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Advanced Development of PV Encapsulants

Semiannual Technical Progress Report 30 June 1995 - 31 December 1995

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A national laboratory of the U.S. Department of Energy
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EXECUTIVE SUMMARY

After 40 weeks in an Atlas xenon-arc Weather-Ometer at 0.55 watts/m^2 /nm at 340 nm and 100°C, glass/encapsulant/glass laminates using four new experimental EVA-based encapsulants showed no visible yellowing. Control laminates with "standard-cure" A9918P and "fast-cure" 15295P exposed at the same conditions were a dark brown.

Laminates of the four experimental EVA-based encapsulants, three which cure under standard conditions - X9903P, X9923P, and X9933P - and one which laminates under fast-cure conditions - X15303P - all registered Yellowness Indexes between 2.0 and 4.9. The A9918P and 15295P controls have Yellowness Indexes of 88.1 and 78.6, respectively, following the same 40 week Weather-Ometer exposure.

Also, 40 weeks of accelerated outdoor EMMA exposure in Phoenix at a nominal 5 suns has caused no measurable yellowing of glass/encapsulant/glass laminates prepared with experimental X9903P.

After 16 months of EMMA exposure, glass/encapsulant/glass laminates prepared with fast-cure 15295P and cerium-oxide containing Solatex II glass had almost no measurable yellow. Tefzel film/A9918P/glass laminates also had no detectable yellow. By comparison, 15295P and A9918P glass/encapsulant/glass controls registered Yellowness Indexes of 4.8 and 34.7 after 16 months of EMMA.

The four experimental EVA-based materials were extruded into sheet of sufficient size and quantity for module manufacturer team members to prepare mini-modules and full size modules for additional testing.

INTRODUCTION

The goals of the NREL PVMaT program are, among others, to reduce module manufacturing costs and improve the quality, and we might add here the reliability, of manufactured PV products. One component critical to the service life of PV modules is the useful life of the EVA resin-based encapsulant which is employed extensively by module manufacturers on a worldwide basis.

This pottant has been in commercial use since 1982 [1, 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 the EVA resin-based A9918 and similar formulations for PV encapsulation, some module producers, end-users, and investigators have reported a yellowing or browning phenomenon with EVA resin-based encapsulants in the field. While the incidence of this discoloration/degradation appeared at comparatively few sites at the time that this present program was conceived, it raised serious concern as to the long term reliability of EVA resin-based encapsulation systems.

Consequently, under the NREL PVMaT program, Springborn Laboratories proposed a comprehensive study of the EVA aging and discoloration problem and its possible solution(s). During the first year of this program, accelerated U.V. aging methods were surveyed. On careful review of the various types of accelerated U.V. aging equipment available, an Atlas Ci35A Weather-Ometer Xenon Exposure System was selected as appropriate equipment for this work.

The following report summarizes how this accelerated aging technique has been used to develop a family of solutions to the discoloration problem, the most significant of which is a series of EVA-based encapsulants which are resistant to discoloration.

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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, application and Economics, Solarex Experience with Ethylene Vinyl Acetate Encapsulation, (Elsevier Sequoia, 1991). pp 383-387.

Purpose: Using the results of Tasks 2 and 3 (see Annual Report for the period ending June 30, 1995) efforts under Tasks 4 and 5 sought to: 1 - develop possible approaches for stabilizing the EVA-based encapsulant against discoloration/degradation including alternate encapsulation systems that might be more inherently resistant to discoloration/degradation, and 2 - evaluate the performance of promising systems by AAS (accelerated aging studies) using xenon-arc Weather-Ometer.

Strategies considered included cerous and uranium salts and metallocene compounds as UVA (UV absorbers), other organic compounds with the ability to strongly absorb radiation in the 285 to 350 nm range as UVA, other hindered amine light stabilizers (HALS) as alternatives to Tinuvin 770, higher concentrations of existing additives, alternate phosphites to Naugard P as peroxide decomposers, UV absorbing coatings on the glass superstrate, and UV-absorbing glass superstrates.

Also investigated were other low-cost polyolefin-based resins as alternatives to EVA resin Elvax 3185.

Results: On the basis of these investigations, we have developed four experimental formulations, X9903P, X9923P and X9933P, EVA-based encapsulants which cure under the same conditions as A9918P; and X15303P, a material which cures under the same conditions as 15295P.

Preliminary accelerated weathering results appeared in our annual report for the period ending June 30, 1995 (page 12 and Table 4). Now, after 40 weeks in the Ci35A Weather-Ometer, glass/encapsulant/glass laminates prepared with all four experimental encapsulants show a negligible 2.0 to 4.9 Yellowness Index (Table 1). It is noteworthy, that visible color does not occur until a Yellowness Index of approximately 10.

Figure 1 provides a graphical comparison of Yellowness Index of these experimental materials with control encapsulants A9918P and 15295P after 34 weeks of Weather-Ometer exposure. The differences are dramatic; the controls are very brown while the four experimental EVA-based materials show no visible yellow.

It should be noted that all four experimental encapsulants were laminated with Starphire glass, which is slightly more transparent to UV-B than Solite glass and thereby represents a "worst-case" for simulating outdoor exposure. Also, all four experimental grades are based on the same Elvax 3185 EVA resin used in 15295P and A9918P and are comparable in cost to these earlier EVA-based encapsulants.

Experimental formulation X9903P is also being subjected to EMMA testing at DSET laboratories in glass/encapsulant/glass laminates. After 40 weeks of exposure, there was no measurable yellowing of the new encapsulant (Table 2).

PREPARE PILOT SCALE QUANTITIES OF PROMISING ENCAPSULANTS

Purpose: Task 6 involved extruding the four more promising experimental EVA-based encapsulants into thin sheet of the required size and quantity for module manufacturer team members to prepare coupon-size mini-modules for accelerated aging and full-size modules for field testing.

Sample Preparation: "Virgin" Elvax 3185 EVA copolymer pellets were blended with the appropriate additives and extruded into 0.018 inch thick sheet. Extrusion equipment consisted of a Hartig 2 1/2 inch extruder, sheet die, and roll stand.

Promising formulations included three encapsulants which cure under "standard-cure" conditions: X9903P, X9923P, and X9933P; and one which laminates under "fast-cure" conditions: X15303P. Extrusion conditions were the same as used for A9918P and 15295P.

6.3: Results: The experimental materials were extruded with no difficulty and processed and handled essentially the same as their A9918P "standard-cure" and 15295P "fast-cure" counterparts. Appearance and surface character also seemed no different.

Small rolls of each material were shipped to team member module manufactures for mini-module and full-size module fabrication. Manufacturers included ASE Americas, Inc.; EBARA Solar, Inc.; Global Photovoltaic Specialists, Inc.; Photocomm, Inc.; Siemens Solar Industries; Solarex Corp.; Solec International, Inc.; and United solar Systems Corp.

Table 1

AVERAGE YELLOWNESS INDEX OF CURED
EVA/GLASS LAMINATES WITH WEATHER-OMETER AGING (1)

			Yellowness Index (5)			Difference
Sample Construction (2)	0 weeks	4 weeks	8 weeks	12 weeks	40 weeks	0-40 wks
Encapsulants Which Cure Under "Standard" Conditions						
X9903P/Starphire	0.2	2.6	2.3	1.8	3.0	2.8
X9933P/Starphire	0.5	3.3	4.8	5.8	4.9	4.4
X9923P/Starphire	0.4	2.2	2.4	--	2.0	1.6
A9918P/Starphire (Control)	0.7	7.0	16.7	30.6	88.1 (4)	87.4 (4)
A9918P/Solatex II or Solarphire	1.2	6.8	8.0	9.2	23.8	22.6
Encapsulants Which Use "Fast-Cure" Conditions						
X15303P/Starphire	0.4	2.5	2.3	1.3 (3)	3.1	2.7
15295P/Starphire (Control)	-0.4	0.4	2.2	5.7	78.6	79.0
15295P/Solatex II	0.0	1.3	1.8	2.2	8.2	8.2

(1) Ci35A xenon-arc Weather-Ometer, 100 degrees C, 0.55 watts/square meter at 340 nm;
(2) Glass/EVA/Glass laminates with Starphire on the back side;
(3) Data taken by different technician;
(4) Solite glass superstrate;
(5) ASTM D 1925; average deviation, ±0.3 Yellowness Index Units

APPENDIX

"Advanced Development of Non-Discoloring EVA-Based PV Encapsulants"

Paper Presented at

13th European Photovoltaics Conference

Nice, France, October 1995

ADVANCED DEVELOPMENT OF NON-DISCOLORING EVA-BASED PV ENCAPSULANTS

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ABSTRACT: This paper discusses the resistance to photothermal browning offered by a series of stabilization strategies for ethylene vinyl acetate (EVA) based photovoltaic (PV) encapsulants, most important of which is a new family of EVA-based encapsulants. These new grades include three "standard-cure" formulations--X9903P, X9923P, and X9933P--and one material that cures under "fast-cure" conditions. After 32 weeks in a Weather-Ometer, these encapsulants showed a Yellowness Index of 4.8 or less, a level that is undetectable by eye.

1. INTRODUCTION

EVA resin-based PV encapsulant is employed extensively by solar module manufacturers worldwide, has been in commercial use since 1981 [1], and has proven dependable from the standpoint of production, module fabrication, and end-use. But despite the widespread acceptance of EVA resin-based A9918P and similar formulations for PV encapsulants, some module producers and end-users have reported cases of browning with field-aged modules. While isolated, these reports raised serious concern as to the long-term reliability of EVA resin-based encapsulants.

Problem definition was conducted using accelerated UV aging studies (AAS) to evaluate the influence of compositional, processing, and operating parameters on A9918P discoloration. Also, instrumental analysis was used to verify suspected chemical degradation mechanisms. Field-aged and Weather-Ometer-aged modules and laminates, prepared with EVA-based encapsulant, were analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) and Gas Chromatography/Flame Ionization Detection (GC/FID) for UV absorbers, by Fourier Transform Infrared Spectroscopy (FTIR) and Raman Spectroscopy for unsaturation and evidence of oxidation, and by Thermogravimetric Analysis (TGA) and X-Ray Photoelectron Spectroscopy (XPS) for vinyl acetate content of the EVA resin. Based on the results of these studies, approaches for stabilizing the EVA-based encapsulant against discoloration/degradation were investigated, and included reformulated systems more inherently resistant to discoloration. These "stabilization strategies" were then evaluated by AAS using an Atlas Ci35A Xenon Arc Weather-Ometer, and by equatorial mount with mirrors for acceleration (EMMA) accelerated outdoor weathering with periodic measurement of Yellowness Index.

2. EXPERIMENTAL

2.1 Sample Preparation

For AAS, vacuum-laminated, coupon-sized laminates measuring 2.70 x 2.75 inches were used. All were prepared with commercial cure schedules based on either A9918P "standard-cure" or 15295P "fast-cure" EVA. For most of this work, glass/glass laminates were selected to facilitate colorimetric and spectrographic measurements.

2.2 Superstrates

The superstrate was commercially used low iron glass to allow maximum transmission of UV-B light (i.e., 285 to 350 nm), the wavelength region suspected of being responsible for encapsulant discoloration. Low iron glasses included Solite (AFG - samples from the mid 1980s), Starphire (PPG), Solatex II (AFG - containing cerium oxide, estimated at less than 4 percent), and Solarphire (PPG - also with cerium oxide). During development work it was speculated that Solarphire (previously named Airphire) and Solatex II would benefit this application by removing most of the UV-B radiation.

2.3 Sample Exposure and Evaluation

Laminates were exposed to 0.55 watts/m^2 (@ 340 nm), > 95 percent R.H., and 100°C in an Atlas Ci35A Xenon Arc Weather-Ometer using quartz/borosilicate glass filters. The nominal lower end UV cutoff was 285 nm. Coupons were monitored for Yellowness Index during AAS, per ASTM D-1925, and percent light transmission (%T) between 250 and 900 nm by UV-VIS spectrophotometer. Some analysis of additive and vinyl acetate contents was also done.

3. RESULTS AND DISCUSSION

3.1 Additives Are Key to Browning

One hypothesis is that browning in EVA-based encapsulants is due to the formation of long sequences of conjugated double bonds (polyenes). These result from loss of acetic acid by EVA's vinyl acetate units [2]. However, a sequence of eight or more conjugated double bonds is required to absorb visible light, as has been observed with polyvinyl chloride [3]. The EVA used in A9918P contains 33 weight percent or 15 mole percent vinyl acetate. Thus, the reactivity ratios for this random copolymer are unity during high pressure polymerization, and it is difficult to imagine the formation of sequences of eight or more units as would be required to create color when thermolyzed to conjugated unsaturation.

For example, when Sung and Noggle conducted carbon-13 NMR studies on a 40 percent vinyl acetate EVA, they found that for sequences of three and five VA units the intensity of the NMR peak was "too weak to be observed [4]." And, if sequences of three and five VA units were undetectable, then certainly there would be almost no chains of eight units or more, as needed to induce color.

When instrumental analysis supported our view that conjugated double bonds did not appear to be a major cause of browning, other possible contributors were examined. Specifically, stabilizing and curing additives and their interactions in the presence of elevated temperature and intense UV-B light were studied. The following summarizes conclusions of the analyses:

- Neither FTIR nor Raman spectroscopy indicated the presence of measurable levels of unsaturation in discolored EVA-based encapsulant.

- The acetate contents of numerous samples, covering the spectrum from unaged to field- and Weather-Ometer-aged laminates, were virtually identical and at the expected levels (see Table 1).

Table 1: Analysis of EVA encapsulants shows no significant loss of acetic acid.

% vinyl acetate content by TGA			
Standard-cure A9918P		Fast-cure 15295P	
Description	%VA[1]	Description	%VA[1]
Uncured sheet	33.2	Uncured sheet	32.4
Cured, unaged	34.9	Cured, unaged	32.8
Weather-Ometer aged, 12 weeks (light yellow)	33.5	Weather-Ometer aged, 25 weeks (yellow)	32.1/32.6
Carrizo modules (brown)	33.9 to 35.5	Weather-Ometer aged, 34 weeks (amber)	33.0/33.6

[1] Corrected for ash residue.

- When treated with peracetic acid, a severely discolored EVA-based sample did not lose any of its color. But a PVC control, which had been purposely degraded to generate conjugated unsaturation and a dark brown color, was bleached to translucent white when the unsaturation was oxidized using the same method. These results supported our hypothesis that browning of EVA-based encapsulant arises from some cause other than polyenes, likely the additives.

- AAS of a laminate of A9918P without Lupersol 101 showed little reduction in the stabilizing additive concentrations, while AAS of A9918P with the normal level of Lupersol 101 showed a significant reduction in stabilizing additives after 12 weeks. The latter also exhibited significant yellowing while the former did not.

3.2 Reformulated EVA-Based Encapsulants Resist Browning

Using the above analyses as a guide, four new EVA-based encapsulants were developed, and glass/encapsulant/glass laminates prepared from each. After 30 weeks AAS, all four evidenced slight Yellowness Index increases of 1.8 to 3.8, a level not detectable by eye. Controls with A9918P and "fast-cure" 15295P had Yellowness Index increases of 72.0 and 64.3, respectively (Fig. 1). Yellowness becomes visible at an index of approximately 10.

3.3 Glass Superstrates Containing Cerium Oxide Reduce Browning

After 30 weeks exposure in the Weather-Ometer, glass/encapsulant/glass laminates prepared with "fast-cure" 15295P and cerium oxide-containing glass superstrate had a Yellowness Index of 5.2--a level not readily detectable by eye. Exposure for a full year resulted in a 13 Index. By comparison, a control with 15295P and Starphire low iron glass had an Index of 87 after the same 30 weeks AAS.

In addition, one year of accelerated outdoor EMMA exposure (52,464 MJ/m^2 total annual irradiance) in Phoenix, Arizona, USA, resulted in almost no color formation for samples with cerium oxide-containing glass. Yellowness Index values of 0.8 and 2.2 were determined for the "fast-cure" and "standard-cure" EVA samples with cerium oxide-containing glass, respectively. The Yellowness Index for "fast-cure" 15295P EVA using Solite glass was 3.6, or 4.5 times worse, while the Index for "standard-cure" A9918P EVA with Solite glass was 28.8, or 13 times worse. In all cases, the "fast-cure" 15295P EVA proved more stable than "standard-cure" A9918P EVA (Fig. 2).

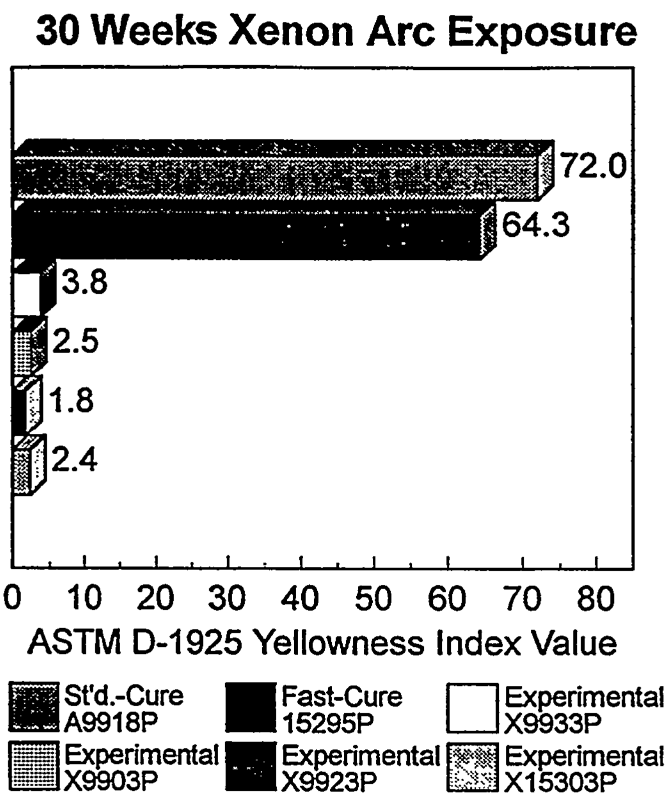

Figure 1: Yellowness of experimental encapsulants on extended Weather-Ometer exposure.

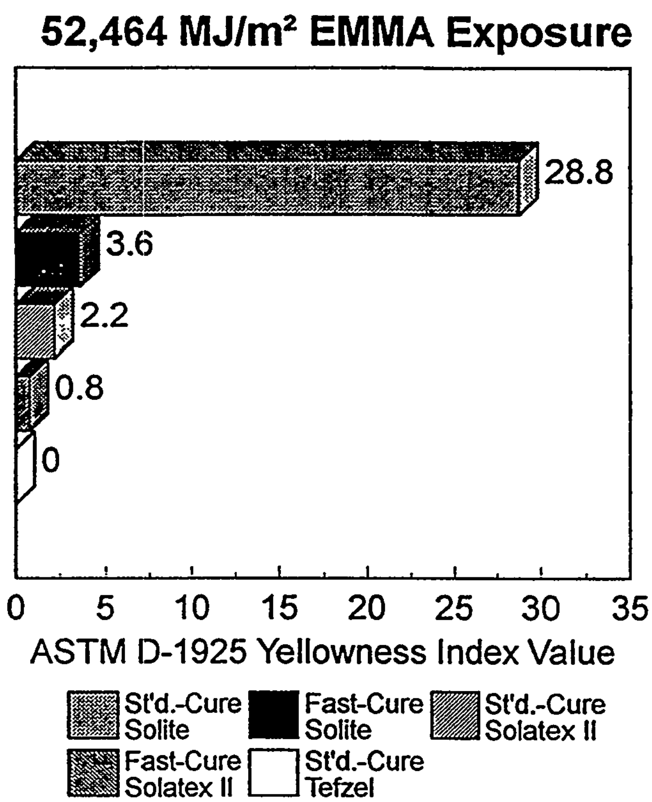

Figure 2: Yellowness of various encapsulants/glass superstrates on accelerated outdoor light exposure.

3.4 Tefzel Superstrate Reduces Encapsulant Browning

After 60 weeks of AAS, a Tefzel/A9918P/glass laminate had a Yellowness Index of 2.0 (Fig. 2). Exposure to one year EMMA weathering also resulted in no measurable yellowing.

4. CONCLUSIONS

Extensive analysis of field- and Weather-Ometer-aged EVA-based encapsulants discounts the hypothesis that browning is based on the deacetylation of repeating vinyl acetate groups, leading to conjugated polyenes in sequences of eight or more. No conjugated unsaturation or loss of acetate group was detected, and therefore no measurable free acetic acid found.

Instead, there are strong correlational AAS data and analysis results to support the hypothesis that additive interaction is a key to browning. Fully formulated A9918P encapsulant browns significantly during extended AAS, while EVA with advanced stabilization and cure packages demonstrates almost no browning, and up to 40 times more resistance than A9918P.

In addition, when EVA with the A9918P stabilizing additives and peroxide crosslinker is subjected to AAS, the stabilizing additives tend to significantly deplete and the laminates show measurable yellowing. On the other hand, when the peroxide is omitted, AAS results in no loss of stabilizers and almost no color development.

Browning of EVA-based encapsulant can thus be attributed to transformation products formed by the consumption of stabilizing additives by alkoxy radicals. These radicals originate from the photolysis of the residual peroxide that remains in the encapsulant after cure.

In conclusion, this development work yielded three "stabilization strategies" for greatly limiting photothermal browning. These are:

- The use of cerium oxide-containing glass superstrates, especially those formulated with "fast-cure" 15295P;
- Specification of Tefzel cover film in place of glass;
- And, most importantly, a choice of four new EVA-based encapsulants--three "standard-cure" (X9903P, X9923P, and X9933P) and one "fast-cure" (X15303P)--all which do not require the utilization of special superstrates.

For added protection, it is recommended that cerium oxide-containing glass, either Solatex II or Solarphire, be used as the superstrate. These glasses contain sufficient cerium oxide to provide a lower end light transmission cutoff of approximately 325 nm.

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13. ABSTRACT *(Maximum 200 words)*

The goals of the NREL PVMaT program are, among others, to reduce module manufacturing costs and to improve the quality and reliability of manufactured PV products. One component critical to the service life of PV modules is the useful life of the ethylene vinyl acetate (EVA) resin-based encapsulant that is employed extensively by module manufacturers on a worldwide basis. However, some module producers, end-users, and investigators have reported a yellowing or browning phenomenon with EVA-resin-based encapsulant in the field. Under the NREL PVMaT program, Springborn Laboratories proposed a comprehensive study of the EVA aging and discoloration problem and its possible solution(s). This report summarizes how an accelerated aging technique has been used to develop a series of EVA-based candidate encapsulants resistant to discoloration under accelerated testing. These candidates are now under outdoor test in Arizona.

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