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FURTHER ANALYSIS OF ACCELERATED EXPOSURE TESTING OF THIN-GLASS MIRROR MATRIX

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ABSTRACT

Concentrating solar power (CSP) companies have deployed thin-glass mirrors produced by wet-silver processes on ~1-mm-thick, relatively lightweight glass. These mirrors are bonded to metal substrates in commercial installations and have the confidence of the CSP industry. Initial hemispherical reflectance is ~93%–96%, and the cost is ~\$16.1/m^2–\$43.0/m^2. However, corrosion was observed in mirror elements of operational solar systems deployed outdoors for 2 years. National Renewable Energy Laboratory (NREL) Advanced Materials Team has been investigating this problem. First, it was noted that this corrosion is very similar to the corrosion bands and spots observed on small (45 mm x 67 mm) thin-glass mirrors laminated to metal substrates with several different types of adhesives and subjected to accelerated exposure testing (AET) at NREL. The corrosion appears as dark splotches in the center of the mirror, with a corresponding 5%–20% loss in reflectivity. Secondly, two significant changes in mirror manufacture have occurred in the wet-chemistry process because of environmental concerns. The first is the method of forming a copper-free reflective mirror, and the second is the use of lead-free paints. However, the copper-free process requires stringent quality control and the lead-free paints were developed for interior applications. A test matrix of 84 combinations of sample constructions (mirror type/back-protective paint/adhesive/substrate) was devised for AET as a designed experiment to identify the most-promising mirrors, paints, and adhesives for use with concentrator designs. Two types of accelerated exposure were used: an Atlas Ci5000 WeatherOmeter (CI5000) and a BlueM damp-heat chamber. Based on an analysis of variance (ANOVA), the various factors and interactions were modeled. These samples now have more than 36 months of accelerated exposure, and most samples have completed their test cycle. We will discuss the results of the final exposure testing of these mirror samples. Glass mirrors with copper back-layers and heavily leaded paints have been considered robust for outdoor use. However, the basic mirror composition of the new mirrors is radically different from that of historically durable solar mirrors, and the outdoor durability must be determined.

INTRODUCTION

The widespread application of CSP generation depends largely on developing a durable, low-cost reflector. The U.S. Department of Energy (DOE) CSP Program has the goal, defined in 1992, to develop a solar reflector with a specular reflectance above 90% into a 4-mrad half-cone angle, with a lifetime of at least 10 years under outdoor service conditions, and a cost of less than \$10.76/m^2 (\$1/ft^2) for large-volume manufacturing [1]. Unofficially, 95% reflectance and a 15–30-year lifetime have been sought. Adjusting the cost goal for inflation, a \$10.76/m^2 (\$1/ft^2) reflector would be equivalent to \$15.46/m^2 (\$1.44/ft^2) when corrected from 1992 to 2006 dollars [2]. Companies within the CSP (mainly dish/Stirling) and concentrating photovoltaics (CPV) industries are using solar concentrators that comprise thin glass mirrors bonded to metal substrates. Several forms of degradation have been observed on mirror facet elements comprising thin glass mirrors bonded to stainless-steel substrates with pressure-sensitive and contact adhesives that have been deployed outdoors as part of operational CSP systems. The pattern of discoloration and corrosion observed in the field exhibits strong similarities to those seen in AET. The corrosion appears as dark splotches in the center of the mirror, with a corresponding 5%–20% loss in specular reflectivity. Evidence suggests that water wicks through the adhesive, permeates through the paint, and facilitates corrosion of the metal layers [3]. Nitrogen found in the paint layer suggests the presence of amines that can break down into compounds that dissolve the copper. Copper and silver are both corroded by the chloride ions found in the paint.

Mirror-backing coatings are produced by traditional wet-chemistry processes: the clean glass is sensitized with $SnCl_2$, the Ag layer is applied by chemical reductive processes, the Cu layer is applied by chemical processes, the mirror-backing paint is applied by various techniques, and the applied paint is force-cured by heating. A new copper-free process has been developed that replaces the copper layer used to inhibit silver-layer corrosion in mirror manufacturing [4]. However, the copper-free process requires the silver deposited on fresh, clean glass and stringent quality control. Silvered mirrors made with the new copper-free process, the application of ~100-Å layer of SnO_2, have several advantages compared to the older copper protective layer: improved chemical resistance; the SnO_2 still allows adhesion of the paint layer; the SnO_2 is a good diffusion barrier for oxygen and water and is immune to further oxidation; the Ag/SnO_2 system does not suffer from the known problems of copper/silver interdiffusion implicated in mirror degradation; and it does not produce copper-containing waste streams that must be environmentally processed and treated for recycling [5].

The mirror-backing paint systems and resulting coatings are typically based on solvent-borne alkyd resins, which are relatively complex paint systems and are proprietary to the paint manufacturers. The paint formulations that afford the best protection against the corrosion of the copper layer protecting a silvered mirror contain lead pigments as the active corrosion-inhibitor component. Historically, solar systems built 10–20 years ago used glass mirrors with multiple-layer paint systems, where one layer contained specially formulated highly leaded (10%–20% lead by weight) paints. The original Flabeg trough mirrors, produced between 1975 and 1985 (used by the Solar Electric Generating System [SEGS] plants in California), used silvered 4-mm-thick, low-iron slumped glass with copper back-layers and a highly leaded multilayer paint system designed for outdoor exposure, that has proven durable [6]. Likewise, McDonald Douglas mirrors that have proven durable in the field for nearly 20 years used a highly leaded multilayer paint system.

Now, highly leaded paints containing more than 10% lead by weight are not available because of environmental and health concerns and most leaded paints contain 0.5%–2% lead by weight. Flabag reported to NREL they had converted their mirror line in 2003 to run 4- or 5-mm glass and a new low-lead paint system, where the lead was reduced to the point that the durability remained equivalent. The base paint of the new three-layer paint system now contains 2.5% lead; the intermediate paint contains 1% lead; and the white outermost coat is still acrylic based and has high ultraviolet (UV) stability [7]. Unfortunately, although the coatings with high lead content are robust, they have been mostly phased out because lead pigments are toxic and their use is discouraged for environmental health reasons.

Mirror-backing paint companies have developed new lead-free paint systems that perform quite well in accelerated tests, but, notably, are intended for indoor conditions. A (Ni^{2+} and Co^{2+})-bis-hydrogen cyanamide is considered to be one of the best-performing, lead-free, corrosion-inhibitor pigments on the market at this time [8]. A second type of lead-free mirror back-coating incorporates antioxidant pigments, which are also cyanamide derivatives of metals, within a melamine-based resin [9]. A third type of lead-free mirror back-coating can be applied as a film and hardened to form a protective layer on the back of the mirror. It comprises a fluid organic resin and a corrosion inhibitor [10, 11]. Lead-free paint systems are capturing significant market share in the indoor mirror market.

Glaverbel in Belgium developed and patented the copper-free process, and launched the copper-free process and the lead-free paint systems in their commercial mirror line in 1998. Pilkington in the United Kingdom commercially introduced the copper-free process in 2000 for thick (3–6 mm) soda-lime glass. In 2000, Naugatuck in the United States began pilot production of mirrors using this process on thin (1.0- and 1.2-mm-thick) glass. It has been claimed that the new construction will have greatly increased resistance to weathering, but other than the Soltys patent [4], there is no evidence in the open literature to support this claim. In addition, experts in mirror paint systems have little expectation that pigments designed for interior applications will have long-term durability in outdoor applications [12,13].

EXPERIMENTAL DESIGN

Several experts recommended using epoxy-based paint systems, which are more appropriate for outdoor applications compared to the traditional alkyd-based paint systems [12-14]. Generally, they recommend a two-component solventless epoxy. However, epoxy paint systems specifically designed as mirror back-coatings appear to be in the developmental stage and are not now commercially available. Additional recommendations included adding a protective paint that is dense and impervious to water might prevent failure. Other possibilities would be to coat the paint either with metal or other inorganic layers that are highly impermeable to water, or with hydrophobic coatings. Use of nonwicking adhesives and strategies that provide an effective edge seal to prevent moisture ingress might also be advantageous.

To experimentally test the numerous recommendations, a D-optimal fractional factorial algorithm was used (Design-Expert® software) to accommodate seven different factors (each having a different number of test levels) into an efficient experimental design to test the durability of thin-glass mirrors

TABLE 1. FACTORS AND LEVELS USED FOR DESIGN OF THIN-GLASS MIRROR TEST MATRIX

Levels	Factors					
	A: Mirror Type[1]	**B: Back Protection[2]**	**C: Adhesive[3] / Substrate[4]**	**D: Edge Protection[5]**	**E: Substrate Cleaning[6]**	**F: Back Cleaning[7]**
1	Naugatuck/Cu	Epoxy	3M 504FL / Al steel	None	SAIC	3M
2	Naugatuck/no Cu	Polyurethane	3M 504FL / Al	Exuded adhesive	SES	None
3	Glaverbel	None	3M 966 / Al steel	CPF film		
4			3M 966 / Al			
5			Mactac / Al steel			
6			Mactac / Al			
7			Epoxy / Al steel			
8			Epoxy / Al			
9			Urethane / Al steel			
10			Urethane / Al			
11			Contact / Al steel			
12			Contact / Al			
13			None			

1: *Naugatuck/Cu*: Naugatuck's standard product with single-coat no-lead paint system.
Naugatuck/no Cu: Naugatuck pilot production run of improved version, which eliminates copper layer with single-coat no-lead paint system.
Glaverbel: Glaverbel's Mirox MNGECological clear standard product (similar copper-free construction) with two-coat mo-lead paint system.
2: *Epoxy*: Benjamin Moore amine M70/M71
Polyurethane: DuPont Imron 3480-S/193-S
None: No additional back-protection layers
3: *3M 504FL*: 3M504 FL pressure-sensitive adhesive (PSA)
3M 966: 3M 966 PSA
Mactac: Mactac's acrylic MACbond 1B-2101 PSA
Epoxy: Extreme 3010 epoxy
Urethane: Ciba Uralane 6100 A/B urethane
Contact: Eclectic E6100 contact cement
None: No adhesive or substrate
4: *Al steel*: ASTM 463-B aluminized steel, with a T1-40 aluminum-silicon coating Stirling Energy Systems, Inc. (SES) standard substrate.
Al: 5052 H32 aluminum Science Application International Corporation (SAIC) standard substrate.
None: No substrate or adhesive
5: *Exuded adhesive*: Excess adhesive exuded out around the periphery of the mirror as a sealant bead
CPFilm: CPFilm Spectraseal ACL1307
None: No edge sealant
6: *SAIC*: standard cleaning practice—Custom Buildings Products T.S.P. (trisodium phosphate) soap and water
SES: standard cleaning practice—Chemetall Oakite Ardrox® 154-A, silicated alkaline immersion cleaner
7: *3M*: Dow Corning Z-6040 silane adhesion promoter diluted in a 50:50 isopropyl alcohol:water cleaning solution
None: As received

[15]. Adhesive/substrate effects were combined as a matter of experimental design convenience (to reduce the number of required samples and to ensure that the experimental design process would not specify application of an adhesive when no substrate was used). The resulting six experimental factors investigated were: (a) thin-glass mirror type, (b) back protection, (c) adhesive/substrate combination, (d) edge protection, (e) substrate cleaning procedure, and (f) mirror-back cleaning procedure. Table 1 summarizes these factors and their respective categorical levels. A series of accelerated screening tests were performed to minimize the number of levels required within each factor [16]. The test matrix includes 84 samples and incorporates all the combinations of factors to be considered.

Mirror types included Naugatuck's standard product having the construction: thin glass / wet-chemistry silver / wet-chemistry copper / back-protective paint (where the paint system is a single-coat no-lead [0.0% Pb] formulation), the Naugatuck pilot-production run of the copper-free process with the same paint formulation ("no Cu"), and Glaverbel's Mirox MNGECological product (having a similar copper-free construction, but a two-coat lead-free paint system where the first layer, in all likelihood, contained <1% lead because of the difference in the definition of lead-free paint between E.U. and U.S. regulations.) Additional back-protection layers of commercially available epoxy (Benjamin Moore amine M70/M71) and polyurethane (DuPont Imron 3480-S/193-S) sealants (along with "none") were incorporated as the second factor. These constructions were then laminated onto two types of metal substrates (ASTM 463-B aluminized steel, with a T1-40 aluminum-silicon coating, and 5052 H32 aluminum used by dish/Stirling manufacturers at the time the experiment was initiated) using six candidate adhesives (3M's 504 FL and 966, Mactac's acrylic MACbond 1B-2101, Extreme 3010 epoxy, Ciba Uralane 6100 A/B urethane, and Eclectic E6100 contact cement). These 12 combinations of adhesives/substrates (along with "none") resulted in 13 levels for this factor.

Several edge-protection concepts were used. One approach was to apply the excess adhesive exuded out around the periphery of the mirror during the lamination process as a sealant bead. After review of the literature and discussions with window vendors, a CPFilm window sealant product (Spectraseal

ACL1307) was recommended as a promising edge protectant. The third level of edge protection ("none") was used as a benchmark to determine the relative effectiveness of edge-protection strategies.

Mirror, paint, and adhesive manufacturers suggested that how the substrate is prepared (the fifth factor) and how the backside of the mirror is cleaned (the sixth factor) prior to lamination are important parameters. Consequently, we incorporated two procedures (levels) for each of these factors into the experimental design. The two processes for substrate cleaning were those currently in practice by two solar manufacturers [16]. The backsides of the mirrors were laminated either as received (uncleaned) or following a 3M priming procedure [16].

To generate the test matrix, we modeled all six of the primary factors (A through F). Two-factor effects that were included were mirror-type interactions with the other five factors (AB, AC, AD, AE, and AF) and the interaction of the back-protection coating with the adhesive/substrate (BC), because these are in intimate contact in the mirror construction. No other interaction terms were modeled. This design resulted in 81 sample constructions that were needed to test all of the factors and interactions of interest. Three randomly chosen samples were replicated to allow the estimation of the pure error associated with the modeled results. Physical test samples roughly 67 mm x 44 mm with the basic architecture of glass mirror / back protection / adhesive / substrate were constructed according to the test matrix.

TEST PROTOCOL

Once the various sample constructions were prepared, we began testing. Optical performance was characterized by measuring spectral hemispherical reflectance, $\rho_{2\pi}(\lambda)$, with an ultraviolet-visible-near-infrared spectrophotomer. This instrument has an accuracy of ±0.8% and a repeatability of ±0.2%. To obtain a single quantity for comparison purposes, $\rho_{2\pi}(\lambda)$ is typically weighted by an air-mass 1.5 terrestrial direct-normal solar spectrum over a specified bandwidth of interest ($\Delta\lambda$) [17,18]. Typically, broadband solar-weighted hemispherical reflectance, $\rho_{2\pi}(\Delta\lambda=250\text{–}2500)$, is used. Alternatively, the bandwidth between 400–650 nm has been found to be particularly sensitive to degradation effects for many glass mirrors, thereby providing a more rapid quantification of performance loss. Both of these quantities were used to analyze the test data. Two types of accelerated exposure were used, namely, an Atlas Ci5000 WeatherOmeter (Ci5000) and a BlueM damp-heat chamber (BlueM). Exposure conditions in the Ci5000 were filtered xenon-arc light intensity (~2 suns), 60ºC sample temperature, and 60% relative humidity (RH). A single day of testing (24 hours) is roughly equivalent to six times the outdoor exposure in terms of light intensity. The BlueM conditions were: no light, 85ºC, and 85% RH. This test is used by the adhesive industry to greatly accelerate weathering effects.

Mirror samples were optically characterized prior to exposure testing, and after about every 3 months of exposure in the Ci5000 (i.e., samples were measure at 0.0, 0.7, 2.1, 5.0, 6.2, 6.4, 9.0, 11.8, 14.6, 18.1, 23.2, 28.3, 34.8, and 38.9 months of exposure) and after about every 2–4 weeks of exposure in the BlueM chamber (i.e., 0.0, 0.9, 1.2, 1.5, 2.1, 2.9, 4.0, 5.9, 7.2, 8.1, 10.2, 11.1, 14.9, 20.7, 24.6, 29.4, and 36.1 months). The optical response variable for the samples is defined as the change in weighted hemispherical reflectance:

$$R_{Opt} = \rho_{2\pi}(\Delta\lambda, t=0) - \rho_{2\pi}(\Delta\lambda, t) \qquad (1)$$

for $\Delta\lambda$=250–2500 nm (Sol Wt). To account for the removal of samples as they failed, the optical response variable was weighted over time by:

$$R_{wt} = R_{Opt} * \frac{\tau_{dis}}{\tau_f} \qquad (2)$$

where τ_{dis} is the exposure time when the samples were discontinued and τ_f is the exposure time for the final sample measurement in the experiment (to date, 36.1 months in the Ci5000 and 38.9 months in the BlueM).

A number of visual attributes were used to characterize mirror appearance, including cracking, corrosion, delamination, silver agglomeration, haze, and three forms of degradation observed outdoors, namely, "banding" (the formation of snake-like bands or zones of discoloration), mottling (the presence of non-reflective spots, often caused by pit corrosion), and darkening. The visual response variable was calculated as:

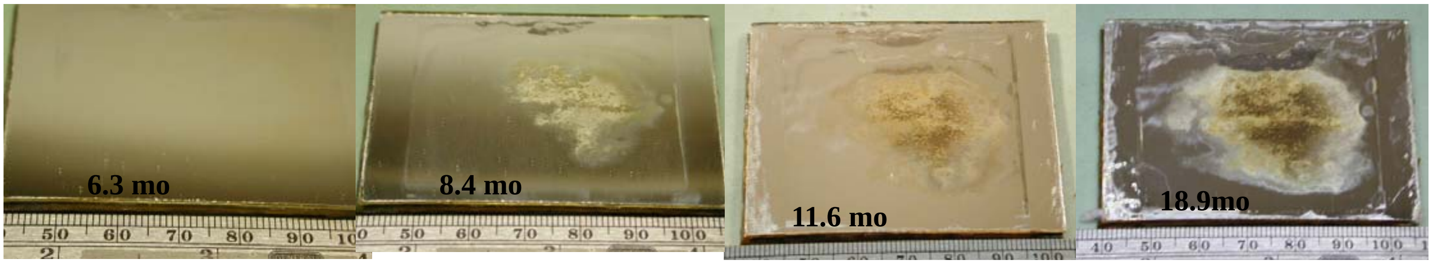

FIG. 1. PROGRESSION OF SPOT CORROSION OVER CI5000 EXPOSURE TIME FOR NAUGATUCK/COPPER-FREE/EPOXY BACK PROTECTION /CONTACT ADHESIVE/AL STEEL.

$$R_{vis} = \sum_{i=1}^{n} R_i * A_i \tag{3}$$

where R_i is an assigned severity rating (0–10 with 0 = unexposed condition) of the i^{th} visual effect, A_i is the fraction of area (0–1) that experiences visual degradation, and n is the number of attributes considered. Two values of R were calculated and used for analysis: n=1 (haze) and n=7 (haze + corrosion + delamination + Ag agglomeration + mottling + darkening + banding), cracking is more a measure of handling than inherent degradation). Samples were judged to have failed if their reflectance dropped more than 10% from their original value (i.e., below 85.82%); the glass mirror delaminated from the substrate; or from visual observations if corrosion, mottled spots or banding, silver agglomeration, or darkening occurred over more than 80% of the sample.

SUMMARY OF PREVIOUS RESULTS

We used the Design-Expert® software to analyze the reflectance data. Based on an ANOVA, we modeled the various factors and interactions, and we found the model to be significant. Mirror type, back protection, and adhesive/substrate combination were found to be significant factors; the only significant interaction term was between mirror type and back protection. Edge protection, substrate cleaning, and back cleaning had no effect on the model. The "Lack of Fit" was not significant relative to the pure error. Non-significant lack of fit is desirable—we want the model to fit.

After initial exposure, 61% of the samples exposed in the Ci5000 showed a slight improvement in the reflectivity (less than 2.7%), whereas only 13.7% of the BlueM samples showed a slight improvement (less than 1%). Forty-six percent of the Naugatuck with copper samples, 52% of the Glaverbel no-copper samples, and more than 96% of the Naugatuck no-copper mirrors exhibited improved reflectance values after initial exposure in the Ci5000. Samples showed no further improvement with subsequent exposure.

Initially, after 2.9 months of Ci5000 exposure, the Naugatuck mirror without copper was found to be significantly better than the other types of mirrors [19]. However, this result was due to the increase in reflectance (response variable) as discussed above, and was considered an anomalous effect because small improvements in reflectivity after initial exposure (solarization) are commonly observed for glass mirrors during exposure testing. Solarization is the initial change in the optical transmission spectrum of glass after exposure to simulated or high-flux terrestrial solar irradiance and temperature [20]. Solarization effects are dependent on the glass type, glass additives, radiation wavelength, and temperature. Solarization is permanent at room temperature but may be reversed by thermal annealing. Depending on the glass composition the transmission of commercial low-iron can either increase or decrease and is thought to be caused by changes in the valence state of the elements in the glass [21,22]. Exposure testing of these mirror samples was continued.

Most samples exposed in the Ci5000 exhibited no perceptible changes in visual appearance for the first year of exposure (Fig. 1). But almost all of the samples exposed to damp heat exhibited some visual change immediately (Fig 2). This can be explained because the humidity and temperature in the BlueM is much higher than in the Ci5000, mirror backing paints were not designed for high humidity and the silvered thin-glass mirrors are more sensitive to exposure to high humidity and temperatures than to exposure to simulated sunlight. The first Ci5000 samples to reach failure were discontinued after 14.6 months of exposure, whereas samples in damp heat began to fail at 0.9 month. Far fewer samples failed catastrophically (i.e., delamination, Fig. 3) following exposure in the Ci5000 than in the damp-heat test. After two years of exposure, 3% of the Naugatuck with copper, 14% of the Naugatuck copper-free, and 10% of the Glaverbel copper-free samples delaminated in the Ci5000. However, about half of the Naugatuck with copper samples and about a third of the Naugatuck and Glaverbel copper-free samples delaminated in the damp-heat test.

After 23.4 months of Ci5000 exposure, the Glaverbel (noncopper) mirrors ranked slightly better than the standard Naugatuck (copper-containing) mirrors for epoxy and polyurethane [23]. Naugatuck thin-glass mirrors without copper were found to be slightly worse than the other types of

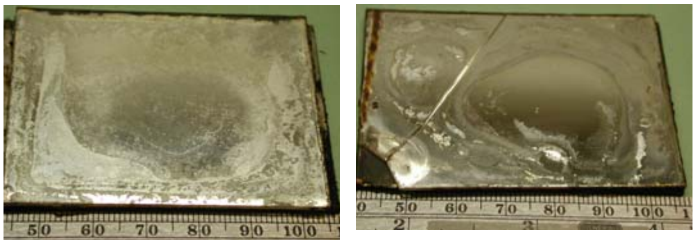

FIG. 2. CORROSION OF TWO MIRRORS AFER 2.9 MONTHS IN BLUEM

Left-same as Fig 1 (Naug/no Cu/Epoxy back/contact ADH/Al steel)
Right- (Naug/Cu/Epoxy back/Epoxy ADH/Al)

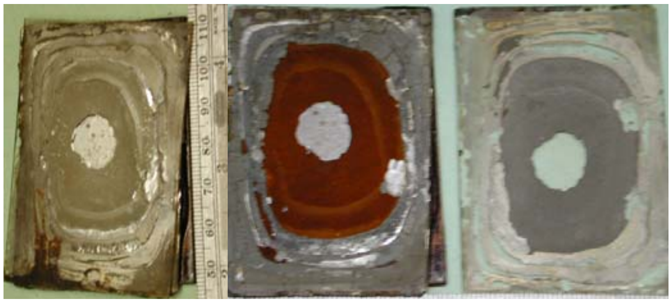

FIG. 3 DELAMINATION OF MIRROR AFER 15.4 MONTHS IN BLUEM

Left- from top, Center-mirror interior-substrate side, Right-mirror interior-glass side (Naug/Cu/Epoxy back/Epoxy ADH/Al steel)

TABLE 2. MOST-DESIRABLE SOLUTIONS FOR EACH TEST METHOD FROM NUMERICAL OPTIMIZATION

Solution #	Tested in Model	A: Mirror Type	B: Back Protection	C: Adhesive / Substrate	D: Test Method	Predicted Average Reflectance	Measured Reflectance	Predicted Average Exposure Time (mo)	Exposure Time (mo)	Corrosion (n=1)	Delamination (n=1)	Appearance (n=7)	Desirability
16	Y	Glaverbel	None	Epoxy/Al steel	BlueM	92.92	94.08	35.20	29.42	1.6	0.4	5.7	0.692
31	Y	Glaverbel	None	Epoxy/Al	BlueM	89.72	90.21	33.58	36.10	1.6	0.6	2.2	0.631
38	Y	Glaverbel	None	Mactac/Al steel	BlueM	93.43		28.89		1.6	1.5	5.0	0.593
47	N	Glaverbel	None	3M 504FL/Al steel	BlueM	90.38		26.08		1.6	1.6	4.7	0.488
50	N	Glaverbel	None	Mactac/Al	BlueM	91.04	91.71	26.85	36.10	1.6	0.1	5.9	0.469
54	Y	Naugatuck/no Cu	None	Epoxy/Al steel	BlueM	89.42	93.60	25.01	36.10	2.6	-0.8	5.2	0.332
1	Y	Glaverbel	None	Epoxy/Al steel	Ci5000	96.59	93.13	41.48	38.89	1.6	0.7	5.5	0.836
2	Y	Glaverbel	None	Epoxy/Al	Ci5000	95.65	95.31	43.28	38.89	1.6	0.9	2.0	0.815
3	Y	Glaverbel	None	3M 966/Al steel	Ci5000	94.72	92.66	39.04	38.89	1.6	0.8	3.6	0.795
4	Y	Naugatuck/Cu	Polyurethane	3M 504FL/Al steel	Ci5000	94.94	89.79	34.91	38.89	0.9	-0.2	1.6	0.790
5	N	Glaverbel	None	Mactac/Al steel	Ci5000	96.03		47.62		1.6	0.4	4.7	0.789
6	N	Glaverbel	None	3M 504FL/Al steel	Ci5000	93.34		47.49		1.6	0.3	4.4	0.785
7	Y	Glaverbel	Polyurethane	Urethane/Al steel	Ci5000	94.80	92.15	39.75	38.89	1.2	0.7	5.0	0.764
8	Y	Glaverbel	Polyurethane	3M 504FL/Al steel	Ci5000	92.57	92.82	32.64	38.89	1.2	0.2	1.5	0.760
9	Y	Naugatuck/Cu	Polyurethane	3M 504FL/Al	Ci5000	90.60	88.23	48.32	38.89	0.9	0.1	1.3	0.758
10	Y	Naugatuck/Cu	Polyurethane	Urethane/Al steel	Ci5000	96.49	92.62	42.25	38.89	0.9	0.3	5.2	0.744
11	Y	Naugatuck/Cu	Epoxy	Mactac/Al	Ci5000	92.30	88.23	31.46	38.89	0.9	0.5	0.3	0.737
12	Y	Glaverbel	None	3M 504FL/Al	Ci5000	94.77	93.34	36.89	38.89	1.6	0.7	6.4	0.727
13	N	Naugatuck/Cu	Polyurethane	Urethane/Al	Ci5000	91.67		41.26		0.9	0.4	1.0	0.727
14	Y	Naugatuck/Cu	Polyurethane	Epoxy/Al steel	Ci5000	95.60	93.41	43.45	38.89	0.9	0.1	4.1	0.700
15	Y	Naugatuck/no Cu	Polyurethane	Epoxy/Al	Ci5000	94.89	93.97	35.24	38.89	2.2	1.1	5.2	0.693

mirrors and none, but were best for polyurethane. For the adhesive/substrate factor, the main result was that mirrors laminated to aluminized steel substrates generally performed better than when they were laminated to aluminum substrates. In general, the 3M504FL pressure-sensitive adhesive and the epoxy adhesive performed the best and the urethane and contact adhesive performed the worst. The mirror-type/back-protection interaction effect suggested that epoxy was a poor choice relative for the Glaverbel and Naugatuck copper-free mirrors. Although the data fell within the experimental uncertainty, the exposure results were beginning to distinguish themselves from the experimental uncertainty. After 20.7 months of BlueM exposure, the degradation observed for the mirror, adhesive/substrate, adhesive, and back-protection factors were, in most cases, equivalent, but possibly at a rate 10 times faster than observed in the Ci5000. Further exposure testing and research would be needed to correlate the damp-heat and Ci5000 results, help resolve the results from the experimental error, correlate the acceleration factor for many types of samples, and attain a confidence level for the damp-heat test.

RECONFIGURING THE EXPERIMENTAL DESIGN

We reconfigured the design that the Design-Expert® software used to analyze the data following recommendations from an expert statistician at Stat-Ease®, the makers of the software [24]. First, we removed the three covariate factors (Edge Protect, Subs Clean, Back Clean) because the model terms were found to be insignificant relative to noise and no useful statistical analysis could be performed. As a result, any effect these factors may have on the responses has been moved to the total variation. Second, we were able to stack the two designs for the two accelerated exposure conditions (BlueM vs. Ci5000) on top of one another and include "Test Method" as a new factor because we had two identical designs done under differing exposure conditions.

Third, too much information was lost in the middle ranges (between the 25th and 75th percentiles) that are critical to development of useful models by averaging across the different responses. The weighting over exposure time was confusing the intermediate responses and obscuring the conclusions, so only the unweighted exposure time (τ_f) was used.

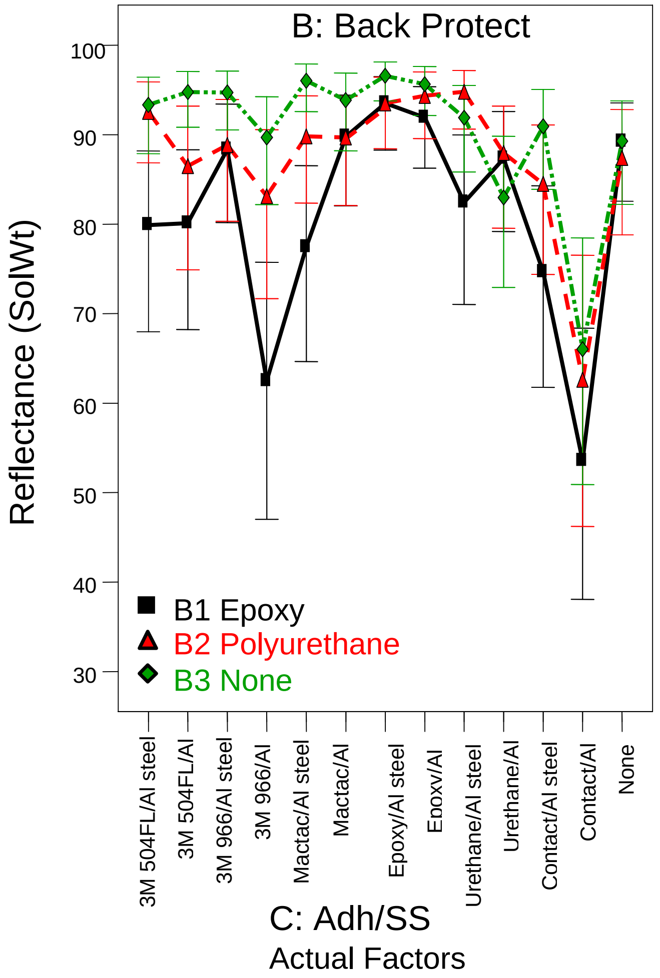

FIG. 4. INTERACTION PLOT OF SOLAR-WEIGHTED HEMISPHERICAL REFLECTANCE OF BACK PROTECTION VS. ADHESIVE/SUBSTRATE (BC) FOR GLAVERBEL MIRROR AFTER 38.9 MONTHS IN THE CI5000.

Fourth, the visual-response variable also was contributing to problems in understanding the middle conditions. Was it the average of everything; or poor haze, corrosion, and banding with good delamination, Ag agglomeration, mottling and darkening? How bad was the haze? This information was lost in a combined metric. Therefore, the Ri and Ai data were separated, and assigned a different (lower) weight than the combined metric R_{vis} for each n=1 (haze, corrosion, delamination, agglomeration, mottling, darkening, and banding) were assigned. The individual R_{vis} for n=7 (haze + corrosion + delamination + agglomeration + mottling + darkening + banding) were added, assigned a higher weight, and used for the analysis.

Fifth, the visible response variables were redefined because a mirror whose appearance is unchanged should have a rating of 0 for 100% of the mirror. Using the previous definition, all of the 0's covered 0% of the area. Therefore, Ri was redefined as the severity rating of the worst case on the mirror and Ai the amount of mirror at level 0 or Ai_{NEW}=1-Ai_{OLD}.

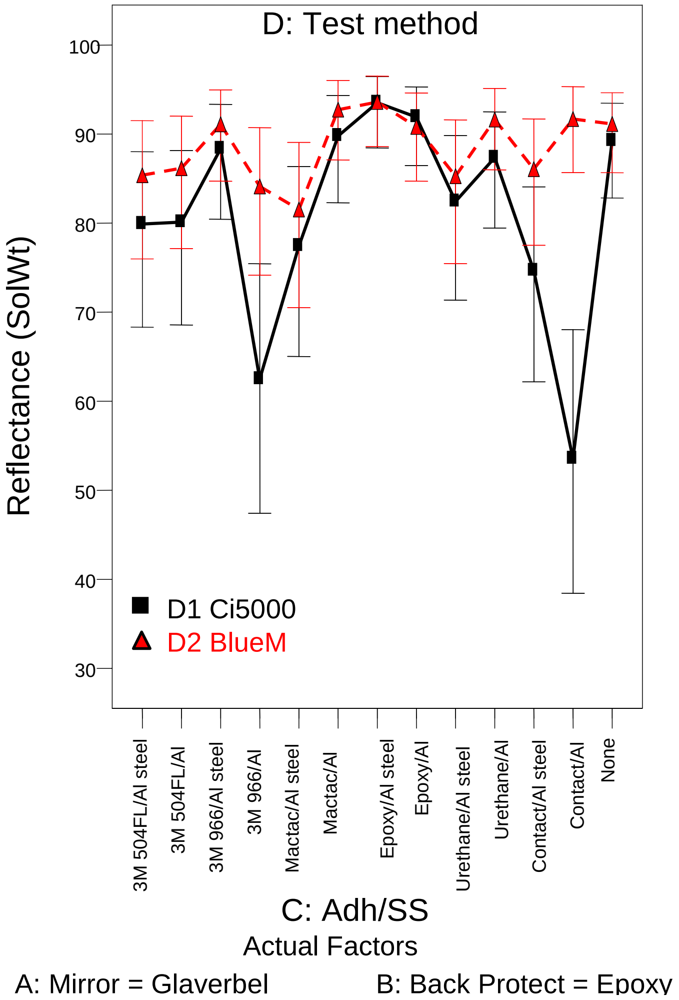

FIG. 5. INTERACTION PLOT OF SOLAR-WEIGHTED HEMISPHERICAL REFLECTANCE OF BACK PROTECTION VS. ADHESIVE/SUBSTRATE (BC) FOR GLAVERBEL MIRROR AFTER 38.9 MONTHS IN THE CI5000.

RESULTS

Performing an ANOVA on the reconfigured experimental design produced reasonable models for the various factors, interactions, and each response. “Reasonable” means that the models do a good job predicting the average responses. The model and the model terms were found to be significant relative to noise, and the “Lack of Fit” was insignificant relative to the pure error. Optimization goals were chosen to maximize reflectance above 85% and an upper goal of 99.99% (nearly perfect), and to maximize exposure time, setting a minimum goal of 25 months, optimization goals were maximized for individual Ai and minimized Ri; the combined metrics R_{vis} for each n=1 (haze, corrosion, delamination, agglomeration, mottling, darkening, and banding) and n=7 (haze + corrosion + delamination + agglomeration + mottling + darkening + banding) were minimized.

The numerical optimization gave 54 solutions; the top 15 are listed in Table 2. These solutions are estimates based on the samples in the model and predict the mirror type, additional back protection, and adhesive combinations that should have the highest reflectivity for the longest life, with the least appearance change. It should be noted that some solutions predicted do not include samples actually tested in the test matrix; this is indicated by a blank cell in the "Measured Reflectance" and "Exposure Time (mo)" columns. The solutions have an average predicted reflectance of 84.43%. The 95% prediction interval ranges from 49.65% up to 96.77%. Exposure varies from as low as 17.92 up to 68.67 months. This prediction interval indicates that roughly 95% of the individual mirrors will have a reflectance somewhere between 50% and 97% and an exposure between 18 and 70 months. Further experimentation will be necessary with several replicates of the best solutions to confirm that the solution truly has better reflectance and durability and to reduce these ranges to more interpretable results. There is enough data to predict what will occur on average, but we lack the data to give a narrow width around this average.

A few rows exhibited high (approaching 1.0) leverages because of the structure of the design rows. Leverages judge how a particular run (row) of the design will influence the fit of the model coefficients. Leverages of 1.0 indicate that the model is forced to go through the point and the model will always perfectly fit the observed value of these rows. Our rows with high leverage points were the Nagatuck/Cu/Polyamide/3M 504FL/Al and Glaverbel/None/Mactac/Al samples both in the BlueM and Ci5000. We ran a design of 84 runs, which is a subset of the 117 runs for all possible combinations of a 3 x 3 x 13 matrix. Although D-optimal designs can estimate a given model—in this case, the two-factor interaction model—the loss of experimental space causes all of the individual points to have increased leverages. Whenever designs are created that do not actually cover all possible combinations of factor levels, the leverages tend to increase. High leverages are only a problem if the data collected are badly flawed. Small variations from the true average will only cause a slight problem. Replicating the points having leverages of 1.0 is a good way to reduce the effect, but requires more runs.

The Glaverbel mirror is the best overall mirror and the epoxy-based adhesive seems to be a good choice based on ANOVA. As shown in Fig. 4, back protection is more difficult to interpret. In general, the Glaverbel and Naugatuck mirrors survived the longest without any back protection. In addition, the polyurethane back protection may be a poor choice based on the observation that only one polyurethane sample has survived 36 months of exposure in the BlueM chamber.

Interactions with the exposure conditions were also found: the test method caused a change in how the system behaved. The "Test Method" effect was found to be significant, with test methods producing different average results. Figure 5 is the interaction plot for the two epoxy-based Adh/SS on Glaverbel mirrors. The Least Significant Difference (LSD) bars overlap, which indicates that the two test methods are not significantly different. But they are clearly different when using the urethane-based Adh/SS. The symbols are the predictions for average exposure, with the LSD bars indicating the interval through which averages will vary based on these data. The reflectance and exposure times are averages; so several mirrors, built with Glaverbel, Epoxy, and Epoxy/AL steel, will have an average solar-weighted reflectance of 88.88% with an average exposure time of 36.97 months. From this sample, the actual mirrors can vary significantly. In general, BlueM is the more accelerated exposure chamber, but the acceleration rate depends on what is being tested, as shown in Table 3. At best, only an average upper bound on the acceleration factor can be estimated; the lower bound is uncertain because 41/84 samples in the Ci5000 and 10/84 samples in the BlueM have not yet reached their end of life. Therefore, it cannot yet be determined that the BlueM accelerates the exposure of all mirrors X times faster than the Ci5000.

TABLE 3. CI5000/BLUEM ACCELERATION FACTOR

Mirror	**Back**	**AVE ACC Factor**	**AVE Upper Bound**	**AVE Lower Bound**
Glaverbel	Epoxy	2.80	6.09	1.62
Glaverbel	Polyurethane	3.28	6.98	1.77
Glaverbel	None	1.94	3.52	1.25
Naugatuck/no Cu	Epoxy	6.10	10.90	2.46
Naugatuck/no Cu	Polyurethane	8.65	32.07	2.49
Naugatuck/no Cu	None	4.25	16.28	1.51
Naugatuck/Cu	Epoxy	8.54	27.06	2.34
Naugatuck/Cu	Polyurethane	10.15	39.95	3.02
Naugatuck/Cu	None	4.74	22.68	1.90
	AVE	5.60	18.39	2.04

CONCLUSIONS

The pattern of discoloration and corrosion observed in the field exhibits strong similarities to those seen in AET. The loss in specular reflectance of 4.4% is quite significant, as about 5%–10% of the area exhibited some level of discoloration after 21 months of field service. Evidence suggests that water wicks through the adhesive, permeates through the paint, and facilitates corrosion of the metal layers [3].

A matrix of sample constructions has been prepared to identify the most-promising combinations of paints and adhesives for use with solar reflectors. Data after over 3 years of exposure in the Ci5000 and in BlueM indicate that the Glaverbel mirror tends to outperform the Naugatuck mirrors in test.

The best back-protection cannot yet be determined, but the application of additional back-protection post-mirror production is not very effective and likely contributes to the catastrophic delamination failures observed. The epoxy adhesive/substrate show slight advantages over other adhesive/substrates. Edge protection and substrate and glass back-cleaning have no effect.

Based on recommendations from the mirror-backing paint industry [12,13] and the performance of the trough mirrors [6], there is some evidence that a multilayer or epoxy back-protection would be useful to increase the durability of the thin-glass solar mirrors. The development of a mirror paint-system suitable for outdoor applications requires the expertise of the mirror paint-system industry. Therefore, it is recommended that mirror paint manufacturers develop a back protection that can be applied during mirror production for solar applications.

Interactions with test methods were also found. The high humidity and temperature (85%RH and 85ºC) in the BlueM has more influence causing silvered thin-glass mirror to degrade than the simulated light with lower humidity and temperature (60%RH and 60ºC) in the Ci5000 does. In general, the BlueM is the more accelerated exposure chamber, but it cannot yet be determined that the BlueM is X times faster than the Ci5000.

The most basic aspect of this analysis is in the numerical optimization (Table 2), but it must be kept in mind that these are all estimates based on a sample. The results of the mirror matrix give good indications about where to gather more data efficiently—and more importantly, where not to gather more data and pointlessly expend valuable experimental resources—to improve our understanding about thin-glass mirror durability. For example in future experiments, Mirror Type, Back Protection, and Adhesive would be modeled because the four factors found to be insignificant relative to noise (Substrate, Edge Protection, Substrate Cleaning, and Back Cleaning) would be excluded. Obviously, the most-desirable solutions from numerical optimization for each test method should be considered and design points with high leverages would have more replicates. However, in all likelihood, additional post–mirror production back-protection would be excluded because of the catastrophic delamination of mirrors with this additional back protection. In addition, only production mirrors would be compared because when these mirrors were acquired and testing was initiated, Glaverbel had been making copper-free mirrors for several years and Naugatuck supplied samples from their preliminary copper-free run; comparing full-production vs. initial-production mirrors may be distorting the results. Fewer adhesives would be used; the adhesives that performed well (e.g., epoxy) would be emphasized and the adhesives that performed poorly (e.g., contact) would be excluded.

A fundamental problem with lifetime testing is that for a reflector with good durability, it takes long exposure times to get meaningful results; frequently the materials and constructions of commercial reflectors change prior to the conclusion of the test and the results are published. Preliminary results from this study and others led Naugatuck to make changes in their glass-cleaning process to improve the adhesion of the silver and to switch from a lead-free one-coat paint system to a two-coat paint system in their copper-free mirror production line. In addition they are exploring adding humidity- and adhesive-resistant protective coatings to their solar mirror product.

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REFERENCES

1. Short, W.D., 1988, *Optical Goals for Polymeric Film Reflectors*, SERI/SP-253-3383, Golden, CO: National Renewable Energy Laboratory.
2. Sahr, R., Inflation Conversion Factors for Dollars 1665 to Estimated 2013, Oregon State University, http://oregonstate.edu/Dept/pol_sci/fac/sahr/sahr.htm. Last modified January 18, 2007; accessed January 31, 2007.
3. Perkins, C., Kennedy, C., and Jorgensen, G., *Identify Reasons for Failure of Thin Glass Mirrors and Recommend Solutions to Industry to Avoid Further Problems in the Field*, CSP FY01 Milestone Report, February 28, 2001,Golden, CO: NREL.
4. Soltys, J., 25 January 2000, U.S. Patent 6017580.
5. Czanderna, A., Masterson, K., and Thomas, T.M., 1985, *Silver/Glass Mirrors for Solar Thermal System*, SERI/SP-271-2293, Golden, CO: Solar Energy Research Institute, p. 22–37.
6. Kennedy, C.E.; and Terwilliger, K., May 2005, “Optical Durability of Candidate Solar Reflectors,” ISEC2004-65111, *ASME J Sol Energy Eng*., 127, pp.262–269.
7. Emberger, R., E-mail memorandum, Flabeg GmbH & Co. KG, Glaserstraße, Germany, 16 January 2007.
8. Sinko, J., 24 September 1996, U.S. Patent 5,558,706.
9. Hughes, Z.J. and Torgussen, O.G., 6 August 1996, U.S. Patent 5,543,227.
10. Sanford, T.J., 6 January 1999, U.S. Patent 5,863,611.

11. Laroche, P. and Boulanger, P., 14 November 2000, U.S. Patent 6,147,803.
12. Hughes, J., Telephone conversation. Standard Paints, Inc., Mansfield, TX, 3 April 2001.
13. Sinko, J., E-mail memorandum, Wayne Pigment Corp., Milwaukee, WI, 27 April 2001.
14. Bahls, H. J., Telephone conversation. Lilly-Valspar, 5 April 2001.
15. Whitcomb, P., 2007, *Design Expert*, 6.0.11, Minneapolis, MN: Stat-Ease Inc.
16. Kennedy C., May 2002, "Standard Mirror Practice–Survey and Screening Test Result", NREL Internal Memo,.
17. ASTM Standard E1175-87(2003), "Standard Test Method for Determining Solar or Photopic Reflectance, Transmittance, and Absorptance of Materials Using a Large Diameter Integrating Sphere," *Ann. Book of ASTM Standards 2003*, American Society for Testing and Materials, Philadelphia, PA.
18. ASTM Standard G173-03e1, "Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface," *Ann. Book of ASTM Standards 2003*, American Society for Testing and Materials, Philadelphia, PA.
19. Kennedy, C.E., Perkins, C.L., and Jorgensen, G.J., 2002, "Durability Testing of Thin Glass Mirror Constructions", *Proc. ASES 2002 Solar Conf., Portland, OR*.
20. White, J.F.., and Silverman, W.B., 1949, "Some Studies on the Solarization of Glass", J. Amer. Cer. Soc..,Vol. 33 No. 8, pp. 252-257.
21. Escoubas, L., Gatto, A., Albrand, G., Roche, P., and Commandré, M., 1998, "Solarization of Glass Substrates during Thin-Film Deposition", App., Optics, Vol. 37, No. 10, pp. 1883-1889.
22. Vitko, J., and Shelby, J.E, 1982, "Effect of Fining Agents on the Solarization of a Borosilicate Glass", *Comm. Amer. Cer. Soc.*, June, pp. c86-c87.
23. Kennedy, C, Terwilliger, K., and Jorgensen, G.J., 2005, "Analysis of Accelerated Exposure Testing of Thin-Glass Mirror Matrix", *Proc. ISEC2005 Solar Conf., Orlando, FL*.
24. Adams, W. F., E-mail memorandums, Stat-Ease Inc., Minneapolis, MN, 29 January 2006–2 February 2006.