major U.S. module producers. However, the rate and degree of discoloration do appear to vary from company to company. Also, discoloration is not limited to EVA encapsulant sheet from any one supplier.

Task 2 of this PVMaT project involves conducting laboratory problem definition work with an emphasis on controlled aging studies to evaluate the influence of various compositional, processing, and operating parameters on EVA discoloration. In support of future laboratory accelerated UV aging studies (AAS) of coupon-size EVA laminates, an Atlas xenon arc Ci35A Weather-Ometer was procured, installed, and calibrated for temperature and irradiance.

In the process of preparing for the AAS studies, UV-visible spectroscopy measurements were performed on various types of low iron glass, representative of materials used for module superstrates. It was discovered that the transmission spectra of some of the grades in the UV region from 250 to 400 nm was significantly different. Older grades of Solatex and Solite, and StarPhire "cut off" well below 290 nm, while newer grades of Solatex and Solite (post 1990) and Airphire greatly reduce the UV transmittance between 280 and 330 nm. Using the newer glasses may have important implications for the stability of EVA encapsulant, since it is our understanding that <u>only</u> the newer Solatex/Solite has been available to module manufacturers since about 1990.

Controlled aging studies are presently underway at 0.55 watts per square meter @ 340 nm and 100 degrees C, and we expect comparative data on yellowing to be available in the next semi-annual report.

1.0 INTRODUCTION

The goals of the NREL PVMaT program are, among others, to reduce module manufacturing costs and improve quality, and we might add here the reliability, of manufactured PV products. But lower production costs will require economies of scale, and this means that the large potential market of central power generating stations needs to be opened up. In a 1989 report, DOE concluded, "...that utilities are 'a key factor in achieving large-scale markets' that would drive down costs."[1]

The report goes on to say, "However, in general, utility companies are not ready to embrace the PV technology on a large scale, in spite of several potential advantages of PV as a large-scale power-generating source."[1] Electric utilities seem to be in a "wait-and-see" mode, and show no interest at the present time in making investments of the magnitude that would make PV more competitive with other power sources.[1]

One component critical to the service life of PV modules is the useful life of the EVA encapsulant which is employed extensively by module manufacturers on a worldwide basis. This pottant has been in commercial use since 1982[2], and over that time has proven to be a dependable material from the standpoint of production, module fabrication, and end-use. But despite the widespread acceptance of EVA for PV encapsulation, some module producers, end-users, and investigators have reported a yellowing or browning phenomenon with EVA in the field. While the incidence of this discoloration/degradation appeared at comparatively few sites, in January 1992 when this proposed PVMaT program was conceived (Proposal to NREL under RFP No. RR-2-11219, titled "Teamed Research and Development on Photovoltaic Manufacturing Technology, Phase 3A - Shared Process Issues" by Springborn Laboratories, Inc., dated January 1992) , it raised serious concern as to the long term reliability of EVA encapsulated systems.

While there had been considerable discussion of the discoloration/degradation of EVA in the industry at the time this study was proposed to NREL, there was insufficient published information from which to draw meaningful conclusions regarding its cause(s).

The browning/degradation of the EVA encapsulant at the Carrizo Solar Corporation's Carrisa Plains Photovoltaic Power Plant in California had a profound effect on the PV industry with respect to consumer confidence and reliability standards. The news of the browning and ultimate demise of the plant quickly transcended boundaries of small circulation PV industry newsletters, making headlines in national publications such as Barron's.[1]

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1 A. Zipser, "Solar Eclipse, Will the Mideast Crisis Make it a Hot Item Again?", Barron's, pp 16, 31 (August 20, 1990).

2 J. H. Wohlgemuth and R. C. Petersen, Solar Cells Their Science, Technology, Applications and Economics, Solarex Experience with Ethylene Vinyl Acetate Encapsulation, (Elsevier Sequioa, 1991).pp. 383-387.

Prior to December 1992, the discoloration of EVA, reported at the facility at Carrisa Plains[1], had been attributed to high operating temperatures, approximately 90°C, and increased light intensity resulting from mirror-enhanced light exposure.[2,3]

In addition, more than one of the manufacturers who supplied modules to the Southwest Regional Experimental Station (Southwest RES), in Las Cruces, NM, had reported browning of the EVA encapsulation layer(s) on site. One company reported cases of severe discoloration and loss of power, while another experienced only slight tinges of brown and yellow with essentially no power loss.

One PV module supplier to the Southwest RES reported signs of yellowing as early as 1984, only four years after installation of the array. By 1993, the condition of these modules had deteriorated to a point where the cells were barely visible through the cover glass.

Another supplier reported yellowing of EVA encapsulant in modules fielded in the Arizona desert, but at that time, similar installations located in Concord, MA (Northeast RES) and Cape Canaveral, FL (Southeast RES) had not exhibited discoloration of substantial degree.

Could this discoloration/degradation phenomenon be attributed only to exposing EVA to energy levels above and beyond those for which it was designed? Many industry representatives said not, and this question really needed to be explored. More information needed to be documented for those reported cases of discoloration, especially as regarded parameters such as EVA supplier/source, module construction, curing/processing conditions, operating conditions in the field, etc.

Therefore, under the NREL PVMaT program, Springborn Laboratories proposed to conduct a thorough review of published information and internal reports and documentation, where available, from proposed team members and other sources. More importantly, Springborn Labs proposed to conduct a detailed survey of module manufacturers, primarily proposed team members (see Appendix 1 - Team Member List) - both those who had experienced EVA discoloration and those who had not, with an emphasis on well documented case histories.

Using phone survey, field visits, and a written questionnaire, detailed information was gathered regarding module design and construction, fabrication/curing techniques, use of primer, grade and supplier of EVA sheet, type of modules, field exposure conditions - especially operating temperature and solar insolation, etc. The primary purpose of this Task 1 survey was to establish correlations between these variables and the incidence of EVA discoloration, leading to a more detailed investigation of causes and mechanisms in Tasks 2 and 3.

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1 D. D. Sumner, Proceedings of 20th IEEE Photovoltaic Specialists Conference, (New York, 1988), p. 1289.

2 A. Zipser, "Solar Eclipse, Will the Mideast Crisis Make it a Hot Item Again?", Barron's, pp 16, 31 (August 20, 1990).

3 A. L. Rosenthal and C. G. Lane, Solar Cells Their Science, Technology, Applications and Economics, Field Test Results for the 6 MW Carrizo Solar Photovoltaic Power Plant, (Elsevier Sequioa, 1991).pp. 563-571.

The following discussion details the results of this literature search and survey of case histories of EVA discoloration, as well as initial work on Task 2 laboratory accelerated aging studies.

2.0 LITERATURE SEARCH ON EVA DISCOLORATION/DEGRADATION

2.1 Studies of EVA Discoloration/Degradation of Fielded Modules

Comparatively little technical information has been published on the experience of EVA discoloration/degradation in fielded modules, and most of that which has appeared has only been released since late in 1990. EVA discoloration was discussed in detail at a meeting held at SERI in February 1990 between selected module manufacturers, SERI staff, and representatives from Springborn Laboratories, Inc. In October of that year, A. Rosenthal and C. Lane of the Southwest Technology Development Institute prepared a paper reporting on "EVA degradation" at the now notorious Carrizo Solar Photovoltaic Power Plant, Carrisa Plains, CA.[1,2]

The Carrizo plant was constructed by ARCO Solar (now Siemens) between 1983 and 1985, and was intended as a "demonstration of photovoltaics' potential for commercial power production."[3] The facility comprised ten segments, each with its own PCU (power conditioning unit). Each of the first 9 segments employed 84 mirror-enhanced, 2-axis trackers (Carrisa 1A), while segment 10 (Carrisa 1B) used 43 larger trackers, but without mirror enhancement. Concentrated solar radiation from the mirrors was reported to be equivalent to a nominal 2 suns.[3]

ARCO indicated that discoloration of EVA was first noted in Carrisa 1A modules after approximately 2.5 years of field exposure, and J. Schaefer of EPRI et. al., reports that the facility experienced "steady degradation in electrical performance since 1986." As of February 1990, discoloration of modules in the mirror-less Carrisa 1B had just started to occur, and J. Schaefer reports "less, but increasing, browning as of 1991."[1,3]

It might be noted that this site was visited by Springborn Laboratories program team members in late March 1992. They reported that segment 10 continues to brown (darken) and is now perhaps half as brown as the mirror enhanced segments.

Since this discoloration phenomenon was unexpected, two complications arose, not only for this site but also for other locations where EVA discoloration has been observed. Because discoloration occurred only over the dark blue-grey silicon cells, it is not clear exactly when the change began; it may have gone unnoticed for some time.

Secondly, because the focus of evaluations was on module performance, discoloration was only considered a side issue, and consequently was never quantified. So various terms have been used to describe the discoloration, such as yellowing,

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1 J. Galica, Internal Memorandum, Springborn Laboratories, Covering Meeting at SERI, Feb. 22, 1990, (Feb. 26, 1990).

2 A. L. Rosenthal and C. G. Lane, Solar Cells Their Science, Technology, Applications and Economics, Field Test Results for the 6 MW Carrizo Solar Photovoltaic Power Plant, (Elsevier Sequioa, 1991).pp. 563-571.

3 J. Schaefer, L. Schlueter, A. Rosenthal, H. Wenger and A. E. Luque, Electrical degradation of the Carrisa Plains power plant, E. C. Photovoltaic Sol. Energy Conf., Proc. Int. Conf., 10th, P1248-53, (1991).

browning, brown cell, amber, and degradation, but all of them only qualitatively at best.

Early in 1990 a major module manufacturer claimed to have seen evidence of browning in modules produced by four different manufacturers, but would not at that time disclose the names of those producers.[1] This same manufacturer reported that discoloration had been noted in its own modules both at Southwest Regional Experimental Station (Southwest RES), Las Cruces, NM, and at Southeast Regional Experimental Station (Southeast RES), Cape Canaveral, FL.[1]

Since that time, J. Schaefer et. al. have reported the evidence of "brown cells" in the modules of manufacturers, other than ARCO (Siemens), at Las Cruces, NM, and San Ramon, CA.[2] Also, F.J. Pern and A. Czanderna claim reports of "yellowing of EVA" in non-mirror-enhanced arrays at Phoenix, AZ; Las Cruces, NM (Southwest RES); Albuquerque, NM (likely the Solarex array at Sandia as noted below); Cape Canaveral, FL (likely Southeast RES); as well as in Morocco, Australia, Saudi Arabia, and Nambia, South Africa.[3]

Regarding discoloration and power loss, Pern and Czanderna state, "Wide variations in the performance of PV modules have been reported ranging from essentially no loss in 10 years with discernible yellowing to over 40% loss in 5 years and forming a dark brown color." And they have indicated exposure times for the onset of discoloration ranging from 3 to 12 years.[3,4]

In September 1992, at the PV Performance and Reliability Workshop, C. Whitaker of ENDECON reported on module reliability at Pacific Gas & Electric's PV Test Facility (PTF) in San Ramon, CA, near Oakland. This site contains roughly 75 modules from 27 module manufacturers worldwide, and represents a variety of module types, constructions, and placements, both fixed and tracked. Roughly a dozen of the modules use a "concentrator" of some type.[5]

According to Whitaker, "approximately 9 PTF modules show various degrees of browning."[5] Again, little detail was provided, and it is not clear if the

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1 J. Galica, Internal Memorandum, Springborn Laboratories, Covering Meeting at SERI, Feb. 22, 1990, (Feb. 26, 1990).

2 J. Schaefer, L. Schlueter, A. Rosenthal, H. Wenger and A. E. Luque, Electrical degradation of the Carrisa Plains power plant, E. C. Photovoltaic Sol. Energy Conf., Proc. Int. Conf., 10th, P1248-5, (1991).

3 F. J. Pern and A. W. Czanderna, AIP Conference Proceedings 268 Photovoltaic Advanced Research and Development Project, Rommel Noufi, (American Institute of Physics, New York, 1992), p. 445-451.

4 F. J. Pern and A. W. Czanderna, Solar Energy Materials and Solar Cells, Characterization of Ethylene Vinyl Acetate (EVA) encapsulant: Effects of Thermal Processing and Weathering Degradation on its Discoloration, (Elsevier Science Publishers, 1992).pp. 3-23.

5 C. Whitaker, Pacific Gas and Electric Company's Perspective on Module Reliability, Photovoltaic Performance and Reliability Workshop, (1992), p. 279-289.

affected modules were all supplied by one manufacturer or whether they used a concentrator.

Module producer Solarex has reported two instances of EVA discoloration, both in non-mirror-enhanced arrays. After 8 years of exposure in Albuquerque, the "Sandia Array" showed some darkening of EVA in the center 7 cm x 7 cm area over 9.5 cm x 9.5 cm cells.[1] But Solarex reports no measurable power loss from the array as of September 1992, and no measurable power loss from modules returned to the Solarex plant for "flash tests."[1]

In addition, Solarex reported visible browning of modules after 9 years exposure at the Southwest RES in Las Cruces, NM, but again claimed no power loss and also indicated that the browning disappeared "when textured glass is covered with alcohol."

At best, the information on discoloration of EVA in fielded modules is vague and incomplete. This fact has prompted a more detailed survey of case histories of discoloration in the field as discussed in section 3.0 of this report, page 25.

It should also be highlighted here that there have been no documented cases of EVA discoloration from modules located in northeast or central USA or in Western Europe. This fact tends to lend weight to the argument that EVA discoloration is only taking place in those locations where there is a high operating temperature and/or high solar insolation, especially at shorter U.V. wavelengths. More will be said about this correlation in Section 3.0 of this report, covering the survey of case histories.

2.2 Laboratory Studies of EVA Discoloration/Degradation

In laboratory studies of fielded, glass-superstrate PV modules, which had been in service for more than five years and in which the EVA encapsulant was discolored/degraded, Pern and Czanderna found a gradient to the yellowing or browning. Cross-sections of the encapsulant were discolored on the glass side, but were clear in the remainder, down to the cell.[2] Other investigators have made similar observations.[3] In addition, "EVA in direct contact with the Silicon solar cell top surface displays a yellow-brown image pattern identical to that of the metallization grid lines and buslines underneath."[2]

As experienced in the field, Pern and Czanderna found in the lab that there was a percent reduction in cell efficiency for EVA-encapsulated test cells exposed

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1 J. H. Wohlgemuth and R. C. Petersen, Photovoltaic Performance and Reliability Workshop, September 16-18, 1992, Golden, CO, Laxmi Mrig, (1992), p. 313-326.

2 F. J. Pern and A. W. Czanderna, Solar Energy Materials and Solar Cells, Characterization of Ethylene Vinyl Acetate (EVA) encapsulant: Effects of Thermal Processing and Weathering Degradation on its Discoloration, (Elsevier Science Publishers, 1992).pp. 3-23.

3 J. Galica, Internal Memorandum, Springborn Laboratories, Covering Meeting at SERI, Feb. 22, 1990, (Feb. 26, 1990).

to accelerated aging, that ranged from 0.5 to 3.1% for those with light-yellow EVA to 10.1 to 19.3% for test cells containing brown EVA.[1]

What appears to be causing this phenomenon?

In the following sections, we will attempt to examine in a systematic way those factors, as reported in the literature, that appear to be contributing to EVA discoloration/degradation and the associated loss in PV module efficiency. These parameters include elevated temperature, U.V. light, the combination of high temperature and U.V., and effects of module construction, as well as catalytic effects of acetic acid and metal and metal oxide interfaces. We will also review reported findings of "photo-bleaching" of discolored EVA, effects of aging on EVA structure, and the impact on additive levels.

2.2.1 Effects of Temperature: Thermolysis of EVA by deacetylation at elevated temperatures is well known, leading to acetic acid as the main decomposition product and unsaturated groups in the backbone of the polymer.[2] Where vinyl acetate homopolymer blocks occur, especially in high vinyl acetate content grades of EVA such as the Elvax 150 used for PV encapsulation, the result is the formation of polyenes or conjugated unsaturated sequences that result in yellow color development.

This degradation occurs in the absence of U.V. radiation at 150°C, and possibly lower temperatures, and the rate is reported to increase with increasing vinyl acetate content in the EVA copolymer.[2,3]

While 150°C exposure of modules in end-use is not expected, deacetylation at this temperature remains significant to PV applications. Liang et. al. state, "it was observed that during outdoor deployment, hot spots (up to 150°C) are developed in the PV modules. These hot spots can cause accelerated degradation leading to premature failure of the encapsulant."[4]

But what about the effect on EVA of more moderate temperature exposure?

Wohlgemuth and Petersen reported that when EVA-encapsulated minimodules were given a high temperature soak at 130°C for 7,200 hours, there was "major mechanical and optical degradation," thermolysis of the EVA, and evolution of acetic acid.[5] But these same investigators indicated that when EVA-encapsulated minimodules with glass substrate and superstrate were heated for 5,303 hours at

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1 F. J. Pern, Photovoltaic Performance and Reliability Workshop, September 16-18, 1992, Golden, CO, Laxmi Mrig, (1992), p. 327-344.

2 B. A. Sultan and E. Sörvik, Thermal degradation of EVA (ethylene-vinyl acetate copolymer) and EBA (ethylene-butyl acrylate copolymer) - a comparison. I. Volatile decomposition products, J. Appl. Polym. Sci, 43, 1737-45 (1991).

3 B. A. Sultan and E. Sörvik, Thermal degradation of EVA (ethylene-vinyl acetate copolymer) and EBA (ethylene-butyl acrylate copolymer) - a comparison. II. Changes in Unsaturation and Side Group Structure., J. Appl. Polym. Sci, 43, 1748-59 (1991).

4 R. H. Liang, S. Chung, A. Clayton, S. Di Stefano, K. Oda and S. D. Hong et al., Photothermal degradation of ethylene/vinyl acetate copolymer, Polym. Sci. Technol, 20, 267-78 (1983).

5 J. H. Wohlgemuth and R. C. Petersen, Photovoltaic Performance and Reliability Workshop, October 25-26, 1990, Lakewood, CO, Laxmi Mrig, (1990), p. 247-258.

125°C, there was no odor of acetic acid and yellowing only approximately 3.5 cm in from the cell edges.[1] Module operating current was reduced by 1.5 to 2%, but there was no change in fill factor or voltage.[1]

Wohlgemuth and Petersen concluded that within expected limits of operation of PV modules, yellowing or browning is not caused by temperature alone.[2]

In 1983, Liang reported that when EVA (A9918) films were heated at 105°C for 800 hours in the absence of U.V. light, there was a gradual increase in absorption at wavelengths longer than 400 nm, which coincided with the appearance of yellowing of the EVA.[3] More recently, Pern and Czanderna reported that, "Heating EVA in capped vials in an oven (no light available) from 85-130°C for 120 h to 240 h results in increased yellowing."[4]

But Wohlgemuth and Petersen reported that when minimodules were subjected to a 90°C temperature soak for 7,200 hours, there was "no change." [5]

One factor that needs to be taken into account regarding heat induced yellowing of EVA is the presence or absence of oxygen. In 1983, Lewis and Megerle found that when 15 mil thick free-standing films of EVA were exposed to 150°C in a circulating air oven for 26 days, there was "very little yellowing." But at the same time tensile strength and elongation at break decreased significantly.[6,7] More recently Pern and Czanderna found that "Heating EVA in open vials at the same temperatures results in less yellowing at each temperature."[4]

The above experiments, conducted in the presence of oxygen, indicate that simultaneously with the deacetylation and formation of unsaturation, these unsaturated groups are being further oxidized leading to chain scission and crosslinking reactions and embrittlement of the EVA. However, Lewis and Megerle go on to add that "tear strength and elastic moduli at 10% and 100% elongations, which are within the regions of concern for PV use, remained relatively constant," and there was no effect on the electrical volume resistivities.[6]

Lewis and Meagerle's work suggests that a partially degraded EVA encapsulant with no significant degree of yellowing/browning may continue to function satisfactorily in flat plate PV modules.

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1 J. H. Wohlgemuth and R. C. Petersen, Photovoltaic Performance and Reliability Workshop, September 16-18, 1992, Golden, CO, Laxmi Mrig, (1992), p. 313-326.

2 J. H. Wohlgemuth and R. C. Petersen, Photovoltaic Performance and Reliability Workshop, September 16-18, 1992, Golden, CO, Laxmi Mrig, (1992), p. 313-326.

3 R. H. Liang, S. Chung, A. Clayton, S. Di Stefano, K. Oda and S. D. Hong et al., Photothermal degradation of ethylene/vinyl acetate copolymer, Polym. Sci. Technol, 20, 267-78 (1983).

4 F. J. Pern and A. W. Czanderna, AIP Conference Proceedings 268 Photovoltaic Advanced Research and Development Project, Rommel Noufi, (American Institute of Physics, New York, 1992), p. 445-451.

5 J. H. Wohlgemuth and R. C. Petersen, Photovoltaic Performance and Reliability Workshop, October 25-26, 1990, Lakewood, CO, Laxmi Mrig, (1990), p. 247-258.

6 K. J. Lewis and C. A. Megerle, Encapsulant degradation in photovoltaic modules, ACS Symp. Ser, 220, 387-406 (1983).

7 C. A. Megerle and K. J. Lewis, Encapsulant degradation in photovoltaic modules, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.), 23, 250-1 (1982).

In conclusion, at the moderate temperatures to which fielded modules are subjected (e.g. 60 to 85°C), both mirror-enhanced and not, temperature alone does not appear to be causing the discoloration phenomenon. That yellowing of EVA encapsulant in fielded modules is not uniform through the cross section, but proceeds from the glass superstrate inward, leads us to conclude that U.V. radiation, in addition to temperature, are required for yellowing/browning at these comparatively low temperatures.

At Springborn Labs, the contribution of U.V. to EVA yellowing at moderate temperatures has been further supported by our observation that in "browned modules" the EVA beneath the cells, where it is protected from U.V. exposure, has not exhibited discoloration and has retained most of its low tensile modulus and tensile elongation.

2.2.2 Effects of U.V. Radiation: One of the first questions that needs to be asked, is what intensity and wavelengths of U.V. radiation? Obviously we're concerned with radiation that strikes the earth's surface at various locations around the globe, and in designing an encapsulant we really need to consider the "worst case" situations -those regions where the light is most intense and the spectrum of U.V. wavelengths the broadest, especially below 300 nm.

Conventional wisdom has it that little radiation below 300 nm reaches the earth surface, but in a joint meeting with module producers and SERI, it was indicated that there can be bursts of sunlight penetrating the atmosphere having wavelengths of 220 nm.[1] Of course, the "white" glass superstrate will filter out most of the radiation below approximately 280 to 285 nm.

Finally, H.W. Zussman claims that while the solar spectrum does not extend below 285 nm at sea level, radiation between 290 and 300 nm routinely falls on the earth's surface, and while relatively small in intensity, this band can do significant damage to resins sensitive to these wavelengths.[2]

Low ambient temperature: When minimodules (edges unsealed) were continuously exposed to RS-4 sunlamps at Springborn Laboratories (nominal 1.4 UV suns) at 50°C (with a total acceleration factor estimated to be 16), there was no visible change in the encapsulant after 35,000 hours of exposure, equivalent to 27 years of solar UV.[3] It should be pointed out that the RS-4 radiation was directed through a pyrex filter, so all radiation below 275 to 280 nm was effectively eliminated.[4]

When Liang exposed EVA films (A9918) to a 450 watt medium pressure mercury lamp (6 to 10 suns; 295 - 380 nm) at 25°C, he found no significant change in molecular

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1 J. Galica, Internal Memorandum, Springborn Laboratories, Covering Meeting at SERI, Feb. 22, 1990, (Feb. 26, 1990).

2 H.W. Zussman, Ultraviolet Absorbers for Stabilization of Materials and Screening Purposes, Modern Plastics Encyclopedia, September 1959, 37, 1A, p 372.

3 J. H. Wohlgemuth and R. C. Petersen, Photovoltaic Performance and Reliability Workshop, October 25-26, 1990, Lakewood, CO, Laxmi Mrig, (1990), p. 247-258.

4 Pyrex brand filter panes #7740 typically will transmit 1% at 278 nm, 5% at 285 nm, and 50% at 306 nm. (as required for ASTM G23 "Operating Light-Exposure Apparatus (Carbon-Arc Type) With and Without Water for Exposure of Nonmetallic Materials").

weight nor percent methylene chloride extractables.[1] But when Pern and Czanderna exposed both Elvax 150 and EVA (presumably fully formulated A9918) to RS-4 at 46°C for 237 hours, they observed increased cross-linking, the evolution of acetic acid, but no yellowing.[2] Since this work was conducted with free-standing films, photobleaching of the polyenes may have been occurring.

Moderate ambient temperatures: When minimodules were exposed to 70°C temperature and natural sunlight (one sun at Enfield, CT using OPTAR racks, outdoor photothermal accelerated reactors) there was no visible change in the EVA encapsulant after 12,000 hours. At 90°C under the same conditions, the EVA showed "slight yellowing" after 12,000 hours, but not enough to degrade electrical performance.[3,4] When minimodules were exposed to 105°C and one-sun there was "moderate yellowing."

Pern and Czanderna report that when Elvax 150 and EVA (A9918) films were exposed to the radiation from three RS-4 sunlamps at 87°C, "a light yellow color develops." "With one RS-4 present, a yellow color is detected."[2]

So in conclusion, it appears that as with temperature, U.V. alone is not sufficient to induce significant degrees of yellowing/browning. However, when U.V. and temperature are combined, e.g. 85 to 90°C and above and one or more suns, and EVA is exposed for extended periods of time, discoloration can be expected.

2.2.3 Photobleaching of discolored EVA: As indicated above, when polyene-based color develops in EVA, these unsaturated groups in the polymer backbone are susceptible to further degradation by oxidation. This process appears to be enhanced by heat but more notably by U.V. radiation.

This photobleaching phenomenon was first reported in fielded modules at Carrisa Plains. Personnel there noted that browned modules, which had been taken out of service and had the glass over the cells cracked or broken in handling, gradually lost their brown color and regained optical clarity. Complete photobleaching reportedly took approximately a year.[5]

In 1983, Liang noted this photobleaching effect in the laboratory. According to Liang, photothermal degradation of A9918 EVA, "...initially causes yellowing, i.e., increase in absorption at 400 nm and a greater rate of increase at 360 nm. This increase in absorption then causes accelerated photolysis which in turn

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1 R. H. Liang, S. Chung, A. Clayton, S. Di Stefano, K. Oda and S. D. Hong et al., Photothermal degradation of ethylene/vinyl acetate copolymer, Polym. Sci. Technol, 20, 267-78 (1983).

2 F. J. Pern and A. W. Czanderna, AIP Conference Proceedings 268 Photovoltaic Advanced Research and Development Project, Rommel Noufi, (American Institute of Physics, New York, 1992), p. 445-451.

3 K. J. Lewis and C. A. Megerle, Encapsulant degradation in photovoltaic modules, ACS Symp. Ser, 220, 387-406 (1983).

4 J. H. Wohlgemuth and R. C. Petersen, Photovoltaic Performance and Reliability Workshop, October 25-26, 1990, Lakewood, CO, Laxmi Mrig, (1990), p. 247-258.

5 J. Schaefer, L. Schlueter, A. Rosenthal, H. Wenger and A. E. Luque, Electrical degradation of the Carrisa Plains power plant, E. C. Photovoltaic Sol. Energy Conf., Proc. Int. Conf., 10th, P1248-53, (1991).

leads to bleaching of these absorbing species. The result is attainment of a photostationary equilibrium in transmission at 400 nm."[1] We might add that this equilibrium can shift more towards color-producing conjugated unsaturation or more towards colorless, fully oxidized EVA depending on the relative presence or absence of oxygen.

Pern and Czanderna demonstrated the photobleaching of yellow-brown, field-discolored EVA by heating the material in air at 57°C for 120 to 150 hours. During this exposure, samples were subjected to radiation from either three RS-4 sunlamps, a 150-W Xenon light source, or a 150-W Xenon source that was focused and filtered to remove all radiation below 440 nm. In each case, the yellow color of the EVA as well as the absorbance decreased.[2]

2.2.4 Catalytic Effects of Acetic Acid: A principal by-product of the thermolysis or photothermolysis of EVA copolymer is acetic acid, as discussed in section 2.2.1 on page 6. Bubbles on the back side of discolored modules at Carrisa plains, "as well as those built by other manufacturers," suggests that EVA degradation results in evolution of a gaseous product.[3] Also, investigators who have dissected discolored modules from Carrisa Plains have noted the smell of acetic acid.[3]

However, it should be pointed out that in some cases Springborn has found that bubbles in the backing film of fielded modules were located between plies of the laminated backing material and were obviously caused by residual solvent or other components of the laminating adhesive.

What effect, if any, does this acetic acid have on the further degradation of EVA, especially if the acid is trapped between two relatively impermeable layers, such as glass superstrate and foil backing material?

Sultan and Sörvik report that the deacetylation rate of EVA copolymers increases with increasing vinyl acetate content, and they attribute this phenomenon to an increased amount of block sequences and "an enhanced acid catalytic effect."[4]

When Razuvaev et. al. conducted isothermal studies of a 33% vinyl acetate containing EVA copolymer at 260°C, they noted that the thermolysis was "strongly catalyzed by $SnCl_2$, HCl, and to some extent evolved HAc." They also observed that inhibitors of radical reactions did not affect the rate of deacetylation.[5]

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1 R. H. Liang, S. Chung, A. Clayton, S. Di Stefano, K. Oda and S. D. Hong et al., Photothermal degradation of ethylene/vinyl acetate copolymer, Polym. Sci. Technol, 20, 267-78 (1983).

2 F. J. Pern and A. W. Czanderna, AIP Conference Proceedings 268 Photovoltaic Advanced Research and Development Project, Rommel Noufi, (American Institute of Physics, New York, 1992), p. 445-451.

3 J. Schaefer, L. Schlueter, A. Rosenthal, H. Wenger and A. E. Luque, Electrical degradation of the Carrisa Plains power plant, E. C. Photovoltaic Sol. Energy Conf., Proc. Int. Conf., 10th, P1248-53, (1991).

4 B. A. Sultan and E. Sörvik, Thermal degradation of EVA (ethylene-vinyl acetate copolymer) and EBA (ethylene-butyl acrylate copolymer) - a comparison. II. Changes in Unsaturation and Side Group Structure., J. Appl. Polym. Sci, 43, 1748-59 (1991).

5 G. A. Razuvaev, B. B. Troitskii, L. V. Chochlova and Z. B. Bubova, Polymer Letters, 11, 512-523 (1973).

A major U.S. module manufacturer indicated that when it subjected the formulated EVA A9918 to RS-4 sunlamp at 90°C with the EVA sandwiched between two glass plates, discoloration of the EVA occurred in only five weeks. The trapped acetic acid evolved is thought to be "autocatalytic for decomposition."[1]

Pern and Czanderna subjected several different cured EVA encapsulation formulations, including A9918, 15295, 16718A, and 18170, to heat only - no U.V. Samples were placed in capped vials and heated at 87, 100, and 130°C for 240 hours. Half had acetic acid vapor introduced into the vials; the other half did not.[2] They report that greater yellowing occurred in the acid containing vials, and attribute this to "acetic-acid-catalyzed yellowing."[3]

Some investigators have noted corrosion of metallization and interconnects in degraded EVA-encapsulated modules from the field, and have speculated that the corrosion was created by acetic acid from the degraded EVA which lead to fill factor degradation in some modules. However, when Solarex immersed cells in 50% aqueous acetic acid in the lab for 5,390 hours, there was no loss in conductivity of the silver bus and no metal corrosion.[3]

In addition, Solarex exposed cells to acetic acid vapors by sealing them inside polyethylene bags which contained open beakers of 50% acetic acid. After 3,550 hours of exposure at room temperature, there was no evidence of corrosion of cell metallization, but the tin-lead solder did corrode.[4]

Solarex also pointed out that "none of the modules from the field, including Carrisa modules, show any visible corrosion of the front interconnects or solder joints." They concluded that "acetic acid corrosion does not appear to be the mechanism causing the fill factor degradation."[4]

2.2.5 Effects of Metal and Metal Oxide Interfaces: Over the years several investigators have noted browning of EVA over the contact grid lines of cells in flat plate modules.[3,4,4,5,6] This phenomenon has been distinguished from more

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1 R. A. White, Internal Memorandum, Springborn Laboratories, (August 8, 1991).

2 F. J. Pern and A. W. Czanderna, AIP Conference Proceedings 268 Photovoltaic Advanced Research and Development Project, Rommel Noufi, (American Institute of Physics, New York, 1992), p. 445-451.

3 J. H. Wohlgemuth and R. C. Petersen, Photovoltaic Performance and Reliability Workshop, September 16-18, 1992, Golden, CO, Laxmi Mrig, (1992), p. 313-326.

4 K. J. Lewis and C. A. Megerle, Encapsulant degradation in photovoltaic modules, ACS Symp. Ser, 220, 387-406 (1983).

5 C. A. Megerle and K. J. Lewis, Encapsulant degradation in photovoltaic modules, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.), 23, 250-1 (1982).

6 F. J. Pern and A. W. Czanderna, Solar Energy Materials and Solar Cells, Characterization of Ethylene Vinyl Acetate (EVA) encapsulant: Effects of Thermal Processing and Weathering Degradation on its Discoloration, (Elsevier Science Publishers, 1992).pp. 3-23.

general discoloration of EVA which appears to proceed from the glass/EVA interface inward. As one module manufacturer has pointed out, with grid-line browning, the grid lines appear dull and brownish while the areas over the ribbons, generally tin-plated copper, remain water-white and the ribbons appear shinny.

Also, grid-line browning is reported to take place at the metal/EVA interface and proceed outward. Solarex, for example, reported that when the EVA was stripped from the surface of a fielded module which had exhibited this grid-line browning, the yellow color remained on the silver metallization, and there was "no sign of this yellow in EVA."[1]

Megerle and Lewis reported that, "When browned EVA, protected by Tedlar, was peeled from the metallization of a cell in an oven aged module, the tear surface on the EVA film showed only a minor amount of oxidation, similar to that observed on EVA tear surfaces which had not been in contact with the metallization. Analysis of the corresponding metallization surface, on the other hand, showed that several hundred nanometers of heavily oxidized polymer remained behind on the metallization surface after the tear. This suggests that the oxidation of the polymer initiated at the interface between the metallization and the polymer, and a reaction front proceeded through the polymer as the catalyzed oxidation progressed. When the polymer was peeled from the cell, the tear occurred along this reaction front." [2]

Lewis and Megerle observed this grid line browning as early as 1983.[2,3] Since the grid-line metallization uses transition metal oxide-containing glass frit, as well as silver, they speculated that the EVA discoloration at the grid lines was being catalyzed by one or more of these materials.[2,3]

To confirm this hypothesis, Lewis and Megerle added 1 to 10% of each of various metal oxides to a lead borosilicate glass matrix, and encapsulated samples of these glasses in panels using EVA. When these test modules were oven aged and monitored for browning, it was observed that EVA over those glass samples containing vanadium oxide, antimony oxide, or a mixed copper/nickel oxide showed accelerated browning.[3]

It was also observed that "certain primers" had the ability to retard browning of the EVA when applied to "solar cell contacts" prior to encapsulation.[3]

Since that time, Pern and Czanderna have also studied the effect of metals on accelerated discoloration of EVA. They added silver, copper, lead, and tin to EVA formulations A9918 and 18170 via metal acetates, and then heated the specimens in an oven for 264 hours at 85°C. They reported, "EVA turned yellow-

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1 J. H. Wohlgemuth and R. C. Petersen, Photovoltaic Performance and Reliability Workshop, September 16-18, 1992, Golden, CO, Laxmi Mrig, (1992), p. 313-326.

2 C. A. Megerle and K. J. Lewis, Encapsulant degradation in photovoltaic modules, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.), 23, 250-1 (1982).

3 K. J. Lewis and C. A. Megerle, Encapsulant degradation in photovoltaic modules, ACS Symp. Ser, 220, 387-406 (1983).

brown in 24 h with Ag+, pale greenish yellow in 264 h with Cu++, and did not discolor with Pb and Sn ions."[1]

They concluded that EVA discoloration is catalyzed by these metals and in the following order of activity: Ag++ > Cu++ >> Sn 4+, Pb++.[1]

2.2.6 Effects on Crosslinking of EVA: In 1983, R.H. Liang et. al. subjected samples of EVA film, formulation A9918, to roughly 6 to 10 U.V. suns (295 to 380 nm) from a 450 watt medium pressure mercury lamp. At 85 and 105°C, Liang indicates that, "Apparently EVA undergoes chemical crosslinking when it is subjected to photothermal aging which result in a decrease in the proportion of the extractables and in apparent modulus, and an increase in the chemical crosslinking density." This is shown in the Table 1 below.[2]

Table 1 - Percentage of Extractable, Molecular Weight Distribution (Mw) of the Extract, and Crosslinking Density of EVA as a Function of Photothermal Aging

TEMPERATURE °C	TIME OF TEST (HOURS)	TEST CONDITIONS	% EXTRACTABLE	$\bar{M}_w$	CROSSLINKING DENSITY (mole/cm³)
CONTROL		AS RECEIVED	48	206,000	1.12×10^{-6}
85	800	OVEN	35	168,000	2.29×10^{-6}
		UV/AMBIENT AIR	33	118,000	4.32×10^{-6}
		UV/NO EDGE SEAL	29	75,000	7.80×10^{-6}
105	800	OVEN	37	174,000	1.33×10^{-6}
		UV/AMBIENT	33	91,000	5.86×10^{-6}
		UV/NO EDGE SEAL	34	44,000	10.10×10^{-6}

When Pern and Czanderna determined gel content, a measure of the degree of cross-linking, of cured but unaged strips of EVA by THF extraction, they reported values in the range of 68 to 71%.[3] This is in good agreement with the gel content recommended by Springborn, which is a minimum of 60% but preferably 80% or above. It should be noted that gel content is influenced significantly by the lamination and curing cycle used during module manufacture.

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1 F. J. Pern and A. W. Czanderna, AIP Conference Proceedings 268 Photovoltaic Advanced Research and Development Project, Rommel Noufi, (American Institute of Physics, New York, 1992), p. 445-451.

2 R. H. Liang, S. Chung, A. Clayton, S. Di Stefano, K. Oda and S. D. Hong et al., Photothermal degradation of ethylene/vinyl acetate copolymer, Polym. Sci. Technol, 20, 267-78 (1983).

3 F. J. Pern and A. W. Czanderna, Solar Energy Materials and Solar Cells, Characterization of Ethylene Vinyl Acetate (EVA) encapsulant: Effects of Thermal Processing and Weathering Degradation on its Discoloration, (Elsevier Science Publishers, 1992).pp. 3-23.

However, when Pern and Czanderna evaluated EVA over the cells of field-aged modules, they found a gel content of 85 to 88 percent "around the cell edges" and 90 to 92 percent in the yellowed region directly over the cells.[3] This suggests that a significant amount of crosslinking has taken place as a result of photooxidative degradation.

2.2.7 Effect on additive levels in EVA: When R.H. Liang et.al. subjected EVA films (A9918) to the U.V. of a 450 watt medium pressure mercury lamp (reportedly 6 to 10 U.V. suns) at room temperature they found an insignificant effect on additive levels.[1,2] Using high pressure liquid chromatography, they followed the effect of U.V. radiation on the phenylphosphite ester antioxidant (Naugard-P) and 2-hydroxy-4-n-octyl benzophenone U.V. absorber (Cyasorb UV531) levels. After 1400 hours of irradiation, the additive levels were essentially unchanged.[2] However, there was "efficient removal of residual curing agent" (Lupersol 101) after only about 60 hours of exposure.[2]

But at increased temperatures there was a significant change. At 70°C and with the same U.V. exposure, there was steady weight loss up to 0.5% after 500 hours, which the authors equate to 2 years of outdoor conditions. A 1% weight loss was observed after 800 hours at 80°C, and roughly 1.5% was lost with the sample open to the air after 800 hours at 105°C.[2]

While some of the weight loss is attributed to the formation of volatile photooxidative degradation products, such as acetic acid, Liang indicates that a portion of this weight change was due to loss of additives. Unfortunately, no further analytical work was done to quantify the loss of additives, either individually or collectively.

Using UV-visible spectroscopy, Pern and Czanderna investigated the residual Cyasorb UV531 levels in a number of "virgin cured EVA, aged but unexposed EVA (stored in dark for 6 years) and EVA degraded for various times in field-deployed PV modules." The result are shown in the following figure.[3]

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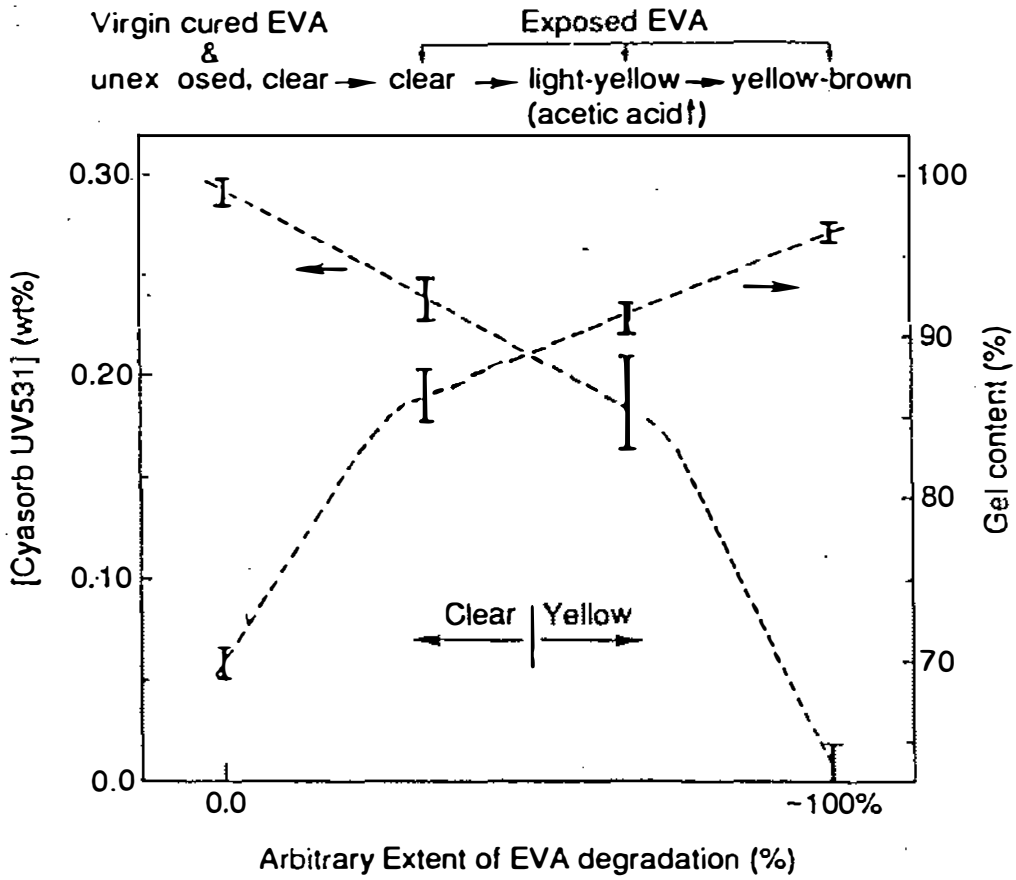
1 S. Di Stefano and A. Gupta, Photocatalytic degradation of a crosslinked ethylene-vinyl acetate (EVA) elastomer, Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem, 21, 178-9 (1980).

2 R. H. Liang, S. Chung, A. Clayton, S. Di Stefano, K. Oda and S. D. Hong et al., Photothermal degradation of ethylene/vinyl acetate copolymer, Polym. Sci. Technol, 20, 267-78 (1983).

3 F. J. Pern and A. W. Czanderna, Solar Energy Materials and Solar Cells, Characterization of Ethylene Vinyl Acetate (EVA) encapsulant: Effects of Thermal Processing and Weathering Degradation on its Discoloration, (Elsevier Science Publishers, 1992).pp. 3-23.


Virgin cured EVA
&
unex osed, clear
Exposed EVA
clear
light-yellow
(acetic acid↑)
yellow-brown
[Cyasorb UV531] (wt%)
0.30
0.20
0.10
0.0
100
90
80
70
Gel content (%)
Clear
Yellow
0.0
~100%
Arbitrary Extent of EVA degradation (%)

The Cyasorb UV531 concentration values range from 0.3% (original concentration) for virgin EVA, through 0.18 to 0.22% for light yellow exposed encapsulant, to 0 to 0.02% for browned material. The Cyasorb concentration of the 6-year aged but unexposed sample was essentially unchanged.[1]

When Pern and Czanderna exposed cured EVA film to DSET 1500W Xenon light filtered by a plate of glass, they reported roughly a 10% loss in Cyasorb UV531 concentration after 900 hours. Temperature was not indicated, but is assumed to have been 60°C.[2]

Thermal loss of Cyasorb at 57 to 60°C was said to be "insignificant."[2]

2.2.8 Probable Mechanisms: Acetic acid is the principal product of decomposition when EVA copolymer is heated at elevated temperatures.[3,4,5,6] Lesser quantities of chain fragments as well as ketene, carbon monoxide, carbon dioxide, and water have also been noted. The latter products are thought to be formed from further thermal decomposition of the evolved acetic acid.[3]

Photothermolysis is thought to proceed in a similar manner. Andrei and Hogea have proposed a mechanism that is in agreement with the work of several other investigators. This mechanism comprises a transition stage, with the formation of a six membered ring, leading to the formation of double bonds and evolution of acetic acid.[7,8,9]

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1 F. J. Pern and A. W. Czanderna, Solar Energy Materials and Solar Cells, Characterization of Ethylene Vinyl Acetate (EVA) encapsulant: Effects of Thermal Processing and Weathering Degradation on its Discoloration, (Elsevier Science Publishers, 1992).pp. 3-23.

2 F. J. Pern, Photovoltaic Performance and Reliability Workshop, September 16-18, 1992, Golden, CO, Laxmi Mrig, (1992), p. 327-344.

3 B. A. Sultan and E. Sörvik, Thermal degradation of EVA (ethylene-vinyl acetate copolymer) and EBA (ethylene-butyl acrylate copolymer) - a comparison. I. Volatile decomposition products, J. Appl. Polym. Sci, 43, 1737-45 (1991).

4 G. A. Razuvaev, B. B. Troitskii, L. V. Chochlova and Z. B. Bubova, Polymer Letters, 11, 512-523 (1973).

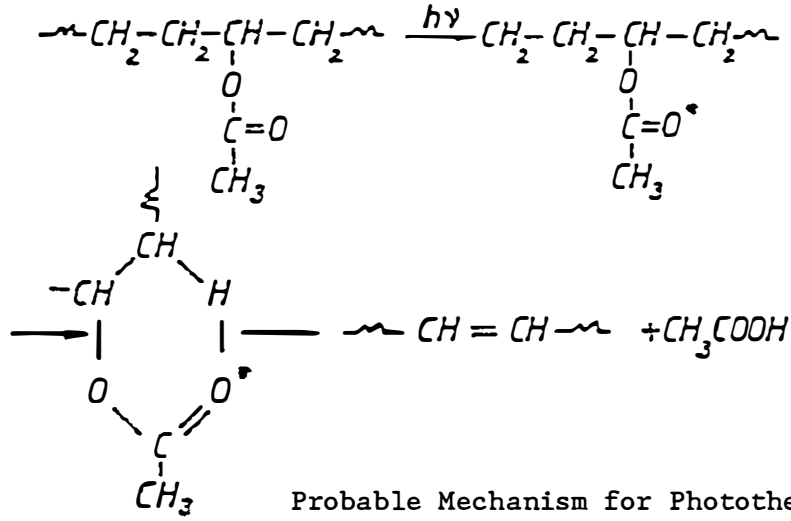
5 P. Bataille and B. T. Van, Journal of Thermal Anal., 8, 141-153 (1975).

6 I. K. Varma and R. K. Sadhir, Angew. Makrom. Chem., 40, 1-10, 11-21 (1975).

7 C. H. Andrei, I. Hogea, and V. I. Dobrescu, Photodegradation and photostabilization of the ethylene-vinyl acetate copolymers. I. Aspects of the mechanism of photodegradation reactions, Rev. Roum. Chim, 30, 865-73 (1985).

8 D. H. Grant and M. Grassie, Trans. Faraday Soc., 56, 445 (1960).

9 G. Geuskans, M. Borsusi and C. David, Europ. Polym. J., 8, 883 (1972).



Probable Mechanism for Photothermolysis

Since EVA copolymers are thought to contain small quantities of vinyl acetate homopolymer blocks, photolysis of the acetate groups followed by formation of polyene or conjugated unsaturated groups results in the development of a yellow to brown color. With a vinyl acetate group in every repeating unit of the block - that is every other carbon in the chain - photolysis results in sequences of alternating double and single bonds in the chain. Such conjugated double bonds are known to develop color, with degraded polyvinyl chloride being a notable example.[1]

The presence of vinyl acetate blocks is supported by U.V. spectroscopy work by Gardner and McNeill.[2,3] They report that an EVA copolymer with 12% vinyl acetate had 18.6% of its vinyl acetate groups in blocks of two and 3.6% in triads or longer sequences. We would expect that Elvax 150, with its comparative high 33% vinyl acetate content, would tend to have even greater proportions of the vinyl acetate groups occurring in triads or longer sequences.

Of course, these double bonds within the chains then are susceptible to further photooxidative degradation leading to chain scissioning and crosslinking by mechanisms that are well known for polyolefins.[1]

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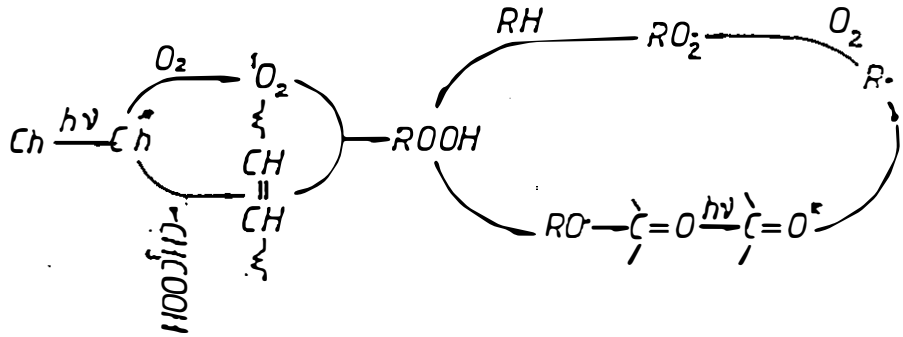
1 Encyclopedia of Polymer Science and Engineering, (Wiley-Interscience, New York, 1988).pp. 145-154.

2 B. A. Sultan and E. Sörvik, Thermal degradation of EVA (ethylene-vinyl acetate copolymer) and EBA (ethylene-butyl acrylate copolymer) - a comparison. I. Volatile decomposition products, J. Appl. Polym. Sci, 43, 1737-45 (1991).

3 D. C. Gardner and I. C. McNeill, J. Therm. Anal., 1, 300-407 (1969).



Ch - chromophore

Oxidation of Chromophores

2.3 Alternative Low Cost Encapsulation Materials

During the original work performed by Springborn Laboratories, Inc. under contract[1] to JPL, several alterative materials were investigated as encapsulants for photovoltaic cells. The initial screening criteria for the ideal encapsulation material included the characteristics presented in Table 2. The fabrication processes for the specific materials investigated in this work were either liquid casting or vacuum lamination.

A survey of materials was conducted during this work, and the findings were organized by price category. The polymers identified included polyvinyl chloride (PVC) homopolymers and copolymers, polystyrene, polyolefin homopolymer and copolymers, polyesters, polyvinyl alcohol, ionomers, acrylics, polyamides, cellulosics, polyurethanes, and silicones, among others. From this survey, the possible candidates were further reduced, based upon optical transparency, modulus, processability, and material cost. The final candidates selected for further development in the JPL program included two types of liquid casting resins, polymerizable butyl acrylate syrups and aliphatic urethanes, and two lamination polymers, ethylene vinyl acetate copolymer (EVA) and ethylene methyl acrylate copolymer.

The main purpose of the development of the liquid systems was to offer module manufacturers the flexibility to pursue fabrication concepts other than vacuum lamination. A final stabilized butyl acrylate system was formulated to produce a transparent low modulus rubber which was found suitable as a pottant material. However, major objections to the use of this material were the pungent odor of the monomeric butyl acrylate which requires good ventilation when handling, and the high exotherm which results from the high heat of polymerization during cure.

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[1] Willis, P.W., Investigation of Test Methods, Material Properties, and Processes for Solar Cell Encapsulants, Jet Propulsion Laboratory, JPL Contract 95427, Final Report, August 1986.

Table 2 - Encapsulant Material Specifications[a]

1.	Glass transition temperature (Tg)	<-40°C
2.	Total hemispherical light transmission through a 20 mil thick film integrated over the wavelength range from 0.4 μm to 1.1. μm	> 90% of incident
3.	Hydrolysis	None at 80°C, 100% RH
4.	Resistance to thermal oxidation	Stable up to 85°C
5.	Mechanical creep	None at 90°C
6.	Tensile modulus as measured by initial slope of stress-strain curve	< 3000 psi at 25°
7.	Fabrication temperature	<170°C for either lamination or liquid pottant systems
8.	Fabrication pressure for lamination pottants	≤ 1 atm
9.	Chemical inertness	No reaction with embedded copper coupons at 90°C
10.	UV absorption degradation	None at wavelength >0.35μm
11.	Hazing or clouding	None at 80°C, 100% RH
12.	Minimum thickness on either side of solar cells in fabricated modules	6 mils
13.	Odor, human hazards (toxicity)	None
14.	Dielectric strength	Sufficient to electrically isolate the cells and interconnects
15.	Process compatibility	Compatible with automated cell handling and encapsulation equipment
16.	Cost	As low as possible

(a) Willis, P.W., Investigation of Test Methods, Material Properties, and Processes for Solar Cell Encapsulants, Jet Propulsion Laboratory, JPL Contract 95427, Final Report, August 1986.

A two part aliphatic polyurethane system was also developed with the assistance of Development Associates, Inc., a supplier of liquid urethane systems. The water white developmental material demonstrated resistance to UV degradation in the laboratory. Inadequacies with this system were primarily due to poor bond strengths to substrates other than glass and the limited pot life of the mixed two part system, i.e. 15 minutes. Primers from the manufacturer for improved bond strengths were available, but this system was not pursued to commercial status during this program.

Of prime choice in the JPL-funded development work were the lamination systems based upon Elvax 150 (Dupont) EVA having a 33% vinyl acetate content and 43 gm/10 min melt index. This resin was formulated to be cured in place during module lamination and further formulated for outdoor use. The current commercially available lamination encapsulants sold by Springborn Laboratories, Inc., and others, are based upon this technology.The second lamination formulation was based upon ethylene methyl acrylate copolymers from Chevron Chemical Co. (formerly Gulf Oil Chemicals Co.). This system was not commercialized in lieu of the satisfactory laboratory and field results achieved with EVA system as the primary encapsulant material. However, from the laboratory work conducted with the EMA material, it appears that the EMA systems process similarly to the EVA. Furthermore, the EMA may be found to demonstrate comparable or improved final product properties when compared with the Elvax 150 encapsulant, e.g. higher thermal stability and creep resistance at lower gel contents.

Alternative resin system(s) with equivalent properties, but better overall outdoor stability may be one possible solution to eliminate the module discoloration phenomena which occurs with the EVA encapsulant. For example, studies have shown that ethylene n-butyl acrylate (EBA) copolymer is more thermally stable than EVA[1]. In this work, significant levels of decomposition product in the form of acetic acid were detected at the pyrolysis temperature of 150°C whereas the EBA was found to produce small amounts of butene, the main degradation product, after 30 minutes at 280°C.

Since the completion of the development work with JPL, several new grades of ethylene copolymers have become commercially available. These new resins along with the EMA formulations developed but not fully tested during the JPL program are of potential interest as alternative encapsulant materials. It is anticipated that the alternative materials investigated will be those which process using similar lamination techniques to the currently used EVA encapsulant system. Atochem, for example, produces a grade of EBA which has a 35% comonomer content and 40 gm/10 min melt index.

Prime candidate material types include:

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[1] Sultan, Bernt-Åake; Sörvik, Erling (Dep. Polym. Technol. Chalmers Univ. Technol. S-412 96 Göteborg Swed). Thermal degradation of EVA (ethylene-vinyl acetate copolymer) and EBA (ethylene-butyl acrylate copolymer) - a comparison. I. Volatile Decomposition Products. J. Appl. Polym. Sci; 1991; 43: 1737-45.

* Ethylene n-Butyl Acrylate Copolymer (Quantum, Atochem)

* Ethylene Methyl Acrylate Copolymer (Exxon, Chevron, Atochem)

* Ethylene/Ethyl Acrylate Copolymer (Custom made - Atochem)

Other possible materials to investigate include:

* EVA Maleic (acid or anhydride) Terpolymer; Carboxylated EVA (Dupont Bynel)

* Ionomers (Dupont Surlyn, Allied)

* Ethylene/Methacrylic Acid Copolymer (Dupont Nucrel)

Specific grades of commercially available alternative copolymers will be identified, and the basic properties summarized in Task 4 of the current NREL program. This information will be procured by contacting the above manufacturers directly and searching the "materials" computer databases such as Plaspec and Materials Selector. From this tabulation, samples of the most promising grades of materials will be procured. Light transmission spectra will be measured on compression molded films and bulk costs on each investigated. Further development work will continue on those systems whose optical clarity, properties, and processing characteristics are similar to those of the commercial EVA encapsulant. Of course, the alternative candidate materials will have to be fully screened to identify any other potential problems associated with these materials. All evaluations will be compared to the behavior of the Elvax 150 EVA based encapsulant currently used in the PV modules.

This work is to be carried out concurrently with Task 4 "Enhance EVA Formulation". It is understood that any new polymer system will require extensive testing to prove its performance in PV applications (Tasks 7,8, and 9).

2.4 Accelerated U.V. Aging Methods

An investigation was undertaken to compare and evaluate the various artificial UV aging systems available for aging EVA samples with the ultimate goal of selecting the most suitable aging apparatus for future work on this program. One objective of the aging work is to reproduce the yellow/brown color change of the EVA encapsulant as seen in the field, but in a much shorter time frame. Furthermore, it is also our concern to choose a method that closely simulates the spectral output of sunlight in order to reproduce "realistic" degradation processes.

Manufacturers of commercially available UV weathering equipment, Atlas Electric Devices Co., Heraeus DSET Laboratories, Inc., and Q-Panel, were contacted for information and equipment details. In addition, telephone calls were placed to bulb manufacturers including GE, Sylvania, Hanovia, American Ultraviolet Co., Superior Quartz, Jelight Company, Ultraviolet Resources international, Apollo Lighting, and North American Philips Lighting Corporation in search of commercially available bulbs that emit UV light in both the UVB (280 - 320 nm) and UVA (320 - 400 nm) ranges.

Information gathered on the light sources in general and equipment/bulbs in specific is highlighted below:

XENON ARC SYSTEMS

* The spectral irradiance of the filtered (borosilicate/borosilicate or quart/borosilicate) Xenon lamp in the UV - visible range most closely resembles the spectral output of natural sunlight of any of the systems investigated, and includes the low (280 - 300 nm) wavelengths of interest.

* The Xenon lamp spectra does not contain large "spikes" as do spectra of other sources, i.e. RS-4 bulbs, Sunshine Carbon Arc.

* Atlas Electric and DSET Heraeus both make several models of Xenon weathering equipment with controlled irradiance for improved reliability of weathering results. The equipment identified includes:

  Xenon Arc Weather-O-Meters/Fad-O-Meters
  - Atlas C-series: Ci3000,Ci35, Ci65
  - Atlas SunChex (benchtop model)
  - DSET Xenotest CPS 1200
  - DSET Suntest CPS (benchtop model)

CARBON ARC SYSTEMS

* The spectral output of the Sunshine Carbon ARC has extremely large spikes in the 350 to 450 nm range which are not found in natural sunlight. This alone makes this system suspect for unrealistic weathering findings/degradation when compared to natural outdoor exposure.

* The "testing community" is moving away from Carbon Arc to the preferred Xenon Arc accelerated test methods.

* This light source was not considered further as an option for UV aging in lieu of the alternative, more promising light sources, e.g. Xenon.

FLUORESCENT UV MERCURY BULBS

* American Ultraviolet has 40 watt Westinghouse fluorescent sunlamp bulbs which can be used in a standard 4-bulb fluorescent light fixture. It would be necessary to operate one UVB and one UVA fluorescent together in order to properly simulate the significant UV range. The problem with this set-up would be that in order to get a uniform mixture of both UVB and UVA light, the test specimens would have to be at least 12 inches away. Considering that the total wattage of the bulb system would be 160 watts, the testing would take a long time. Ultraviolet Resources International has similar UVB and UVA fluorescent bulbs.

* The UVA bulbs do not emit down below 295 nm whereas the UVB bulbs emit much lower (beginning around 275nm). It is speculated that the primary wavelength range responsible for causing EVA degradation lies somewhere

between 285 and 295 nm. However, it would not be wise to assume that other higher wavelengths do not solely or synergistically contribute to the browning. Therefore, such bulbs as the UVA or UVB alone are not the best choice for this investigation unless, perhaps, a combination of bulbs in a single apparatus could be used.

* Both Atlas (UVCON) and Q-Panel (Q-U-V) sell weathering cabinets which use fluorescent UVA and UVB bulbs. As the names state, these low wattage bulbs emit most all of their energy in the UV range of the spectrum. However, in both weathering cabinets, only one type of bulb can be used at a time - either UVA or UVB.

  At present, use of combined bulbs does not appear to be a commercially available option.

MERCURY VAPOR AND SUNTANNING BULBS

* One practice for artificial UV weathering in the past was to expose plastic samples to a Mercury Arc lamp (discontinued ASTM D795, Exposure of Plastics to S-1 Mercury Arc Lamp). The S-1 lamp (400 W) and the more recent RS-4 (100 W) lamp were made by GE. Springborn Laboratories, Inc. has several RS-4 test chambers made by Test Lab Apparatus, Inc. which were used in numerous aging studies in the past, including the JPL-funded solar encapsulant work. However, ASTM D795 was discontinued some time in the early 1980's and the production of RS-4 bulbs was recently discontinued by GE. Therefore, the search for alternative sources of Mercury Vapor and Suntanning bulbs were investigated as one possible aging scheme for this program.

* GE, Superior Quartz, American Ultraviolet, and North American Philips Lighting Corp. specialize in medium pressure mercury bulbs. Sylvania manufactures mercury high intensity discharge lamps and Jelight Company specializes in low pressure mercury bulbs. GE and Sylvania have discontinued production of the RS type suntanning bulbs. The RS suntanning bulbs, formerly made by GE, were used for accelerated UV aging of plastics. North American Philips imports a metal halide bulb.

  Sylvania makes 400 watt high intensity discharge mercury lamps. These lamps have a glass outer tube which cuts off all wavelengths below 300 nm. The principal wavelengths generated by these bulbs are in the visible spectrum, however there are ultraviolet wavelengths generated at 334.2 nm and 365 nm.

  GE makes a series short arc mercury bulb, designated HBO series, which has a peak wavelength at 360 nm and cuts off at 270 nm. This series bulb is supplied at 50, 200, and 500 watts and requires a special power supply to operate.

  American Ultraviolet has a medium pressure mercury bulb that appears to be similar to the GE HBO series. The Portacure 1000 energy spectral distribution emits approximately 15 relative units of energy in the 280 -

300 nm range and approximately 100 relative units at 380 nm. This bulb requires a special power supply.

Superior Quartz is a specialty bulb manufacturer specializing in custom medium pressure mercury bulbs. It is possible that they could custom manufacture the RS-4 bulb, but they generally do not manufacture "R40"-shaped bulbs.

Jelight Company manufactures low pressure mercury vapor lamps. The low pressure mercury bulbs generate most of their energy at 250 nm or below and comparatively little at 282, 302, 313, 365, 404, 436, and 546 nm.

North American Philips has a 400 watt metal halide bulb that emits light from 275 nm to 380 nm and appears to have a more uniform spectral distribution than the discontinued RS-4 bulb. The HPA400 metal halide bulb is approximately 4.2" x 0.7" and has a special ballast that must be used. One possible drawback to this bulb is its 350°C temperature.

* Mercury vapor and/or suntanning bulbs emit UV light. However, the spectral emission is considered to be "spiky".

* Many commercially available bulbs have a filter (the outer glass itself) which may filter out the harmful UVB wavelengths which are of interest in our work.

* There are no commercial aging devices employing these bulbs. We would need to purchase a ballast and to design chambers in which to run our tests. Since we have no data on the ability of a home made "box" to degrade the EVA, it would not be prudent to rely solely on this method. Reliability and reproducibility of a custom made system is questionable.

Conclusions

* The fluorescent UV bulbs are lower wattage, less expensive, and do not require a separate filter - the glass on the bulb itself is the filter. However, their spectral output is limited to a small portion of the UV range and may yield unrealistic results in exposed samples.

* Since there are no commercial aging devices employing Mercury vapor and/or suntanning bulbs, we would need to purchase a ballast and to design chambers in which to run our tests. Since we have no data on the ability of a home made "box" to degrade the EVA, it would not be prudent to rely solely on this method. Concerns of reliability and reproducibility once again come into play. Perhaps this less expensive system could be used as a secondary screening tool, keeping in mind its limitations.

* Since the objective of our work is to find a suitable accelerated aging scheme which causes the EVA to discolor and simulates outdoor conditions, the best lamp source for our purpose is the Xenon lamp. There has been extensive research on Xenon weathering systems, and there is equipment available which has been optimally refined to adjust for variations in irradiance and other critical factors.

* If the encapsulant program progresses to where we are concerned about water/moisture absorption, we would have the added ability to run humidity in the C-series and Xenotest Weather-Ometers to simulate hot/humid regions and other combinations.

* The benchtop Xenon models have limitations of size and flexibility. Of the two reviewed, the Atlas Sunchex and DSET Suntest, the latter appears to be a much better quality piece of equipment with controlled irradiance.

* Of the Xenon systems, the favored full-size units are the Atlas Ci35 and the DSET Xenotest 1200 CPS.

The various commercially available accelerated UV aging cabinets are compared in detail in Appendix 2 on page 47

3.0 RESULTS OF THE SURVEY ON THE DISCOLORATION OF EVA ENCAPSULANTS FOR PHOTOVOLTAIC MODULES

3.1 Objective

The objective of this survey was to investigate case histories of fielded EVA encapsulated photovoltaic modules in an effort to make correlations between the discoloration of the encapsulant and various material, fabrication, placement, and exposure parameters.

3.2 Scope

Survey participants were selected from the industry based on a minimum 4 year history of fielded, EVA- encapsulated, photovoltaic modules. Information was obtained from both module manufacturers and module test facilities. The participants included: Advanced Photovoltaic Systems, Inc., Arizona Public Utility, ENDECON, Florida Solar Energy Center, Global Photovoltaic Specialists, Inc., PG&E, Photocomm, Inc., Sandia, Siemens Solar, SMUD, Solar Web, Inc., Solarex Corp., Solec International, Inc., Southwest Regional Experimental Station (SWRES), Texas Instruments, United Solar Systems Corp., US Navy China Lake, and Utility Power Group, Inc.

The survey was introduced by a brief telephone interview of potential participants. This interview established a suitable contact and determined whether there was a history of EVA encapsulant use. Once a reasonable history was discovered, a written questionnaire (refer to Appendix 3) was sent to key individuals. The questionnaire asked detailed questions about module construction, processing, field placement, and operation. As necessary, the written survey was followed by a telephone conversation or meeting in which the survey answers were discussed in more depth. Supplementary information was also obtained from individuals active in the photovoltaic community. Site visits were arranged in order to obtain comparative data from manufacturer/to/manufacturer and test-site/to/test-site.

3.3 Results

A brief outline of the survey results is presented in Table 3. The survey uncovered incidences of EVA encapsulant discoloration occurring after exposure periods ranging from 4 years to 10 years. It should be stressed that the dates reported for discoloration of the EVA do <u>not</u> necessarily reflect discoloration at its inception. The reported dates, rather, describe the point at which the discoloration was first realized. Very often the discoloration was not noticed until its advanced stages. The rate of discoloration for most modules could not be determined definitively because of poor documentation and a lack of quantitative browning measurements.

It should also be noted that the information provided by the module manufacturer and the testing facility sometimes contradicted. The contradictions were due, in part, to the fact that the testing facilities often did not report key observations to the manufacturer. For example, Table 3 information provided by Manufacturer "E" reported a ten year history of module operation in the Mohavi

Table 3 - The History of Fielded, EVA- Encapsulated PV Modules

Location	Mfg	EVA Source	Formulation	Color	Approx. Max.[a] Temperature	Observation Time	Construction[b]	Elevation
SWRES Las Cruces, NM	A	-	A9918	brown	-	3-4 years	-	1198 m
Hawaii	B	a	A9918P	clear	-	4 years	B	-
Detroit	B	a	A9918P	clear	-	4 years	B	191 m
California	B	a	A9918P	clear	-	4 years	B	-
San Ramon, CA	C	b	other	brown	64°C[c]	4-5 years	B	8 m
Davis, CA	D	c	A9918	brown[d]	-	4-5 years	D	8 m
China Lake, CA	A	-	A9918	discolored	-	5 years	A?	-
China Lake, CA	E	a	A9918	brown	-	5 years	-	681 m
Sells, AZ	C	b	other	80% brown	-	6-8 years	B	-
City of Austin, TX	C	b	other	slight brown	60-71°C[3],[e]	7 years	B	250 m
SMUD, CA	D	c	A9918	light amber	65°C[f]	7 years	B	8 m
Caples Lake, CA	C	b	other	clear	52°C[g]	> 7 years	B	2400 m
Carrisa Plains, CA	C	b	other	slight brown	-	8 years	B,D	640 m
John Long, Phoenix, AZ	C	b	other	moderate	77°C[3]	8 years	B	340 m
Sandia, Albuquerque, NM	D	d	A9918	light amber	-	8 years	B	1619 m
SMUD, CA	C	b	other	slight brown	77°C[3]	9 years	B	10 m
San Ramon, CA	F	c	A9918P	clear	-	9-10 years	B	8 m
Carrisa Plains, CA[h]	C	b	other	dark brown	80-90°C[8]	10 years	B,D	640 m
Costa Rica	G	-	A9918	clear	-	10 years	B,C	-
Mohavi Desert	E	a	A9918	clear	-	10 years	B	-
"Around the World"	E	a	A9918	clear	-	10 years	B	-
Cape Canaveral, FL	A	-	A9918	discolored	-	10 years	A	-
SWRES Las Cruces, NM	D	c	A9918	light amber	75°C[6]	10 years	B	1198 m

(a) Estimated, no "hard" data available, (summer) measurements taken mostly from back-side of module

(b) A- Glass/EVA/Cell/EVA/Foil, B- Glass/EVA/Cell/EVA/Film laminate, C- Tefzel/EVA/Cell/EVA/Film laminate, D- Bifacial

(c) Average ambient temperature plus 30°C

(d) Browning varied from one cell to another within the same module

(e) High and low mounted racks

(f) Manufacturer's data

(g) Estimated based on high wind velocity (ambient temperature plus 20°C)

(h) Modules operated at approximately 2 suns (mirror enhanced)

Desert without discoloration of the EVA. At the same time, there was a contradicting report of Manufacturer "E" browned modules after 5 years exposure at China Lake (in the Mohavi Desert).

In most cases, there was concrete information provided with respect to: EVA source, the formulation of the EVA encapsulants, and the construction design of the modules. The information provided on the discoloration of the modules, however, was often too subjective to enable a direct comparison from one testing facility to the next, and the onset of browning was generally not realized until it was quite advanced.

3.4 Overview of Results

a. The module manufacturers depend on the testing facilities for information that is pertinent to EVA discoloration. Typically, the module testing has not focused on EVA discoloration, and consequently there is limited documentation on the incidence of browning. Most of the manufacturers had never heard of EVA encapsulant browning until the test site sent them discolored modules.

b. In most cases, the exact time for EVA discoloration to develop is not known. Generally, discoloration was not documented until its advanced stages.

c. The survey contacts generally did not have exact data with respect to module operating temperatures and insolation. Generally, the maximum module operation temperatures were approximated as 30°C above ambient temperature.

d. Data collected from "project"-type modules generally was pertinent only to determining the overall module efficiency. Module operation temperature, circuitry flaws, module replacement, module rewiring, and array downtime were rarely documented.

e. There is no quantitative information on discoloration. A typical browning analysis is based on visual observation without color standards or quantitative measurements.

f. There have been no reported cases of EVA browning from Eastern and Central United States or Western Europe.

3.5 Correlations Between EVA Discoloration and Various Material, Fabrication, Placement, and Exposure Parameters

3.5.1. EVA Supplier

The EVA encapsulants that were reported during this survey were manufactured by Miles, Inc. Berlin, CT (formerly Mobay and Rowland), Richmond Technology, Inc. Redlands CA, and Springborn Laboratories, Inc Enfield CT. Discoloration was not limited to the EVA sheet stock of any one supplier.

It is possible that the formulation and process used to produce the EVA sheet stock had an effect on the discoloration of the fielded modules. It was impossible, however, to determine the effect of each manufacturer on the discoloration, since none of the module manufacturers used EVA from more than one supplier.

There appeared to be distinct differences in the discoloration rates of each photovoltaic manufacturer. It is possible that the EVA sheet stock supplier was a factor due to differences in formulation and processing parameters.

Formulation:

Virtually all of the fielded EVA encapsulants reported during this survey were Lupersol 101 cured formulations. There were two basic EVA formulation types represented in fielded modules; self-priming, and unprimed. All three of the compounders supplied self-priming sheet to the module manufacturing industry. Only two of the compounders, Miles and Springborn, supplied unprimed sheet stock.

EVA sheet from two of the manufacturers appeared to be identical in composition. The third manufacture, however, use a different ratio of ingredients than the other manufacturers.

It is possible that formulation composition had an effect on the rate and degree of discoloration of the EVA encapsulant materials. It should be noted, however, that there are examples of discolored modules containing each of the EVA compositions previously described.

Processing:

The processing parameters of each EVA sheet manufacturer, were not investigated as part of the survey. Likely each compounder processed the raw materials differently.

EVA sheet from each of the manufacturers was found to have discolored after field exposure of 4 to 10 years. It can therefore be concluded that the discoloration of the EVA encapsulant is not caused by any one formulation or film processing procedure. It is likely that the processing procedure for the EVA sheet-stock has an effect on the rate of discoloration in fielded photovoltaic modules since the EVA sheet-stock contains reactive ingredients.

A correlation between processing parameters and the discoloration of EVA encapsulants was impossible to make since the photovoltaic manufacturers generally used EVA encapsulants from only one supplier. The performance of the different EVA encapsulants could not be directly compared since there were other variables such as cell design, module manufacturing, and module operation, to consider when evaluating the encapsulants for discoloration.

3.5.2. Module Manufacturer

There were some definite correlations found between the rate of discoloration of the EVA encapsulant materials and the manufacturer of the modules. The Sacramento Municipal Utility District (SMUD), Pacific Gas and Electric (PG&E), and Southwest Regional Experimental Station (SWRES) facilities had representative modules from several manufacturers.

The reasons for the differences in module discoloration rate from one manufacturer to another manufacturer were difficult to ascertain based on the test facilities' field reports. Testing sites at SMUD and at PG&E provided information from multiple manufacturers. Modules at these testing facilities were fielded under identical conditions with respect to ambient environment, power load, and mount design. This would suggest that manufacturer dependent variables including raw materials, module fabrication processes, module design, and module operation have a significant effect on the rate of discoloration of the photovoltaic modules.

A third test site, SWRES, provided test reports for two different manufacturers. The operating conditions were similar for all the modules at this testing facility with the exception of the mounting design, and manufacturer-dependent variables. The modules having the least discoloration had been mounted on elevated racks which enabled them to operate at cooler temperatures than the more discolored modules that were mounted as part of an integral roof rack. Despite the differences in mounting, however, the relative rates of discoloration at SWRES correlated with the reports from the SMUD and PG&E facilities.

3.5.3. Module Construction

There were four basic module construction types reported during our survey: Glass/EVA/Cell/EVA/Foil, Glass/EVA/Cell/EVA/film laminate, Tefzel/EVA/Cell/EVA/-film laminate, and bifacial. Each manufacturer had its own proprietary silicon cell, circuitry, and engineering parameters.

The majority of the modules that were reportedly discolored were glass/EVA/Cell/EVA/film laminates since this was the most common construction. It was beyond the scope of the investigation to make correlations between the rate of discoloration and the module construction since there is little long term field data for the other three, less popular, construction designs.

There have been general observations by the photovoltaic industry that suggest that modules appear to discolor more quickly if the module has poor vapor permeability. Theoretically, the Tefzel construction should have better permeability than the glass/film laminate, and the glass/film laminate should have better permeability than the glass/foil laminate.

The permeability versus EVA discoloration theory appears to have been supported by data collected during the survey. There were several reports of accelerated discoloration over areas in the modules where non-permeable junction boxes or aluminum labels were adhered to the back-side of the modules.

3.5.4. Geographic Location and Climate

There appeared to be a strong relationship between geographic location and the incidence of EVA- encapsulant discoloration. There have been no reported cases of EVA discoloration from Eastern and Central United States or Western Europe while browning is reported in Southern and Western United States.

The annual average solar irradiance varies from region to region throughout the country.(Figure 1 - Average Daily Direct Normal Solar Radiation (MJ/m^2), page 31) Reports of browning in the Southern and Western regions of the country are not surprising when considering the actual solar insolation distribution. Based on published information[1], the southern and western regions of the United States have greater solar irradiance than the eastern or central regions. Arizona and New Mexico have approximately 26 MJ/m^2, California has approximately 20-24 MJ/m^2, Colorado has approximately 20 MJ/m^2 average irradiance, Texas has approximately 16-24 MJ/m^2, Florida, Illinois, and Minnesota have approximately 14 MJ/m^2 and the Northeast averages 10-12 MJ/m^2. These differences in irradiation from north to south, and east to west in the United States, likely results from differences in latitude, elevation, and the composition of the atmosphere/troposphere.

Photovoltaic modules that have been fielded in the northeast region of the United States, have approximately a ten year history without discoloration. Some modules fielded in California have discolored in as few as 4 years of fielded exposure. Differences in the performance of the EVA encapsulant materials between the Northeast and other parts of the United States appear to correlate with the direct normal solar radiation data. Overall, it was impossible to quantify the effect of normal solar radiation on the discoloration rate of the EVA encapsulants. The manufacturers generally reported when the EVA discoloration was first realized, rather than at its onset.

One major deficiency in the available solar radiation data available was the absence of measurements of the actual solar spectral emission at each test location. Direct normal solar radiation is a measure of the total solar radiation, but it does not indicate the energy irradiance for each spectral wavelength.

The ratio of short-wavelength ultraviolet to total radiation potentially is believed to be the same throughout the United States on a given day.[2] Regions of the United States that have higher solar insolation will, therefore, have proportionally greater amounts of UV. The proportion of short to long wavelength ultraviolet changes with season, local conditions and time of day. No data was reported on the exact composition of UV energy at each module site, however.

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1 Insolation Data Manual and Direct Normal Solar Radiation Data Manual, SERI/TP-220-3880 , July 1990.

2 R.W. Singleton and P.A.C. Cook, Textile Res. J. 39, 43-49 (1969)

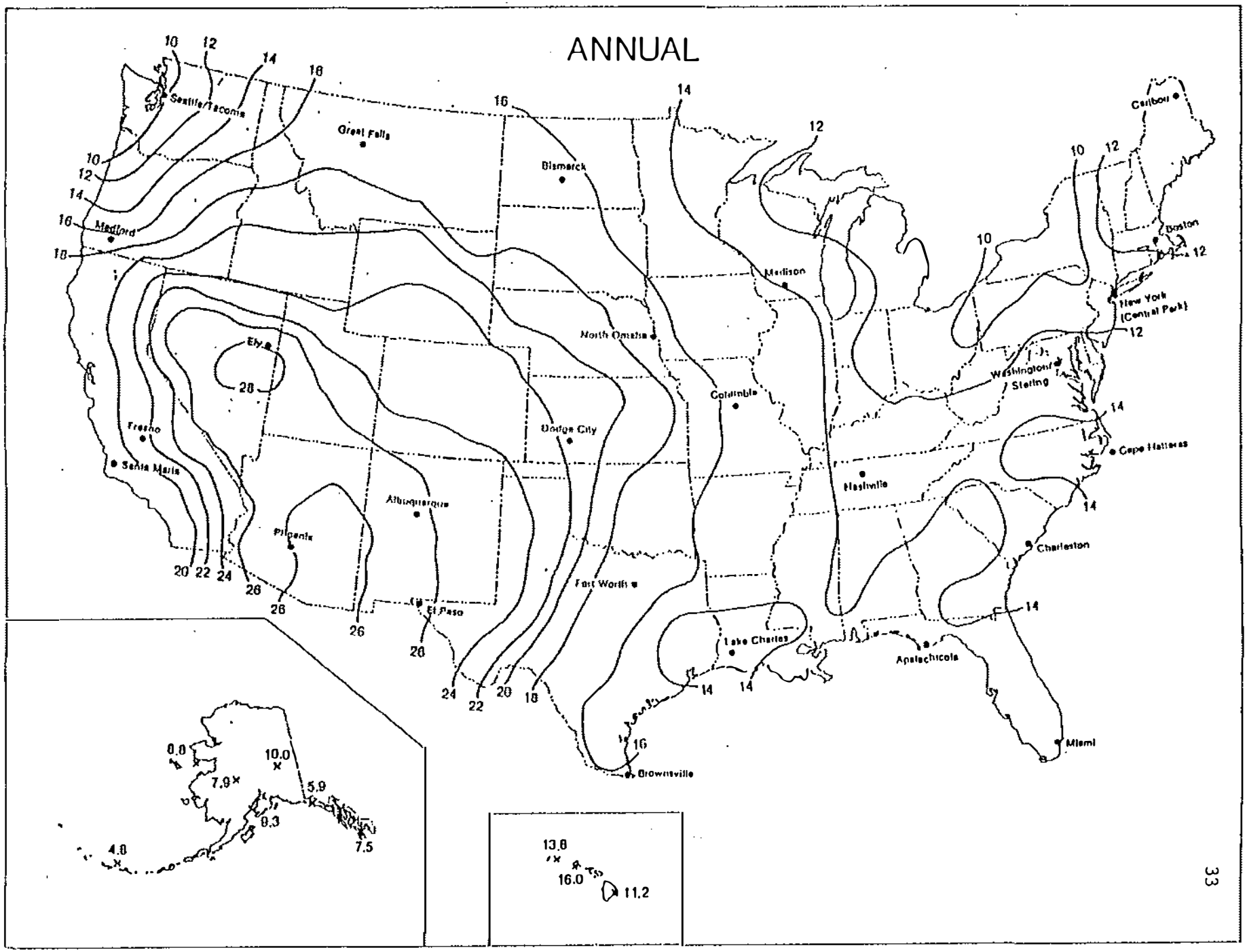
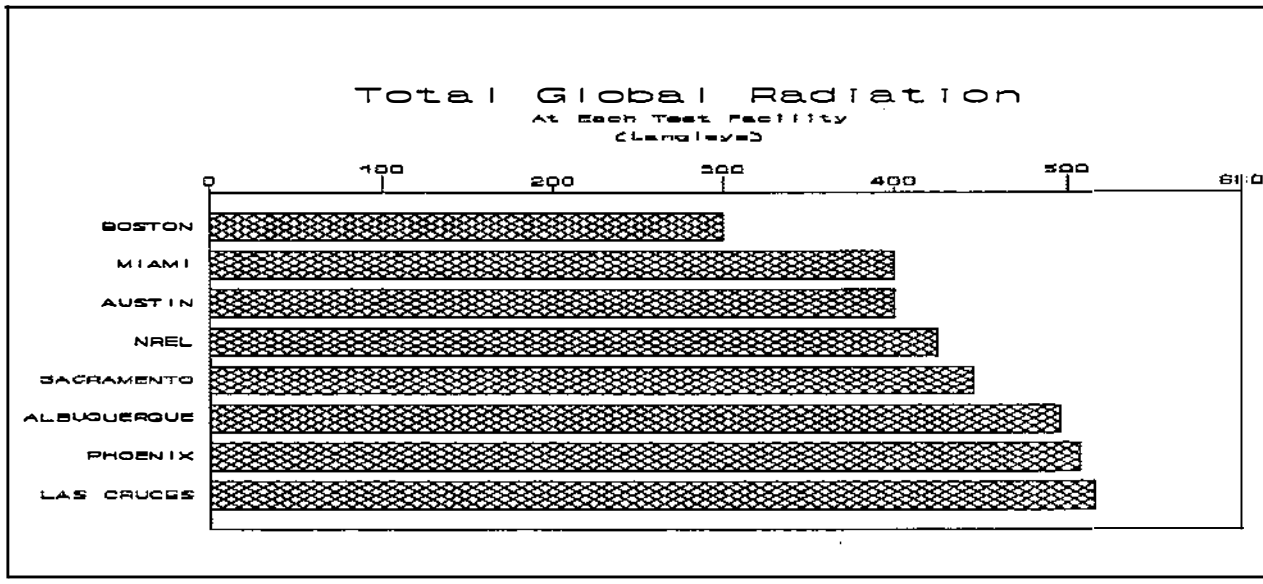

ANNUAL
Seattle/Tacoma
Great Falls
Bismarck
Medford
Ely
Fresno
Santa Maria
Phoenix
Albuquerque
El Paso
Dodge City
North Omaha
Madison
Columbia
Fort Worth
Nashville
Lake Charles
Brownsville
Apalachicola
Miami
Charleston
Cape Hatteras
Washington/Sterling
New York (Central Park)
Boston
Caribou
10
12
14
16
18
20
22
24
26
28
0.8
10.0
7.9
5.9
8.3
4.8
7.5
13.8
16.0
11.2

Figure 1

The solar insolation varies with latitude since the sunlight's angle of incidence that the sun shines on the earth changes with distance from the equator. The terrestrial solar irradiance is strongest at the equator where the sun has the most direct path to the earth's surface and, therefore, less air mass to filter out the sun's energy. At latitudes north and south of the equator, the sun hits the earth's surface at a lower angle of incidence and must penetrate through a larger volume of atmosphere in order the reach the earth's surface.

The composition of the atmosphere is very important in terms of the spectral composition of solar radiation that reaches the earth's surface. If one assumes that the stratosphere is fairly uniform above the entire United States, it would appear that variations in the troposphere might affect the overall solar radiation that reaches the earth at similar latitudes. Areas of the United States (West, Southwest) that are very dry with little precipitation, would then tend to get more solar irradiance than areas that are humid with high amounts of precipitation (East, Southeast).

Figure 2



Based on total global radiation measurements at each testing location (Figure 2 - Total Global Radiation at Each Test Facility), Southwest Regional Experimental Station (SWRES) at Las Cruces NM should have the most severe discoloration, followed by Phoenix, AZ; Albuquerque, NM; Sacramento, CA; NREL; Austin, TX; Miami, FL; and then Boston, MA. In actuality, however, the module manufacturer reported EVA encapsulant discoloration did not directly correlate with the total global radiation reported at each location. For example, there are reports of discolored EVA at Miami, FL and Austin after 7 years, while at NREL, where there is a higher amount of solar insolation, there are separate reports of no discoloration and slight discoloration after 10 years. Phoenix, AZ was reported to have moderately discolored EVA while Las Cruces, NM, with the same approximate total global radiation as Phoenix, reported much less discoloration.

While it does appear that total solar insolation correlates with the EVA discoloration rate, it does not singularly affect the rate of EVA discoloration.

3.5.5. Mounting Variables

Photovoltaics that were fielded at the same test location were not always fielded under identical conditions. Depending on the facility, module discoloration from competing manufacturers could not be directly compared due to variables in mounting.

Module Mount Angle

Depending on the mount angle, it is possible for the modules to receive different levels of solar radiation. An angle that is perpendicular or normal to the sun's radiation will have the maximum possible irradiance for that location. It has been reported that a mount angle of 10° less than the latitude will result in the maximum ultraviolet irradiance since this will ensure a nearly perpendicular presentation to the sun's radiation during the summer months when the ultraviolet content is the highest.[1] If ultraviolet exposure is indeed a contributor to EVA discoloration, the angle at which the module is mounted could have an accelerating effect. Manufacturers and test facilities failed to provide sufficient data on mounting angle to draw any conclusions, however.

Tracking Systems

Single axis and double axis tracking systems are often utilized to maximize the modules' irradiance exposure by maintaining an optimally direct angle of incidence with the sun as it moves across the horizon. The single axis tracking systems, used by two of the test sites reporting data, theoretically should increase the total irradiance exposure of the modules by one third[2]. It is, therefore, assumed that modules mounted on these systems are exposed to one third more ultraviolet light than modules mounted on stationary mounting systems and that the rate of EVA discoloration should also increase by one third.

The SMUD and Austin modules, mounted on single axis tracking systems appeared to have more pronounced browning than the total average global irradiance data would indicate. When the tracking system was considered (Figure 3 - Tracker Enhanced Global Radiation), modules at SMUD should have had, by far the greatest discoloration and modules at Austin should have been slightly more discolored than modules at Phoenix. The rate of discoloration of modules mounted on tracking systems does not appear to correlate proportionally with the one third increase in apparent solar irradiance, however.

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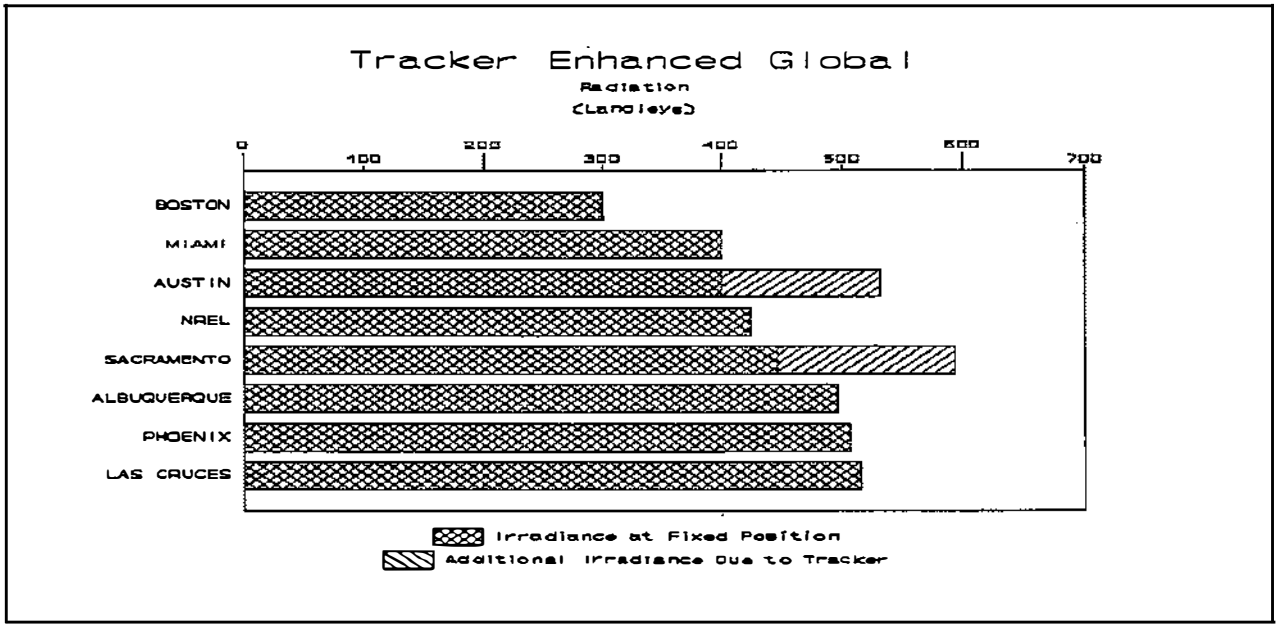
1 G.C. Newland, R.M. Schulken, Jr. and J.W. Tamblyn, Mater. Res. Stand. 3, 487-488 (1963)

2 J.E. Clarke, Encyclopedia of Polymer Science and Engineering, Volume 17 p. 796-824, John Wiley and Sons, inc. 1989

Figure 3



Module Mounting Systems

A second mounting variable that was considered during this survey was the module mounting system. Generally, modules were fielded using one of four basic mount designs; pole, rack, integral roof mount, standoff roof mount and direct roof mount. Modules fielded on integral and direct roof mounted systems tended to operate at higher temperatures than modules that were mounted on free standing racks or poles. The temperature differential between the free standing and the roof-mounted systems was most likely due to the lack of air circulation around the integral roof mounted racks and to the fact that the free standing racks were exposed to the cooling effects of the wind.

It was not possible to isolate the effects of the mounting design on the discoloration rate of the modules since there were no locations where similar modules were tested on different types of mounting structures. Similarly, each testing facility had different insolation and varying weather conditions which prevented a direct comparison of mounting design with the rate of discoloration. One of the testing sites had modules on both the rack and the integral roof mounted systems. The module operation from each type of rack was not quantified, however.

One example of the cooling potential of the mount design on the discoloration rate of the EVA encapsulant might be at the CALTRANS facility at the top of Donner Pass, Caples Lake, CA in the Sierra Nevadas. This rack-mounted array is elevated high off the ground so that the winter snow will not cover the modules, and is exposed to maximum wind speeds of 160 KM/h. This system has been in operation for 7 years without discoloring. The lack of discoloration at the CALTRANS facility might be puzzling if comparing the geographic location and solar insolation data. It is has been demonstrated in the laboratory, however,

that module operation temperature can accelerate EVA discoloration[1]. If the potential difference in the operation temperatures is considered, it is not surprising that the CALTRANS modules have not discolored.

In terms of the discoloration of EVA encapsulant materials, representative modules of all mount designs and mount-angles have discolored. It was beyond the scope of the survey to make inferences between the mounting design and the speed or quantity of the discoloration since there were no examples of similar modules that were mounted at the same testing facilities but at different angles of incidence or different mount types. Some of the module manufacturers considered the module installation in the field proprietary in terms of mount angle and tracker systems. Others suggested that modules fielded with 2 axis tracking systems were quicker to discolor than those fielded with fixed tilt systems. This observation on the rate of discoloration of modules on 2 axis tracking systems was unsupported by data that was collected during the survey and also by the literature[2] (see "Tracking Systems" p. 33 of this report).

3.5.6. Module Operation Temperature

The module operation temperatures reported for fielded photovoltaics appeared to be full of contradictions. The module manufacturers generally provided approximate temperature rather than actual data. Exact temperature data was generally not available since very few of the testing facilities monitored module operation temperatures over a period of time.

For lack of better data, most manufacturers supplied a 30°C correction factor for determining the module temperature based on the ambient temperature. There were poorly documented exceptions to the ambient plus 30°C temperature based on the prevailing winds and module mount design, however.

The 30°C correction factor appears to be supported by the reported data from research conducted under EPRI contract GS-6696[3] at arrays located at Sacramento Municipal Utility District (SMUD), and the City of Austin, Texas. Computer-acquired data detailed in the EPRI report indicates that the maximum temperature experienced by the modules during operation is 65-70°C. Generally, this appears to be approximately 30°C above the reported ambient temperature.

If the correction factor were applied to the ambient temperature data that was reported by one module manufacturer, modules operating at SMUD would have an approximate maximum operating temperature of 77°C. This was 7°C higher than the actual data that was continuously collected at the SMUD facility. It was not clear whether this information was contradictory to the EPRI study since the study did not indicate whether the data was based on an average of temperatures collected from modules of all three manufacturers, or whether the data reflected

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1 P.B. Willis, Investigation of Test Methods, Material Properties, and Processes for Solar Cell Encapsulants, 9th Ann. Rep. JPL Contract 954527, 1985 (Jet Propulsion Laboratory, Pasadena, CA).

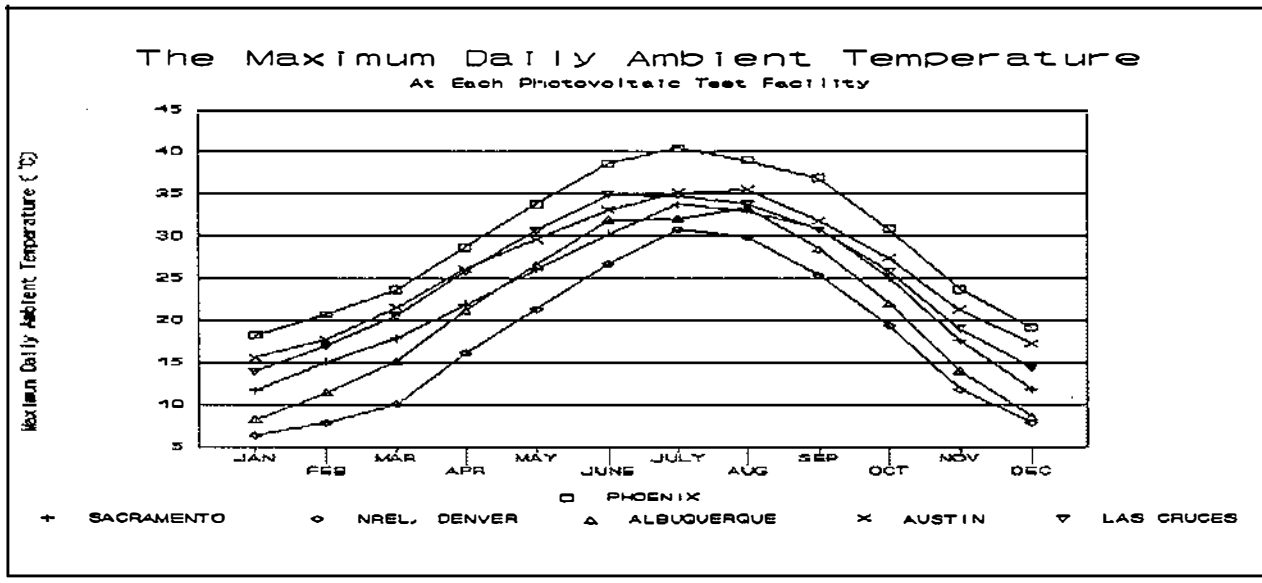
2 C.R. Caryl in W.E. Brown, ed., Testing of Polymers, Vol. 4, Wiley- Intersciences, New York, 1969, pp. 379-397

3 "Photovoltaic System Performance Assessment for 1988", Prepared by Southwest Technology Development Institute, Las Cruces, New Mexico. Final Report; project 1607-6.

only an example of one module/one manufacturer in the entire photovoltaic array. It is likely that the module operation temperatures vary depending on the individual manufacturer and the module design.

Due to the approximate nature of the module operation temperature data provided by the module manufacturers, the National Weather Service average maximum temperature data[1] was later used to more accurately correlate the module operation temperatures with EVA discoloration. Based on National Weather Service Station maximum average daily temperature data (Figure 4 - Maximum Daily Ambient Temperature at Each Photovoltaic Test Facility), modules in Phoenix, Az potentially operated at annual maximum temperatures greater than other test site locations.

Figure 4



The ambient temperature profiles for test sites located in Sacramento, CA; Albuquerque, NM; Austin, TX; and Las Cruces, NM[2] were similar. The average ambient temperature at NREL was much cooler than at the other Western test sites. The average Denver, CO temperature is approximately 10°C cooler than Phoenix, AZ.

When considering the ambient temperature data alone, one might predict that the John Long array in Phoenix, having a 41°C annual maximum ambient temperature, would have the most intense discoloration of all the fielded modules. The modules located at Austin, Sacramento, Albuquerque, and Las Cruces would be less discolored than modules in Phoenix, while modules located at NREL would have the least discoloration of all the testing facilities.

The degree of discoloration of EVA encapsulant materials appears to loosely correlate with the ambient temperature information from the National Weather Service. NREL has a ten year history without browning. Austin, Sacramento, and

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1 Insolation Data Manual and Direct Normal Solar Radiation Data Manual, SERI/TP-220-3880, July 1990

2 Based on National Weather Service Data for EL Paso,TX

Albuquerque have slight browning. Phoenix is reported to have moderate browning (Figure 5 - Comparison of Operation Temperature with Degree of Browning).

Figure 5

Location	Max. Daily T (°C)(July)	Approx. Module T(°C	Degree of Browning
Phoenix	41	71	moderate
Austin	35	65	moderate/slight
Las Cruces	35	65	slight
Sacramento	34	64	slight
Albuquerque	33	63	slight
Denver	31	61	no browning
Boston	27	57	no browning

Other arrays that appear to operate under cooler average maximum ambient temperatures are the CALTRANS array on the top of Donner Pass (32°C ambient, maximum daily average July) and the Gardner array in Boston MA (27°C ambient, maximum daily average July). CALTRANS has a 7 year history without discoloration while Boston has a ten year history.

3.5.7. Photothermal Effects

Literature in the field of EVA encapsulant materials reports a combined effect of temperature and light with respect to discoloration.[1,2,3,4,5] Information collected during the survey of fielded photovoltaic modules illustrates the combined effect of temperature and light on the discoloration of EVA encapsulant materials (Figure 6 - The Effects of Radiation and Module Temperature on EVA).

Phoenix, which has both the highest average annual radiation and the highest average annual module temperature of the surveyed test sites, appears to have the most severe EVA discoloration. Boston, on the other hand, has the coolest average module temperature and the lowest average annual radiation, with no EVA discoloration.

While the insolation or temperature data alone can be used to explain the discoloration patterns at Phoenix and Boston, this analysis becomes over-simplified when referring to the comparative discoloration of modules at Austin,

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1 "EVA Degradation Mechanisms Simulating Those in PV Modules", F.J Pern and A.W. Czanderna; Report from DOE contract DE-AC02-83CH10093

2 "Solarex Experience With Ethylene Vinyl Acetate", J. H. Wohlgemuth and R.C. Petersen, Solar Cells Their Science, Technology, Applications and Economics: Elsevier Sequioa; 1991; 30: 563-571

3 "Encapsulant Degradation in Photovoltaic Modules", K.J. Lewis and C.A. Megerle, Journal Polymer Solar Energy Util.; 1983; 220: 387=406; CODEN: ACSMC8; ISSN: 0097-6156.

4 "Investigation of Test Methods, Materials, and Processes for Solar Cell Encapsulants", 7th Ann. Rep., JPL Contract 954527, 1983 (Jet Propulsion Laboratory, Pasadena, CA.)

5 "Photothermal Degradation of Stabilized EVA", Liang et. al. (JPL), Polym. Sci. & Tech. 20 (1982) 267-278

Figure 6

The Effects of Radiation and Module Temperature on EVA

Location	Ave. Annual Radiation kJ/m2	Approximate Av. Annual Module T(°C)	Degree of Browning
Phoenix	21216	60	moderate
Austin	16755	56	slight
Las Cruces	21559	55	slight
Sacramento	18645	53	slight
Albuquerque	20740	51	slight
Boston	12537	45	no browning
Denver	17800	38	no browning

Las Cruces, Sacramento, Albuquerque, and Denver. When comparing the average annual insolation at the Austin test facility and the Denver test facility, one might expect modules at Denver to have more discoloration than modules at Austin. If, instead, the combined module operation temperature and annual insolation data are considered as factors, one would correctly predict that the modules at Austin would be more discolored than the modules at Denver. Similarly, modules at Phoenix and Las Cruces did not have the same degree of discoloration despite similar amounts of annual radiation. If the average annual temperature difference of 5°C is considered, however, one would correctly predict that modules from Phoenix would be more discolored than modules in Las Cruces.

The reports of discolored modules were not quantitative enough to make further observations relating the discoloration of modules at Las Cruces, Austin, Sacramento, and Albuquerque. Based on insolation and ambient temperature data obtained from the National Weather Service, however, one might predict that modules at Las Cruces would be more discolored than modules at Austin, Albuquerque, and Sacramento.

3.6 Survey Conclusions

a. The incidence of EVA discoloration is not limited to the modules of any one particular manufacturer.

b. The incidence of EVA discoloration is not limited to the EVA encapsulant of any one particular supplier.

c. The rate of browning appears to be module manufacturer dependent. There is one module manufacturer who's modules consistently discolor less than any other manufactured modules that have been tested in the field in excess of 4 years.

d. Possible variables affecting the differences in discoloration from manufacturer-to-manufacturer include: EVA suppliers, EVA formulations, processing variables, cell/module design, and operation and/or operation temperature.

e. The incidence of EVA discoloration appears to be primarily in the West and Southwest where there is comparatively high solar insolation and higher operating temperatures.

f. EVA discoloration appears to be more intense at test facilities that have a combination of high module operation temperature and high solar insolation.

4.0 FURTHER PROBLEM DEFINITION - LABORATORY AGING STUDIES

4.1 Aging Equipment Selection

On careful review of the various types of accelerated U.V. aging equipment available (see Section 2.4 of this report), an Atlas Ci35A Weather-Ometer Xenon Exposure System was selected as the preferred equipment for this work. To summarize, some of the more significant advantages of the Ci35A include:

1. The spectral irradiance of filtered xenon light in the UV and visible range of the spectrum closely resembles that of natural sunlight, with no large spikes as is often found with mercury lamp or carbon arc sources. (see figure 7)

2. While both Atlas Electric Devices Company and DSET (Heraeus) offer full-scale xenon-arc weathering equipment with controlled irradiance for improved reliability, we thought that Atlas offered an advantage in being a domestic source for parts and service.

3. The xenon-arc source is widely accepted by industry (e.g. textile, automotive, plastic) and Government for accelerated weathering.

4. The Ci35A is flexible in that the operator is able to set, monitor, and control the irradiance, temperature, humidity, and water spray.

5. The Ci35A has the capacity for many more samples than the table top models - more than 60 2.6 x 5.0 inch samples, and twice that number if 2.6 x 2.5 inch samples are used. This is particularly important considering the scope not only of the Task 2 problem definition studies, but also the Task 5 evaluation of improved encapsulant formulations.

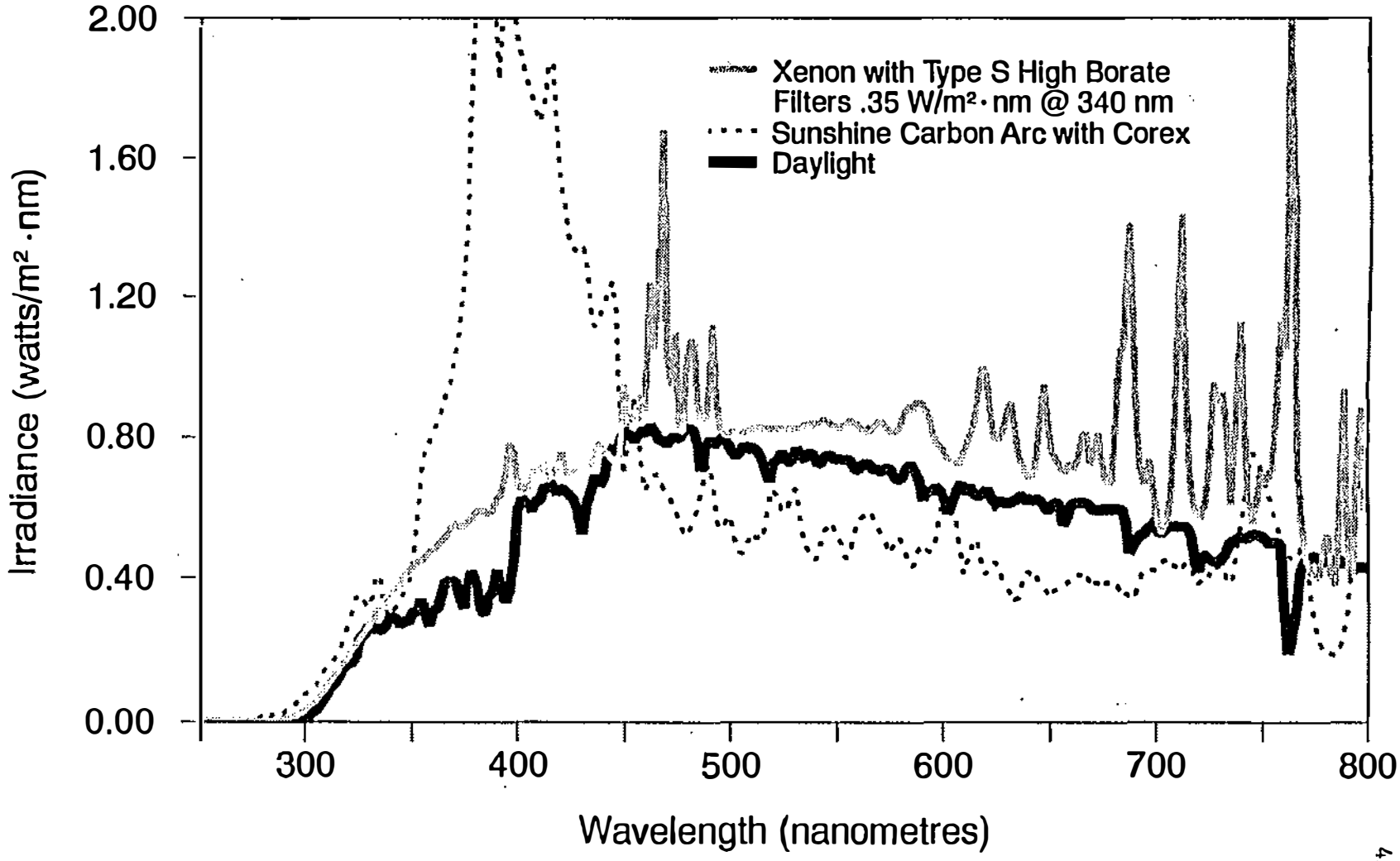
Disadvantages of the Ci35A include degradation of filters and the air-cooled lamp, requiring periodic replacement of both, generation of ozone by the lamp, and comparatively high cost of the equipment and replacement parts. See page 59 for more details.

A Ci35A device was purchased for the program, and has been calibrated for panel temperature and irradiance.

4.2 Accelerated Aging Studies

4.2.1: Sample Preparation: For these comparative accelerated aging studies, coupon-size laminates, measuring 2.6 x 2.5 inches and preferably less than 0.25 inches thick, are being used. These are being prepared by vacuum lamination using the normal time/temperature/vacuum schedule used for encapsulation work when using EVA formulation A9918, except when the cure schedule is purposely varied in order to assess its effect. A laboratory vacuum laminator and pump are being used for this work. A data logger and multiple thermocouples were used to

Xenon Arc vs. Sunshine Carbon Arc vs. Miami "Average" 45°S Daylight



Courtesy of Atlas Electric Devices

verify the temperature profile used during the cure for samples cured in the laminator. To cut cycle times, most samples are being removed from the laminator once laminated and are being post cured in a circulating air oven.

Samples being prepared are outlined in the attached Table 4. For most of this work, glass/glass laminates are being used to facilitate visual, colorimetric, and spectrographic measurements. However, some laminates contain cells in order to investigate such effects as cell/EVA and metallization/EVA interfacial chemical changes. The general constructions being used are shown at the top of Table 3.

4.2.2: Glass superstrate being used is low iron glass so as to allow the maximum amount or UV-B through (ie. 285 to 350 nm), that wavelength region suspected as being responsible for EVA discoloration/degradation. Also, low iron glass is the superstrate most commonly used in those fielded modules which have shown a discoloration problem. TPE refers to standard Tedlar/polyester/EVA laminate backing material.

The glass of choice for most domestically prepared flat plate modules based on crystalline and semi-crystalline silicon cells has been Solatex manufactured by AFG Industries, Inc., Kingsport, TN, or Solite - also by AFG - which is the same material as Solatex but with a stippled pattern on one surface. These were also the glass superstrates that were used most significantly for module manufacture during the mid 1980s, the period when most of the discolored modules studied in Task 1 were produced. For this reason, Solatex was selected for this Task 2 work.

However, in the process of preparing for sample lamination, it was noted that recent samples of Solatex had a different appearance than the older material on hand in the laboratory - annealed pieces that dated from the 1980s. This observation prompted the running of transmission spectra of both samples by U.V. visible spectroscopy. As seen from the attached spectra (Figures 8 and 9), the transmissions are significantly different in the 270 to 350 nm range.

AFG has not to our knowledge officially acknowledged a change in composition for Solatex, and does not distinguish between newer and older lots in their product literature. However, AFG representatives will refer to the newer material as Solatex II, and we have adopted that terminology as a means to distinguish the two types.

In addition, we were contacted by PPG Industries regarding a new grade of glass called Airphire that they claim contains cerium oxide. PPG also makes a similar glass called Starphire, without the cerium oxide, that the firm markets for various furniture, appliance, architectural and commercial applications. UV-visible spectra were run on these glasses as well, and are also attached (Figures 10 and 11). The transmissions of the Airphire and Solatex II are strikingly similar in the 300 to 350 nm region.

Unfortunately, the older Solatex (or Solite) is in extremely short supply. While there are sufficient quantities available to complete the Task 2 work, future development work and scale up for field studies will require the use of an alternate superstrate material which will permit EVA yellowing to occur. The

Figure 8
UV-VIS Transmission
(28921 Run #1)

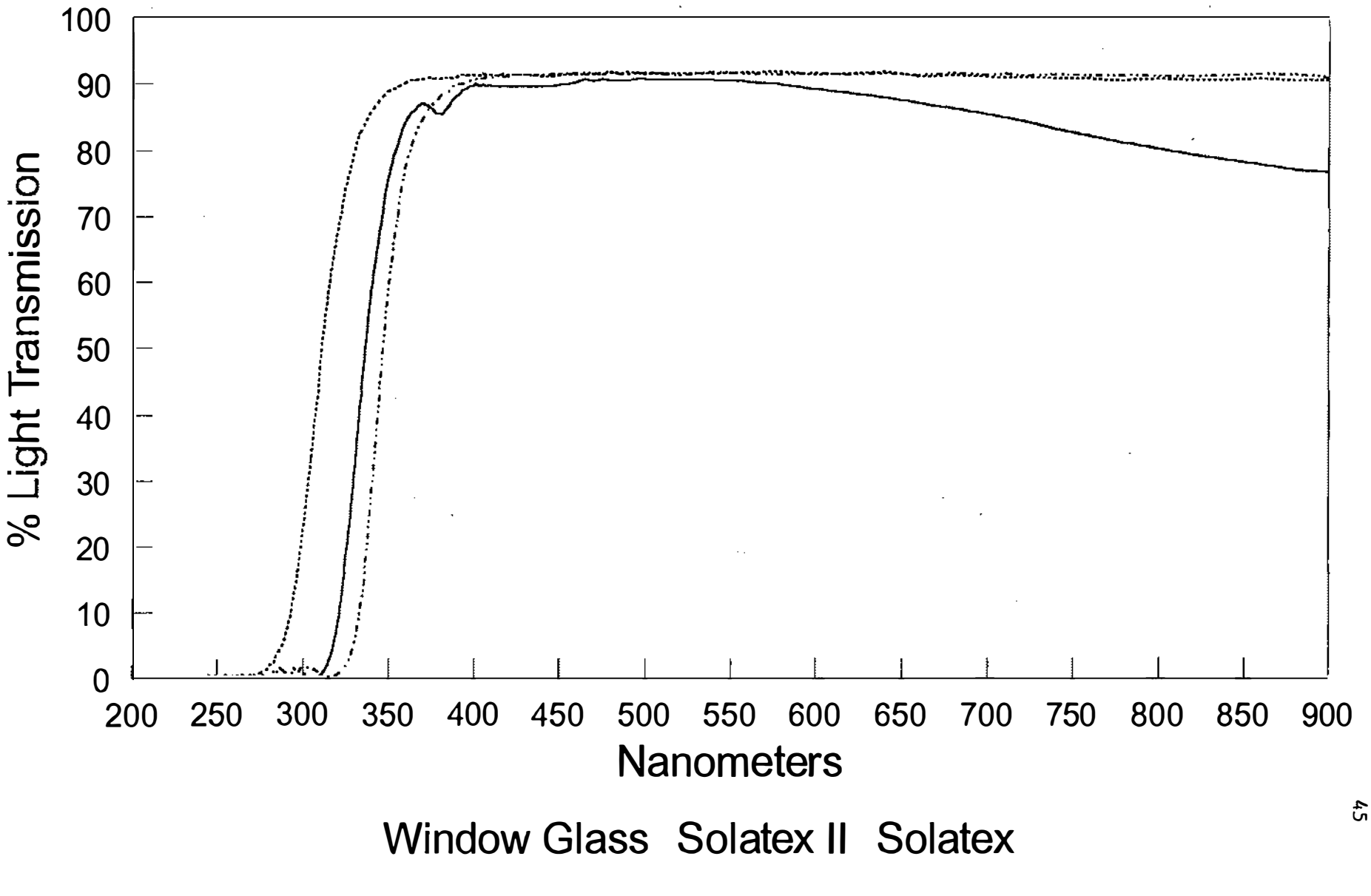


Figure 9
UV-VIS Transmission
(28921 Run #1)

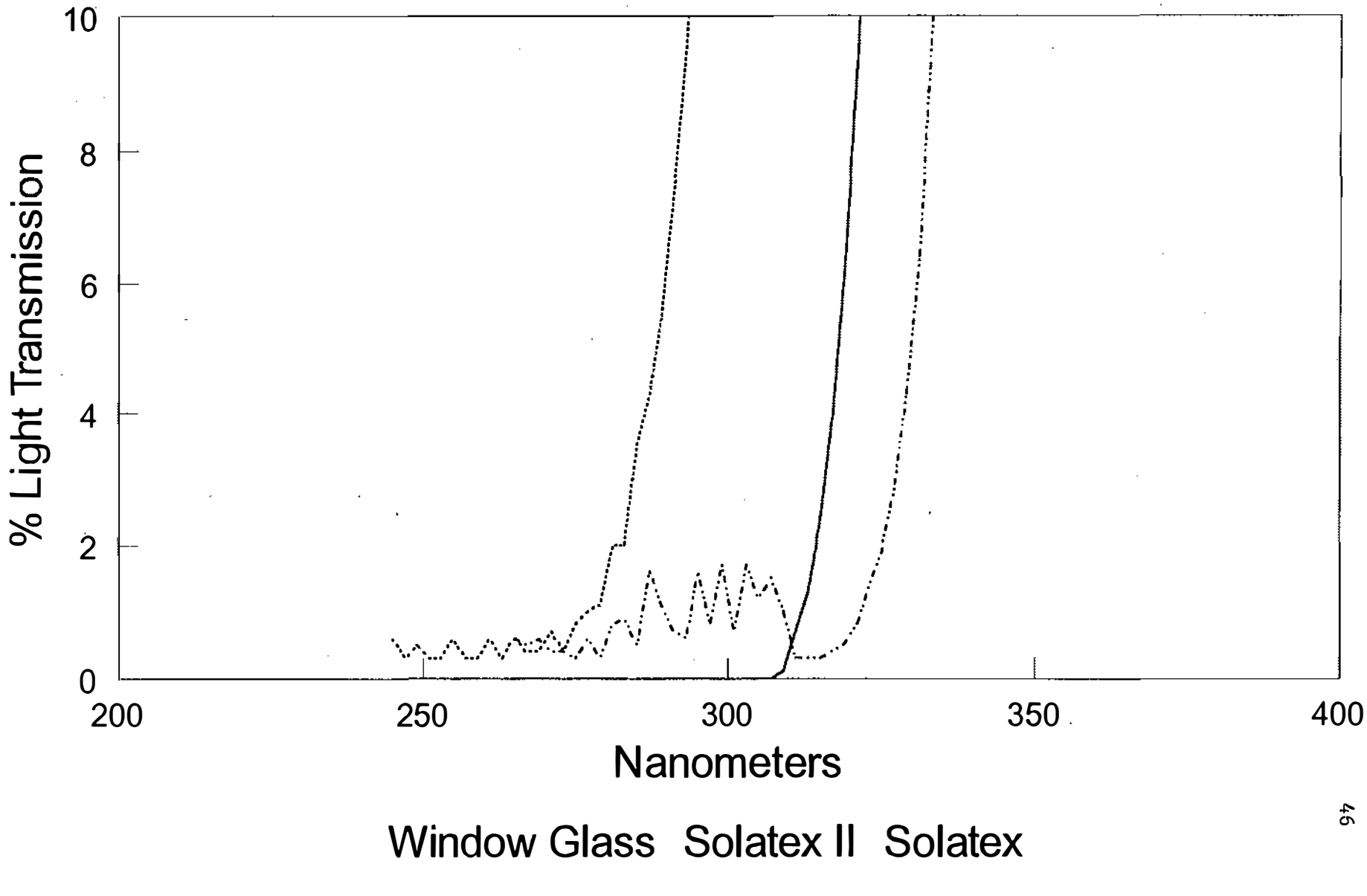


Figure 10
UV-VIS Transmission
(28921 Run #2)

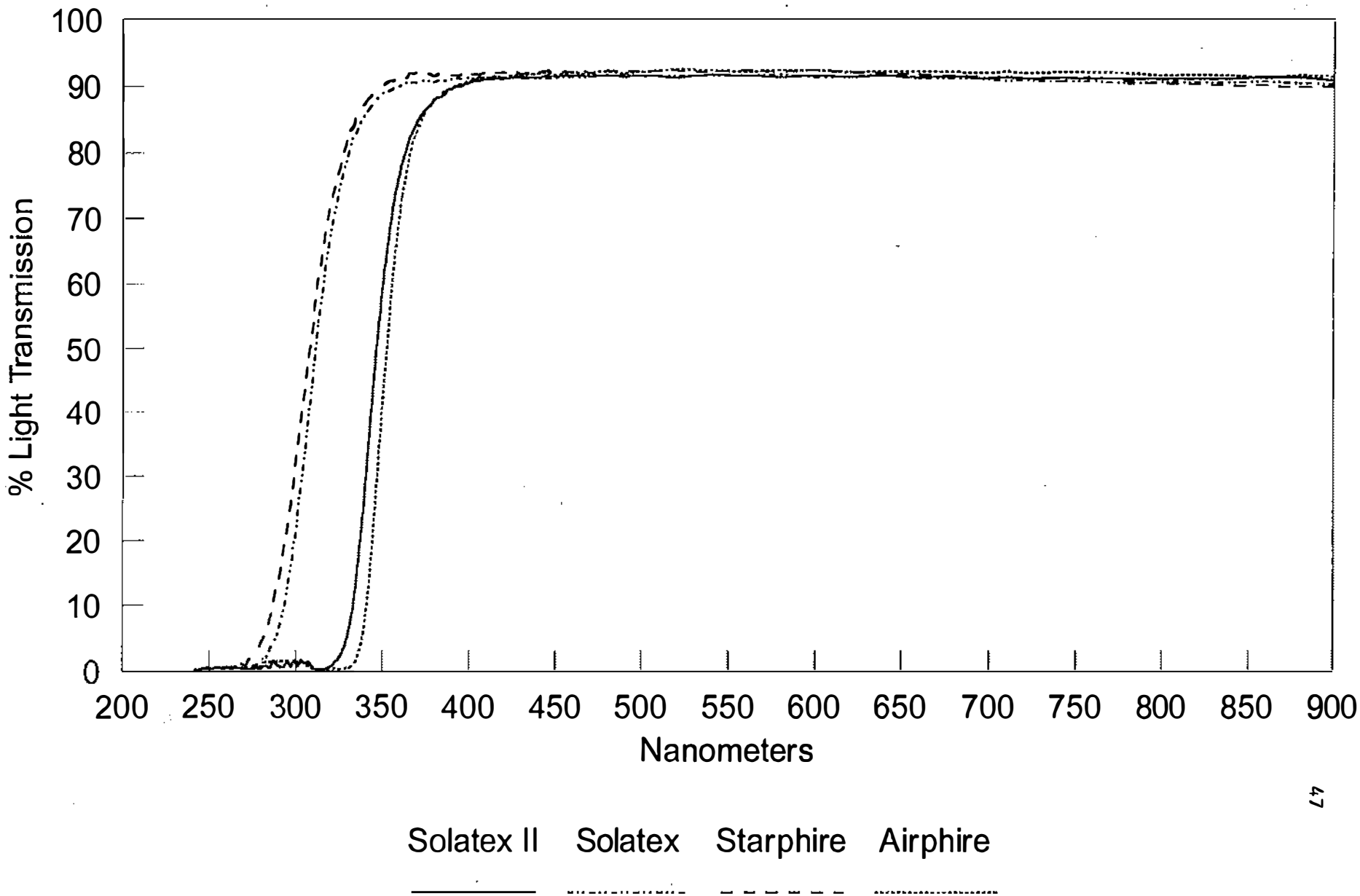
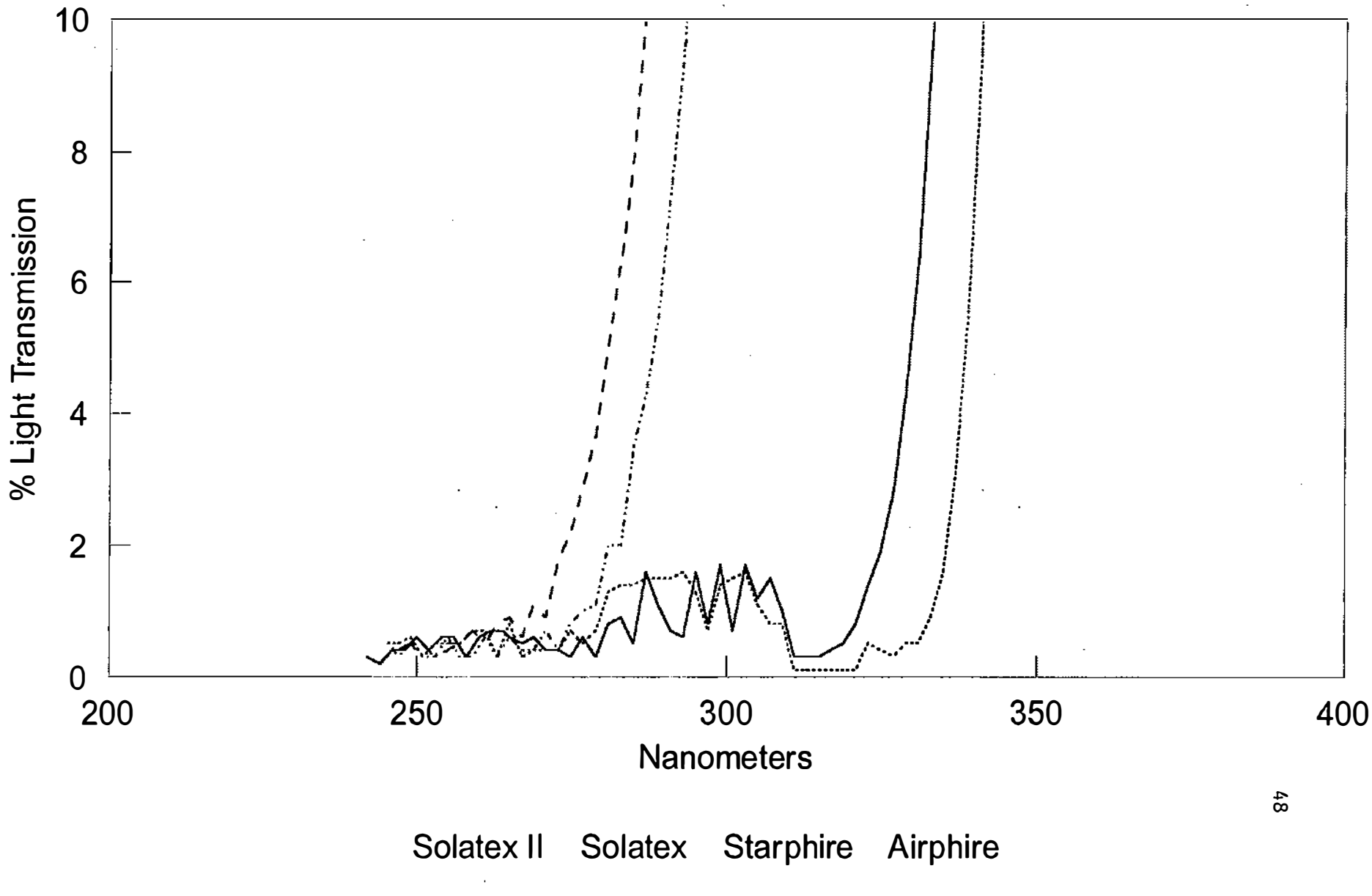


Figure 11
UV-VIS Transmission
(28921 Run #2)



logical choice for use in future investigations is Starphire. For this reason, it can be noted that the Table 4 plan of Task 2 studies contains samples which compare the various types of glass.

Naturally, there is considerable interest in both Airphire and Solatex II/Solite as well, since both cut off much of the radiation in the 270 to 330 nm region, a band which is known to be detrimental to organic polymer stability. Also, it is fortuitous that PPG has now released Airphire, as the use of cerium-containing glass superstrates was a Task 4 "stabilization strategy" suggested in our proposal of January 1992.

4.2.3: Sample Exposure: Coupon laminates are being exposed to 0.55 watts/square meter (taken @ 340 nm) and 100 degrees C in a Ci35A Atlas xenon-arc Weather-Ometer using quartz/borosilicate glass filters. The nominal lower end U.V. cut-off is 285 nm. Samples will be exposed for a minimum of 13 weeks or until significant degradation/discoloration of the EVA has occurred.

In most cases, samples are being run in duplicate. In the interest of time, Series 1 and 2 samples (Table 4) are being exposed simultaneously.

Calibration work on the Ci35A revealed that slight temperature and irradiance variations exist between samples placed in the top, middle, and bottom racks. Some samples were placed so as to assess the effect of this variation. However, since the purpose of the testing is to develop comparative data, most of the samples are being rotated between racks on a weekly basis to normalize any minor T/I differences.

Again, it should be emphasized that the Weather-Ometer is being used <u>only as a screening tool</u> - that is, a laboratory technique for conducting preliminary evaluation of various module encapsulation materials/constructions in order to assess their relative U.V. aging resistance and to obtain a relative ranking of those materials/constructions. There will be no attempt to correlate accelerated aging results with field information or to develop acceleration factors, both of which are beyond the scope of this investigation.

4.2.4: Sample Evaluation: Coupons are being monitored for color/chemical changes during the exposure. Non-destructive tests on the samples include visual fluorescence at 360 nm under a hand held "mineral light" (qualitative test for development of unsaturation in the EVA), Yellowness Index per ASTM D-1925, and Percent light transmission (%T) at 285 to 900 nm by U.V.-VIS.

Some destructive testing will also be done. Especially at the conclusion of the accelerated UV exposure period, selected samples will be forwarded to Al Czanderna and John Pern at NREL for fluorescence spectroscopy and to UCONN/IMS for Task 3 analysis.

Quantitative yellowing results are expected early in year two of the program and will be reported in the next Semi-Annual report.

Table 4

Phase I - Task 2 Testing Program

Accelerated Aging in Atlas Ci35A Weather-Ometer

Sample: #1 Glass/A9918P EVA/ Cell/A9918 EVA / TPE backing
Sample: #2 Glass/A9918P EVA/ Glass

Size of Samples: 2.6 x 2.5 inches (two per holder)

Rack: t=top, b=bottom, m=middle, rot=rotate

Glass superstrate type: S-I="old" Solatex (or Solite), S-II= Solatex II
A=AirPhire St=StarPhire

SERIES 1 - Find the "bad Actors": Irr=0.55 W/square meter @ 340 nm, T=100°C

Objective: Isolate potential problems of construction/ingredients, etc.
Samples: All Sample #2 configuration unless specified otherwise

# of samples	Rack	Sample Variables	Glass superstrate
2	m	Sample #1	S-I
3	t,m,b	Sample #2 (no rotation)	S-I
2	rot	Sample #2	S-I
2	rot	Sample #1	S-I
2	rot	Sample #2	S-I
2	rot	Sample #2	S-II
2	rot	Sample #2	A
2	rot	Sample #2	St
2	rot	Sample #2	Window

The following samples all use #2 configuration:

2	rot	double EVA layer (36 mils)	S-I
2	rot	1/2 thickness EVA (9 mils)	S-I
2	rot	A9918P - Hand milled	S-I
2	rot	A9918P - Hand milled	St
2	rot	15295P (TBEC)	S-I
2	rot	15295P (TBEC) hand milled	S-I
2	rot	15295P	S-II
2	rot	15295P	St
2	rot	15295P	A

2	rot	A9918P - No peroxide, epoxy sealed edges	S-I
2	rot	A9918P - Epoxy sealed edges	S-I
2	rot	A9918P	
2	rot	A9918P - No Tinuvin 770	S-I
2	rot	Elvax 3185 - As rec'd, epoxy sealed edges	S-I
2	rot	Elvax 3185 - As rec'd, epoxy sealed edges	St
2	rot	A9918 - No silane	S-I
2	rot	A9918P - No Phosphite	S-I
2	rot	A9918P - No backing	S-I
2	rot	A9918P - No backing	St
2	rot	A9918P - No backing	S-II

SERIES 2 - Investigate Other Variables: Irr.=0.55 W/square meter @ 340 nm, T=100°C

The following samples are being rotated on the Ci35A racks from top to middle to bottom, on a weekly basis:

2	cure 15 minutes @ 150 C in oven	S-I
2	no post cure once removed from laminator	S-I
2	cure 60 minutes in laminator under vacuum	S-I
2	Tedlar superstrate	none
2	Tefzel superstrate	none
2	A9918 with primer applied to glass	S-I
2	A9918P with metal (oxide) strips embedded	S-I

5.0 FUTURE WORK

Future investigations will involve the following tasks, as they appear in the subcontract Statement of Work:

TASK 3: In conjunction with the task 2 investigation discussed in section 4.0 of this report, "Further Problem Definition - Laboratory Aging Studies," we will also define possible chemical mechanisms of degradation. With assistance from the University of Connecticut's Institute of Materials Science, instrumental analysis will be conducted on various field and laboratory aged EVA laminates and modules to verify degradation/discoloration hypotheses.

TASK 4: Based on the results of tasks 2 and 3, we will develop a family of stabilization strategies to overcome discoloration by exploring U.V. absorbers in the EVA; U.V. absorbing glass, coated glass, or coated cover films; and alternate low-cost encapsulation polymers.

TASK 5: Simultaneously with task 4, we will conduct accelerated weathering testing of laboratory-size laminates to verify the stabilization strategies.

TASK 6: The more promising new encapsulant formulations will be extruded in pilot-scale quantities into sheet for evaluation by team members - ten domestic module manufacturers.

TASK 7: Team members will prepare test coupon laminates, using the sheet materials from task 6. We will subject these samples to accelerated aging in our Atlas Ci35A xenon arc Weather-Ometer.

TASK 8: Team members will prepare full size modules from the two best encapsulant formulations. These modules will be subjected to IQT testing by Arizona State University.

TASK 9: At Arizona Public Service's STAR facility in Tempe Arizona, ASU will conduct field testing of full sized modules, with regular data acquisition and analysis. Modules will include those using improved encapsulant materials as well as control modules prepared with A9918P "standard cure" EVA encapsulant.

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Siemens Solar Industries
4650 Adohr Lane
P.O. Box 6032
Camarillo, CA 93011
* Ms. Theresa L. Jester
  Senior Director

Photocomm, Inc.
7681 East Gray Road
Scottsdale, AZ 85260
* Mr. Walter O'Niel
  Vice President
  Gov't & Intl. Marketing

United Solar Systems Corp.
1100 West Maple Road
Troy, MI 48084
* Subhendu Guha, Ph.D.
  Vice President
  Research & Technology

Solarex Corp.
630 Solarex Court
Frederick, MD 21701
* John H. Wohlgemuth, Ph.D.
  Director
  Research and Development

Texas Instruments
13532 North Central Expressway
P.O. Box 655012- MS 35
Dallas Texas, 75265
* Mr. Russell R. Schmit
  Operations Manager

Solar Web, Inc.
P.O. Box 10864
Pittsburgh, PA 15236
* Mr. Richard Rosey

Solec International, Inc.
12533 Chadron Avenue
Hawthorne, CA 90250
* Mr. Stephen Olah
  Vice President, Operations

Utility Power Group, Inc.
9410-G Desoto Avenue
Chatsworth, CA 91311
* Mr. Gilbert Duran
  Vice President

Advanced Photovoltaic Systems, Inc.
P.O. Box 7093
Princeton, NJ 08543-7093
* Mr. Ron Matlin
  Director, Power Sys. & Gov't Cont.

Global Photovoltaic Specialists, Inc.
21525 Parthenia St.
Canoga Park, CA 91304
* Mr. Howard Somberg
  President

Arizona State University
Center for Energy Systems Research
College of Eng. and Applied Sciences
Tempe, AZ 85287-5806
* Mr. Robert Hammond
  Director, Alternative Energy Dev.

Arizona Public Service Company
P.O. Box 53999
Phoenix, AZ 85072-3999
* Mr. Joe McGuirk
  Manager, Research & Development

University of Connecticut
Institute of Material Science
Storrs, CT 06269-3136
* Dr. Myer Ezrin

Appendix 2 - Comparison of Xenon Weathering Equipment

ATLAS CI35 OR CI65 XENON WEATHEROMETERS

Pros/Features

* The spectral output of a Xenon lamp is a fairly close match to that of natural sunlight.

* Standard features include controlled irradiance at either 340 or 420 nm, specimen rack, microprocessor based program cycle control, direct setting for black panel temperature control, direct setting for dry bulb temperature, 3 channel data collector ring, Vibra Sonic humidification system, temperature calibration convenience package, calibrated Xenon reference lamp, air heater, water heater, air intake dust filter, circulating system with tapwater-cooled heat exchanger, and stainless steel construction. Note: lamp/filters/specimen holders not included.

* These units use one 6500 watt water-cooled long arc Xenon lamp.

* The lamps are water cooled and MUST be used with filters by virtue of the apparatus design. As a bonus, the water acts as an IR filter (NOTE - the Xenon bulb tends to have a large spiky IR irradiance which is not characteristic of that of sunlight).

* Interchangeable inner and outer (Borosilicate, Quartz esp.) filter are available which allow the low, we believe most critical, UV wavelengths through.

* The irradiance level can be manually set to a desired setpoint using either 340 or 420 nm.

* Features of equipment: Temperature can be set digitally ranging from 45 to 90°C; Eprom chip has set of programs for light/dark cycles.

* The C series have control-loop internal irradiance monitoring that continually adjusts the light output to maintain a constant irradiance level.

* Depending upon the rack and holders selected, from 66 to 85 3" X 5" samples can be exposed at any given time.

* The Ci35 can be used as a 1 - 2 sun weathering apparatus as received by virtue of the irradiance setting. With the purchase of a special rack (smaller diameter rack, less samples, but closer to the light source), the Ci35 series can be converted into a 3 sun weathering device.

* Purchase of a Ci65 allows the buyer to have 20 4" X 12" panels exposed outdoors, free of charge for one year with complete reporting by South Florida Test Service in Miami, Arizona, Illinois, or Holland. (with Ci35 purchase, they will expose 10 panels)

Cons

* Cost of equipment and replacement parts is higher than the UVCON/QUV or Sunchex/Suntest systems.

* The filters degrade over time and must be replaced after a specified amount of usage. The time varies from 400 to 2000 hours depending on whether the filter is an inner or outer filter, and the irradiance at which the equipment is operating.

* The air-cooled lamps degrade in output over time. Atlas guarantees the bulbs for 1200 hours, but states that the statistical lifetime of the bulb is 2000 - 2500 hours.

* At the low UV ranges, ozone is generated and must be removed from the system. Atlas suggested putting another filter in place and suctioning the ozone away from the area. This additional filter may further complicate our situation in terms of spectral output.

DSET HERAEUS XENOTEST 1200 CPS XENON WEATHEROMETERS

Pros/Features

* Spectral output of Xenon lamp is a fairly close match to that of natural sunlight.

* Standard features include: controlled irradiance in UV range of 300-400 nm, carousel for sample holders, sample holders, user guided microprocessor for programming, control and data acquisition, temperature control by measuring black standard thermometer or test chamber, humidification system, rain spray, dark time heater, Xenon lamps, UV filters, thermal printer, diagnostic software, RS232 port.

* This unit uses three 2800-6000 watt air cooled "Hanau" Xenon lamps.

* The use of "air" cooled lamps (versus water) eliminates the optical filter contamination. They claim filters are pre-aged at the factory and do not have to be replaced unless you break one.

* Max UV filter is used for high UV radiation.

* The irradiance level can be fixed at a desired setpoint using either 300-400 nm range or at 340 nm.

* Temperature (black standard) is adjustable between 45 and 120°C and humidity between 30 and 95%.

* This unit is programmable for light/dark cycles, temperature, irradiance, and relative humidity.

* Control-loop internal irradiance monitoring continually adjusts the light output to maintain a constant irradiance level.

* Depending upon the rack, stationary or turning mode holders, 75 3" X 5" samples can be exposed at any given time.

* Ozone generation is not a problem with this equipment; the lamp air cooling system carries the ozone away.

Cons

* Cost of equipment and replacement parts is higher than the UVCON/QUV or Sunchex/Suntest systems.

ATLAS SUNCHEX BENCHTOP XENON WEATHEROMETER

Pros/Features

* Uses one 1500 watt Xenon lamp - spectral output close match to that of sunlight.

* The UV 280 filter appears to allow the critical low wavelengths of light through to the sample. Need spectral output to be sure.

Cons

* There is only a small area of uniform irradiance inside the chamber. Only six to eight 2" X 2" samples can fit in the (500 cm^2) chamber at any one time. Since there is only a small area of uniform irradiance inside the chamber (as acknowledged by Atlas and Al Czanderna, NREL), the area is further reduced, but it is not clear by how much. Considering that a control sample is needed for each exposure and a place is required to put the sensor, even less area is available for samples.

* For these small benchtop units, one must purchase separate irradiance and temperature sensors for each unit and a single multimonitor to measure/check, but not control irradiance.

* The sensors take up sample space in the exposure chamber which is very limited to begin with (500 cm^2 or 80 in^2). NOTE: This is total area, not total USABLE area - see previous comments.

* This unit is not an accepted weathering apparatus for the textile industry.

* The degradable 280 filters must be replaced after a certain usage period (400-2000 hours).

* The lamps are guaranteed for 1200 hours and then must be replaced. Atlas says the lamps usually last 1500 - 1800 hours.

* Air-cooled bulb does not screen out IR emitted from bulb.

* Five to six Sunchex cabinets would be required to hold all anticipated test specimens for this program. Each unit may have a different temperature or irradiance due to difficulties in standardizing these parameters. Comparison of samples between boxes is in question.

DSET HERAEUS SUNTEST BENCHTOP XENON WEATHEROMETER

Pros/Features

* The price of the Suntest units is lower than the Xenotest.

* This unit uses one 1500 watt Xenon lamp - spectral output close match to that of sunlight.

* The Max UV filter appears to allow the critical low wavelengths of light through to the sample. They claim the filter is non-degradable.

* This equipment has a closed-loop control for constant irradiation monitoring/control.

* The exposure area of the chamber gets uniform irradiance levels, even at the corners.

Cons

* There is only a small area of uniform irradiance inside the chamber. Only six to eight 2" X 2" samples can fit in the 500 cm^2 chamber at any one time.

* It is not clear if this unit is an accepted weathering apparatus for the textile industry.

* The lamps are guaranteed for 1500 hours and then must be replaced.

* Air cooled bulb does not screen out IR emitted from bulb.

* Five to six Suntest cabinets would be required to hold all anticipated test specimens for this program. Each box might have a different temperature or irradiance due to difficulties in standardizing these parameters. Comparison of samples between boxes is in question, but probably more reliable than the Suntest chambers.

Appendix 3 - Written Questionnaire

Written Survey of the

"Ethylene Vinyl Acetate Encapsulant Discoloration
in Photovoltaic Modules"

March 1993

Conducted by

SPRINGBORN LABORATORIES, INC.
10 Springborn Center
Enfield, CT 06082

A. Discolored Ethylene Vinyl Acetate

1. What grade of EVA did you use? Who was the supplier of this material?

2. What were the storage conditions for the EVA prior to its use? Were the rolls themselves protected by foil or a plastic bag?

3. How old was the EVA at its time of use?

B. Module Construction(s) for those that Discolored

1. What materials were used in the construction of the module(s)?

   What was the substrate design?

   What was the superstrate design?

   What was the cover material?

   What was the backing material?

   What was the back metallization of cell?

   What was the metallization on top of cell?

   What type of solder was used?

   What type of flux was used?

2. What were the metallic components for the grids?

3. What were the metallic components for the buses?

4. Were the metallized solar cells subject to a cleaning process to remove the residue of solder flux? If so, was the cleaning process a dry or wet method? Chemicals used?

5. What was the thickness of the EVA over the cells before and after curing?

6. If glass was used in the construction of the module, what type of glass (low iron, window glass)? Who manufactured the glass? How was the glass cleaned prior to use? Was a primer applied directly to the glass?

7. Did the cover material have any special surface treatments, anti-reflective coatings, anti-reflective patterns, or primers on either surface? Which side of the cover material had this quality? inner?_____ outer?_____ .

8. What was the background color of the module?

9. Did the module contain Craneglas• fibers? yes_____ no_____

Where was the Craneglas• positioned within the module?
On top of the cell _____ below the cell _____ both top and below_____

10. Were any of the EVA encapsulants tested (qualified for suitability) prior to field use? If so, how were they tested?

11. Did the modules have by-pass diodes? How many cells per diode?

C. Module Processing for those which Discolored

1. What type of laminator did you use? (make and model number)? Was its performance equal to or better than specifications (e.g. accuracy of temperature)? What was the vacuum level? Temperature ramp rate?

2. What was the processing profile for the module(s) beginning from the uncured state and including curing time, lamination time, temperature, vacuum level, and duration? Was the module cooled before removal? How was the module cooled?

3. Were the module(s) post cured? yes _____ no _____ If yes, describe the post cure time-temperature and other -parameter profile.

D. Module Field Placement of Modules which Discolored

1. Describe how the module(s) were installed in the field? (include the mount angle, tracker, mirror enhancement, and Fresnel concentrator) If mirror enhancement, how many suns?

2. Where are/were the modules located? Elevation?

3. What was the installation date of the modules?

4. Once in service, how often were the modules cleaned?

5. Describe the typical module temperature profile for each of the four seasons including the maximum and average operating temperatures. Where were the thermocouples located relative to the cells (over, behind, or between the cells)? Provide a separate temperature profile for each location where discoloration occurred (if different).

6. Describe the typical relative humidity profile for the modules during each of the four seasons. Provide a separate humidity profile for each location where discoloration occurred (if different).

6. What was the solar insolation at each module site?

E. Operation of Modules which Discolored

1. Approximately what percentage of modules placed in the field discolored?

_____ clear ____ yellow _____ amber _____ brown

2. How long had the module(s) been in operation before they discolored?

3. Where on the module did the discoloration appear? Are these areas random, between the cells, or over cells? Does the discoloration continue all the way to the edge of the cell or the module itself? Is the intensity of the discoloration uniform across the surface of the cell? Were there clear areas between the cells (How wide?)?

4. Were there any associated problems with the discolored modules, i.e. delamination, corrosion of grid pattern or interconnects, bubble or void formation, delamination, wiring problems, or shading?

5. What was the initial voltage/power/efficiency rating for the modules? How did the measured values after initial use compare with the ratings? What are the present values today for the voltage/power/efficiency? How were these values measured (e.g. on separately monitored modules, on an array, on a system)? Were any other measurements taken?

6. Are voltage/power measurements of the discolored modules consistent with those of clear modules that were in operation for the same length of time?

7. Were any of the modules cracked? If so, what is the color of the EVA surrounding the crack compared to the overall discoloration?

8. What was the condition of the EVA if/where the back of the module was cut through to mount something or cut for some other reason.

9. If similar modules were operated at several different geographic locations, was EVA discoloration observed at one location and not another? Describe in detail.

10. Were there modules with identical exposure histories at the same geographic location that did not have similar coloration/discoloration? If so, were there any differences in preparation, deployment, or operation?

11. Was an analysis of the discolored modules conducted by you or any other organization? Was there an odor noted especially on peeling off the back film?

12. Can the discoloration of the modules be connected with a particular curing agent, priming process, EVA supplier, or some other factor in particular? (Describe)

F. Action Taken

1. Was any change made in design, procedures, or EVA because of past discoloration?

G. Additional Comments

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Enfield, Connecticut 06082

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11. SUPPLEMENTARY NOTES

NREL Technical Monitor: H. Thomas

12a. DISTRIBUTION/AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

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13. ABSTRACT *(Maximum 200 words)*

This report describes work under Phase II of a Photovoltaic Manufacturing Technology project to conduct laboratory problem definition with an emphasis on controlled aging studies to evaluate the influence of various compositional, processing, and operating parameters on ethylene vinyl acetate (EVA) discoloration. In support of future accelerated UV aging studies (AAS) of coupon-sized EVA laminates, an Atlas xenon arc Ci35A Weather-Ometer was procured, installed, and calibrated for temperature and irradiance. In preparing for the AAS studies, UV-visible spectroscopy measurements were performed on various types of low-iron glass, representative of materials used for module superstrates. It was discovered that the transmission spectra of some of the grades in the UV region from 250 to 400 nm was significantly different. Older grades of Solatex and solite, and StarPhire "cut off" well below 290 nm, while newer grades of Solatex and Solite, and StarPhire and Airphire greatly reduce the UV transmittance between 280 and 330 nm. Controlled aging studies are presently underway at 0.55 W/m^2, 340 nm, and 100°C, and we expect comparative data on yellowing to be available soon.

14. SUBJECT TERMS

photovoltaics ; solar cells

15. NUMBER OF PAGES

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