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Silver Deterioration in Second Surface Solar Mirrors

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SILVER DETERIORATION IN SECOND SURFACE SOLAR MIRRORS

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ABSTRACT

The suitability of various heliostat mirror module designs for large solar central power systems, depends in part on the ability of the reflective surface to survive over the expected lifetime, with little loss in reflectivity. Recent observations on several module designs revealed significant deterioration of the silvered surface in an unexpectedly short time span. This report documents current information on the extent and nature of the deterioration noticed on several mirror module designs, on the accelerated tests designed to simulate field deterioration, on the potential design solutions available, on the parameters necessary for conducting useful accelerated weathering tests, and on the nature of commercially prepared mirrors.

*Currently on leave of absence

ACKNOWLEDGMENTS

The authors wish to thank Clarence Karfs (8316) for numerous sessions on both optical and scanning electron microscopes and Cal Feemster (8315) for infra-red and atomic absorption analyses.

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SILVER DETERIORATION IN SECOND SURFACE SOLAR MIRRORS

Introduction

The current choice of reflective surfaces for large solar thermal central power systems is a second surface mirror made with low iron float glass and silvered with conventional high volume mirror silvering techniques. Glass was chosen among other reasons for its weatherability and reasonably high transmittance while the silvering process was chosen for its high reflectivity and economic application to the glass with current technology. Several modules constructed with these mirrors and either polystyrene foam cores or aluminum honeycomb cores exhibited significant amounts of deterioration of the silver layer in less than eight months of exposure to the outdoor environment at Livermore, California. An investigation was launched to determine the cause of this deterioration, it involved a coordinated effort between Sandia Livermore, McDonnell Douglas Astronautics (MDAC), Martin Marietta Aerospace (MM), Jet Propulsion Lab (JPL), Solar Energy Research Institute (SERI), Battelle, Pacific Northwest Labs (PNL), Sandia Labs Albuquerque (SLA), and several other organizations. These organizations were represented either officially or unofficially on the Mirror Deterioration Committee whose charter was to identify the cause of the deterioration, identify potential design solutions, and specify some type of accelerated weathering tests.

As used in this report, the term deterioration refers to any change in the condition of the silver reflective surface on second surface glass mirror modules that would result in a noticeable drop in the reflectance of the mirror over its predicted lifetime. This definition specifically excludes any effects that are so long term as to escape external detection over the normal life of the mirror and any losses in reflectance due to changes in the glass itself. In the course of these investigations it seemed plausible that the mechanism that was responsible for the silver deterioration could also generate some glass erosion. If this is the case, this erosion is also not considered as deterioration.

The work accomplished to date indicates that the deterioration problems observed up to now can be overcome with current technological designs to produce reflective surfaces lasting 15 years or longer with acceptable optical characteristics. There is, however, an undercurrent of evidence which suggests the existence of slower, less damaging deterioration mechanisms that can impact the long term (20 years or more) economics of large scale solar power plants. These potential mechanisms are not proper topics for this study as they involve more detailed analysis of the silver-glass interface, a very complex area with several options in materials and processes.

One final introductory comment. Although specific materials and commercial products are mentioned in this report, that is not to be construed as endorsement or condemnation, for the specific reason that most products purchased were manufactured for an entirely different market. The various manufacturers have been marketing their products for some time with excellent success in the more conventional applications. It is the peculiar requirements of the solar industry that have imposed restrictions on the use of certain classes of materials, not specific products.

Observations

The first signs of mirror deterioration were observed in the heliostat test facility at Sandia Livermore in September 1978. These mirror modules were of two basic designs manufactured by three different organizations: Martin Marietta (MM) designed and built, McDonnell Douglas designed and built, and McDonnell Douglas (MDAC) designed - Sandia Livermore (SLL) modified and SLL built (see Figures 1a, 1b, 1c for module designs). All of the modules were made of low iron float glass silvered by a commercial mirror manufacturer, and all had been exposed to the weather since February 1978. A detailed "mapping" of the deterioration was completed in November 1978 in order to obtain some quantitative value for deterioration rates. Examples of these "maps" are shown in Figures 2 and 3. It should be noted that the deterioration patterns noticed on the MDAC designed and built modules, matched exactly the adhesive joints of the pieced styrofoam core. During the next few months, detailed examinations were made on several mirror modules located in Baltimore, Maryland and St. Petersburg, Florida. The modules in Maryland were also designed and built by MM but they did not use low iron float glass or the same mirroring company or the same adhesive application as the SLL located modules. Figure 4 is a picture of one of the two modules that had been stored outdoors in a moderately humid and polluted environment (downwind from a steel mill) and also considerably vandalized. After about one year of exposure there was no detectable deterioration. Examination of plain mirrors enclosed in a crate at the same site revealed deterioration on some mirrors made by one manufacturer and the beginning of deterioration on the other mirrors. The geometry of the crate and packing material was such that the mirrors remained very wet for many days. Those plain mirrors that had shown some deterioration contained the same backing paint as the modules located in Livermore while the mirrors showing only the beginning of deterioration (no copper under paint blisters) contained the same backing paint as the vandalized module.

In addition to the observations made first hand by the authors, there were reports of deterioration on some mirror modules at Sandia Albuquerque[1] (small mirror facets bonded to concrete supports) and deterioration on foamed glass modules (float glass mirrors bonded to foamed glass cores) designed by Jet Propulsion Lab.[2] It should also be noted that the mirrors (laminated glass mirrors) at the Central Receiver Test Facility (CRTF) in Sandia Albuquerque (SLA) showed no deterioration along with a few unprotected mirrors stored outdoors also at SLA.

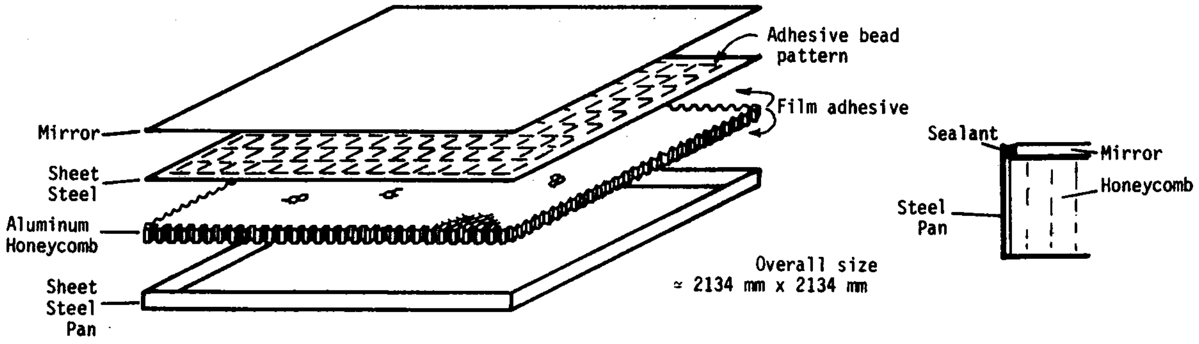


Figure 1a. Martin Marietta (MM) Module

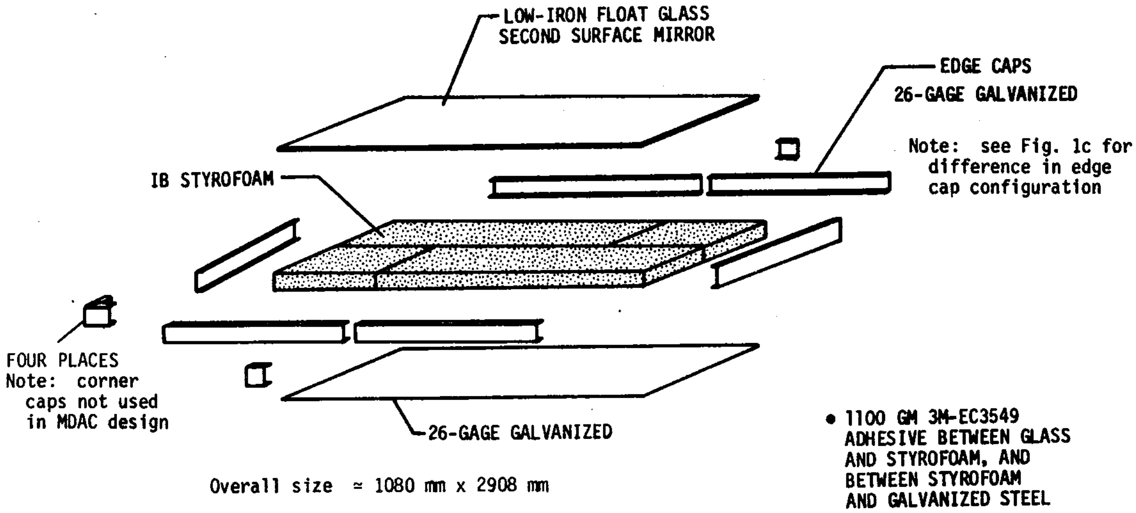


Figure 1b. Sandia Modified, McDonnell Douglas (MDAC) Module

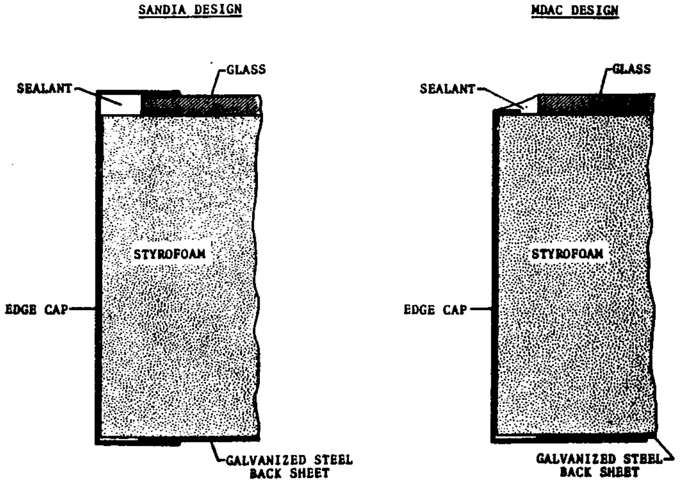


Figure 1c. Design Differences Between SLL and MDAC Modules

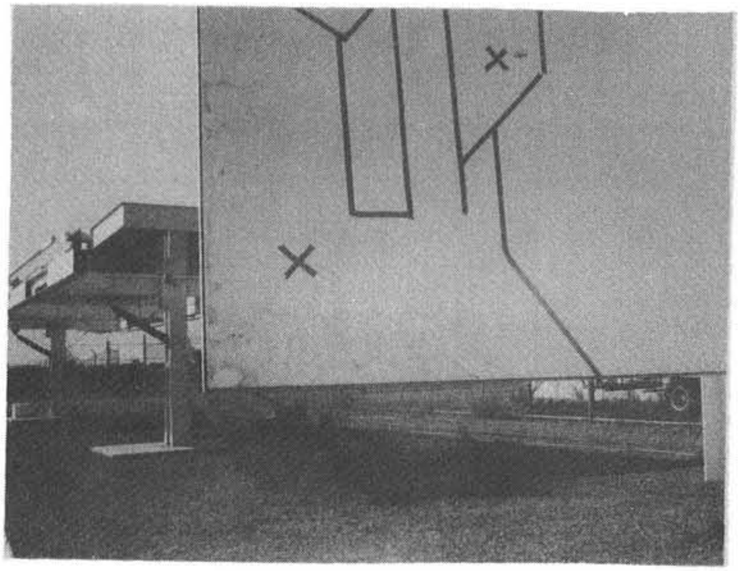


Figure 2. Photo Showing Deterioration Pattern on MM Module

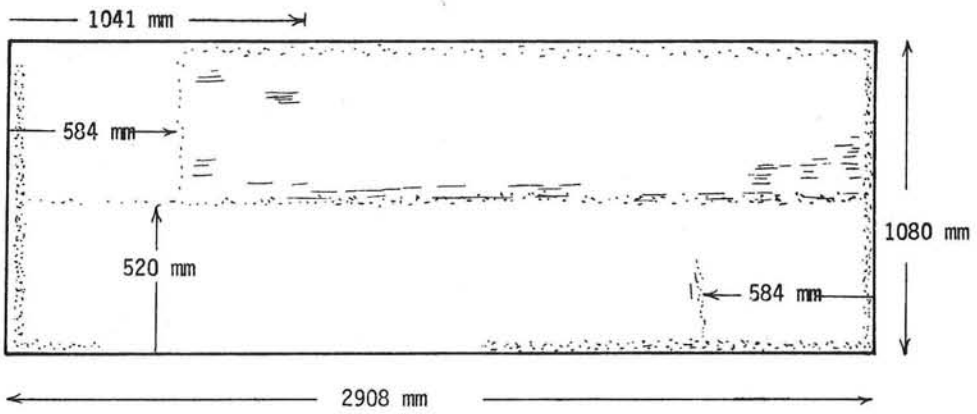


Figure 3. Drawing Depicting Deterioration Pattern on MDAC Module

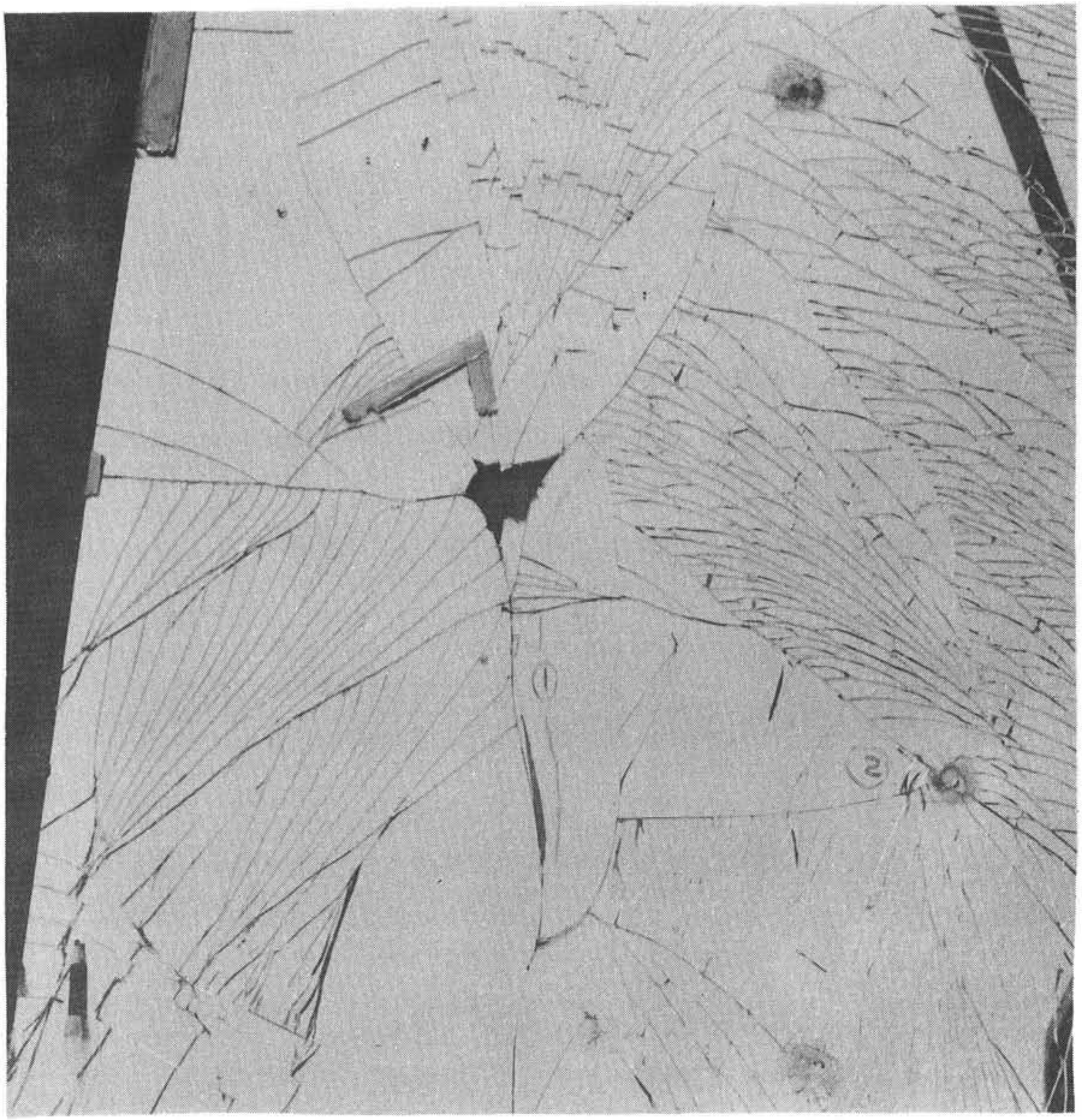


Figure 4. Vandalized MM Module Showing No Deterioration

The deterioration observed was categorized three ways: streaking, spotting and delamination. The streaks appear as grayish bands on the silvered surface (effects on the silvered surface can be distinguished from dirt or anomolies on the first surface by the absence of a second, reflected image) the spots appear as dark irregular areas and the delamination which is literally the separation of the silver from the glass appears as water droplets on the silvered surface. Figures 5 through 7 show examples of each.

Detailed Destructive Examinations

Three deteriorated mirror modules were opened and examined for clues to the deterioration mechanism. One MDAC module was examined at McDonnell Douglas, one MM module at Martin Marietta and one SLL built module at Sandia Livermore.

SLL Built Module

Careful examination of this module revealed no failure of the sealant visible to the eye. However, once opened sufficient water was found in the module to cause severe corrosion on the inside of one of the galvanized edge caps (see Figure 10) and to be sensed by touch. The other three edge caps had no corrosion noticeable. In all cases the deterioration seemed to start as a very small spot which grew larger with time. In some cases the spots (if in a line) would seem to grow and merge to form a continuous dark streak. This linear arrangement of spots to form a continuous streak was attributed to the adhesive lay down pattern used in some of the modules as shown in Figure 9. At times the bonding pressure was sufficient to flatten the adhesive ridges into a continuous fairly even film in which case the deterioration, if any, would take the form of randomly distributed spots. The adhesive in a portion of the deteriorated area had not been flattened and hence still formed ridges allowing a direct path for water to migrate in from the edge. The deterioration was confined to one area of the module (adjacent to the corroded galvanized edge) but contained both streaking and spotting. Several microliters of liquid were extracted from the region between adhesive ridges and subjected to infra-red (IR) analysis. Microscopic examination gives reason to believe that all deterioration begins with some form of delamination, so small as to be undetectable to the unaided eye.

MDAC Built Module

Examination of the MDAC built module revealed some pinholes in the sealant and areas where the sealant was not bonding well to the glass. There was again very noticeable amounts of water in the module and again the deterioration followed adhesive ridges that had not been flattened in bonding. The moisture content of the foam was as high as 6% by weight near the back of the mirror. Some of the deterioration patterns were identifiable as fingerprints or other obvious contamination before silvering and many of the examined deterioration products that were high in silver were also high in chlorine.

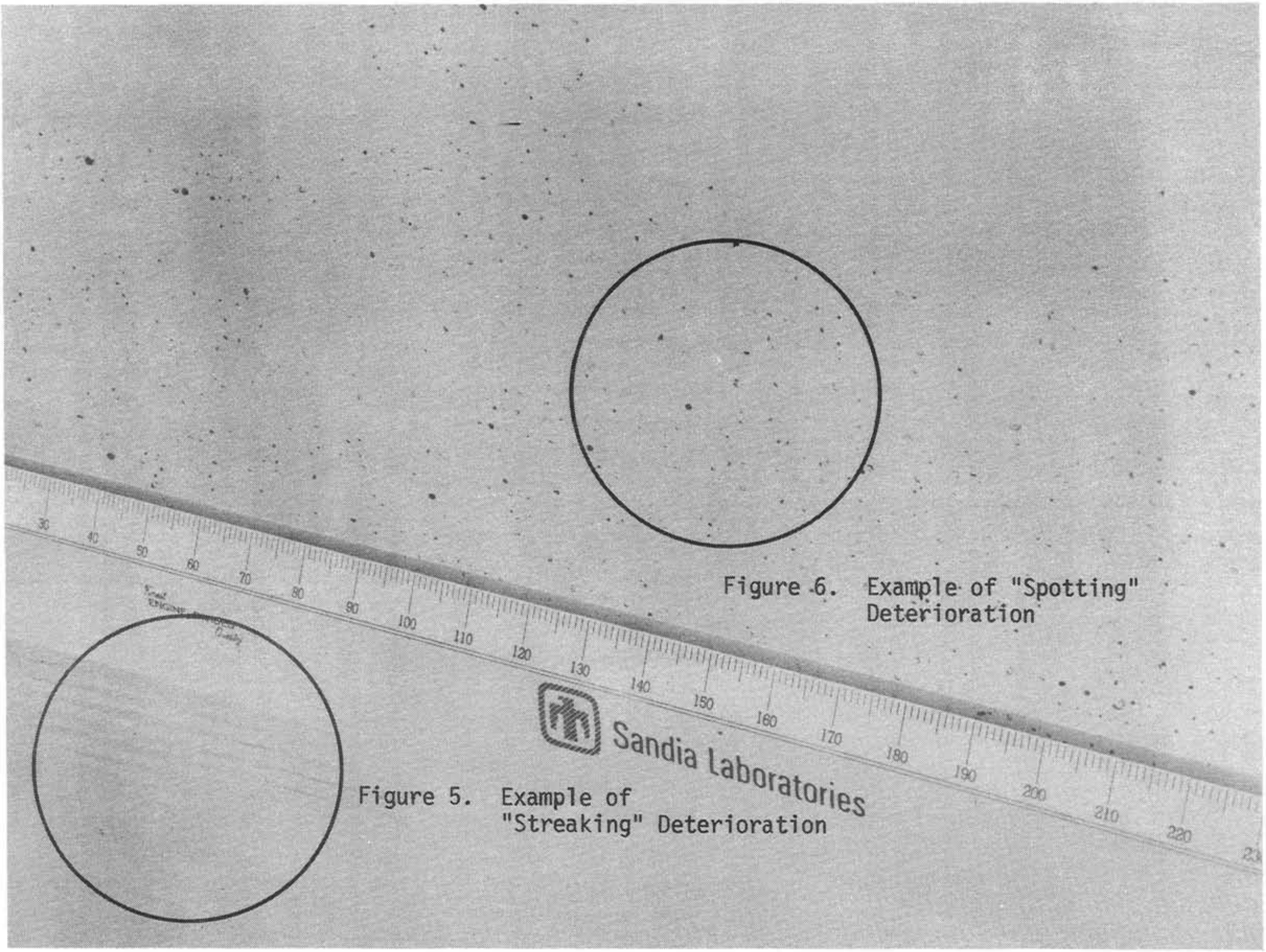


Figure 6. Example of "Spotting" Deterioration

Figure 5. Example of "Streaking" Deterioration

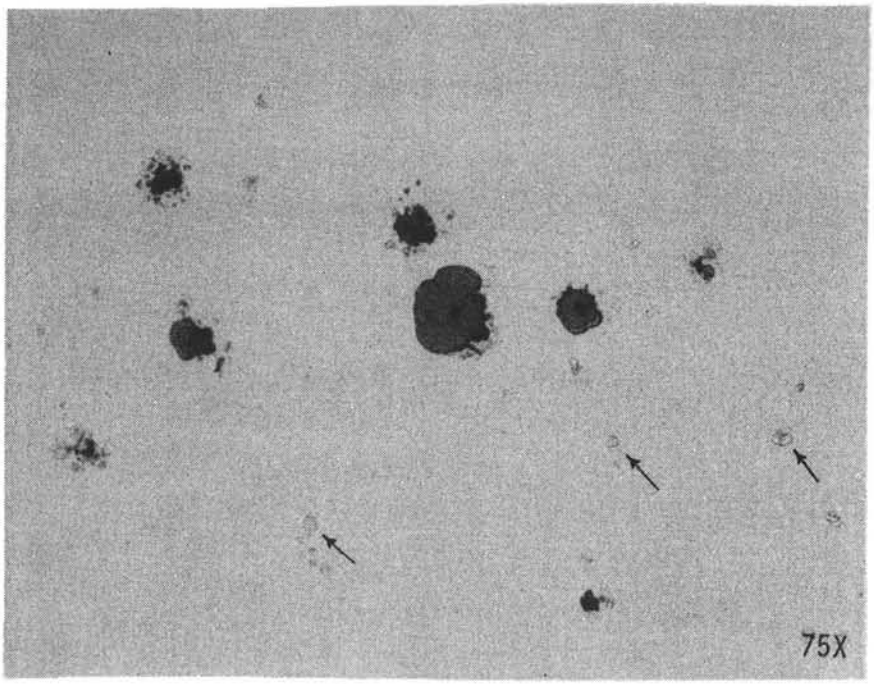


Figure 7. Magnified View of Deterioration Showing Delamination Sites (Arrows)

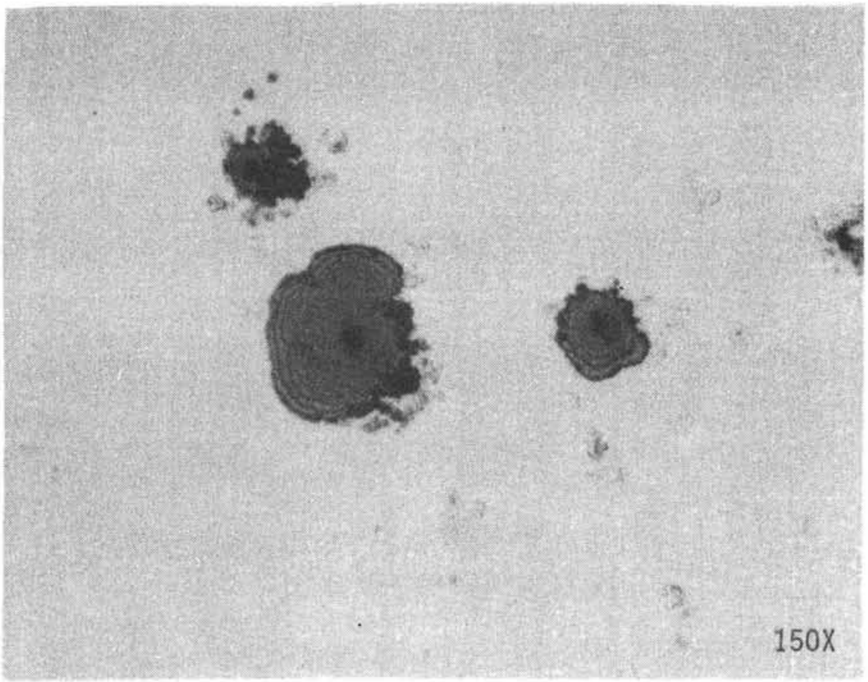


Figure 8. Magnified View of Several Deterioration Spots

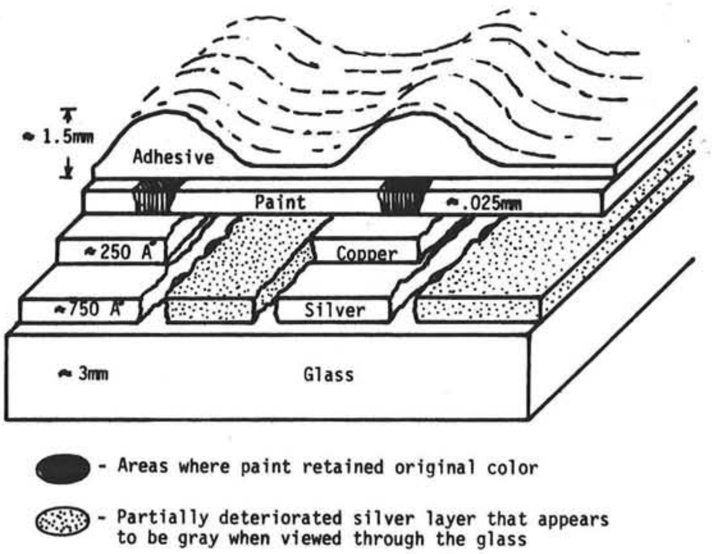
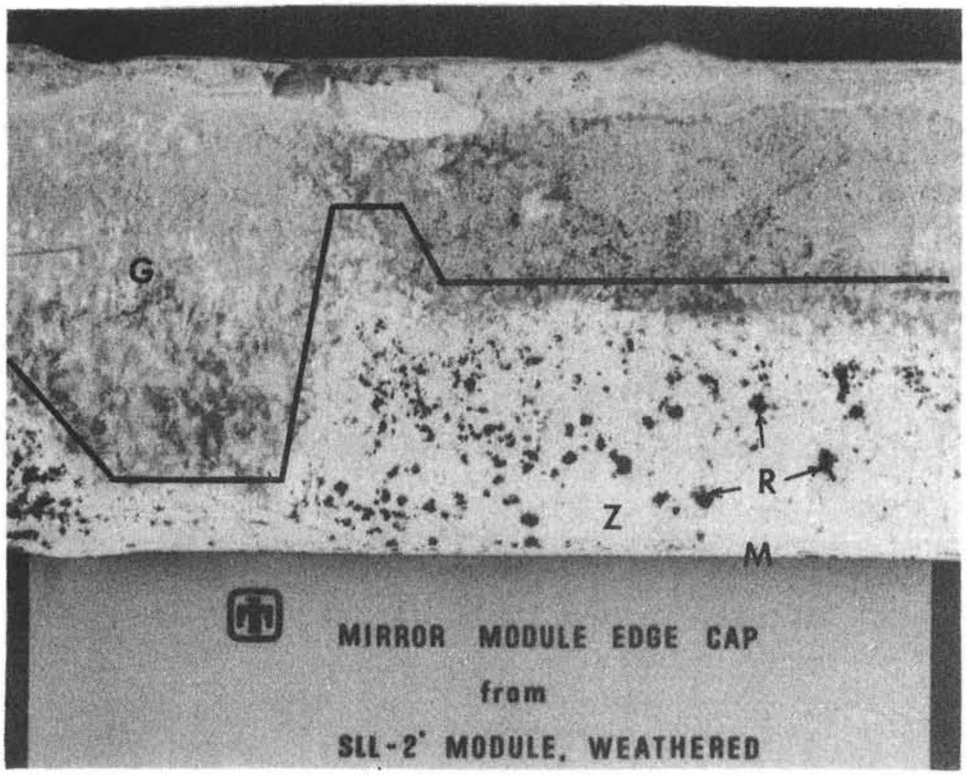


Figure 9. Exploded View of Deterioration Found on Field Sample (Not to Scale)



G - Normal Galvanized Steel Z - Zinc Oxide
R - Iron Oxide M - Side of edge cap closest to mirror

Figure 10. Galvanized Edge Cap From Deteriorated Sandia Module

Martin Marietta Built Module

The MM module differed from the others in that the core was not in contact with the mirror. Rather, it was sandwiched between two metal sheets and the sandwich bonded to the mirror. Careful examination of this module revealed significant quantitites of water wherever the adhesive did not form a continuous barrier to water penetration. There was very gross corrosion of the steel sheet and obvious blistering of the mirror backing paint below the water line.

In every instance, wherever deterioration was present, the uniform copper layer was mostly absent and wherever there was silver remaining there was no discoloration of the silver layer. In fact what was actually being seen from the front surface was the gray backing paint. In other words the streaks or spots were actually areas devoid of silver and copper (see Figure 9).

Laboratory Tests

Accelerated deterioration tests:

Without exception, the field deterioration observed was accompanied by the presence of liquid phase water at some time in the history of the module. Infra-red (IR) analysis of minute quantities of liquid found in some modules indicated the presence of some unidentifiable organic compounds. The source of the organic contaminant is unknown but there are three possibilities: the sealant, the adhesive, and in the case of the MDAC design, the polystyrene foam core. The polystyrene foam (Type IB) is manufactured by Dow Chemical and is blown with Freon 12 and methyl chloride. The methyl chloride dissipates rather rapidly and although it is capable of dissociating into hydrogen chloride and methanol, it would do so very slowly unless enhanced by heat or a catalyst. The sealant (DOW Corning DC 790) used in the MDAC designed module and the MDAC designed Sandia modified module was found to generate copious amount of a very aggressive liquid. This concentrated liquid if allowed contact with the back of the mirror would dissolve the copper layer in a matter of minutes at 60°C, with or without the mirror backing paint present.

Because of the obvious compatibility problem with the sealant and the mirror, a series of laboratory tests were designed to try to simulate and accelerate the deterioration seen in the field. The test apparatus is shown in Figure 11. This test was accomplished on mirrors with and without applied adhesive by bonding a plastic cup to the back of the mirror and inserting ≈ 20 ML of a solution of distilled water +1% isopropyl alcohol with and without sealant extract. The entire arrangement is then placed in an oven at 60°C. In all cases where the sealant extract was used on mirrors with adhesive, the deterioration discoloration was not the same but the pattern was. In all other cases where adhesive was applied to the mirrors the laboratory sample could not be distinguished from the exposed mirrors and the growth of small spots to larger ones was verified. In all cases when there was no adhesive, merely water, the deterioration did eventually appear but after as much as a 5 fold increase in time.

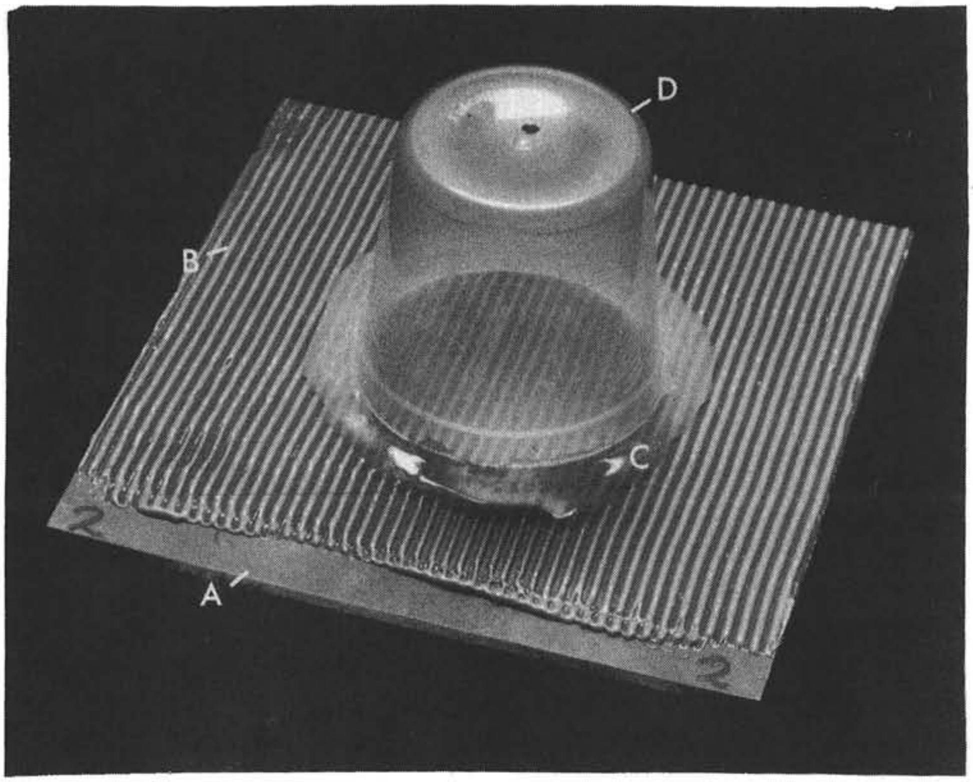
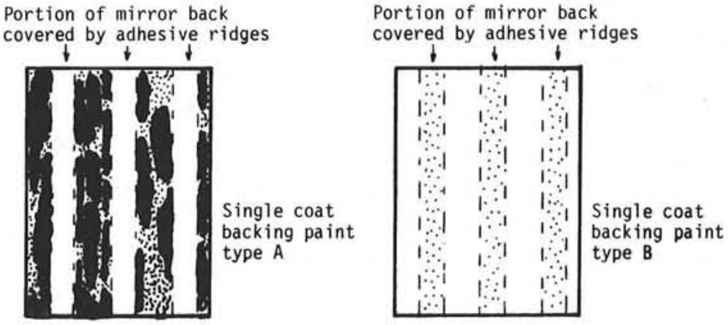


Figure 11. Inverted Cup Deterioration Test

A - Mirror, Glass Side Down
B - Adhesive Being Evaluated
C - Sealant Around Base of Cup
D - Plastic Cup with Hole in Top to Hold Water + 1% Isopropyl Alcohol



After 625 hours, severe deterioration noted **between** adhesive ridges

After 3480 hours, minor deterioration noted directly underneath adhesive ridges

Figure 12. Comparison of Trends in Lab Deteriorated Mirrors

Much later in the program, some evidence arose that indicated a potential stress enhanced deterioration mechanism. To ascertain the validity of this mechanism, to evaluate other classes of adhesives, and to determine the potential benefit of additional paint layers, the inverted cup test was repeated on a number of mirror samples (see Tables I & II). Those mirrors of a different manufacturer (using a different mirror backing paint) showed much better resistance to deterioration by as much as a factor of 10 to 20. All the adhesives tested seemed to be much more chemically compatible than the adhesive used in the field mirrors. Indeed that was not surprising in that they were chosen for the inertness of their chemical constituents.

Some mirrors with paint layers in addition to the standard backing paint proved to be the most resistant to attack of all the mirrors. These mirrors however, may have also revealed the existence of two distinct deterioration mechanisms as the very slight deterioration noted on them was in the areas where no deterioration was noted on the same mirror without the additional layer of paint (see Figure 12). The accelerated deterioration tests in the lab were able to duplicate in about 500 hours, the effect observed in the field after 8 months. Using different backing paints only, this effect was reduced approximately ten fold after almost 3500 hours of testing. This translates to an overall factor of 70, which implies that with better backing paints it would take more than 45 years to observe the effects seen on the exposed mirrors after 8 months. If the degree of acceptable deterioration were reduced to one third (hardly noticeable), then a reasonable lifetime estimate becomes 15 years.

More recently, a test has been developed at SERI[3] that exposes mirror samples to atmospheres containing H_2S or HCl gas. The mirrors that had been shown to be the first to deteriorate in all other tests, also were first to deteriorate in these tests (see Table IV). The advantage being that these tests require substantially less time to complete. It is not to be inferred that the mechanism is the same in both tests, rather only that the ability of the paint, copper and silver layers to resist attack is being measured equally well.

Early in the investigation we received a report of mirror deterioration problems with a foamed glass mirror module designed by JPL.[2] The investigation that followed linked the deterioration to the type of adhesive used. In a screening and evaluation process, it was determined that the pH of the water extract from the adhesive under test, could be directly associated with the severity of deterioration that adhesive could cause. To state it simply, the further from neutral the pH of the water extract, the greater the severity of the deterioration. The water extract of the adhesive used on the modules under investigation for this study had only a slightly non-neutral pH.

Mechanical Stress Compatibility:

If a specific adhesive proves itself to be compatible chemically with the mirror, it must also be tested for mechanical compatibility as was demonstrated by the last series of deterioration tests. One epoxy adhesive had sufficient strength to cause the glass to fail internally while another managed to remove the silver quite nicely (see Figure 13 and 14). This may

TABLE I

RELATIVE COMPARISON OF SEVERAL MIRROR SYSTEMS FOR RESISTANCE TO DETERIORATION[1]

Mirror Maker	Glass	Backing Paint(s)	Exposure to Water[2] + Isopropyl @ 60°C	Location of Deterioration	Rating
Buchmin	LIF[3]	Glidden	After 625 hrs > 10% area badly deteriorated	Underneath adhesive troughs	Poor
Northrup[4]	----	PPG	After 1390 hrs very minor deterioration	Underneath adhesive ridges	Good
			After 3480 hrs estimated < 5% loss in reflectivity	Underneath adhesive ridges	Good
Northrup[4]	----	PPG & Proprietary Paint	After 1390 hrs no visible deterioration	----	Very Good
			After 3480 hrs estimated <<1% loss in reflectivity	Underneath adhesive ridges	Very Good

---

[1] All mirror backs were wiped clean with methanol and then covered with adhesive (3M EC 3549 + .5% A-187) using a notched trowel with notches 1.5 mm deep and 3.0 mm apart.

[2] Mixture used was 1% isopropyl alcohol in distilled water as shown in Fig. 11.

[3] Low iron float glass 3.2 mm thick from PPG.

[4] Heliostat designer - supplied mirror for testing.

TABLE II

RELATIVE COMPARISON OF SEVERAL ADHESIVES FOR COMPATIBILITY WITH COMMERCIALLY AVAILABLE MIRRORS[1]

Adhesive[2]	Paint	Test Duration[3]	Results[4]
A-spotted[5]	Glidden only	2230 hrs	Severe deterioration at edges of adhesive only with discoloration--no deterioration under adhesive--elsewhere faint hazy deterioration under blisters spread uniformly on paint.
D-spotted	Glidden only	2230 hrs	No noticeable deterioration anywhere, minimal paint blistering, much copper everywhere except under the adhesive where some is gone--very good adhesive, adhesion and cohesion.
A-spotted	Glidden & Aluminum[7] Loaded Paint	2230 hrs	Severe deterioration at edges of adhesive--hazy spots under numerous blisters--beginning of deterioration under adhesive--only trace of copper present anywhere.
D-spotted	Glidden & Aluminum Loaded Paint	2230 hrs	No noticeable deterioration anywhere-blistering of aluminum paint covering 15% of area - no copper under blisters some copper elsewhere - aluminum paint does not seen to be effective water barrier.
A-spread[6]	Glidden only		Silver delaminated from glass during thermal cycling.
D-spread	Glidden only	-----	Mirror remained intact after thermal cycling.
A-spread	Glidden & Aluminum Loaded Paint	-----	Silver delaminated from glass during thermal cycling.
D-spread	Glidden & Aluminum Loaded Paint	-----	Mirror Remained intact after thermal cycling.
B-spread	Glidden & Aluminum Loaded Paint	-----	100% cohesive failure in paint during thermal cycling.
C-spread	Glidden & Aluminum Loaded Paint	2300 hrs	Micro delamination of silver from glass covering < 1% of area--very large adhesive blisters covering 50% of area-- aluminum paint blistering under adhesive blisters - no copper anywhere.
A-spread	Glidden & Aluminum Foil	-----	Could not be fabricated.
B-spread	Glidden & Aluminum Foil	-----	100% planar fracture in glass during thermal cycling.
C-spread	Glidden & Aluminum Foil	-----	Could not be fabricated.
D-spread	Glidden & Aluminum Foil	-----	Could not be fabricated.

---

[1] All mirrors were manufactured by Buchmin Industries with low iron float glass from PPG and with Glidden mirror backing paint.

[2] See Table III for adhesive identification.

[3] Refers to exposure to distilled water + 1% isopropyl alcohol at 60°C as shown in Figure 11.

[4] Prior to water exposure, all mirror sample were cycled between -30°C and 50°C, thirty times over a seven day period.

[5] Adhesive applied to mirror on three isolated areas.

[6] Adhesive applied to mirror in a uniform layer covering entire back surface.

[7] Aluminum loaded paint applied in 2 coats at Sandia Livermore.

TABLE III

ADHESIVE IDENTIFICATION FOR COMPATIBILITY TESTS SHOWN IN TABLE II

Adhesive		Components	Manufacturer	Parts by Weight	
A		EPON 828	SHELL	100	
		*DDSA	--	135	
		NEOCURE 28	TENNECO	2	
B		EPON 828	SHELL	60	
		VERSAMID 125	GE	30	
		MICA (FILLER)	--	40	
C		SS 4155 (PRIMER)	GE	--	
		RTV 630 A/B	GE	10/1	
D	RESIN	POLYMEG 1000	QUAKER OATS	47.6	65.0
		POLYMEG 2000	" "	7.4	
		**MDI	--	45.0	
	CURING AGENT	POLYMEG 1000	QUAKER OATS	85.0	35.0
		1,4- BUTANEDIOL	--	10.0	
		QUADROL	WYANDOTTE CHEM.	5.0	

---

*DDSA- DODECENYL SUCCINIC ANHYDRIDE

**MDI- 4,4' - DIPHENYLMETHANE DIISOCYANATE

TABLE IV

RESULTS OF A SCREENING TEST DEVELOPED AT SERI[3]

Mirror Description	0.1 ATM H_2S 100% R.H. @ 25°C	Results of Adhesion Tests After 12 Hours of Aging
A - No Copper Layer Unbaked Paint	after 60 hours no apparent loss in reflectivity	failure mode unchanged 100% cohesive in paint- some loss in strength
B - Copper Layer Baked Paint (Identical to Field Deteriorated Mirrors)	after 5 hours ≈ 50% loss in reflectivity	failure mode changed from cohesive in paint to 100% adhesive between paint and metal - > 60% loss in strength
C - In House Manufactured Mirror with Copper Layer & PPG Paint	after 60 hours no apparent loss in reflectivity	failure mode unchanged 100% cohesive in paint - some loss in strength

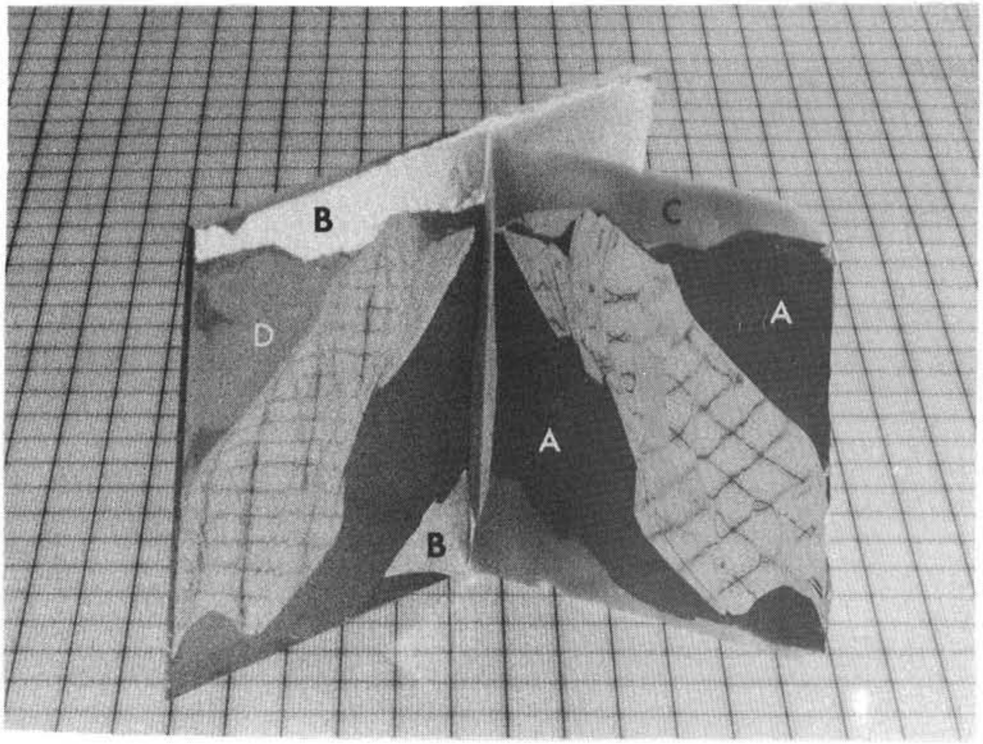


Figure 13. Mirror (15 cm x 15 cm) Fractured in Glass (During Thermal Cycling) by Adhesive: A-Mirror Backing Paint, B-Aluminum Foil, C-Epoxy Adhesive, D-Copper Layer

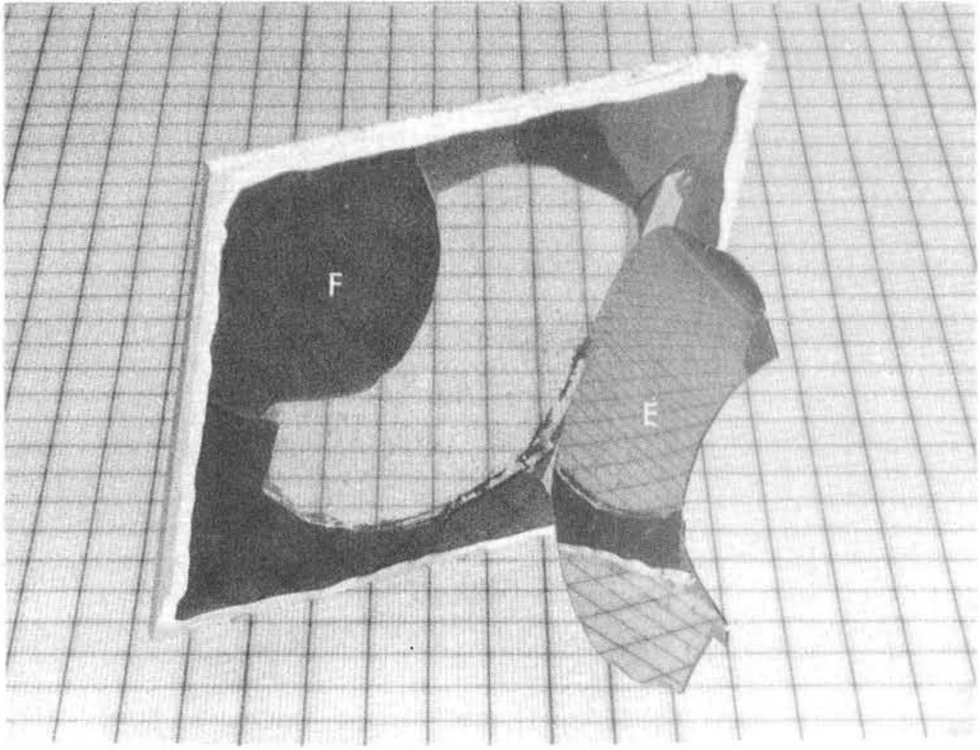


Figure 14. Mirror (15 cm x 15 cm) with Silver Delamination Due to Thermal Cycling: E-Silver Layer Intact F-Epoxy Adhesive

imply that some adhesives have the ability to penetrate the silver layer if indeed the copper and silver layers are porous and bond directly to the glass. However, it may also be indicative of the importance of adhesive layer thickness.

Stability of Copper and Silver Layers--Since the copper-silver interface is capable of forming a galvanic couple, and since the solubility of copper in water varies greatly with the purity of the water, the time it takes for the copper layer to erode becomes important because of its relative thinness (see Table V). A fairly simple apparatus demonstrated the inability of the copper layer to withstand attack even in distilled water under a nitrogen atmosphere. Within 330 hours @ 60°C the copper layer had been completely removed. Such action would not normally be noticed on circuit boards or other "large" scale items since the copper thickness can be a thousand if not many thousands of times thicker. Numerous adhesion tests on the paint-copper-silver-glass structure have shown that the weak "link" in the layers is consistently the paint-copper bond under tensile stress and probably the silver-glass bond in sheer or peel.

Microscopic Examination--In all the observations made, it was never clear what caused the nucleation of the spots. It was originally thought that the spots located themselves at pinholes in the paint layers. Very careful examination of several selected mirrors revealed pinholes only due to rough handling and in numbers, orders of magnitude less than what would be required for the spotting effect (see Figure 15). Indeed accelerated deterioration tests run on mirrors samples with intentionally created pinholes had deterioration start invariably at some location other than the pin holes.

Examination of the silver glass interface was much more difficult as it involved developing a technique to separate the two layers or expose the silver without contaminating it. Extensive use of SEM and AUGER techniques at MDAC, Battelle Pacific Northwest Labs, and Sandia, Livermore, did not firmly establish the presence, in any significant quantities, of any aggressive species that could be responsible for the deterioration. These sputter through profiles did reveal some iron which is understandable in that iron powder is used as the reducing agent for the copper deposition, and the possibility of much diffusion of the copper into the silver and silver into the glass.

Mirror Silvering Techniques

A visit was made to a mirror silvering facility to ascertain if potential sources of deterioration were being introduced in the mirroring process. A typical mirror line would start with the float glass being placed tinned side down on the line. The glass receives a thorough wash with cerium oxide and brushes. After rinsing, the glass surface is activated with a stannous chloride solution to promote silver adhesion and then the silver layer is deposited with three distinct solutions, each sprayed on. Once rinsed again, the copper layer is applied, the mirror is dried and coated with paint using a curtain coating technique. The painted mirror is then run through drying

TABLE V

TYPICAL LAYER THICKNESSES ON SEVERAL SAMPLES OF ONE LOT FROM ONE MIRROR MAKER

SAMPLE		PAINT	COPPER	SILVER
#1	A	61.24	.380	.609
	B	-----	35.3	56.6
	C	-----	424	580
	D	2000	1.67	2.28
#2	A	53.55	.401	.889
	B	-----	37.2	82.5
	C	-----	447	846
	D	1800	1.76	3.33
#3	A	76.40	.470	.709
	B	-----	43.7	65.9
	C	-----	525	676
	D	2500	2.07	2.66
#4	A	73.22	.519	.636
	B	-----	48.3	59.1
	C	-----	580	605
	D	2400	2.28	2.38
Average	A	66.10	.442	.711
	B	-----	41.1	66.0
	C	-----	494	677
	D	2200	1.95	2.66

A - Coverage in gms/m^2

B - Coverage in mg/ft^2 (Industry Standard)

C - Thickness (A°)

D - Thickness (10^{-6}in.)

Assuming 100% Dense Layers

Note: Thickness was calculated (not measured) by weighing individual layers and assuming 100% dense material. Later investigations indicate that the silver is not 100% dense. Paint was removed with methylene chloride, copper with ammonium persulfate $(NH_4)_2 S_2O_8$.

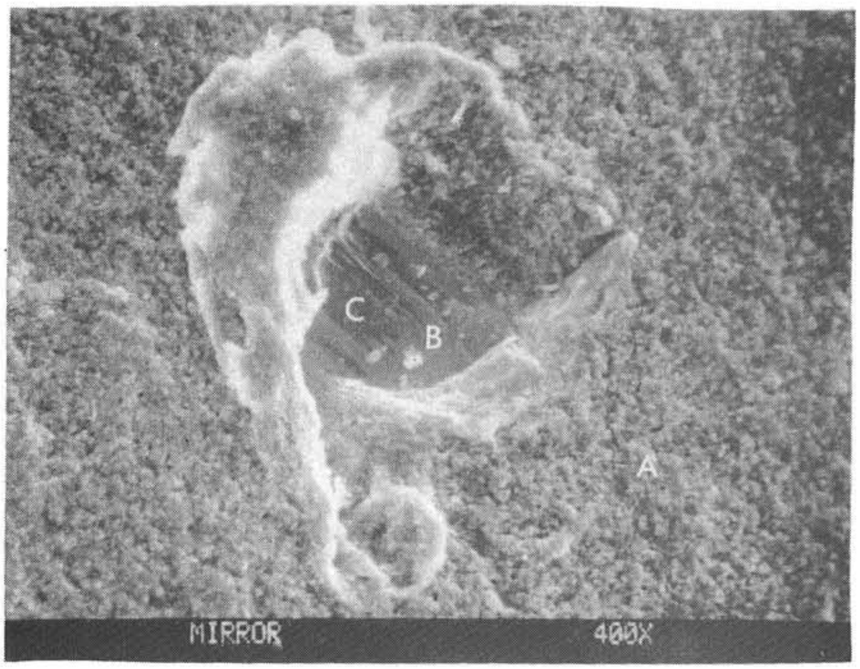


Figure 15a. Magnified SEM View of Mirror Pinhole
A-Mirror Backing Paint
B-Metal Layer(s)
C-Glass

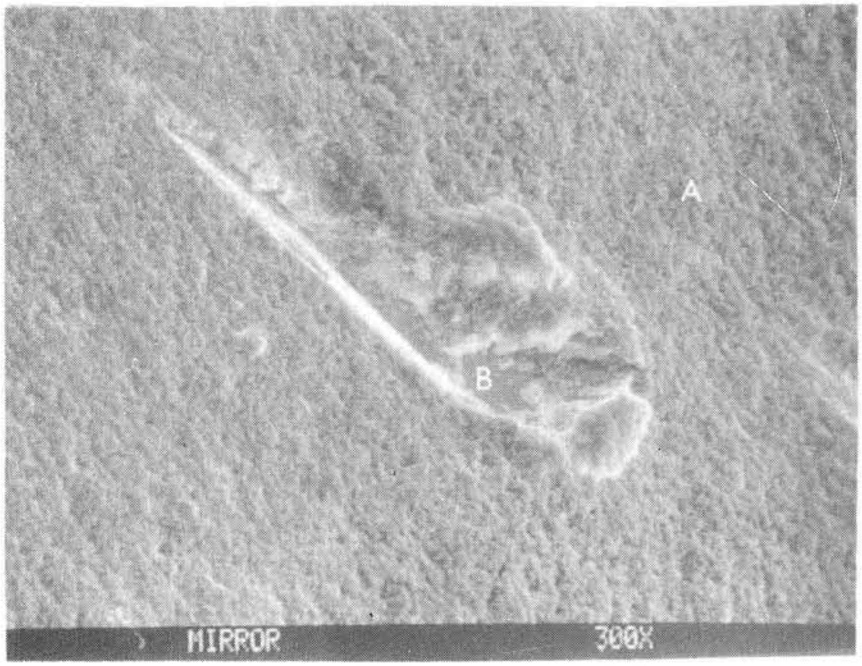


Figure 15b. Magnified SEM View of Mirror Pinhole
A-Mirror Backing Paint
B-Metal Layer(s)

ovens to the inspection area. The process is very acceptable for indoor decorative mirrors but in general most mirror makers do not exercise a great deal of quality control on the solutions used, glass cleanliness and process conditions in general. That is understandable however since the intention is not to produce a mirror capable of surviving a continuously wet environment for 30 years. In fact, the backing paint applied at the end of the run is designed to be porous to allow excess water trapped in the metal layers during the mirroring process to escape. Some paints are more porous than others and local environmental requirements may forbid the use of the more acceptable paints. There is much evidence to indicate that the mirroring process can be improved upon but this is the subject of a report to be published by Battelle Pacific Northwest Labs[4] and will not be discussed here. The lack of control on the mirroring process is best shown by comparing Table V with the desired coverages of 25 mg/ft^2 copper and 75 mg/ft^2 silver which were specified on the purchase order for that lot. Actual copper layers were found to vary between 35 and 48 mg/ft^2, and actual silver layers to vary between 56 and 82 mg/ft^2. There is some disagreement in the industry itself as to the proper thickness of the various layers but some of the more durable mirrors have coverages more like 15 mg/ft^2 copper and 85 mg/ft^2 silver.

Examination of Old Auto Side-View Mirrors

A study of old auto mirrors (side-view) was conducted at JPL[5] to ascertain the durability of the reflective surface. The mirrors that proved most durable used an adhesive with an inorganic filler in an aliphatic hydrocarbon binder. These mirrors were as much as 34 years old with a reflectivity greater than 72%. Although there is no data available on the reflectivity of the mirror when new, there is reason to suspect that a decrease in reflectivty will occur with time even without deterioration of the silver layer. Some work being done at Battelle PNL indicates a diffusion of the silver layer into the glass with time. This diffusion could cause a loss in reflectivity but for the purposes of this report, it is not considered deterioration for it is indeed a long term effect and does not involve destruction of the silver layer.

The work done at JPL also revealed that a properly silvered mirror can transmit more than 1% of the more energetic spectrum of the ultraviolet segment of sunlight. This probably was not a significant contributor to the deterioration seen to date, but it may be for longer term effects.

Mirror Deterioration Committee

This committee was formed soon after the discovery of the silver deterioration problem and consisted of those organizations mentioned in the introduction. The purpose of the committee was to gather as quickly as possible and disseminate, as much information on mirrors as could be found. This enabled us to dispel many "myths" about mirror making and to sort out the truly knowledgeable members of the mirroring industry. The committee was also charged with the responsibility of identifying the major cause of the deterioration and to develop an accelerated aging test to evaluate design solutions to the problem.

Toward the end of May most of the committee felt comfortable in stating that the deterioration seen in all proposed designs for the Barstow heliostats, would not have been produced as quickly as it had if liquid phase water had not been present in the module. Indeed it was also mostly agreed that only module designs that precluded the existence of liquid water standing on the mirror backing could possibly survive a thirty year environment when existing commercially prepared mirrors were used. This does not eliminate the design of a vented module which can dry out rapidly, but it does imply, with varying climatic conditions, that a module remaining sealed against water or water vapor penetration has a better chance of surviving 30 years. This assumes of course, that the seals can survive for 30 years. It was also generally agreed that the thermal pane window industry has sufficient experience in this area to classify the sealing problem as current technology and not something requiring development work. However, work still needs to be done to insure the 30 year integrity of the sealant materials in the more severe environment of the mirror module.

In surveying the mirroring industry, the committee was able to obtain some consensus about several aspects of mirror silvering.

- There appears to be only very vague information on the function of the copper layer in mirrors. In general it is thought to provide stress relief between the paint and the silver layer and also to permit better adhesion than paint directly on silver. Interestingly enough, there is one mirror maker not using the copper layer. Additional details on this should be referred to the Battelle study[4].

- The silver layer appears to be highly porous which is a phenomenon dictated by the nature of the application process. Evidently, the silver bonds well to the tin atoms applied during the sensitization and then forms "bridges" to adjacent tin sites. The process continues until the layer is built up to that necessary for near theoretical reflectivity.

- The adhesion of the silver layer improves with time. Although little knowledge exists as to why this happens, it is not a point of contention.

- The silvering of old glass (more than several months after manufacture) generally leads to stains, dark amber in color, appearing at the silver-glass interface. Although this is not considered deterioration since it occurs during manufacture, it should be noted as a potential problem.

The problems associated with testing any module design proves to be a much more difficult one to solve, if indeed it has been solved. Extensive reference was made to existing reports dealing with accelerated aging and some with the methodology[6] used to develop an accelerated aging test. Given the restraint of a one month test to simulate the Barstow environment, the committee finally selected the temperature humidity cycle shown in Figure 16. The rationale behind the selection of the various parameters follows.

TEMPERATURE: Although it was generally agreed that a truly representative accelerated aging test would include both temperature extremes, the predominant mode of failure most likely occurs at the higher temperatures. Barstow never really sees 55°C weather but again this choice was a compromise between test acceleration and unnatural stress or reactions on the organic materials. The lower temperature of 20°C was chosen to provide significant temperature pumping and a realistic daily temperature swing. Table VI is a summary of 30 years of Barstow weather used to specify typical daily weather extremes and averages. The 20°C limit was also chosen in order to allow condensation for simulation of rain or mirror washing.

HUMIDITY: Several proposed chemical degradation mechanisms (for the organic sealants) involved both a humid environment to enhance oxidative effects and a dry environment to promote bake out of plasticizers or other reactions. To include both conditions and provide for liquid phase water, the humidity was specified to be $> 94\%$ @ 55°C for 4 days and $< 30\%$ @ 55°C for 3 days. The short duration of each cycle was chosen to provide multiple wet dry periods simulating several winter-summer seasons.

UV EXPOSURE: It was generally agreed that the primary mode of sealant material breakdown would be UV radiation in conjunction with water.[7] To accelerate the UV portion, it was decided to increase the time rather than the maximum intensity, therefore, the UV spectrum shining on the mirrors continuously would be equivalent in both intensity and profile to Air Mass 1 solar spectrum UV radiation.[8] This is generally accepted to be the maximum UV intensity that would be seen at Barstow.

ATMOSPHERIC CONTAMINANTS: A careful review of California Air Quality Board data revealed no significantly high levels of airborne contaminants for the Barstow area. It was determined that ambient Albuquerque air would be sufficiently close to Barstow air to preclude extra effort in this area.

The committee generally agreed that an exact number for the acceleration factor accomplished by these tests would be extremely difficult to pin down because of the many unknowns in the process. However, an acceleration factor of 4 to 6 did not seem entirely unreasonable to anyone; some estimates were as high as 10.

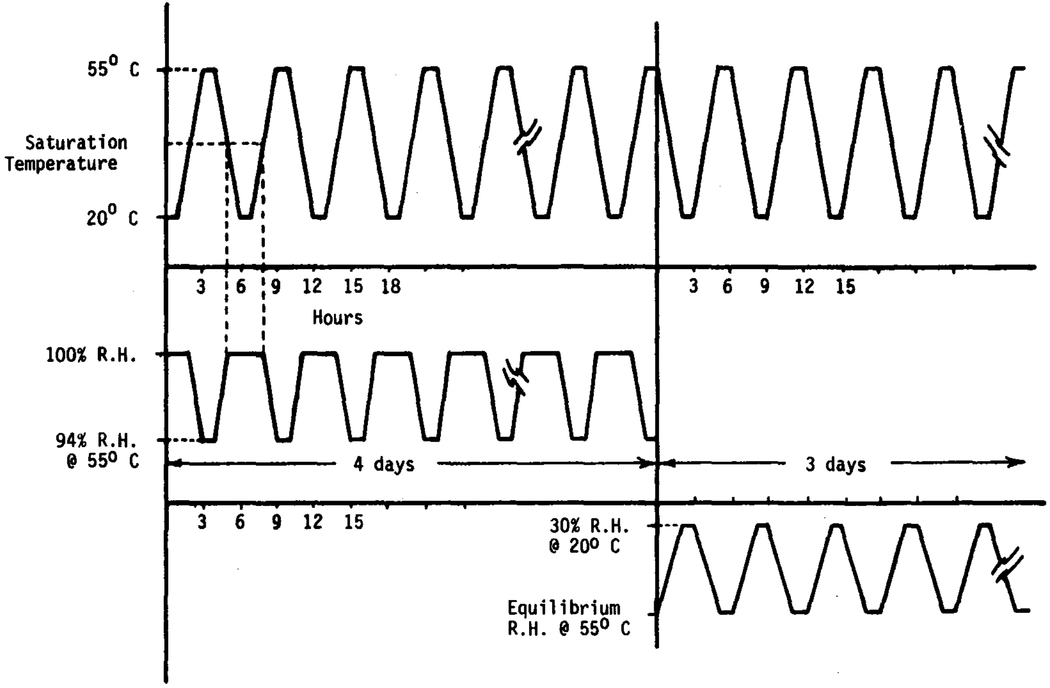


Figure 16. Accelerated Aging Cycle Used on Full Scale Modules - Constant UV Irradiation Equivalent to Air Mass 1 Insolation Not Shown

TABLE VI

SUMMARY OF 30 YEARS OF BARSTOW, CA[9] WEATHER DATA

MAX TEMP	45°C	(113°F)
MIN TEMP	-18°C	(0°F)
Typical summer maximum	35°C	(95°F)
Typical winter minimum	7°C	(45°F)
MAX TEMP change during one day - summer	32°C	(89°F)
- winter	26°C	(78°F)
Typical temp change during one day - summer	16°C	(26°F)
- winter	16°C	(26°F)
Incidents of dew Nov. thru Apr.	64 times in 27 years	
Incidents of dew May thru Oct.	8 times in 27 years	
Incidents of precipitation Nov. thru Apr.	452 times in 27 years	
Incidents of precipitation May thru Oct.	228 times in 27 years	
Typical summer R. H.	15% R. H.	
Typical winter R. H.	40% R. H.	

Mirror Module Testing

On September 3, 1979, testing as outlined in Figure 16 began on 8 mirror modules. Four of the modules were designed and built by MDAC and are very similar in design to that shown in Figures 1b and 1c with the following exceptions (see Figure 17):

- The styrofoam core was one piece not four pieces bonded together.
- The edge cap configuration was the Sandia design (Figure 1c) with the addition of a polyisobutylene sealant bead in the inside corners of the edge cap and an additional silicone sealant fillng the gap between the parallel surfaces of the galvanized sheet steel and mirror on the front and galvanized steel and galvanized steel on the back.
- The edge cap spacing is maintained by dimples in the steel.
- The edge caps are held in place by an adhesive bonding the cap to the styrofoam core.

The MM modules differed from the design shown in Figure 1a in several ways (see Figure 18):

- There was no sheet steel between the mirror and the aluminum honeycomb.
- The adhesive used to bond the mirror to the honeycomb was a B-staged epoxy requiring an elevated temperature curve.
- The edges of the honeycomb cells were prevented from penetrating the mirror backing paint by a layer of very loose weave glass cloth (scrim cloth).
- Aluminum tape was placed on the back of the mirror along all the edges to prevent bonding of the honeycomb to the mirror at the edge (to prevent edge cracks).

Although the tests were designed to include the use of UV radiation, numerous problems with the arc lamp sources prevented this aspect of the test from being initiated. Each module was instrumented with a relative humidity gauge and a pressure gauge. Test data after one month indicate that the MDAC modules were intially sealed and remained totally sealed. The MM modules did not demonstrate the same clear cut behavior and closer examination of the sealant revealed areas of potential leaks. The problems associated with the sealant design appeared to be of a quality control nature, i.e. 1) preventing the scrim cloth from penetrating through the sealant 2) preventing the aluminum tape from penetrating the sealant 3) preventing improper mixing and bead width of the sealant.

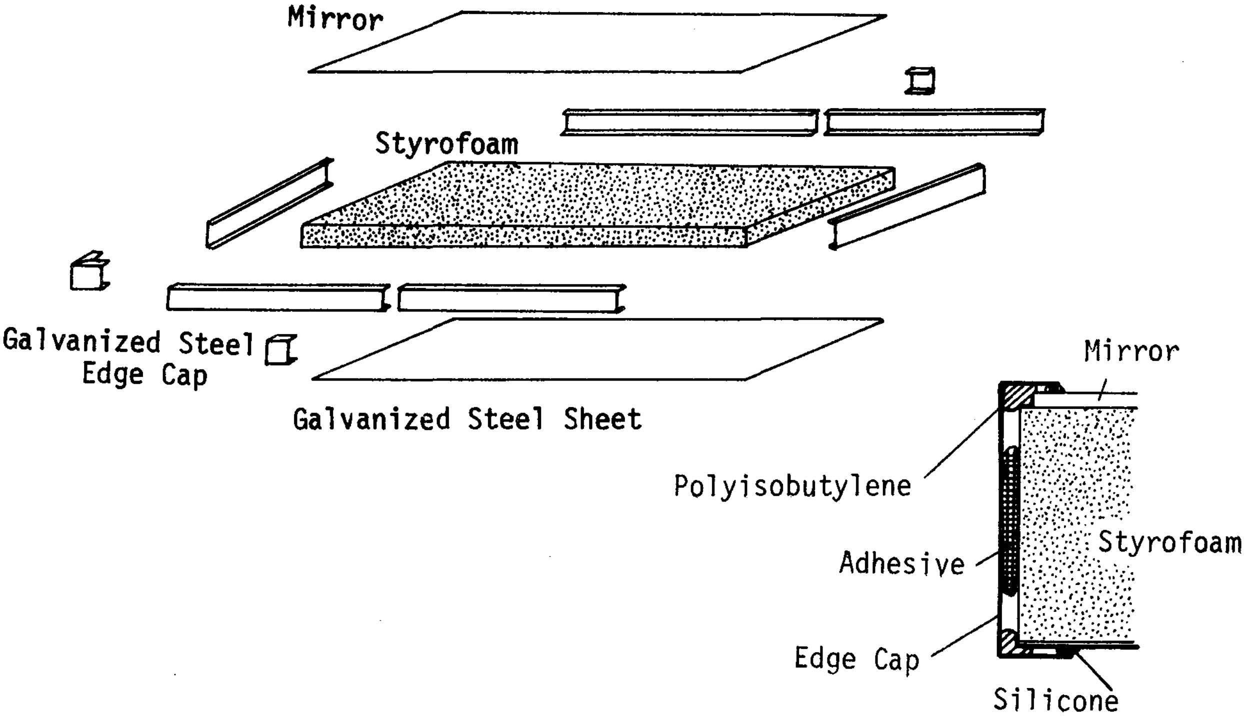


Figure 17. Revised MDAC Mirror Module Design

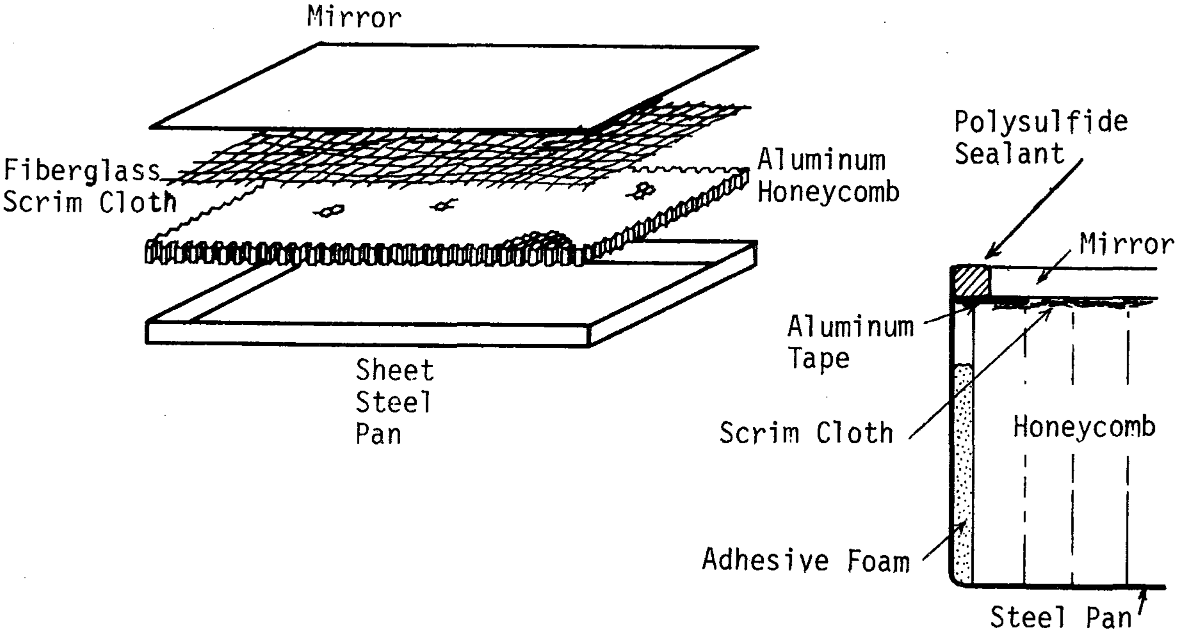


Figure 18. Revised MM Miror Module Design

The MDAC design leans heavily on the experiences of the thermal-pane window industry and shows the greatest promise in providing a module that is as close to being hermetically sealed as can be achieved with polymeric materials.

Conclusions

- The primary causative agent for most of the deterioration seen on the modules described in this report was the presence of liquid phase water in contact with the back of the mirror.
- There are a variety of adhesives that when used on the back of the mirror will greatly accelerate the deterioration caused by the presence of water, for example, any adhesive containing amines or sulfides.
- There are a variety of adhesives that have demonstrated chemical and mechanical (stress) compatibility with the mirrors.
- There are available superior mirror backing coatings that if used could prolong the useful life of the mirrors by as much as a factor of 10 to 20 even under the worst conditions seen to date, for example, PPG UC44409 paint and a variety of acrylic enamel paints.
- Tests to recreate field deterioration have been developed which are very successful in screening out potentially incompatible adhesives or potentially poor mirror backing paints.
- It has been demonstrated that it is possible to construct a full scale (1.3 m x 3.3 m) mirror module that can maintain an internal dew point less than -30°C after thermal cycling between -30°C and 50°C and exposure to high humidity at 50°C. The ability of the sealant materials in this module to survive for 30 years seems reasonable but as yet has not been proven.
- There is reason to believe that a well ventilated mirror module would survive as long as a totally sealed design, although no specific designs were investigated.
- There are available design solutions employing current technology that would provide a minimum of 15 years service life with no significant deterioration. These designs employ the use of superior mirror backing paints and more compatible adhesives. There is every possibility that refinement of this technology could extend the life to 30 years or more.

Recommendations

- Although the ability to fabricate full scale sealed modules has been demonstrated, high volume production of these modules could generate leakers once in a while. To guarantee survivability in these cases the adhesive used should be compatible at a minimum with use of a superior backing paint(s) as a desirable option.

- Totally vented mirror modules should use compatible adhesives and superior mirror backing paint(s) in all cases.
- Laboratory screening tests such as those described in this report should be used prior to the design of any full scale module, to weed out undesirable adhesives and mirror backing paints.
- There is much evidence to suggest the existence of deterioration mechanisms with very long term, non-catastrophic effects. There is clearly a need to better understand the silver glass interface to provide more efficient, economic solar heliostats.

Summary

The deterioration of the silver reflective surface in solar mirrors involves a complicated interaction with all of the materials of construction. However, there appears to be a variety of engineering solutions to the short term (less than 15 years) deterioration problem. These solutions involve the judicious choice of sealants and adhesives as determined by relatively simple compatibility tests and the design of either a well sealed module or well vented module with perhaps glass edge sealants. The solutions to the much less dramatic but nonetheless important long term deterioration problem are far from trivial and require much more analysis and testing.

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