Second Solar Reflective Materials Workshop

Abstracts

Sponsored and Organized by:

Pacific Northwest Laboratory
and
Solar Energy Research Institute
for the
U.S. Department of Energy

San Francisco, California
February 12-14, 1980
SECOND SOLAR REFLECTIVE MATERIALS WORKSHOP
FEBRUARY 12-14, 1980
SAN FRANCISCO, CALIFORNIA

AGENDA AND INDEX TO THE ABSTRACTS

MONDAY, FEBRUARY 11

1900 - 2100 Registration

TUESDAY, FEBRUARY 12

0730 Registration

0830 Introduction to the Workshop
   M. A. Lind, PNL

SESSION 1: Environmental Contamination
   W. F. Carroll, JPL

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1030 Cleaning Agents and Techniques for Concentrating Solar Collectors
   V. L. Morris, McDonnell Douglas

1050 Prevention of Soiling of Heliostat Surfaces
   R. E. Cambron, Springborn

1110 Questions and Discussion on Environmental Contamination

1200 WORKING LUNCHEON

Working Luncheon
WEDNESDAY, FEBRUARY 13

0830 Announcements

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R. B. Pettit, SLA

0840 Deterioration of the Silver-Glass Interface in Second Surface Solar Mirrors
V. P. Burolla, SLL

0900 Reflectance and Aging Studies on Heliostat Mirrors
H. Taketani, McDonnell Douglas

0920 Progressive Changes in Microstructure and Composition During Degradation of Solar Mirrors
J. L. Daniel and J. E. Coleman, PNL

0940 Characterization of New and Degraded Mirrors with AES, ESCA and SIMS
L. R. Pederson and M. T. Thomas, PNL

1000 BREAK

1030 Auger Analysis of Silver-Glass Interfaces
R. Bastasz, SLL

1050 Corrosion of Second Surface Silver Mirrors
B. E. Mills, SLL

1110 Corrosion of Second Surface Mirrors
J. Vitko, Jr., J. E. Shelby, and R. L. Farrow, SLL

1130 Electro-Chemical Evaluation of the Corrosion Resistance of Mirrored Surfaces
S. L. Pohlman and P. M. Russell, SERI

1200 LUNCH

SESSION 4: More on Degradation
P. J. Call, SERI

1320 Failure of Reflective Metal Coatings by Cracking
R. Zito, U. of Arizona

1340 Inhibiting Degradation of Wet Process Manufactured Solar Mirrors
C. Q. Buckwalter and G. L. McVay, PNL
THURSDAY, FEBRUARY 14

0830   Announcements

Session 5:   Polymers and Coatings
             K. D. Masterson, SERI

0840   Reactions at the Silver/Polymer Interface: A Review
       P. Q. Schissel and A. W. Czanderna, SERI  

0900   Exposure Testing of Solar Collector Plastic Films
       M. Berry and H. Dursch, Boeing

0920   Abrasion Resistant Polymer Reflectors
       R. A. Assink, SLA

0940   Thin Film Solar Reflectors
       R. N. Griffin, G.E.

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1030   Silicon Resins for Protection of First Surface Reflectors
       W. E. Dennis, Dow Corning

1050   Plasma-Polymerized Organosilanes as Protective
       Coatings for Front Surface Mirrors
       K. W. Bieg and K. B. Wischmann

1110   Protective Oxide Coatings for Heliostat Mirrors
       P. W. Buckman, Jr., Westinghouse

1130   Optical Properties of Disordered Rare Earth-Aluminum
       Alloys
       D. M. Trotter, Jr., Cornell University

1200   LUNCH

Session 5:  Coatings (continued)
             M. A. Lind, PNL

1320   Silver Aluminum Alloys as Reflector Layers for
       Solar Concentrators
       K. D. Masterson, SERI, R. O. Adams, Rockwell

1340   Reflector Edge Seal Development
       J. J. Dietrich, M. R. Boaner, G. F. Pittinato,
       McDonnell Douglas

1400   Questions and Discussion - Where Do We Go From Here?

1500   BREAK

1530   Introduction to ASTM Activities
The reflectance properties of several solar mirror materials have been studied after the mirrors were subjected to 10 months of outdoor exposure in Albuquerque, NM. The mirror materials include second-surface, silvered float glass, an aluminized acrylic film, an aluminized teflon film, and a roll polished aluminum sheet. The specular reflectance properties were measured as a function of angular aperture using a bidirectional reflectometer while the diffuse reflectance and hemispherical reflectance were measured using an integrating sphere reflectometer. The outdoor exposure resulted in a buildup on the mirror surface of particulates, which can both scatter and absorb incident solar radiation. For the materials studied, the reduction in specular reflectance was approximately five times greater than the reduction in hemispherical reflectance, indicating that the deposited particles are much more effective in scattering radiation than absorbing it. The wavelength dependence of the specular reflectance loss caused by the accumulated dust particles was studied for each mirror after the 10 month exposure. When normalized by the hemispherical reflectance of each mirror, the wavelength dependence of the normalized scattering curves were identical for all mirrors, within experimental errors. The normalized scattering curve changes during the course of the outdoor exposure, indicating that the particle size distribution of accumulated dust is changing with time. Over the 10 month period, the average decrease in the specular reflectance measured at 500 nm was slightly lower for the silvered glass mirror as compared to the aluminized acrylic and aluminized teflon mirrors.

*This work was supported by the Division of Solar Technology, U. S. Department of Energy (DOE), under contract DE-AC04-76-DP00789.
**A U. S. DOE facility.
One of the most significant causes of electrical performance degradation of flat plate photovoltaic modules exposed at outdoor sites throughout the country has been the accumulation of airborne particulates on sensitive optical surfaces. To characterize and understand the "dirt" problem and to minimize its impact on array life cycle costs, a photovoltaic contamination study is being performed by the Jet Propulsion Laboratory's Low-Cost Solar Array Project. This paper contains the more significant results obtained to date in this study.

Comparative electrical and optical performance data from modules exposed in the field and materials from test sites throughout the country have been collected and examined. The results show that there is a significant site dependence. The results also indicate that the rate of particulate accumulation during the dry season is material independent. Whereas, the effect of natural removal of "dirt" by rain or wind is material dependent. Changes in spectral transmission as a function of time and location along with limited scattering data will be presented.
THEORETICAL CONSIDERATIONS OF SOIL RETENTION*

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California Institute of Technology
Pasadena, California 91103

This paper describes mechanisms of surface soiling which results in resistance of the soil to be removed by natural means (wind, rain, etc.). Several of the mechanisms to be described are reported in the limited literature on surface soiling, and the remainder to be discussed are postulated. The primary mechanism of retention involves attractive forces between a surface and a particle, with the magnitude of the attractive forces basically dictated by particle size. It was observed in experiments on soil removal by wind from dry, oil free glass surfaces that particles smaller than $10\mu$ in size resist removal by wind speeds exceeding hurricane velocities. Additional retention mechanisms to be described involve relative humidity, dew, hydrophilic surface properties, and deposition of airborne organic vapors. The various mechanisms suggest directions for chemically defining the requirements for low soil retention surfaces, and for evolving cleaning strategies.

*This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the U.S. Department of Energy through an agreement with NASA.
THE EFFECT OF NATURAL CLEANING ON THE SIZE DISTRIBUTION OF
PARTICLES DEPOSITED ON SILVERED, GLASS MIRRORS*

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Albuquerque, New Mexico 87185

The particle size distribution of naturally soiled, silvered glass mirrors has been measured to determine the separate effects of natural soiling and natural cleaning (wind and rain). One set of three mirrors was exposed at Sandia Laboratories on a rooftop exposure rack (height ~12 m) at a south facing, 45° orientation angle for total periods of 2, 6, and 12 days. The size distribution function for particles deposited on those mirrors was measured as: \( \frac{dN}{d(\log r)} \propto r^{-n} \), where \( n \approx 1.1 \), \( r \) = particle radius, and \( N \) = number of particles with radii less than \( r \). A second set of mirrors was exposed on both the rooftop exposure rack and on a ground level exposure rack and experienced several months of natural soiling and cleaning (wind and rain). The size distribution of particles deposited on these mirrors was measured as: \( \frac{dN}{d(\log r)} \propto r^{-n} \), with \( n \approx 2.1 \). No significant difference was measured in the particle size distribution of the mirrors from the two locations. The increase in the \( n \) value for the mirrors exposed to long periods of natural cleaning represents an increase in the relative number of small particles with respect to the larger particles. This suggests that the smaller particles are less easily removed by natural cleaning forces such as wind and rain.

In order to investigate the soiling deposition mechanisms, a third group of mirrors was exposed at orientation angles of 0°, 45°, 90° and 180° (inverted) only during periods of good weather. These mirrors accumulated substantially more large particles (1 \( \mu \text{m} \leq r \leq 10 \mu \text{m} \)) than mirrors which had been exposed to any natural cleaning forces (sets 1 and 2). The shape of the particle size distribution function was similar for all the mirrors in set 3 but peaked in the range 1 \( \mu \text{m} \leq r \leq 10 \mu \text{m} \) instead of linear as seen for sets 1 and 2. As expected, the total number of particles decreased with increasing orientation angle.

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*This work was supported by the Division of Solar Technology, U. S. Department of Energy (DOE), under Contract DE-AC04-76-DP00789.

**A U. S. DOE facility.
Tests were conducted to determine the nature of the soil which is irreversibly deposited on solar collectors during environmental exposure. Methods of removing this soil were investigated. The mechanism of attachment of the soil to the surface was determined as a potential aid to cleaning agent formulation. Reflector specimens were environmentally exposed at several industrial sites. Three types of reflector surfaces were studied: second surface silvered glass, aluminized FEK-244 film on aluminum substrate, and RTV 670 on aluminum. Cleaning procedures were evaluated by microscopic examination of the solid surfaces before and after cleaning by measurement of specular reflectance. The effect of local environmental degradation specific to an industrial process on solar collector surfaces was investigated.
The objectives of this project are to develop methods for preventing or minimizing soiling of the surface of the glass-mirrored heliostat and the plastic dome over the aluminized Mylar mirror and also to facilitate the cleaning process. The substrates used in this project are regular and low iron float glass, Kynar, and Petra A polyester.

The two general classes of compounds which are being investigated are antistatic and antisoiling agents. The categories of antistatic agents used are amine derivatives, quaternary ammonium salts, phosphate esters, and polyethylene glycol esters. The soil-release agents are either hydrophilic ionic or hydrophilic nonionic in character. These compounds are attached to the substrate surface by silane or titanate coupling agents or as a mixture with a hard, weather-resistant coating. The silanol groups on the surface of glass provide suitable attachment sites; whereas, the plastic substrates require activation by various procedures.

Evaluation of the various coatings on the three substrates is accomplished by a sequential screening procedure. The tests are performed in the following order with ineffective materials eliminated at each step: (1) clarity, (2) adhesion, (3) antisoiling properties, (4) abrasion resistance, (5) antistatic properties, and (6) permanence.

Several coatings have been identified which meet the prescribed criteria when applied to glass. These coatings are not totally dust repellent, but they significantly reduce the cleaning effort. Dust may be removed by a high velocity air stream, an air stream in conjunction with gentle brushing, or by small amounts of water at low pressure. The extensive activation studies for plastics delayed the coating evaluations; however, materials which appear promising are being examined. In addition to promoting the cleaning process, some of these coatings actually improve the light transmission through the plastic.
LOW ABSORPTION FLOAT GLASS FOR BACK SURFACE SOLAR REFLECTORS

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A solar reflector using back surface silvered glass can have a very high solar reflection coefficient, but only if there is little or no absorption of solar radiation within the glass. The reflective surface must also be relatively free of surface wave if the collected beam is to maintain its spatial integrity. Thin glass made by a high production float process can be made to meet the flatness requirements, but absorption due to normal levels of iron oxide degrade the solar transmittance.

The float process is described and normal optical characteristics of float glass are discussed. The Ford Motor Company's Tulsa glass plant recently made over one million square feet of one-eighth inch low-iron glass which meets the rigid transmittance and flatness requirements for heliostat glass for the Ten Megawatt Power Project at Barstow, California. Research has established that the valence state of the iron in the glass is a significant factor in the solar transmittance. Iron in the ferric state absorbs in the ultraviolet while iron in the ferrous state absorbs in the infrared. Since the total solar energy in the UV is small compared to that in the IR, forcing the iron to the ferric state gives a higher solar transmittance for the same overall iron level. The float glass process at Tulsa was optimized for low-iron input through raw material selection and for furnace operating conditions to produce excellent quality low absorption glass. Measurements of the transmittance were in extremely good agreement with the Government selected test laboratory. The mean solar transmittance of the glass measured 89.3% and the calculated reflectance after silvering was 89.6%.
SOLARIZATION OF HELIOSTAT GLASSES*

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ABSTRACT

We have observed a solar-induced decrease in Fe$^{2+}$ absorption in heliostat glasses from the solar furnace at Odeillo, France. This decrease occurs throughout the sample (not just at the exposed surface) and is of sufficient magnitude to result in an increase of 2.5% in solar transmittance in a period of nine years. Optical and ESR studies did not detect a corresponding increase in Fe$^{3+}$ concentration. The implication of these results on a microscopic model for the observed solarization is discussed. Solar simulation studies produced effects of magnitude and sign similar to those observed in the field exposed samples, and appear to offer an attractive means for screening samples for solarization tendencies.

* Research supported by the U.S. DOE
Although soda-lime-silica glass appears to be the most durable low-cost candidate material for second surface solar mirrors in the near term, only limited quantitative information is available on the behavior of this material after long-term natural weathering in an arid environment. In an effort to assess the magnitude and character of any changes that occur, samples of soda-lime-silica glass were examined which had experienced more than forty years of exposure as south-facing vertical windows.

These samples contained areas that were both fully exposed and partially protected from moisture and blowing sand. The interior and exterior surfaces of both exposed and unexposed regions of the glass were compared for structural and compositional changes. The samples were also examined for spectral transmittance, reflectance, optical scatter and surface index of refraction changes. The results of these limited studies suggest that, at least from the optical point of view, the material showed only minor changes. The changes that did occur would not have affected the performance of solar mirrors used in even the most optically demanding heliostat designs.
WEATHERING OF POTENTIAL GLASSES FOR SOLAR APPLICATIONS

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C. Pantano
Pennsylvania State University
State College, Pennsylvania

ABSTRACT

The weathering of a variety of potential heliostat glasses under accelerated testing has been studied by a number of surface characterization techniques including optical spectroscopy, optical and scanning electron microscopy, sputter-through Auger analysis, ESCA, SIMS, dye penetration testing, surface profile measurements, and resonant nuclear reaction profiling. Significant weathering effects were observed only for the soda-lime-silicate glasses. For soda-lime-silicate glasses, the results indicate that the first stage of weathering is the formation of a low-density anti-reflection film on the glass surface. Growth of this film eventually results in spalling of the glass surface and severe degradation of the optical quality of the glass. The rate of weathering is a strong function of the composition of the glass. Float glasses exhibit significantly better weathering resistance on their tin-rich surface than on the tin-poor surface.

* Research supported by the U.S. DOE
Elastically deformed thin glass (thickness = 0.15-0.80 mm) provides an alternate method of forming a curved glass reflector which can eliminate some of the disadvantages of thicker glass. This paper describes a concept where silvered thin glass is laminated to a steel backing to form a reflector laminate with a reflectance greater than 93%. Subsequent bending of the flat reflector laminate to a concentrating profile produces compressive stresses throughout the glass if the laminate is properly designed. These compressive stresses enhance its fracture resistance and the lamination provides protection for the silver. The design of the lamination is outlined for 0.25 and 0.51 mm thickness glass. The factors considered in the design are: (1) stresses in the glass due to handling and forming the laminate to the shape of a parabolic trough; (2) thermal stresses in the glass due to thermal expansion mismatches within the reflector laminate and mismatches between the laminate and its support; (3) fabricability; (4) cost; and (5) weight. Reflector laminates 0.3 m x 2.3 m have been fabricated and the fabrication procedures are discussed. Thermal/humidity cycling, hail impact, bond strength measurements and reflectance results are presented which demonstrate the performance capabilities of this reflector laminate concept.
Most mirrors made today for domestic, indoor applications are coated using a semi-continuous wet chemistry production process. These mirrors generally consist of a float glass superstrate, a silver reflective layer, a copper layer and a protective paint overcoat. The function of the copper layer has not been fully determined at this time even though the basic mirror structure has changed very little since the 1800s. The paint overcoat on mirrors for interior use prevents abrasion during post-production handling.

The generic production process will be described from glass input to removal of the final product. Key aspects of the individual process steps will be emphasized. The organization of the industry will be mentioned briefly.
Some highlights of the electroless deposition of silver on glass

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Water solutions of three chemical species (ammoniated silver nitrate, sodium hydroxide, and formaldehyde) form a battery action deposition of silver when sprayed simultaneously on a sensitized glass surface. It is shown how a series of simple reactions could yield the result of the well known etochrometric equation for the reaction, but one of these reactions is a nucleophilic displacement of a "free" hydron which is not possible. The alternative is a third order reaction which led London Laboratories into a study of the Cannizzaro reaction in 1968. This study suggested a mechanism by which, not only an electron, but an electron which is bonded to a hydrogen atom to form the hydron (\(\tilde{H}\)) is transferred to the catalytic surface. One can then explain how a speck of silver on one sensitized spot can set off the extremely effective catalysis of the finally continuous film.

Also discussed is the metal crystallization theory of Kossel-Stranski. This theory indicates qualitatively how both components of the Hydron (\(\tilde{H}\)) are dealt with on the catalytic surface.

Reaction rates have been determined for the deposition processing the Spinning Dish approach. The analysis shows rates of silver deposition with constant concentrations of reactants. The experiments yield the dependence of deposition rate on the rate of diffusion of a single ion.
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 proposed for the Barstow pilot plant revealed significant deterioration of the silvered surface in an unexpectedly short time span.

The deterioration seen to date is not specific to a particular geographic location or module design and appears in several forms depending upon the geometry of the mirror module and the compatibility of the mirror with adhesives and sealants used in its fabrication. There is evidence of more than one deterioration mechanism that may be a function of the mirror backing paint used. There is strong evidence that water plays a dominant role in any mechanism and that silver delamination is a precursor to silver dissolution. Laboratory tests have been successful to an extent, in generating mirror deterioration similar to that seen in the field.

*Work supported by the United States Department of Energy under Contract No. DE-AC04-76DP00789
A brief review of the principles involved in making reflectance measurements of mirrors over the solar spectrum including air mass correction is given. Using these principles, reflectance measurements of different commercial silvering processes on the same glass showed no significant differences between the processes studied, including vapor deposited silver. In addition, reflectance measurements were made on bare silver, silver/copper, silver/copper/paint over glass together with transmission measurements on the same glass. Using these results, a correlation between transmission and reflectance efficiency after mirroring was developed.

Subsequently, these mirrors, as well as candidate first surface mirrors, were subjected to Mojave Desert environmental conditions for time periods up to 3-1/3 years. Of the mirrors tested, second surface glass mirrors and first surface aluminized acrylic mirrors exhibited the greatest weathering properties.
PROGRESSIVE CHANGES IN MICROSTRUCTURE AND COMPOSITION DURING DEGRADATION OF SOLAR MIRRORS

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ABSTRACT

The long-term degradation of solar mirrors can range from negligible to near total destruction of the reflective silver layer, depending on age and conditions of use. The microstructure and composition of several stages of degradation have been studied using light optical and scanning electron microscopy (SEM) combined with an electron microprobe x-ray fluorescence analyzer (EDX). Newly fabricated mirrors commonly display weak adhesion of the silver layer to the glass; gaps of several micrometers have been measured on mirror specimens polished in profile by metallographic methods for high resolution microscopy. Surface micro-defects such as unsilvered spots, impurity precipitates, and outsize silver grains also are not unusual in new mirrors.

Field degradation of mirrors first appears visually as a random distribution of fine spots in which the silver layer is thickened, and a reaction has occurred with the adjacent glass surface. Continued degradation leads to enlargement or aggregation of spots which may ultimately cover nearly the entire mirror surface. A circular banded structure develops around each spot center, with the silver layer adhering strongly to the glass or backing paint in alternate bands. The degraded regions are devoid of the copper originally deposited over the silver, and the silver grain size has increased about tenfold. The evidence suggests that the extent of degradation, the composition of reaction products, and the type of microstructure are strongly influenced by the presence of water.
CHARACTERIZATION OF NEW AND DEGRADED MIRRORS WITH AES, ESCA, AND SIMS

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A series of samples representing each stage of second surface mirror production were examined using AES and ESCA, in combination with ion sputtering, and SIMS. Finished mirrors that had been exposed to the environment were also analyzed.

Untreated soda lime silicate float glass was found to contain tin and iron on both surfaces. These elements were restricted to depths less than 50Å on the air side, but were detected at depths greater than 5000Å on the float side. Both sides were depleted of calcium and sodium to roughly the same extent; calcium to a depth of about 300Å and sodium to 800Å. On the air side, tin and iron were effectively removed by scrubbing with a CeO₂ slurry, without obviously affecting the extent of sodium and calcium depletion. Sensitization with 0.05% SnCl₂ solution followed by rinsing led to a surface tin concentration of approximately 1 atom percent. The resulting tin layer was less than 30Å deep.

After depositing silver from solution, silver was found to penetrate the glass matrix to depths of several hundred angstroms, which is attributed to ion exchange with sodium and/or calcium ions. Samples having both copper and silver overlayers showed intermixing of the metals greater than that expected from published diffusion and miscibility data. The results are consistent with a model of silver and copper existing as microcrystalline islands, with dimensions less than the spatial resolution of the AES and ESCA spectrometers.

On degraded mirror samples, the thickness of the copper layers was found to vary widely across the surface. Copper was not detectable on and near some corrosion spots. Analysis of corrosion pits showed the presence of C, Cl, S, Ca, K, Si, O, Na, Fe, and Sn. Some of these, particularly S and Cl, may help to accelerate corrosion in these areas.
AUGER ANALYSIS OF SILVER-GLASS INTERFACES*

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ABSTRACT

Long term performance is expected of mirrors used in heliostat arrays. One consequence of this requirement is that the silver reflective layer in a mirror must adhere firmly to the underlying glass substrate so that delamination, which degrades mirror performance, does not occur. Gentle annealing is known to increase the adhesion of evaporated, silver films to glass but the mechanism that enhances adhesion is not understood. In an attempt to gain some insight into this process, Auger electron spectroscopy has been used to study the effects of annealing upon silver/glass interfaces.

Samples of ordinary float glass were coated with ~1000Å of silver in a vacuum evaporation chamber. Control samples were not treated further, while others were annealed at 200°C for periods up to 1 hour. The samples were then placed in an Auger spectrometer having a base operating pressure <100 nPa and the silver was removed in situ by 3 keV Ar+ bombardment so that the silver/glass interface could be examined.

AES data recorded while sputtering indicated the bulk of the silver film in both samples was free of contaminants. Near the silver/glass interface, which was taken as being at the point where significant sample charging was first observed, the composition of the two samples differed. In the control samples there was an abrupt transition in going from the metal film to the glass insulator while in the annealed samples a broader transition region was observed. The oxygen content at the interface, which was estimated from Auger data using empirical sensitivity factors, was greater in the annealed samples than in the controls.

These observations can be interpreted using a model in which intermixing of the silver layer with the glass components occurs upon annealing. Increased adhesion appears to be correlated with this interfacial behavior.

*This work was supported by the U. S. Department of Energy.
Mirrors with up to eight months exposure in the field and with extensive corrosion have been studied to determine the nature of the corrosion. Auger electron spectroscopy of exposed surfaces displaying corrosion indicates that a copper/oxygen species is the first decomposition product. This product tends to form or precipitate in spots or rings and may or may not be accompanied by small amounts of chlorine or sulfur. These elements are superficial, however, and easily removed by sputtering.

In the mirror with eight months exposure, the centers of the copper corrosion areas seem to be the sites for silver degradation. In some cases pinholes have formed in the bottoms of the "craters" which transmit light after the paint backing is removed by a solvent. (The solvent may also remove some corrosion products.) The silver, which is exposed in rings between the copper and the corrosion products, is in the form of the oxide or carbonate, although sulfur or chlorine may also be present.

Model studies of mirrors exposed to a water/isopropyl alcohol mixture by other Sandia investigators have produced separation of paint bubbles from the mirror. Analysis of these areas reveals a silver layer contaminated with numerous elements which must have been leached from the paint. A model mirror exposed to hydrochloric acid has shown extensive chloride formation and massive oxidation of the silver as well as of the copper.

All of the above-mentioned mirrors failed from the paint side. A clean mirror made to fail at the glass/silver interface has been studied as a baseline case to investigate corrosion from the glass side rather than the paint side. It has so far proven impossible to force a corroded mirror to fail at this interface, however.

*Work supported by the U.S. Department of Energy, DOE, under Contract DE-AC04-76DP00789.
A variety of techniques have been used to characterize the corrosion of the reflective layer in second surface heliostats. Initial studies utilized optical and electron microscopy, ESX, Auger, and ESCA analysis of corroded mirrors in which the protective paint backing had been removed by chemical means. These studies suggest that the corroded areas consist of spots from which both the silver and copper have been removed and that the resulting degradation in optical performance results from the removal of reflective material and not from the buildup of corrosion products. This interpretation assumes that the chemical stripping process used to remove the paint does not remove any of the corrosion products or significantly alter the corrosion morphology. Further studies, i.e. (a) microscopic and surface analysis of mechanically stripped mirrors; (b) the use of conventional and laser based optical techniques to probe the corrosion from the front surface of the mirror, hence eliminating the need for any alterations in mirror structure, and (c) the characterization of a nearly identical morphology observed in certain heat treated mirrors, have shown that this assumption is not entirely correct.

*Research supported by the U.S. Department of Energy*
Electrochemical techniques including potentiostatic, dynamic and galvanic measurements were employed to evaluate the corrosion resistance of mirrored surfaces. Corrosion current measurements generated using a potential driven modified scratch test were used to rank order the corrosion resistance of various manufactured "stack" mirrors. The electrochemical ranking compared very well with resistance rankings derived from modified salt spray and alternate immersion tests, but only required a few minutes to complete as compared to hundreds of hours required to complete the environmental tests. This technique is presently being evaluated as a rapid quality assurance test.

Galvanic measurements have shown that silver/copper is not an active galvanic couple and copper does not provide much cathodic protection to the silver. In fact, galvanic titration measurements between copper and silver have revealed that near a pH of 10.3 and at accompanying halide ion concentrations, a polarity reversal occurs and silver will corrode preferentially when coupled to copper.

Electrochemical experiments have also shown that the formation of hydrogen gas at the glass/silver interface will cause deadhesion of the silver from the glass. The silver/tin galvanic interaction is very strong and in the presence of water, even without aggressive species, oxidation of the tin and hydrogen formation on the silver surface will occur.

Changing various process chemicals and/or the mirror "stack" structure will increase the corrosion resistance of mirrors. Suggested changes are presently being evaluated at the SERI mirroring and corrosion facility.
The relationship between point defects and severe cracking of metal films is explored. Tests carried out on coatings of Cr, Cu and Ni show that cracks radiate from pinholes in the metal film. This effect has been attributed to stress concentration in the neighborhood of the pinhole. It seems advisable to fill in as many pinholes as possible during deposition if cracking is to be avoided. Furthermore, reflective coatings intended for high temperature use should not be raised to the pinhole formation temperature or higher.
The impact of heliostat mirror degradation on the performance of central receiver power plants can be significant. Presented in this paper is a probable cause of mirror degradation and a possible method of inhibiting this degradation without encapsulating the mirror.

One possible cause of mirror degradation is the dissolution of the soda-lime-silicate surface at the silver-glass interface. The initiation of this degradation may begin at the time of production and continue as a result of glass/water interaction. Inhibiting this dissolution may be possible by treating the glass surface with trivalent lanthanide ions prior to the silvering deposition. The lanthanide ions can be incorporated into the production line without additional capital investment and without interfering with the efficiency of the silvering reaction.

Leaching experiments have been performed as a form of accelerated weatherization on mirrors and on soda-lime-silicate glasses. The glasses and mirrors doped with a series of different lanthanide ions show that significant gains may be realized towards preserving the integrity of the glass surface.
The corrosion reaction that occurs at the glass/metal interface of a mirrored surface is extremely sensitive to the interfacial environment. Small perturbations to the environment caused by crevice concentration effects, fabrication chemicals, glass leaching, local hot spots or photoactivation of the surface metals produce large variances in the durability of the mirrored surface. Surface analyses of corroded mirrors, selective ion measurements and various electrochemical testing techniques, have been used to correlate the change in interfacial environment with the observed corrosion resistance of the mirrored surface.

Experimental measurements reveal that the "stack" mirror interfaces behave as natural occluded cells and that variations from bulk chemistry in pH and ionic concentrations are significant and occur rapidly. It has been shown that the corrosion of the glass, the dissolution of the metal and the migration of ions through the paint are responsible, in part, for this measured environmental change at the glass/metal interface.

Galvanic measurements between the silver and copper have shown that the galvanic corrosion is extremely sensitive to the environment. Misleading information concerning the importance of silver to copper ratio can be drawn from testing mirrors in an overly aggressive environment. The effect of light impingement on the solver and copper and photoactivation of the cell causes fluctuation in the measured galvanic current and should be examined.

When determining a mechanism to explain the corrosion of a mirrored surface, all the environmental factors and behavior of the individual components must be considered, for it has been shown that they will affect the overall corrosion behavior.
Abstract

An effort to characterize and evaluate reflective surfaces for advanced, point focusing solar thermal concentrators has been undertaken. The UV transmission and visible reflectances of various surfaces have been investigated. Special attention has been given to commercial glass mirrors with a smaller amount of effort on anodized aluminum and aluminized plastic reflectors.

The transmission of the near-ultraviolet between wavelengths of 290 nm-400 nm have been measured on glass mirrors without backing paint. The peak intensities superimposed upon a wide transmission range were observed between 326 and 340 nm. The penetrating UV spectra varied with (a) the thickness of silver and copper overcoat and (b) the uniformity of the metallizations. The purpose of these measurements was to determine the amount of UV energy impinging upon the backing paint and adhesive systems.

One purpose of this research is to ascertain if the UV component has a role in mirror corrosion processes.

In order to test the integrity of the silver-metallization and paint systems, pull testing on high reflectance solar mirrors has been undertaken. The types of failure modes are included along with tensile strengths observed. This new data is different from others working in the field. Postulated reasons for the differences will be given.
Field exposure tests and scientific analysis have demonstrated that the integrity (both the adhesion and permeability) of the protective backing paint on silver/glass mirror systems is a key issue in determining the suitability of a mirror for long-term durability in solar applications. This paper describes simple, safe, and reproducible tests for the exposure of mirror coupons to a well-defined moist atmosphere containing either HCl or H₂S. These tests subject mirrors to a gaseous environment, in contrast to previously available condensing or immersion tests. Commercial mirrors have been subjected to these accelerated tests and the quantitative data derived corroborates observations from field exposure.

The tests consist of placing a known quantity and concentration of solution in a desiccator maintained at a controlled temperature. The hydrogen chloride or hydrogen sulfide molecular concentration in the gaseous environment of the desiccator is quantitatively defined as a function of temperature, volume, concentration, and surface area of the solution. A kinetic model that accounts for the concentration of hydrogen chloride molecules in the vapor phase as a function of time is also presented.
One of the possible solutions for improving mirrors for long-life, inexpensive solar concentrators is to coat the reactive mirror material with a polymer. Polymer-coated reflectors may result both in improved optical efficiency and cost reduction for solar mirrors. Since the existence of a mirror/polymer interface may itself result in long-term instabilities in a solar-stressed environment, it is necessary to isolate those affects attributable to the "bulk" materials from those of the interface. While actual failure mechanisms are speculative, several plausible examples are presented that may lead to failure of the polymer/mirror interface. The purpose of this paper is to review the literature on one of the systems of great current interest, the silver/polymer interface. First, the components of this interface are considered separately. Results of studies of reactions by environmental gases with silver are summarized. Then, several candidate fluoropolymers and polymethylmethacrylate are considered independently of the metal. The thermal, photo, and oxidative degradation reactions are briefly outlined. Finally, the limited data actually obtained on the silver/polymer interface are summarized. Results obtained on the silver/Teflon-FEP interface are emphasized because its use for thermal control panels in the space program resulted in extensive study.
The Boeing Engineering and Construction Co. (BEC) has been involved in the study and use of plastic films for solar collectors during the past four years.

This paper summarizes experimental work accomplished by BEC, aimed at finding low-cost, long-life, highly specular plastic films for collector utilization. Primary investigations include contacting the plastic film industry for potential candidates, screen testing and initiating exposure exposure testing of the most promising materials. Samples have been subjected to up to 18 months of solar exposure in both real time and accelerated testing techniques at a desert test site in Arizona. The changes in mechanical and optical properties for each of the materials and test conditions are presented.

Thermoformed domes (35.5 cm and 61 cm) have been exposure tested at the same desert test site since late 1978. The testing was initiated to verify the weatherability of the various materials and processes of fabrication. Changes in mechanical and optical properties and dust accumulation are discussed.
Metallized polymer sheets and films offer the potential of providing a low-cost, lightweight and easily installed solar reflector surface. One of the primary concerns associated with their use is their susceptibility to abrasion from wind blown sand and cleaning operations. Various approaches to the attainment of an abrasion resistant polymer surface were surveyed and two of the approaches were examined in detail. First, an abrasion resistant acrylic sheet was aluminized by an ion plating process. Although the abrasion resistance of the material was excellent, its reflectivity was fair and its weatherability was poor. Second, a development abrasion resistant coating was applied to an aluminized acrylic film. The abrasion resistance, reflectivity, weatherability and dirt retention properties of the material were excellent.

* This work was supported by the U. S. Department of Energy (DOE) under contract #DE-AC04-76 DP00789.

** A United States DOE facility.
THIN FILM SOLAR REFLECTORS

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No abstract submitted.
SILICONE RESINS FOR PROTECTION OF FIRST SURFACE REFLECTORS

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Silicone resins were evaluated for use as protective coatings for front or first surface silver and aluminum reflectors. The silicone resins encompassed a broad range of chemical compositions and physical properties. The relevant physical properties of the cured resin films were measured and their soiling characteristics were obtained by measuring the transmissivity of cured films at various periods of outdoor exposure. The spectral and specular reflectance of squares of float glass metallized with aluminum and protected with the best candidate coatings were measured before and after exposure to ultraviolet radiation. Float glass squares metallized with both silver and aluminum coated with resin were exposed to moist sulfur dioxide, salt spray and exposed outdoors. These samples were prepared with and without silane coupling agents to promote the adhesion of the resin to the metal surface.

Excellent protection and high specular reflectivity was afforded by certain of the silicone resin coatings throughout the various accelerated tests and in outdoor exposure.

In general the aluminized reflectors were easier to protect than the silvered reflectors. The most common mode of failure of the silvered float glass samples was loss of adhesion between the glass and the silver. Further work is in progress to diminish this mode of failure and to identify the failure modes which have occurred on both silver and aluminum first surface reflectors.
PLASMA--POLYMERIZED ORGANOSILANES AS PROTECTIVE COATINGS FOR SOLAR FRONT-SURFACE MIRRORS*

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A plasma polymerization technique has been investigated as a method to apply uniform, thin (microns) protective coatings to front surface mirrors employed in various solar applications. These coatings were also found to offer anti-static qualities and weather resistance. Specifically, the coatings were organosilicone polymers based on precursors such as vinyltrimethylsilane (VTMS), methyltrimethoxysilane (MTMOS) and vinyltrimethoxysilane (VTMOS).

We found negligible changes in hemispherical and specular reflectance when these coatings were applied. Both silver and aluminum front surface mirrors were evaluated. Surface electrostatic charge decay measured following corona charging mirror surfaces suggest that coatings containing oxygen (MTMOS, VTMOS) had improved anti-static behavior compared to the nonoxygen containing polymer (VTMS). The initial charge decay in the oxygenated materials occurred < one minute versus > hour for the VTMS coating. Weatherability tests conducted in a temperature-humidity cycling environmental chamber showed that the plasma polymerized coatings provided excellent protection for aluminized mirrors (six-month test). Silvered mirrors were observed to degrade after two months; however, unprotected silver mirrors degrade in a matter of days in this environment. Improved abrasion resistance was achieved for MTMOS coatings synthesized in an oxygen rich plasma when compared to the uncoated glass in a falling sand abrasion test (ASTM D968-51). Finally, although no attempts were made to ascertain the economics of this technique, this method of producing thin, uniform, adherent optical quality coatings that conform to virtually any shaped substrate should be further investigated as a means to provide protective coatings for solar applications.

*Work by DOE facility, #DE-AC04-76 DP00789.
The reflective surface of a mirror is rapidly corroded by atmospheric contaminants if left unprotected. One promising technique of providing protection is to coat this surface with a transparent, dense oxide film. Preliminary experimental results indicate that a titanium dioxide coating, applied by a low-temperature process, protects the reflective surface from corrosion in aqueous nitric acid and salt solutions. Reflectivity measurements show that only approximately 2-1/2% of the energy reflected from a front surface mirror is absorbed by the titanium dioxide coating.
An aluminum surface has a solar reflectance $\leq 0.91$. The Drude model predicts a reflectivity $\approx 99\%$ for Al because it neglects interband transitions which arise because of long range translational order in the pure material. By alloying Al with small amounts of gadolinium and samarium, which are large atoms with the same valence (+3) as Al, materials which are still largely Al but lack long range order are created. The reduction in interband transition strength concomitant with reduction in long range order raises the reflectivity of the alloys relative to pure Al, but only over a fairly narrow wavelength range. Over the rest of the solar spectral region the increased Drude relaxation rate $(\hbar/\tau_D)$ resulting from the disorder depresses the reflectivity of the alloys so that a smaller net solar reflectance results.

Specular alloy samples are prepared by simultaneously evaporating Al and a solute onto chilled ($T \approx 100\text{K}$) substrates. Electron microscopy shows that for solute concentrations $\leq 10\%$ the alloys consist of small crystallites embedded in a matrix of disordered material, with the crystallites growing smaller and less organized as the solute concentration increases. Alloys with $\approx 10\%$ solute are totally disordered and are characterized by $\hbar/\tau_D \approx 0.7$ eV, similar to that of liquid Al, and an interband transition strength about 1/3 that of pure Al. Solute concentrations $\geq 20\%$ are required to reduce the interband strength to zero; this increases $\hbar/\tau_D$ to $\approx 2$ eV. For pure Al $\hbar/\tau_D \approx 0.14$ eV.

Supported by SERI XH-9-8158-1 and NSF DMR-76-81083 A02.
SILVER ALUMINUM ALLOYS AS REFLECTOR LAYERS FOR SOLAR CONCENTRATORS

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The area intensive components of concentrating solar energy collector systems are the reflectors. Their relatively high cost has great leverage on the cost of the total system and hence the costs of solar energy collected. In order to minimize the collector area and the costs, one would like to use materials with very high reflectivity. Unfortunately, the material with the highest reflectivity, silver, is quite susceptible to corrosion caused by airborne compounds from the environment. This paper reports on research being carried out cooperatively by Rockwell International's Rocky Flats Plant and SERI to evaluate the potential of silver-aluminum alloys to provide a high reflectance, environmentally stable reflective layer for glass or polymer superstrates.

To provide samples with a wide range of silver to aluminum ratios desired for survey work, co-sputtering of separate silver and aluminum targets arranged in suitable geometry was chosen as the deposition technique. Using this technique, coatings that vary continuously over a 15 cm. length from almost pure aluminum at one end to almost pure silver at the other have been produced. Composition and micro-structure profiles along the samples were obtained using Auger, x-ray and SEM analysis techniques. Data on the spectral reflectance of these alloys as a function of the silver to aluminum ratio is reported. Reflectance almost equal to that of chemically plated silver and with good specularity has been obtained.

Initial studies on the resistance of the films to corrosion by salt spray and HCl vapor are reported and correlated to measurements of the electrochemical potential of the alloys.
Commercialization of Solar Central Receiver Systems requires cost effective heliostats with long life. Mirror modules for these heliostats must, therefore, have no silver degradation/corrosion for the 20-30 year life expectancy. Recent studies have identified water on the backside of the mirror as a major factor in producing this silver degradation/corrosion. An effective edge seal for the reflector panel to prevent water from entering the panel is one concept that can be used to obtain the required life.

This paper presents the results of reflector edge seal development for the MDAC foam core mirror module. First, the various sealing materials are identified and test results that show which sealing materials are effective are presented. Second, several edge seal designs are presented which made use of available insulated glass technology. Sample panels are fabricated using these designs and the most effective materials.

Finally, environmental test parameters are developed and the sample panels are tested in an environmental chamber. Results of these tests and conclusions regarding edge seals are presented.