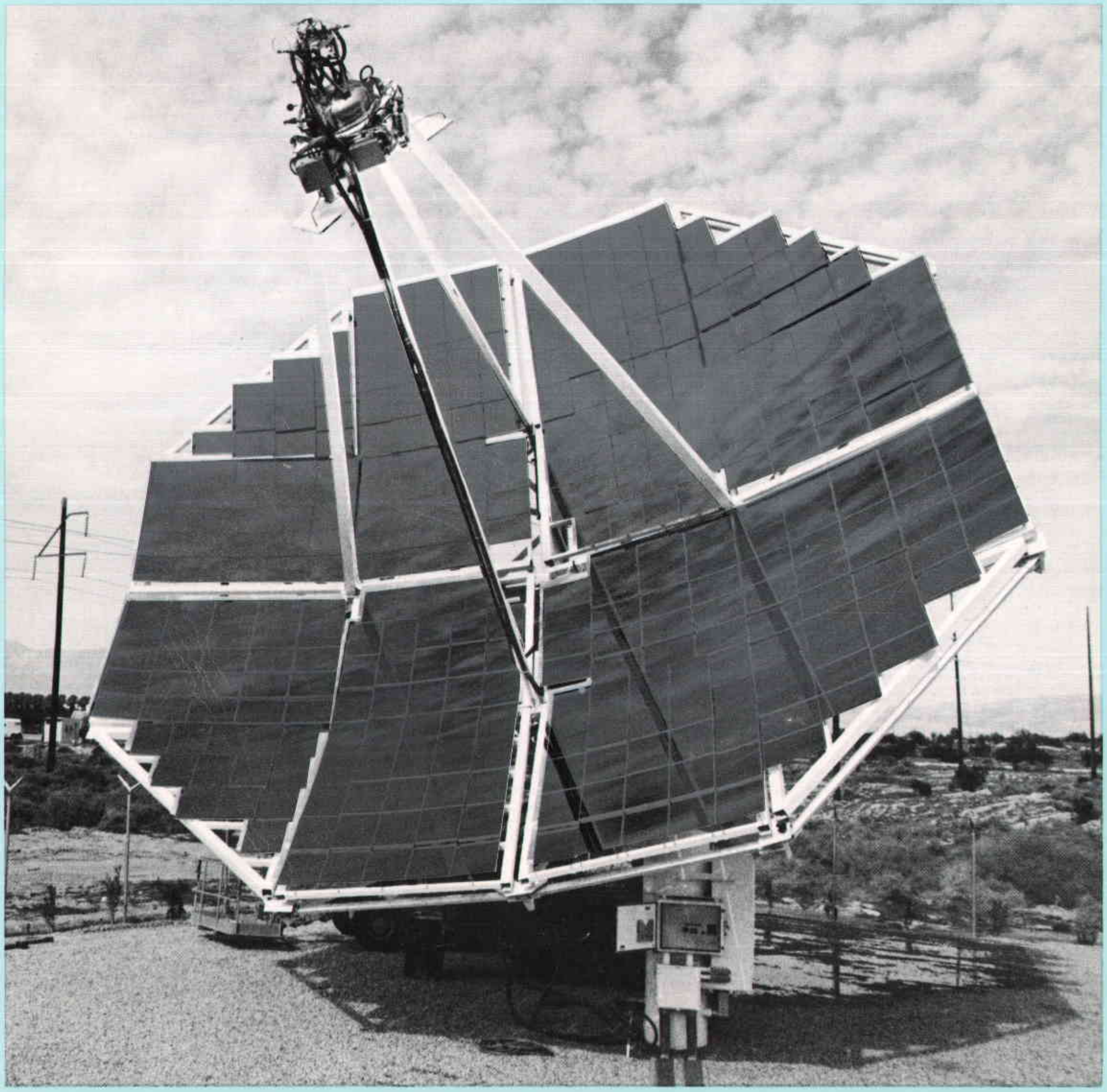
SERI/SP-271-2293

# Silver/Glass Mirrors for Solar Thermal Systems



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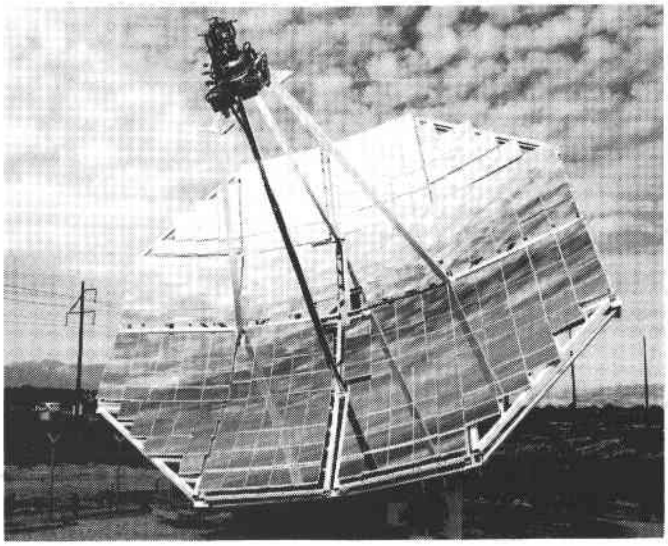
# Silver/Glass Mirrors for Solar Thermal Systems



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## Preface

The research and development (R&D) described in this document was conducted within the U.S. Department of Energy's (DOE) Solar Thermal Technology Program. The goal of the Solar Thermal Technology Program is to advance the engineering and scientific understanding of solar thermal technology and to establish the technology base from which private industry can develop solar thermal power production options for introduction into the competitive energy market.

In solar thermal technology, tracking mirrors or lenses concentrate sunlight onto a receiver. The heat absorbed by the receiver is converted into electricity or used as process heat. The two primary solar thermal technologies, central receivers and distributed receivers, use various point and line-focus optics to concentrate sunlight. Central receiver systems use fields of heliostats (two-axis tracking mirrors) to focus the sun's rays onto a single tower-mounted receiver. Parabolic dishes up to 17 meters in diameter track the sun in two axes and use mirrors or Fresnel lenses to focus radiant energy onto a receiver. Troughs and bowls are line-focus tracking reflectors that concentrate sunlight onto receiver tubes along their focal lines. Concentrating collector modules can be used alone or in a multi-module system. The concentrated radiant energy absorbed by the solar thermal receiver is transported to the conversion process by a circulating working fluid. Receiver temperatures range from 100°C in low-temperature troughs to over 1500°C in dish and central receiver systems.

The Solar Thermal Technology Program is directing efforts to advance and improve each system concept through research and development of solar thermal materials, components,

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and subsystems, and the testing and performance evaluation of subsystems and systems. Work is done under the technical direction of DOE and its network of national laboratories who work with universities and private industry. Together they are pursuing a comprehensive, goal-directed program to improve performance and provide technically proven options for eventual incorporation into the nation's energy supply.

To contribute to the national energy supply, solar thermal energy must eventually be economically competitive with other energy sources. Components and system-level performance targets have been developed as quantitative program goals. The performance targets are used in planning research and development activities, measuring progress, assessing alternative technology options, and optimizing components. These targets will be pursued vigorously to ensure a successful program.

This document reviews the state of the art of the design, manufacture, testing, and performance of silver/glass mirrors for solar thermal systems applications.

## Acknowledgments

This document was prepared by Al Czanderna, Keith Masterson, and Terence M. Thomas of the Materials Research Branch of the Solar Energy Research Institute.

# Contents

# Introduction

## Background

A significant aspect of research and development (R&D) of solar thermal energy systems concerns the design, manufacture, testing and performance of mirrors for solar energy applications. Mirrors have an essential role in various solar thermal technology applications. For these applications, mirrored surfaces are used to redirect and/or to concentrate the rays of the sun. The most extensive application of mirrors is expected to be in solar thermal systems. Most industrial and utility applications of solar thermal energy systems are to produce process heat fluids or develop other forms of energy, such as electricity for mechanical power, requiring concentrating mirrors. Mirrors are needed to concentrate the naturally available solar flux in order to attain higher temperatures.

Mirrors are used mostly in such solar thermal systems/subsystems as parabolic troughs, parabolic dishes, spherical bowls, and heliostats. Each has particular design requirements. However, the principal attributes sought in the design specifications of the "ideal" solar thermal reflector should include the following:

- High optical performance:
  - reflectance/transmittance,
  - specularity,
  - geometrical configuration,
- Low maintenance (dust free),
- Low initial cost, and
- Long life.

Most mirrors presently in use employ either silver (domestic and decorative applications) or aluminum films (automotive applications) for their reflecting surfaces. Mirrors made of silver must be protected from chemical and physical deterioration of the silver; whereas, aluminum mirrors are more resistant to degradation.

Since both silver and aluminum reflecting surfaces in solar applications must retain their highest reflectivity for many years, the reflecting surfaces are protected with transparent covering materials referred to as superstrates. Also, this adds to the physical integrity of the reflector since the superstrate supports the silver.

The material or materials attached to the silver (1) should not detract from the silver's reflective quality, (2) should not contribute to degradation of the silver, and (3) should bond well. Moreover, all of these properties should remain substantially intact over the economic life span of the facility in which they are used, during which time the mirror may be degraded by storms and stressed by temperature cycling, water, humidity, vapor, ultraviolet (UV) radiation, dust, and physical abuse.

Most mirrors have been manufactured by bonding a thin layer of silver to glass — the glass being the protective barrier, light transmitter, and, in part, a structural support. A copper film to protect the silver's back surface and layers of paint to protect the copper also are necessary.

The advantages of using glass as a superstrate are its clarity (high solar transmittance), low cost, smooth surface, physical strength, abrasion resistance, impermeability, resistance to soiling, ease of cleaning, and inertness. Compared with other mirrors, those made of glass and silver are preferred for their high reflectance, good specularity, durability, and resistance to distortion from loads. However, glass is heavy and brittle, requiring massive structural support.

Mirrors of silvered glass are fairly tolerant of mirror compositional variations and/or impurities. They can be expected to provide high reflectance as long as the silver remains intact and in contact with the glass. Retaining this integrity depends on chemical and physical processes that take place in and between the layers of materials composing the mirrors.

Although glass has many advantages as a superstrate for silver mirrors, certain factors can mitigate its use. Glass is a relatively heavy (high density) and brittle material; therefore, it requires either stronger and stiffer mechanical support structures or thinner, more fragile layers than lighter materials.

Mirror manufacturing techniques can play an important role in the performance of glass as a mirror superstrate. Poorly made glass may contain bubbles, which can cause dispersion of the light beam, diminishing mirror specularity. The glass manufacturing technique also influences mirror performance in that it controls surface smoothness and thickness uniformity. Float glasses have problems for solar applications; their facings tend to be wavy and lack parallelism. On the other hand, the float glass process allows the production of very thin glass desired for heliostats. Polished sheet glass has the best uniformity but is thicker than float glass. Thick glass tends to be less wavy than thin glass.

The age of the glass prior to its being silvered can affect the longevity of a mirror's high optical performance. Apparently, the surface of many glasses "foam up" during storage which leads to a destabilization of the subsequent silvering process.

The attributes sought in the design specifications of the "ideal" silver/glass mirror for solar thermal systems cannot be achieved simultaneously. As is the case in all areas of materials technology, the end product is a compromise between performance, durability, and cost; hopefully an optimal one.

## Objective and Scope

The principal objective of this document is to review the state-of-the-art of the design, manufacture, testing, and performance of silver/glass mirrors for solar thermal systems applications.

This document treats each of these topics. Chapter 1 briefly discusses the fundamentals of silver/glass mirrors. Chapter 2 presents the desired and actual mechanical and optical properties of silver as a solar reflector, of glasses as a superstrate for silver, and of silver/glass mirrors. Chapter 3 reviews the research literature on the physics and chemistry of silver/glass mirrors, and includes a discussion of the silver deposition processes and of the interfacial and surface reactions of the layered mirror materials. Chapter 4 describes present testing procedures and results for solar mirrors and indicates improvements needed in future mirror manufacturing. Chapter 5 discusses a summary of the float glass manufacturing process for fabricating commercial silver/glass mirrors, and a preview of a prospective integrated process for manufacturing silver/glass solar collectors in a single manufacturing plant.

# Chapter 1

# Overview of Silver/Glass Mirrors

The use of mirrors in the solar energy industry is extensive and varied. The most extensive application of silver/glass mirrors is for solar thermal electric or industrial process heat (IPH) systems. Most industrial and utility solar-energy-generated applications that produce process heat fluids or develop other forms of energy, such as electricity for mechanical power, require concentrating mirrors.

## Mirrors for Solar Thermal Collectors

Solar thermal mirrors are used in parabolic troughs, parabolic dishes, spherical bowls, and heliostats. The parabolic trough (Figure 1-1) concentrates the sun's rays along a line. The parabolic dish (Figure 1-2) concentrates the sun's rays toward a point. The *spherical* bowl (Figure 1-3) concentrates light along a rod. The compound parabolic concentrator (Figure 1-4) funnels light from a large aperture into a smaller receiver. The heliostat field employs a vast number of reflectors (flat or minimally parabolic) to focus on a central receiver, as shown in Figure 1-5.

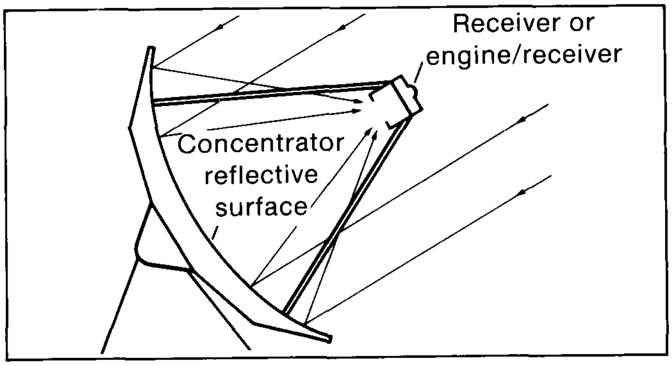


**Figure 1-2 Parabolic Dish**

Although different collectors each have particular design requirements, optimally, none should have surface irregularities that tend to scatter light and reduce system efficiency. The manufacture of curved reflectors for concentrating flux is critical since departure from design contour can diffuse a mirror's focus.

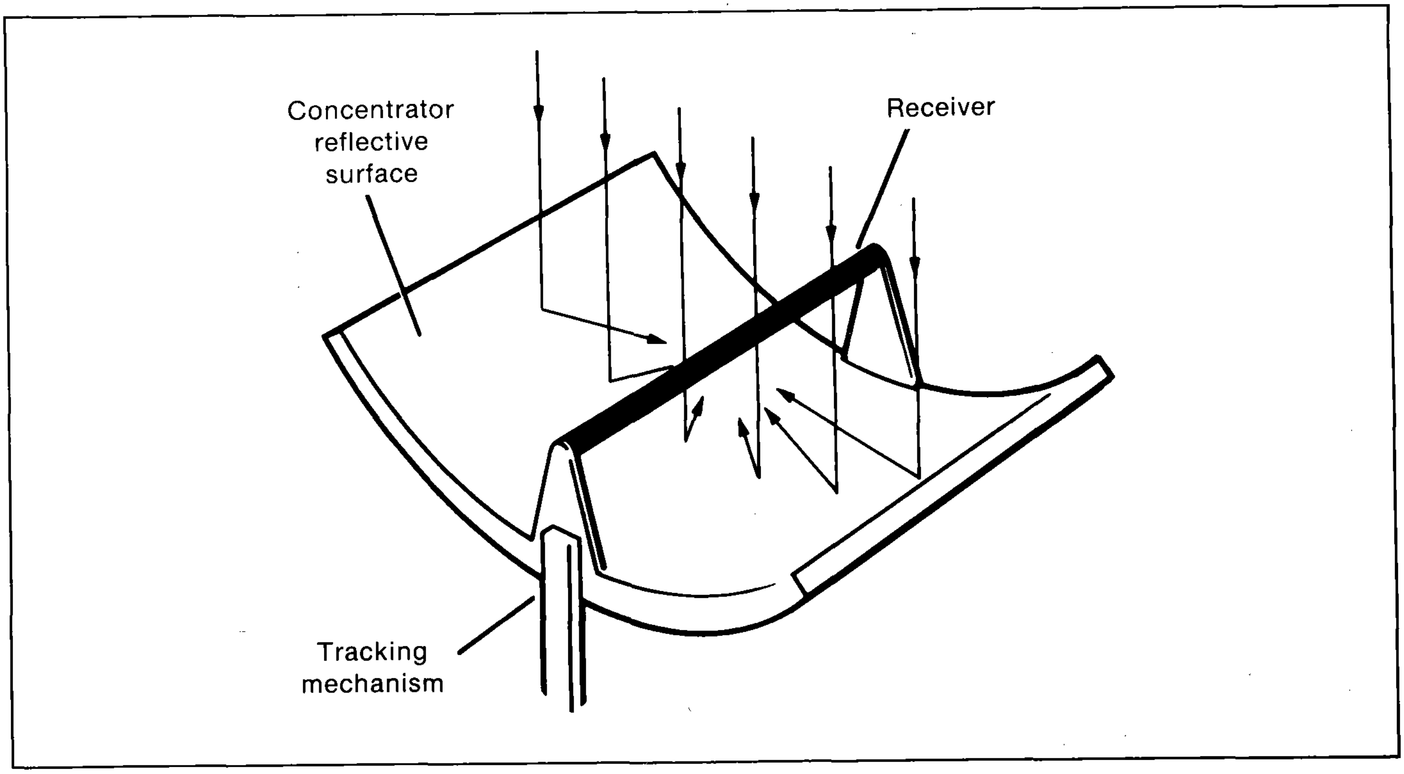


**Figure 1-1 Parabolic Trough**

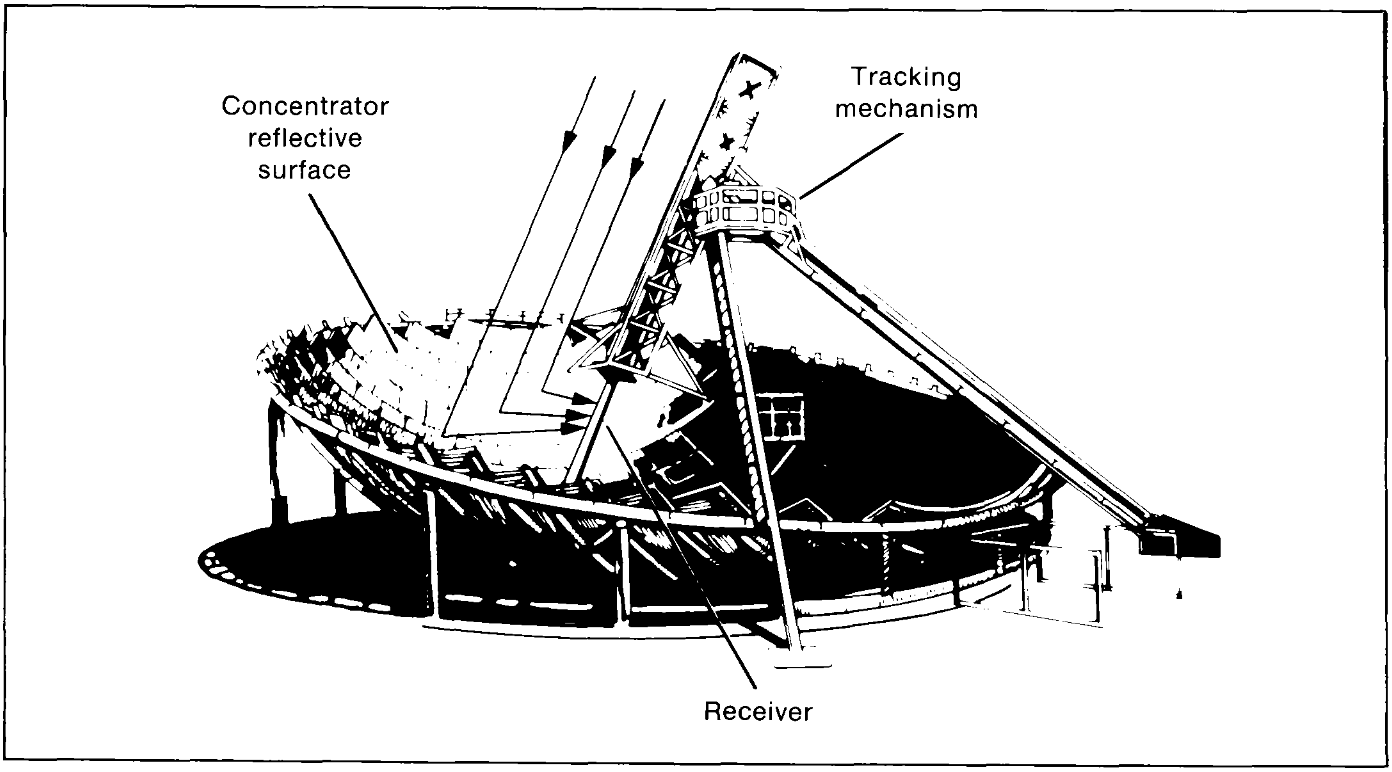


Figure 1-3 Spherical Bowl

Flux concentration ratios (collector area to area of focal point) are ultimately limited by optical factors. For line focusing the sun's rays, the maximum theoretical concentration ratio is 200; for point focusing it is 40,000. Detracting from any theoretical limit are the imperfections contained in real mirrors; i.e., waviness, scattering, and absorption sites, among others. These and other divergencies presently limit line concentration ratios to 60 and point-focus concentrations to about 600. Values of 100 and 5000, respectively, are thought to be achievable with improved technologies.

Eventually, practical achievable temperatures are expected to reach about 800°C and 2700°C using line- and point-focus collectors, respectively. However, present technology is limited to achieving temperatures of 300°C and about 1000°C. Heliostats are expected to provide flux concentration ratios of up to 1000 and, ultimately, temperatures of about 2500°C. A temperature as high as 1370°C is possible with present advanced technology.

## Preference for Silver Mirrors for Solar Thermal Applications

Ideally, the perfect mirror is one for which each ray of incoming solar radiation is reflected — without loss of intensity and without deviation from the ideal state; however, no mirror is perfect. In all mirrors some quantity of solar radiation from part of the solar spectrum will be absorbed by the materials that make up the reflector. Normal surface irregularities will cause the rays of a beam to deviate from an ideal path in all mirrors. Also, mirrors — even those of solid silver with ultraclean surfaces — have a dielectric layer that causes refraction.

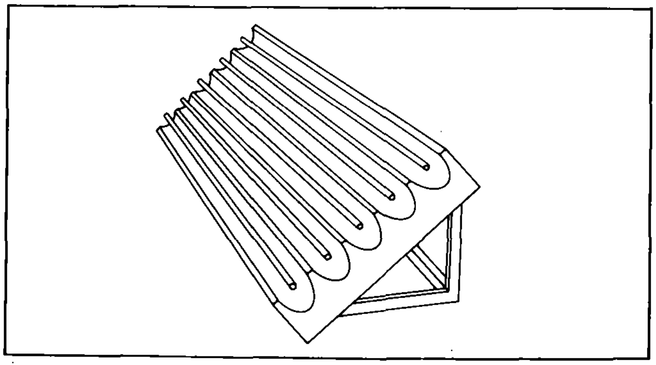


Figure 1-4 Compound Parabolic Concentrator

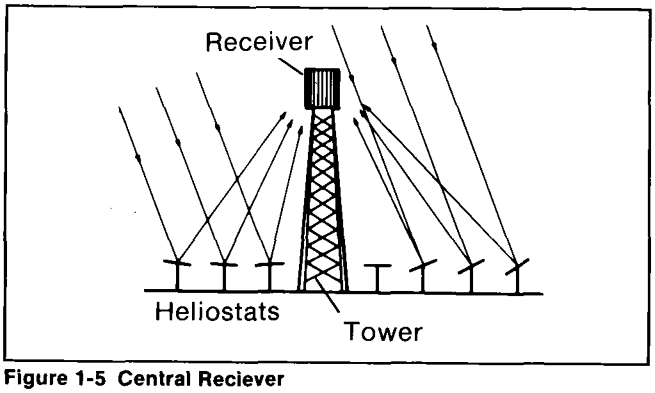


Figure 1-5 Central Reciever

Most mirrors presently use either silver (domestic and decorative applications) or aluminum films (automotive applications) for their reflective surfaces. Mirrors made of silver must be protected from chemical and physical deterioration of the silver; whereas, aluminum mirrors are more resistant to degradation. In many solar applications, however, silver is preferred because of its high reflectivity; 97%-98% compared to 88%-92% for aluminum. Nevertheless, both materials are being tested and used in various solar applications.

Since both silver and aluminum surfaces in solar applications must retain their highest reflectivity for many years, the reflective surfaces are protected with transparent covering materials referred to as superstrates. The mirrors are then called "second surface." Substrates are the base (bottom) materials that protect the back surfaces of the silver or aluminum. A mirror is "first surface" when the reflecting layer precedes the support.

Although, ideally, a transparent covering should behave optically as if it were not present, in practice it reduces optical performance to some degree. Since with silver mirrors the superstrate is chosen for protection of the silver from oxidation and other chemical effects, the superstrate should minimize the deterioration of silver's "original" high state of reflectivity. Also, since the superstrate supports the silver, that support should add to the physical integrity of the reflector. Collectors must survive some difficult environmental stresses, including thermal cycling, hail, ice and snow loads, wind, and dust abrasion.

Reflector integrity for solar applications is paramount. The material or materials attached to the silver should not detract from the silver's reflective quality, should not contribute to degradation of the silver, and should bond well. Moreover, all of these properties should remain substantially intact for about 30 years.

## Glass Mirrors

In the past, most mirrors were manufactured as a construction of silver bonded to glass — the glass being the protective barrier, light transmitter, and, in part, structural support. These so-called second-surface mirrors (because the silver is bonded to the side of the glass furthest from the light source) also include a copper film to protect the silver's back surface and layers of paint to protect the copper.

The advantages of using glass as a superstrate are its clarity (high solar transmittance), low cost, smooth surface, physical strength, abrasion resistance, impermeability, resistance to soiling, ease of cleaning, and inertness. Thus, glass approaches the ideal material for protecting silver. Compared with other mirrors, those made of glass and silver are preferred for their high reflectance (82%-97%), good specularity (generally $\leq 2$ mrad [0.10 deg.]), durability, and resistance to distortion from loads.

Mirrors of silvered glass are fairly tolerant of compositional variations and impurities. They can be expected to provide high reflectance without unreasonable dispersion, providing the silver remains intact and in contact with the glass. Retaining this integrity depends on chemical and physical processes that take place in and between the layers of materials composing the mirrors.

The basic ingredient of most glass is silica. However, many different glass formulas exist to provide such special features as durability, flexibility, special ranges of refraction and thermal expansion, dielectric property, and transmission. Thus, some glasses are better than others for particular uses. Common window glass, for example, contains "fillers" to decrease its cost. One filler is iron oxide, a substance that strongly absorbs the long visible wavelengths of light. This absorption reduces the reflectivity of common silver-backed glass mirrors to values of typically 82%.

There are other ways in which chemical composition can affect performance. For example, although glass is relatively impermeable, a certain flow or diffusion of chemical constituents within the glass can take place. Sometimes these constituents (such as sodium in common glass) can react with the deposited silver, degrading the silver's reflectivity. Composition can also affect the mechanical characteristics of the glass which can influence mirror integrity. A mirror with a glass thermal expansion much different than silver will tend to delaminate during thermal cycling. (Glass can be formulated to cover a range of expansion coefficients, including matchups with specific metals.) In addition, most glass compositions are brittle and vulnerable to fracture from stress and impact.

The manufacturing technique can play an important role in the performance of glass as a mirror superstrate. Poorly made glass can contain bubbles which can cause dispersion of the light beam, diminishing mirror specularity.

# Chapter 2

# Properties of Silver/Glass Mirrors

## The Ideal Solar Reflector

The principal attributes sought in the ideal solar reflector are

- High optical performance:
  - reflectance/transmittance,
  - specularity,
  - geometrical configuration,
- Low maintenance (dust free),
- Low initial cost, and
- Long life.

High optical performance means solar reflectance $R_s$ or solar transmittance $T_s$ values approaching unity, and a Gaussian beam spread due to nonspecularity and slope errors of less than 2 mrad in the most demanding heliostat applications. Figures 2-1 and 2-2 illustrate the basic optical properties of transmitters and reflectors and compare ideal materials with real materials (Lind 1981). These desired properties apply to glass as a superstrate with a silver reflective coating.

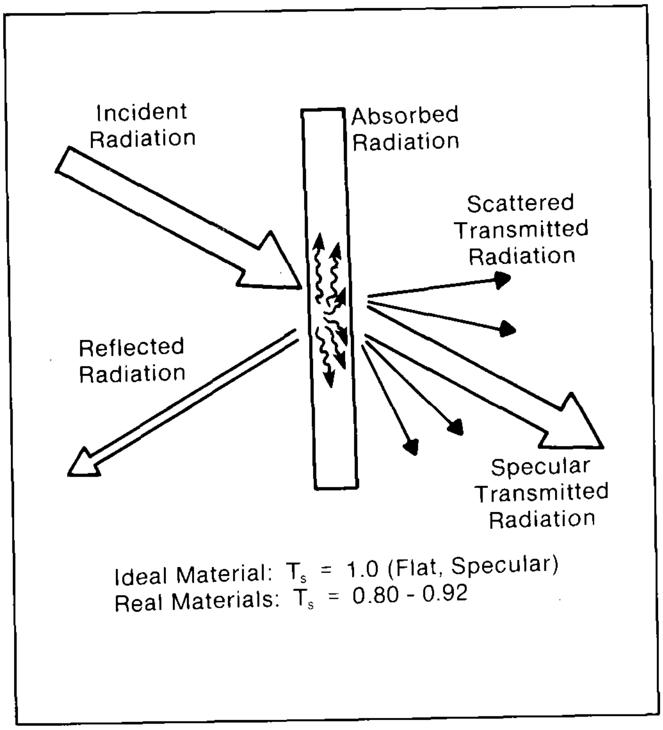


**Figure 2-1 Optical Properties of Transmitters** (Lind 1981)

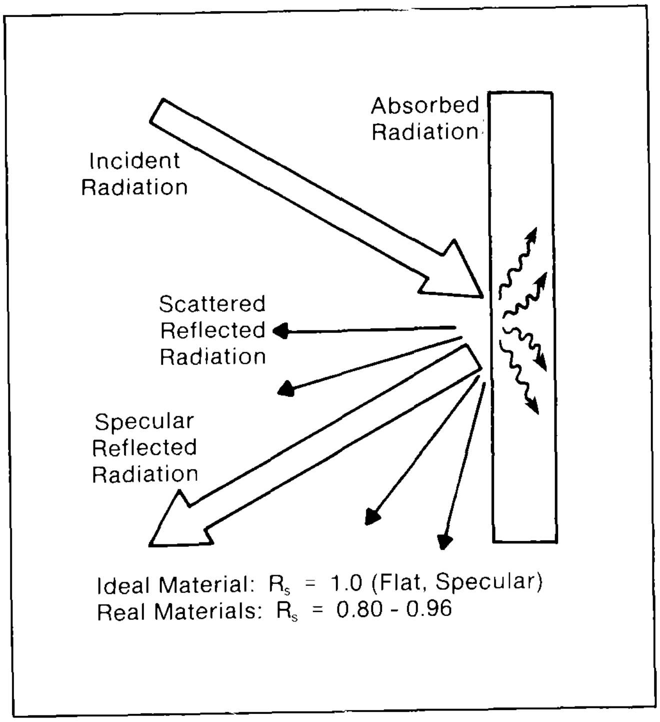


**Figure 2-2 Optical Properties of Reflectors** (Lind 1981)

## Approaches to the Ideal Reflector for Solar Applications

The preferred specifications for ideal solar reflectors can be defined easily but are difficult to achieve. The reflector should be perfectly specular and should have a solar reflectance of unity. A substrate should be capable of supporting the reflective surface and maintaining a given geometrical configuration under all external environmental stresses. The reflector should not degrade in performance over its estimated 20-40 year lifetime. Finally, the cost per unit area of the entire reflector unit should be economically acceptable.

The properties that are important for consideration in an ideal solar reflector are best subdivided into three classifications: (1) mechanical, (2) optical, and (3) chemical. The relevant specific properties within these three classifications are listed in Table 2-1. Definitions and examples of the mechanical and optical properties are provided in the following sections of this chapter; the chemical properties of silver/glass mirrors are discussed in Chapter 3.

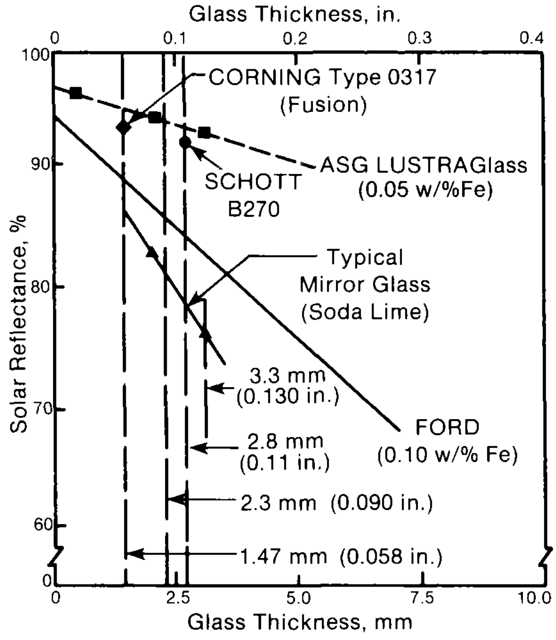
## Mechanical Properties of Second-Surface Glass Mirrors

Table 2-1 provides a listing of the mechanical properties pertinent to mirror materials and reflectors. Since most solar mirrors are often composite layers of several materials, the mechanical properties of both the individual materials and the composite product are important. Generally speaking, the mechanical properties of the individual materials must be compatible with each other for the composite product to achieve the desired set of mechanical properties.

These mechanical properties take on different degrees of importance, depending upon the type of solar mirror; e.g., second-surface glass mirrors or aluminum mirrors. The following discussion of properties is taken from Bouquet (1979, 1980).

**Glass thickness and composition.** Many types of glass, including soda-lime and low-iron glass, are currently being used for solar applications. Reflectance by second-surface glass mirrors varies remarkably with thickness and composition (Bouquet 1980) which produces a corresponding dependence of solar reflectance as shown in Figure 2-3. Typical thicknesses of solar glass are identified by vertical lines. Note that most of the slanted lines shown at zero thickness of glass point to the high (90%) range on the reflectance scale. The criterion for thickness selection is that the glass be as thin as possible to reduce double absorption during the transmission of the incident solar radiation over as wide a spectrum as possible and still withstand the strength specifications or other requirements for a particular application.

The chemical composition of several representative glasses is given in Table 2-2, and a summary of physical properties is given in Table 2-3. It can be seen that the physical properties are highly composition-dependent. These properties will be presented and discussed fully in the next section.



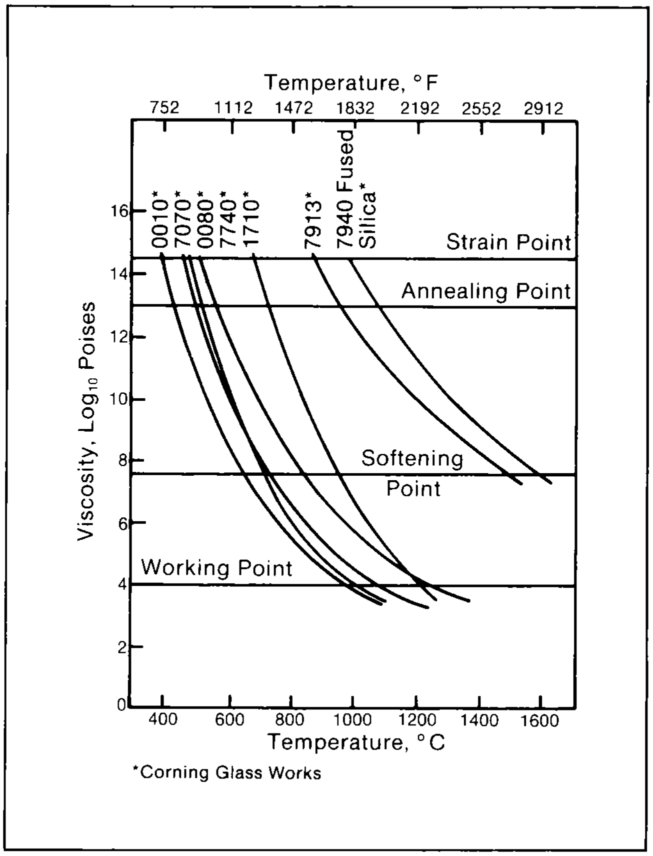
Adapted From Taketani (1977)

**Figure 2-3 Solar Reflectance versus Glass Thickness for Typical Types of Second-Surface Glass Mirrors** (Bouquet 1980)

**Properties affecting glass performance.** In early studies the fundamental physical properties of most commercially available glasses were evaluated for applications to solar mirrors. These properties are summarized in Figures 2-4 through 2-8. Two specific qualities required of flat, one-dimensional, and two-dimensional glass shapes in order to achieve high performance are low coefficient of thermal expansion, and high thermal conductivity.

**Table 2-1 Property Classifications for Solar Receivers**

| Optical | Mechanical Properties | | Chemical and Environmental |
|---|---|---|---|
| Specularity | Flatness | Delamination | Oxidation |
| Surface figure error | Density | Static fatigue | Corrosion |
| Hemispherical reflectance | Coefficient of expansion | Stress corrosion | Solarization |
| Solar-weighted hemispherical reflectance ($\rho_2$) | Thermal conductivity | Crack growth | Weathering |
| | Abrasion resistance | Spring-back | Agglomeration |
| Superstrate transmittance | Hardness | Durability | Outgassing |
| Index of refraction | Softening point | Thermal cycling | |
| | Annealing point | Crazing | |
| | Strain (yield) point | Young's modulus | |
| | Poisson's ratio | Shear strength | |
| | | Bending strength | |



*Corning Glass Works

**Figure 2-4 Viscosity - Temperature Curves** (CIT 1978)

Two newer glasses, in particular, have physical properties that are well-suited to solar mirror applications. These two glasses are Corning Glass Works 0317 aluminosilicate glass and 7809 borosilicate glass. Their properties are tabulated in Table 2-4. Both glasses have high solar reflectance with deposited silver; and both have low coefficients of expansion and, hence, low stress corrosion.

**Measurements of glass strength.** Measurements of the strength of flat glass have been treated by Lewis (1976). Several measurement methods have been used, including the following two approaches: (1) Hertz fractures produced by pressing a steel ball against the glass, and (2) the bending strength of circular glass plates.

The latter test is found to be more reliable, considering the fact that the side of float glass next to the tin bath is observed to be the weakest. Since the side

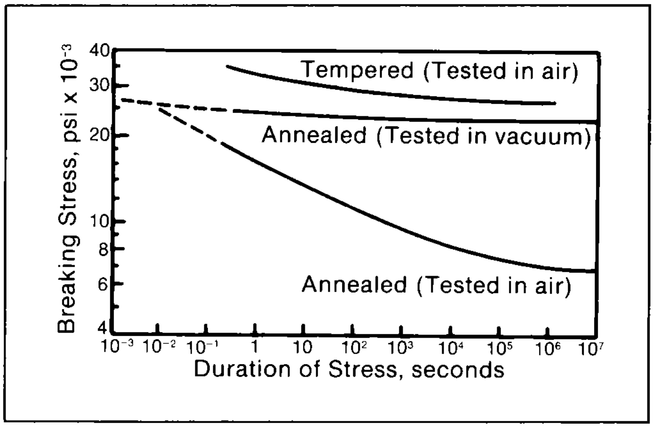


**Figure 2-5 Stress Time Characteristics of Glass** (Bouquet 1979)

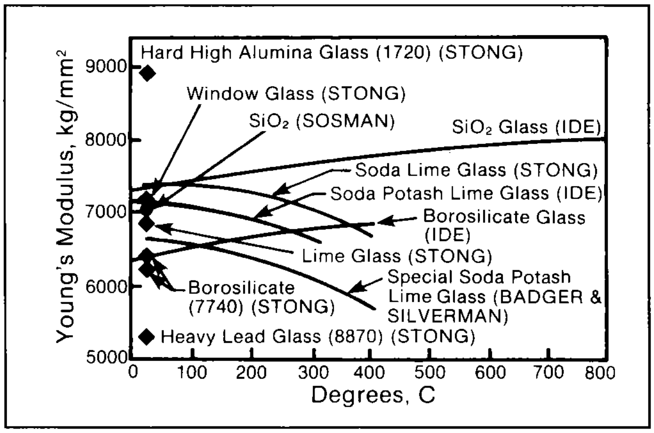


**Figure 2-6 Young's Modulus of Various Glasses** (Bouquet 1979)

**Table 2-2 Analysis and Properties of Representative Glasses** (Bouquet 1979)

| Type of Glass | Analysis, Percent by Weight | | | | | Softening Temp. °C |
|---|---|---|---|---|---|---|
| | $SiO_2$ | Modifiers | $Al_2O_3$ | $B_2O_3$ | PbO | |
| Fused silica | 99.9 | - | - | - | - | 1667 |
| 96% silica (Vycor) | 96.0 | - | - | 4.0 | - | 1500 |
| Borosilicate (Pyrex) | 80.5 | 4.2 | 2.2 | 12.9 | - | 820 |
| Aluminosilicate | 57.7 | 9.5 | 25.3 | 7.4 | - | 915 |
| Soda-lime silica | 73.6 | 25.4 | 1.0 | - | - | 696 |
| Lead-alkali | 54.0 | 11.0 | - | - | 35 | 630 |

opposite the tin bath is silvered by the mirror industry, it follows that the glass side of the mirror is weakest.

One of the greatest limitations in using glass for parabolic dishes is its static fatigue, which can be described by the following equation:

$$t_f = K\sigma_f^{-n}$$

where

$K, n$ = constants
$t_f$ = time to failure
$\sigma_f$ = the stress level at which failure occurs.

In other studies, Tummala (1976) has shown the stress corrosion coefficient *n* to be a function of the bulk glass composition. It changes little with the surface of the glass. Experiments show that the stress corrosion resistance varies inversely with the thermal expansion coefficient over the 25°C to 300°C range.

Slow crack growth in glass that can lead to failure is frequently initiated by edge cracks. Recent information indicates that a "factory cut" edge has better resistance to edge cracking than edge processing (beveling, polishing, or other treatment).

During glass shaping, glass has a tendency to spring back to its original shape upon cooling. An initial effort is needed to ascertain the amount of spring-back allowable when selecting a new type of glass. A tentative criterion is less than a 1% dimensional spring-back along the smallest radii of curvature.

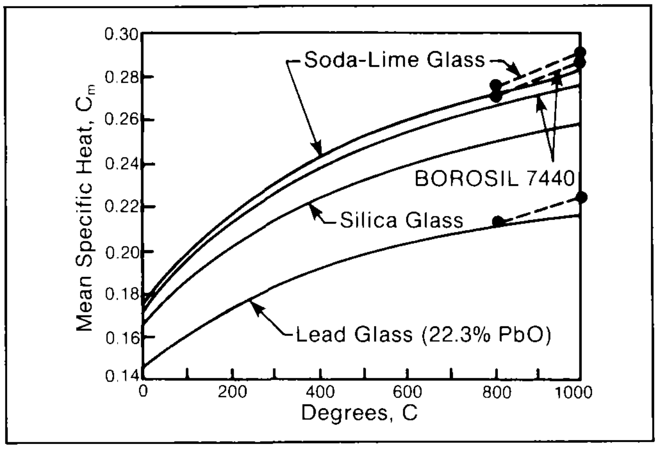


**Figure 2-7 Mean Specific Heat of Glasses** (Bouquet 1979)

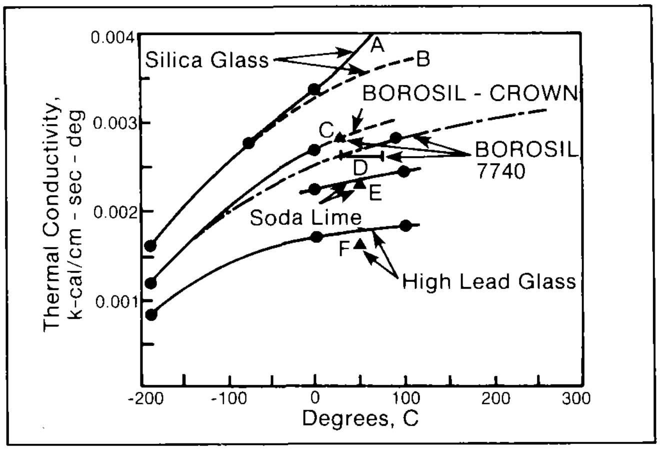


**Figure 2-8 Thermal Conductivity of Glasses** (Bouquet 1979)

**Table 2-3 Physical Properties of Glass**

| Type of Glass | Specific Gravity g/cm³ (lb/ft³) | Young's Modulus 10³kg/mm² (10⁶ psi) | Thermal Expansion* cm/cm° C (in./in.° F) | Refractive Index | Poisson's Ratio |
|---|---|---|---|---|---|
| Soda-lime | 2.47<br>(154) | 7.1<br>(10.2) | $93.6 \times 10^{-7}$<br>$(52 \times 10^{-7})$ | 1.512 | 0.22-0.24 |
| Aluminosilicate | 2.52-2.64<br>(154.6-157.2) | 8.8-8.9<br>(12.5-12.7) | $42.1\text{-}46.1 \times 10^{-7}$<br>$(23.4\text{-}25.6 \times 10^{-7})$ | 1.53-1.547 | 0.24-0.25 |
| Borosilicate | 2.13-2.48<br>(132.8-154.6) | 5.0-6.9<br>(7.1-9.8) | $32\text{-}51.5 \times 10^{-7}$<br>$(17.8\text{-}28.6 \times 10^{-7})$ | 1.473 | 0.2-0.23 |
| 96% fused silica | 2.18<br>(135.9) | 6.9<br>(9.8) | $7.6\text{-}8 \times 10^{-7}$<br>$(4.2\text{-}4.4 \times 10^{-7})$ | 1.458 | 0.19 |
| Fused silica | 2.2<br>(137.2) | 7.4<br>(10.5) | $5.6 \times 10^{-7}$<br>$(3.1 \times 10^{-7})$ | 1.459 | 0.16 |

*Over the range 0° C to 300° C or 32° F to 572° F
Source: Corning Glass Works, Corning, New York

**Table 2-4 Typical Solar Mirrors: Preliminary Properties of Corning 0317 and 7809 Glass** [Thickness - 1.5 mm (0.060 in.)]*

| Property | Type of Corning Glass | |
|---|---|---|
| | 0317 (Aluminosilicate) | 7809 (Borosilicate) |
| Density, g/cm$^3$ | 2.45 | 2.44 |
| Index of refraction | 1.512 | 1.509 |
| Solar transmittance, % | 90.9 (est.)** | 91.7 ± 2 |
| Solar reflectance, % | | |
| (a) Vacuum-deposited silver | 95 ± 1 | 95 (est.)** |
| (b) Chemically deposited silver | 94 ± 1 | 94 (est.)** |
| Weather (glass only), 20 years | Excellent | Excellent |
| Softening point, °C | 870 | 750 |
| Annealing point, °C | NA | 569 |
| Strain point, °C | NA | 529 |
| Strengthening capacity | Yes | No |
| Expansion coefficient | | |
| (a) 0°C-300°C, $10^{-7}$/°C | 88 | 77 |
| (b) -30°C to +50°C, $10^{-7}$/°C | 81 | 72 |
| Poisson's Ratio | 0.22 | 0.20 |
| Young's Modulus, $10^2$kg/mm$^2$ | 68.94 | 76.52 |
| ($10^6$ psi) | (10) | (11.1) |

*Corning Glass Works, Corning, New York
**Bouquet 1980

## Optical Properties of Glass Mirrors

**Definitions.** The principal optical properties applicable to solar reflectors are specular reflectance (specularity), surface figure error, directional hemispherical reflectance, solar-weighted hemispherical reflectance, and superstrate transmittance.

Two measures of surface irregularities that cause loss of redirected sunlight from a solar mirror are surface specularity and surface figure error. Specularity measures the scattering from surface variations with a characteristic spacing of less than approximately 1 mm, whereas scattering from surface contour (slope) variations on a scale greater than approximately 10 mm is referred to as the surface figure error.

Surface specularity values (ASTM 1983)* are generally associated with the fine structure of the reflecting material, e.g., deposited silver; whereas surface figure error (slope) variations typically result from local deviations in the surface normal about the ideal surface shape. Thus, the surface figure error determines the direction of the reflected radiation, and the surface specularity determines the angular spread and intensity of this radiation; see Figure 2-9 for a representation of these two surface irregularity effects.

Directional hemispherical reflectance measures all of the reflected radiation from a surface independently of its angular distribution. This measurement is typically recorded as a function of wavelength from 350 nm to 500 nm, using an integrating sphere reflectometer. The solar-averaged hemispherical reflectance value for a mirror is determined by averaging the spectral hemispherical reflectance data over the solar spectrum. This value represents the maximum available reflected solar energy for a particular mirror; however, depending on the angular distribution of this radiation, only a portion of this reflected radiation may be utilized in a solar collector.

Laboratory measurements by Pettit and Roth (1980) of the specular reflectance at 18 mrad [R(18 mrad)] and the directional hemispherical reflectance

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*There is neither an accepted (ASTM, etc.) measure of specularity nor any proposed measure with a scale from 0 to 1. When one is established, it will probably be in units of milliradians.

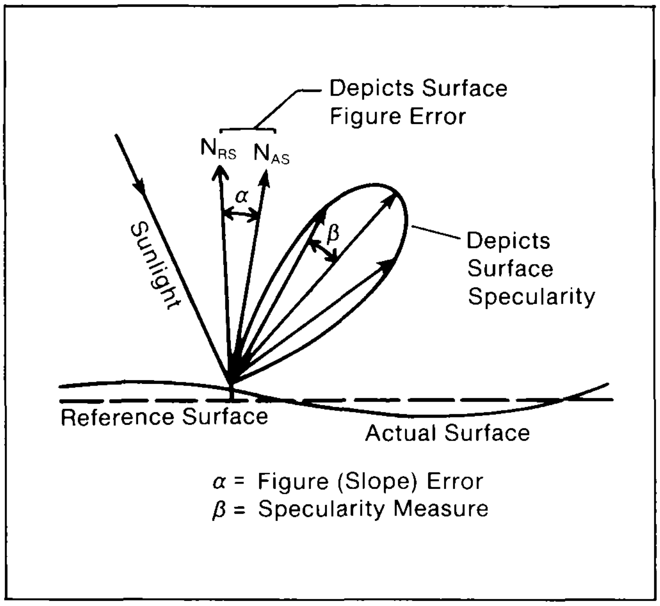


**Figure 2-9 Schematic Representation of a Mirror Surface Showing the Difference Between Figure (Slope) Errors and the Mirror Specularity** (Pettit and Roth 1980)

[Rλ(2π)], both measured at 500 nm, and of the solar-averaged hemispherical reflectance [$R_s(2\pi)$] are illustrated in Figure 2-10 for several solar mirror materials. Silvered float glass (2.7 mm thick) exhibits the highest hemispherical reflectance [Rλ(2π) = 0.92] at 500 nm of the five mirror materials, but has the lowest solar-averaged hemispherical reflectance [$R_s(2\pi)$ = 0.83].

The difference beween the specular and hemispherical reflectance values for these materials is due to large angle scattering at the mirror surface. The reflectance profiles illustrate the importance of measuring both the specular reflectance and hemispherical reflectance properties at the same wavelengths for all mirror materials.

Superstrate transmittance is the ratio of the solar energy transmitted through a plane surface of superstrate in a defined wavelength band to the solar energy incident on the superstrate in that band.

**Reflectance properties of various reflector materials.** Of all possible metals that could be used for solar reflectors, only silver and aluminum have solar-weighted spectral reflectance values above 0.90. All others, including gold, nickel, chromium, stainless steel, rhodium, and copper have reflectance values below 0.82. The spectral reflectance properties of silver and aluminum, together with gold, measured for the metal/vacuum interface are shown in Figure 2-11. The solar-averaged reflectance values are calculated to be: silver, 0.98; aluminum, 0.92; and gold, 0.85. These values represent the practical upper limit of solar reflectance for these materials. The reflectance of aluminum is reduced over the solar region primarily because of an interband absorption centered at approximately 800 nm. It has been suggested that this absorption band may be eliminated by using amorphous aluminum; this would increase the solar reflectance several percent (Trotter 1978). However, efforts to reduce this absorption have not been successful and do not appear to be feasible now.

In most solar applications, the metal-reflecting layer is protected by a transparent coating such as an oxide (e.g., $Al_2O_3$), glass, or plastic film. The index of

| Material | $R_\lambda(2\pi)$ | R(18 mrad) | $R_s(2\pi)$ |
|---|---|---|---|
| 1 Silvered Glass | 0.92 | 0.92 | 0.83 |
| 2 ALZAK - Parallel | 0.89 | 0.78 | 0.85 |
| 3 ALZAK - Perpendicular | 0.89 | 0.72 | 0.85 |
| 4 SHELDAHL Aluminized Teflon | 0.87 | 0.82 | 0.87 |
| 5 3M SCOTCHCAL 5400 | 0.86 | 0.85 | 0.85 |

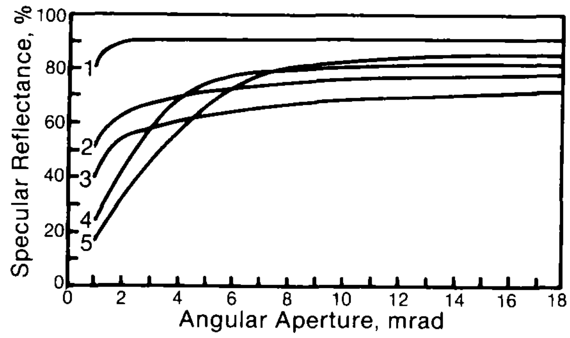
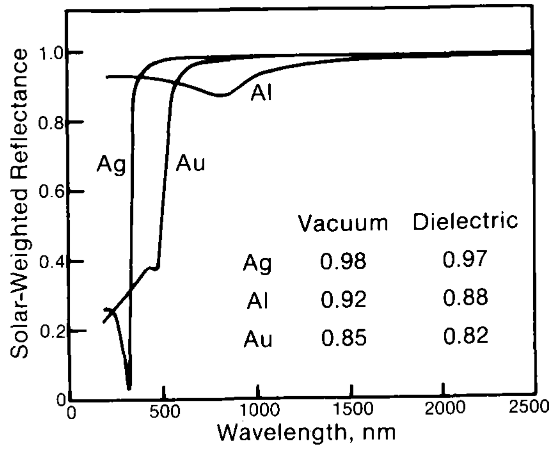


**Figure 2-10 Specular Reflectance Properties for Several Solar Mirror Materials.** The table lists the hemispherical reflectance [Rλ (2π)] and the specular reflectance at 18 mrad [R(18 mrad)] measured at 500 nm. Also listed is the solar-weighted hemispherical reflectance [$R_s(2\pi)$] (Pettit and Roth 1980)



|  | Vacuum | Dielectric |
|---|---|---|
| Ag | 0.98 | 0.97 |
| Al | 0.92 | 0.88 |
| Au | 0.85 | 0.82 |

**Figure 2-11 Reflectance Properties of Silver (Ag), Aluminum (Al), and Gold (Au) as a Function of Wavelength for the Metal/Vacuum Interface.** The table lists the solar-weighted reflectance for a metal/vacuum interface and a metal/dielectric interface with an assumed index of refraction of 1.5. (Pettit and Roth 1980)

refraction of most coating materials is typically 1.5 through the solar spectral region. With a nonabsorbing dielectric layer applied over the metals, the solar-averaged reflectance is reduced by 0.01 reflectance units for silver, 0.03 for gold, and 0.04 for aluminum. Thus, in most applications, silver mirrors will have, at most, a solar reflectance of 0.97, while the solar reflectance of aluminum will be closer to 0.88.

In order to understand the specularity and the reflected beam intensity of various mirror materials, it is helpful to consider the construction of a typical reflector. The typical construction of both a front-surface (substrate) and second-surface (superstrate) reflector are shown in Figure 2-12. In a front-surface mirror, the reflecting layer is applied to the substrate and then overcoated with a protective film.

In a second-surface mirror, the reflecting layer is applied to a transparent superstrate (e.g., glass or plastic film) which is then bonded to a support structure after applying a protective layer. Also shown in Figure 2-12 is a back-protection layer. The entire composite, shown in Figure 2-12, is termed a "reflector," while the outer layers, which include the silver or aluminum film, are termed the "mirror."

Both the specularity and the reflected beam intensity can be affected by all of the components shown in Figure 2-12. Depending upon its optical properties, the outer protective layer can modify the reflected beam's intensity at the metal/dielectric interface as shown previously. In addition, the outer layer can absorb radiation and thereby reduce the solar reflectance. The specularity can be affected by scattering within the layer or at the inner or outer surfaces. If the outer surface is not parallel to the reflecting surface, then multiple reflected images are formed.

The reflecting surface itself can scatter radiation if it has a rough surface (i.e., figure error). In addition, the reflected beam intensity may depend upon the purity of the metal layer as well as the deposition process (vacuum deposition, chemical reaction, ion plating). Both the surface texture of the backing layer, which is typically a thin metal sheet, and the lamination or bonding technique that is used to attach the reflecting surface to the backing layer can be important in affecting the specularity of the reflector. The same is true for the bonding of the backing layer to the support structure.

**Optical properties of second-surface silver mirrors.** *Glass as the superstrate.* (Taketani 1980) has performed solar reflectance measurements on several second-surface silvered mirrors produced by different commercial silvering processes on the same glass superstrate. The results, shown in Table 2-5, together with earlier measurements on bare silver (Taketani 1978), indicate that the reflectance of coatings deposited by different commercial chemical- or vapor-deposition methods are comparable. The measurements, except for the bare silver measurement, were made on a special low-iron-content float glass (3.2 mm thick) manufactured by PPG Industries.

Taketani (1980) also reported recent reflectance and transmittance measurements that were made on various commercial grades of glass of different thicknesses and iron content with and without silver backing. The results are shown in Table 2-6. The value of low-iron-content glass for second-surface solar mirrors is readily apparent.

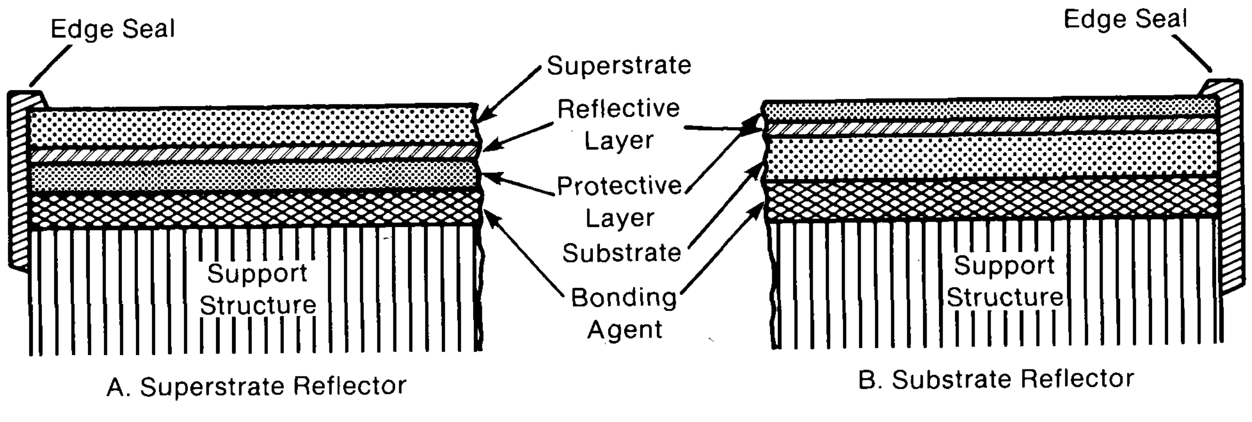


**Figure 2-12 Examples of Typical Reflective Surfaces** (Bouquet 1980)

The solar transmittance of glass is strongly influenced by the iron content and the thickness, as illustrated in Figure 2-13 (Bouquet 1979). The decrease in transmittance with iron content is due to long wavelength absorption by the ferrous state of iron, causing a greenish color in the glass. Ferrous iron exhibits a strong absorption band at about 1000 nm (see Figure 2-14) (Coyle 1981). Removal of the iron or conversion of the ferrous iron to ferric iron in the fusion glassmaking process has been shown to improve the solar transmittance significantly. Figure 2-15, for example, reveals a 4.7% increase in spectral transmittance for the Ford Motor Company's low-iron, 3-mm float glass compared to its own normal production glass (Goodyear 1980). The calculated reflectance of a silvered mirror using this glass is 89.6%.

The effect of iron content became of considerable importance in the manufacture of the heliostats for the Solar One 10-Megawatt Power Project at Barstow, California. The Glass Division of the Ford Motor Company manufactured a low-iron-content float glass for those heliostats.

In addition to the glass composition, Ford Motor Company also had to control the flatness of the glass so that proper directional reflectance could be achieved with the heliostat mirrors. Flatness measurements were made by Battelle Pacific Northwest Laboratories (Goodyear 1980). Figure 2-16 shows a typical laser scan, Curve A, to determine the surface figure error. The short period is called the "wave" and the long period is called the "bow." Curve B shows the wave only and was the basis of acceptance of the glass for the heliostat.

**Optical properties of first-surface silver mirrors.** First-surface, or front-surface, silver mirrors face the inherent problem that exposed silver is reactive with environmental gases (see Chapter 3). First-surface aluminum mirrors, on the other hand, have a natural protective coating of $Al_2O_3$. However, various studies are underway to develop protective overcoatings for silver.

Studies of the reflectance of front-surface silvered float glass, protectively coated with silicone resins, have been carried out by Dennis and McGee (1980) at the Dow Corning Corporation. Samples were prepared with and without silane coupling agents that tend to promote the adhesion of the resin to the metal surface. Table 2-7 provides the measured values of specularity and solar hemispherical reflectances; the reflectance values ranged from 94.8% to 97.8%. However, in environmental exposure tests, the silvered float glass samples usually failed because of loss of adhesion between the glass substrate and the vapor-deposited silver.

**Table 2-5 Reflectance Measurements of Silvered Mirrors** (Taketani 1980)

| Mirror Manufacturer | Silver Deposition | Surface Being Measured | Reflectance (%) |
|---|---|---|---|
| Theoretical Value (Kingslake 1965) | vapor | front | 99 |
| Mirrorlab (Taketani 1978) Texas | chemical | front | 98 |
| Donelley, Michigan | vapor | second | 90 |
| Buchmin, Ind., California | chemical | second | 92 |
| | chemical | second | 92 |
| Binswanger Mirror Co., Arizona | chemical | second | 92 |
| | chemical | second | 92 |
| Carolina Mirror Corp., N. Carolina | chemical | second | 91 |
| | chemical | second | 91 |
| Gardner Mirror Corp., N. Carolina | chemical | second | 90 |
| | chemical | second | 91 |
| | chemical | second | 91 |
| | chemical* | second | 91 |
| | chemical* | second | 91 |
| | chemical* | second | 91 |
| Mechanical Mirror Works, New York | chemical | second | 90 |
| | chemical | second | 90 |

*Enhanced Solaflect formula

## Table 2-6 Glass Reflectance and Transmission Measurements
(Taketani 1980)

| Glass Manufacturer | Glass Thickness mm | (in.) | Reflectance (%) | Transmission (%) |
|---|---|---|---|---|
| PPG Industries, Inc.<br>Clear float | 2.38 | (3/32) | 89 | 87 |
| | 3.18 | (1/8) | 86 | 86 |
| | 6.35 | (1/4) | 79 | 82 |
| Ford Motor Co. | 2.38 | (3/32) | 91 | 88 |
| | 3.18 | (1/8) | 89 | 87 |
| | 6.35 | (1/4) | 81 | 83 |
| PPG Industries, Inc.<br>Low-iron float | 3.18 | (1/8) | 92 | 88 |
| LOF, Inc.<br>Solar 90 sheet | 3.18 | (1/8) | 94 | 90 |

## Optical and Physical Properties of Code 7809 Solar Fusion Glass

Code 7809 solar fusion glass is a product of a collaborative development program between Corning Glass Works (CGW) and the Solar Energy Research Institute (SERI) (Coyle and Livingston 1981; Coyle et al. 1980). SERI sought this new glass to satisfy unique solar requirements such as very low optical absorption, outstanding stability in the weight, and elasticity when forming parabolic mirrors.

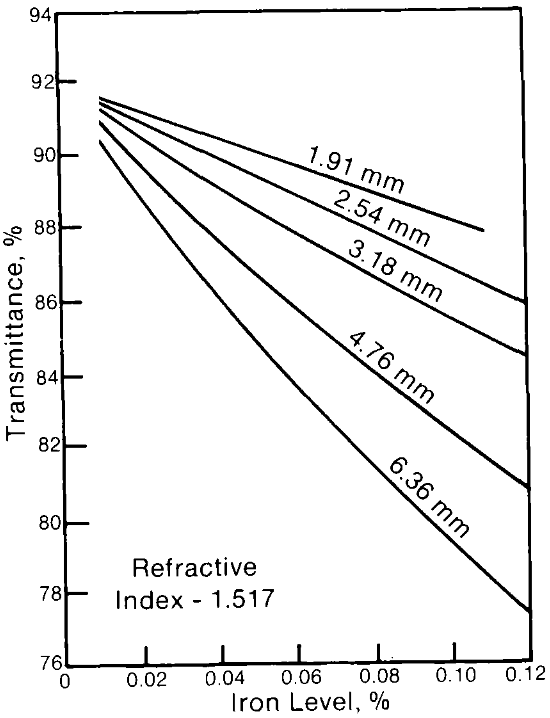


**Figure 2-13 Solar Transmittance as a Function of Iron Content and Glass Thickness** (Bouquet 1979)

**Glass forming and composition.** The fusion process, patented by CGW, is one of several methods used to produce sheet glass. The advantages of this process are (1) compositional flexibility, (2) capability to produce thin cross sections; i.e., 0.5 mm, (3) ease of changing the thickness, (4) excellent surface quality, and (5) operation in oxidizing conditions. Using current equipment, widths to 1.4 m and lengths to slightly over 3 m can be achieved (modifications to present equipment could allow widths up to 1.8 m).

The fusion process is based on an "overflow pipe." Molten glass flows from the fore-hearth into one end of a horizontally oriented hollow trough. An end view of this trough would show a V-shaped configuration. The glass fills the internal cavity and over-

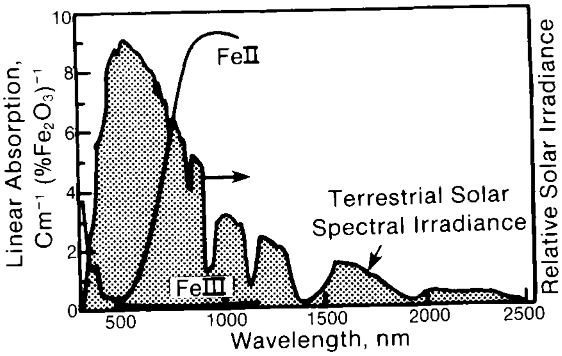


**Figure 2-14 Absorption Coefficients of Fe$^{+2}$ and Fe$^{+3}$ in Soda-Lime Glass** (The shaded curve is the relative spectral solar irradiance) (Coyle 1981)

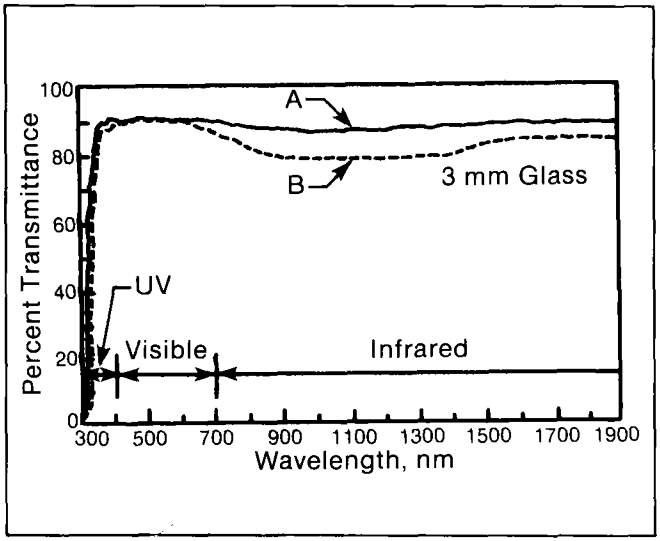


**Figure 2-15 Transmittance for Low-Iron, 3-mm Glass (A) and Normal 3-mm Glass (B)** (Goodyear 1980)

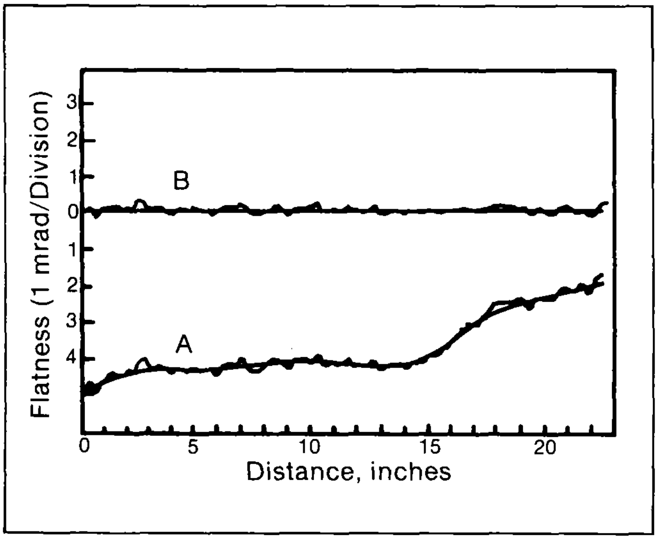


**Figure 2-16 Flatness of 3-mm Glass as Measured by Laser Scan at Battelle Pacific Northwest Laboratories.** (Glass for Curve A is not corrected for bow; that for Curve B is corrected for bow.) (Goodyear 1980)

flows both sides of the trough. Edge-located pulling rolls are used with the surface tension of the molten glass to draw the glass uniformly down the exterior of the "pipe" to the apex of the "V." There the glass "fuses" into a monolithic sheet. Heating and cooling equipment permits the judicious control of temperatures needed to carry the glass through the annealing and strain points. At the appropriate point in the cooling zone, the sheet is cut into required lengths and then is automatically transported to the edge-stripping and final-sizing station.

Corning Glass Works developed the new glass composition (CGW-7809) specifically for solar energy applications (see Table 2-8). Some of the properties of the glass are shown in Table 2-9. The glass was designed to be compatible with the fusion sheet-forming process and to be melted at high rates for low production costs. Compositions originally considered ranged from "improved" soda-lime (float) glass to a hard borosilicate pharmaceutical composition (CGW-7809).

The low solar absorption by the new glass was obtained by reducing the total iron content, and adjusting the batch and melting conditions to oxidize all of the ferrous iron (Fe$^{+2}$) to ferric iron (Fe$^{+3}$).

The levels of alumina and soda were adjusted in the composition to achieve a thermal expansion of $77 \times 10^{-7}$/°C to minimize thermal expansion differences with potential support materials. The resulting CGW-7809 composition represents a suitable compromise among solar transmittance, thermal expansion, lifetime, and cost.

**Solar transmittance and reflectance.** The spectral hemispherical transmittance of the CGW-7809 glass was evaluated by using an integrating sphere spectrophotometer (Coyle and Livingston 1981). The high spectral transmittance of the 7809 glass differs markedly from the transmittance of the more common soda-lime float glass; see Table 2-10. The broad absorption band around 1100 nm in the soda-lime glass due to Fe$^{+2}$ is conspicuously absent in the 7809 glass, as shown in Figure 2-17. The transmittance of

**Table 2-7 Reflectances of Silvered Float Glass** (Dennis and McGee 1980)

| Resin | Solar Directional Hemispherical Reflectances Rλ (2π) | Specularity in mrad at 568 nm for Cone Angles | |
|---|---|---|---|
| | | 10° | 45° |
| A | 0.955 | 3.17 | 3.84 |
| B | 0.957 | 0.89 | 1.60 |
| C | 0.959 | 0.73 | 0.77 |
| E | 0.978 | 0.58 | 0.60 |
| H | 0.949 | 3.20 | 3.60 |
| L | 0.948 | 8.20 | 8.65 |

**Table 2-8 Composition of CGW-7809 Glass**
(Coyle et al. 1980)

| Oxide | % |
|---|---|
| $SiO_2$ | 66.0 |
| $Al_2O_3$ | 9.0 |
| $B_2O_3$ | 8.0 |
| $Na_2O$ | 9.0 |
| $CaO$ | 2.0 |
| $K_2O$ | 5.0 |
| $TiO_2$ | 0.5 |
| $As_2O_2$ | 0.2 |
| $Fe_2O_3$ | 0.0 |

**Table 2-9 Properties of CGW-7809 Glass**
(Coyle et al. 1980)

| | |
|---|---|
| Softening point, °C | 750 |
| Annealing point, °C | 569 |
| Strain point, °C | 529 |
| Expansion, $(°C)^{-1}$, 0-300°C | $77 \times 10^{-7}$ |
| Poisson's ratio | 0.20 |
| Young's modulus, psi | $7.6 \times 10^3$ kg/mm$^2$ |
| Density, g/cm$^3$ | 2.44 |
| Index of refraction | 1.509 |

the 7809 glass is close to the theoretical maximum; it shows little absorption, and only reflective losses.

Figure 2-18 illustrates the solar-spectrum-weighted transmittance of unsilvered glass and the hemispherical reflectance of silvered glass for conventional float glass, low-iron float glass, and 7809 glass for a range of glass thicknesses. It gives theoretical values for reflectance. Values for mirrors silvered by Falconer Glass Company on 7809 glass were about 2% lower. The 7809 fusion glass has higher transmittance and provides higher reflectance than the other two glass types over the full range of thicknesses considered.

An evaluation of 7809 glass for solarization (changes of transmittance due to solar irradiation, particularly in the ultraviolet) showed no detectable change in optical density (less than 0.001) after 500 hours at 10 suns in a solar simulator (Coyle et al. 1980). This result allayed concerns that solarization might reduce the solar transmittance of the glass in its service environment. Comparable experiments on several float glasses (Vitko 1980) revealed a decrease in optical density (i.e., an increase in transmittance) varying from 0.002 to 0.01.

**Optical accuracy.** The surface flatness of a glass sheet determines the optical accuracy of mirrors in redirecting solar energy, as well as the aesthetic appeal of glazings used in passive applications. Figure 2-19 shows the results of a laser-ray tracing of the 7809 glass (Coyle et al. 1980). It shows that glass from the pilot test reflected light less accurately than float glass, probably, CGW believes, as a result of poor surface tension leveling of the glass on the Harrodsburg, Kentucky, "fusion" pipes. However, the 0317 glass made at the Blacksburg, Virginia, full-scale "fusion" facility showed optical accuracy approaching that of the best float glass — more than adequate for solar applications. Thus, CGW is optimistic that the optical accuracy for 7809 obtained at Blacksburg would be adequate since it is expected to be similar to that of the 0317 glass.

**Chemical durability.** Accelerated weathering studies were made on 7809 glass specimens exposed at 70°C and 100% relative humidity (Coyle et al. 1980). CGW observed an increase of about 0.002 in. in the optical density after four weeks of exposure. However, the change was an order of magnitude less than that noticed in float glasses under similar conditions, indicating that the glass was durable in the environment expected for solar applications.

**Table 2-10 Solar Transmittance of Various High-Transmittance Glasses**
(Coyle and Livingston 1981)

| Thickness (in.) | Glass Type | Glass Composition | Solar Transmittance |
|---|---|---|---|
| 0.040 | 7809 fusion | Alumino-borosilicate | 0.919 |
| 0.060 | 7809 fusion | Alumino-borosilicate | 0.917 |
| 0.060 | 0317 fusion | Aluminosilicate | 0.909 |
| 0.090 | 0317 fusion | Aluminosilicate | 0.910 |
| 0.110 | 0317 fusion | Aluminosilicate | 0.910 |
| 0.125 | Low-iron rolled | Soda-lime silicate | 0.910 |
| 0.118-0.125 | Low-iron rolled | Soda-lime silicate | 0.88-0.89 |
| 0.125 | Regular float | Soda-lime silicate | 0.83-0.87 |

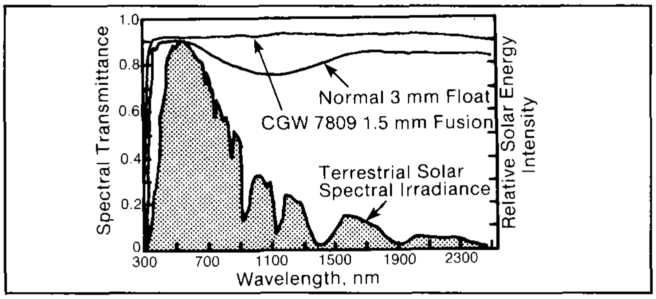
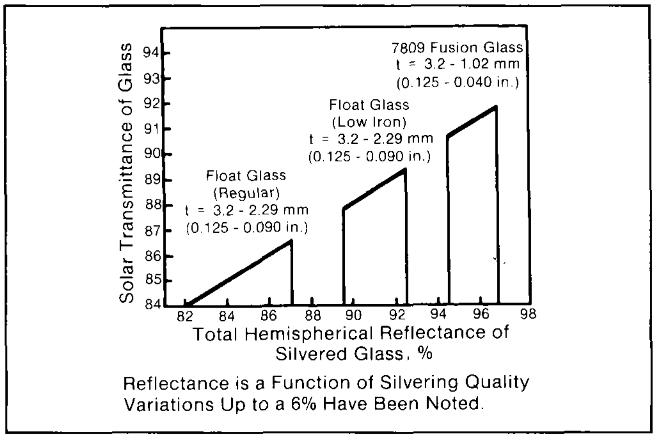


**Figure 2-17 Transmittance in Solar Spectrum of CGW-7809 Fusion and Soda-Lime Glass** (Coyle and Livingston 1981)



Reflectance is a Function of Silvering Quality Variations Up to a 6% Have Been Noted.

**Figure 2-18 Solar Reflectance of Second-Surface Silvered Mirrors on Different Glasses** (Coyle and Livingston 1981)

**Mechanical properties.** The fracture toughness $K_{IC}$ and stress corrosion properties (Kingery 1976) of 7809 glass were evaluated (Coyle and Livingston 1981). The value of $K_{IC}$ was $0.75 \pm 0.01$* which is about 6% greater than for soda-lime float glass, and gives it an advantage over other glasses in resisting hail impact and handling. The stress corrosion coefficient was estimated to be 26, compared with 19 for float glass (Coyle and Livingston 1981). This indicates that 7809 glass will be able to resist the growth of cracks that lead to delayed failure when the glass is held in tension — such as an elastically deformed thin glass mirror (Marion 1980).

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*In units of megapascals × $(\text{meters})^{1/2}$.

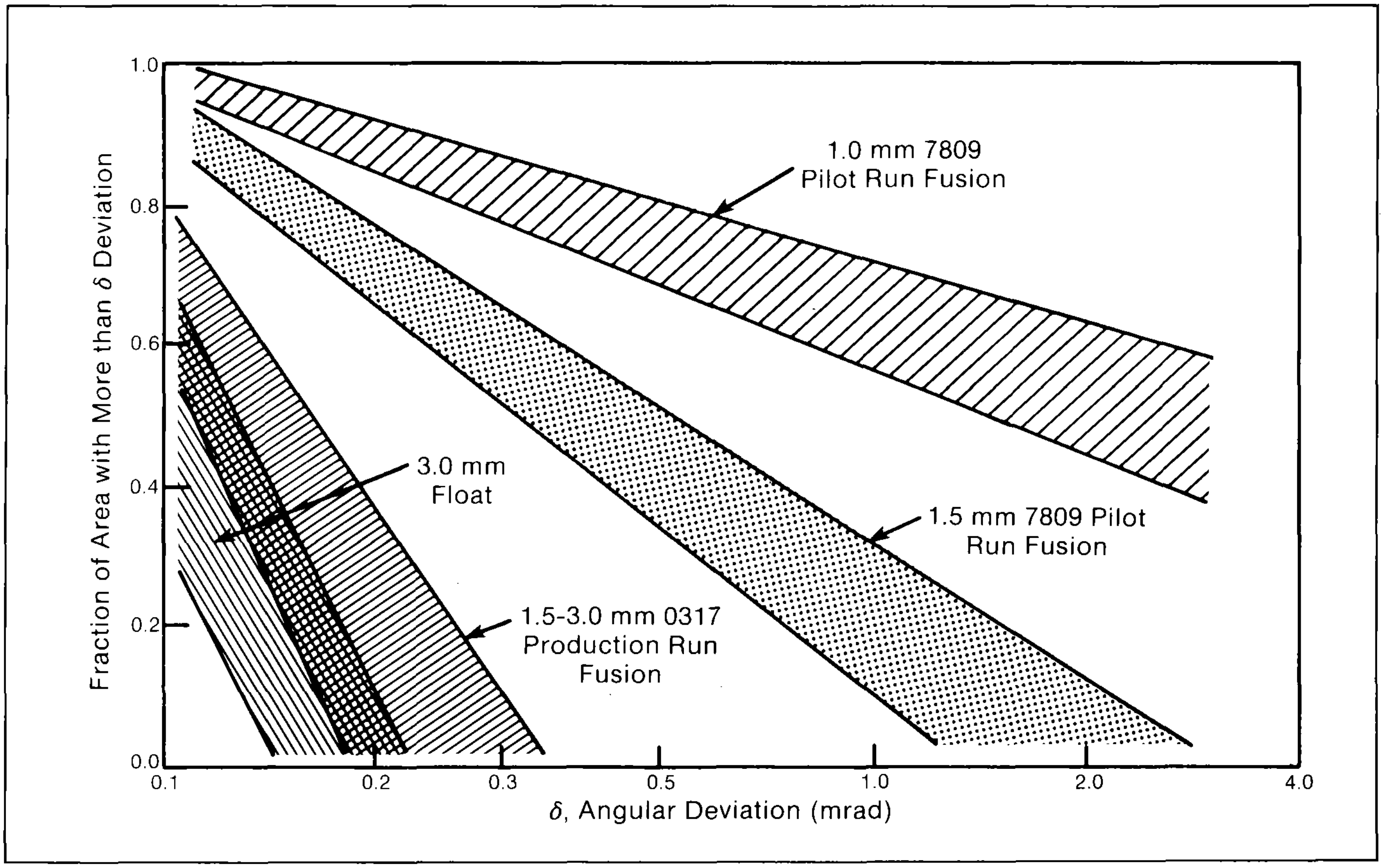

**Figure 2-19 Fraction of Glass Surface Area with More than Angular Deviation from Specular Reflection** (Coyle and Livingston 1981)

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# Chapter 3

# Physics and Chemistry of Silver/Glass Mirrors

## Glossary of Terms in Chapter 3

| | |
|---|---|
| AES | Auger Electron Spectroscopy |
| e.m.f. | electromotive force |
| EPR | Electron Paramagnetic Resonance |
| ESCA | Electron Spectroscopy for Chemical Analysis (see XPS) |
| IR | Infrared |
| ISS | Ion Scattering Spectrometry |
| NRA | Nuclear Reaction Analysis |
| RBS | Rutherford Backscattering Spectrometry |
| r.f. | radio frequency |
| RH | Relative Humidity |
| SAM | Scanning Auger Microscopy |
| SEM | Scanning Electron Microscopy |
| SEXAFS | Surface Extended X-ray Fine Structure Spectroscopy |
| SIMS | Secondary Ion Mass Spectrometry |
| UV | Ultraviolet |
| XPS | X-ray Photoelectron Spectroscopy (see ESCA) |
| XRF | X-ray Fluorescence |

## Introduction

The chemical and physical processes involved in the preparation and degradation of silver/glass mirrors are discussed in this chapter. As illustrated in Figure 2-12 (superstrate) in Chapter 2, the silver/glass mirror consists of a multilayer stack of glass, silver, and a protective backing. The protective backing may also consist of two or more multilayers. The most important stability issues for a multilayer configuration are interface reactions, adhesion, and the choice of the protective backing. In the descriptions of possible causes of mirror degradation in this chapter, reference is made to various analytical techniques to discern the causes. A brief description of the purpose of the techniques is contained in Table 3-1.

Since most mirrors are prepared by an electroless, wet, chemical process method (i.e., chemical-process mirrors), the emphasis of this section is on the chemistry related to preparing these mirrors and the processes responsible for their degradation. Similar but less complete discussions are provided for mirrors made by vacuum, organometallic, and other processes. Recent research results on improving the adhesion in the multilayer stacks and on identifying a more durable protective backing for the silver are then presented. In this section a brief historical development of silver/glass mirrors and a general overview of parameters that degrade the performance of mirrors in multilayer stacks is presented.

**Table 3-1 Surface Analysis Techniques for Evaluating Mirror Degradation**

| Technique | Rationale |
|---|---|
| Auger Electron Spectroscopy (AES) | Identify surface composition including impurities and degradation products; supurb lateral resolution |
| Scanning Electron Microscopy (SEM) | Map topography and surface defects |
| Ion Scattering Spectroscopy (ISS) | Determine surface composition; sensitive to isotopes and the first monolayer |
| Secondary Ion Mass Spectroscopy | Determine surface composition for first few atomic layers, especially ppm detectability of impurities |
| X-ray Photoelectron Spectroscopy | Identify oxidation state, average chemical composition, and nature of chemical bond for the first few monolayers of a surface |

## Historical Development

The historical development of mirrors has been summarized by Schweig (1973), who describes mirrors in use from more than 4000 years ago up to the technology of 1973. The method for making a chemical-process mirror has not changed in principle since Liebig's observation (1835) that a solution of silver is reduced by aldehydes to deposit a brilliant mirror. When the discovery of tin chloride as a sensitizer was made in 1876, the silvered mirror was able to compete with the tin-mercury amalgam mirror for clarity and durability.

The general processes for making mirrors from that point on were almost exclusively used for 80 to 100 years (Schweig 1973). During this time the processes were made more economical and efficient. The optical quality improved, but the durability of the product did not change. The description of the basic manufacturing process has not changed since 1970 when the process was economically optimized by introducing formaldehyde as the spray-process plating accelerator.

Schweig (1973) also traces the worldwide development efforts that have resulted in the current, widely used manufacturing method for preparing chemical-process mirrors; this industrial method is described in Chapter 5. He also summarizes the detailed chemical formulations used for making chemical-process mirrors, as well as equipment used, safety precautions, etc. The 200-page book devotes about 15 pages to mirrors made by methods different from the chemical process.

## General Parameters Causing Degradation

The life-cycle cost of a particular mirror design depends on the durability of the reflector assembly, such as shown in Figure 2-12 in Chapter 2. The purpose of sandwiching the reflective material into a multilayer stack is to limit reactive constituents from reaching the silver; thus, increasing the performance lifetime of the mirror. Mirror durability, therefore, depends on the materials used to form the mutilayers and the environmental exposure parameters. The degradation problems associated with multilayer stacks clearly depend on the ability of the glass and protective backing to exclude reactive materials, the ability of the manufacturer to exclude reactive impurities during manufacture, and the rate of interfacial processes connected with the materials used; e.g., interdiffusion and ion exchange.

All earth-based solar mirror systems will be subjected to terrestrial environmental exposure. The important parameters include atmospheric gases (water vapor, oxygen, and air pollutants), UV radiation, temperatures from -30°C to +150°C, temperature cycling, mechanical stressing from differential thermal expansion, and dust. Generic problems must be addressed such as the reactivity (1) of silver with and without a metallization backing, (2) at the silver/glass interface during UV exposure, (3) of any metallization backing with atmospheric gases and then with silver, (4) of impurities incorporated into the multilayer stack during preparation, and (5) of the glass surface itself with atmospheric gases or attached particulates.

## General Comments About Mirror Degradation

Some field-exposed, second-surface, silver/glass solar mirrors fabricated by conventional wet chemistry processes have experienced significant loss in performance because of degradation in less than one year (Masterson 1983a). Others have been exposed for more than five years without undergoing visible changes (Bomar 1981). The variability in the field durability of mirrors made by the same process is not fully understood. Based on prior work, implementing realistic quality assurance tests for durability and projecting mirror lifetime from accelerated tests is not possible. There is some evidence that the variability in durability is partly a quality control problem, but there is much more evidence that the basic problem is the thermodynamic instability of the glass/silver/copper/paint system when exposed to terrestrial environmental conditions (Thomas 198_).

Research over the past few years identified three failure modes that are common to many of the field-degraded mirrors: (1) debonding of the silver/glass interface, (2) halide formation in the metallic layers, and (3) agglomeration of the silver layer (Masterson 1983a). All of these are consequences of basic mechanisms at work that involve halides, water, oxygen, and other impurities (Thomas 1983). Halides have been reported by numerous investigators (Czanderna 1978; Daniel 1980; Pederson 1980; Mills 1980; Shelby 1980a; and Thomas 1983). Pinholes result primarily from agglomeration; black spots result from dissolution of copper, leaving voids at the silver/glass interface (Delameter 1981).

Early attempts at duplicating these failure modes in the laboratory by subjecting mirror specimens to environments containing high levels of degradative conditions in order to accelerate the process have met with mixed success (Dake 1980; Coyle 1981a; Pellicori 1980). The environments range from boiling water and salt spray to acid vapor and other corrosive gases. Although most of these environments eventually corroded the mirror metallization, the experiments were difficult to duplicate and the microscopic appearance of the specimens was seldom similar to naturally degraded mirrors. Furthermore, these experiments contributed very little to developing a basic understanding of the mechanisms or kinetics of the degradation process.

There are several suspected sources for the different rates of mirror degradation. These include inadequate cleaning of glass prior to mirroring; inadequate control of the mirroring steps, thus preventing optimized deposition of silver, copper, or other components; introducing contaminants during the mirroring steps; and reactions of silver and/or copper, especially in the presence of water vapor and oxygen (Masterson 1983a). Clearly, some of these can be eliminated with rigorous quality control.

Six parameters considered to be primarily responsible for the degradation of a particular type of mirror as a function of time have been identified (Masterson 1983a): (1) humidity (water vapor), (2) temperature, (3) thermal cycling, (4) solar ultraviolet radiation, (5) environmental pollutants, and (6) mechanical force. Including time, a matrix for testing mirrors actually consists of seven parameters. Each of these has a great range of magnitude and gradation, so there is almost an infinite number of possible tests to identify the impacts of the various individual and combinations of parameters. A matrix of finite size was identified for conducting actual experiments to assess the importance of the various parameters (Masterson 1983; Chapter 4, this document).

In addition to the parameters to which mirror systems are exposed, there are several choices that influence durability. These choices are in five major topical areas: (1) glass selected, (2) cleaning and sensitization of glass, (3) method of depositing silver, (4) backing metal for the silver (if any), and (5) reflector backing material (e.g., paint or sputtered quartz). Combining optimum methods and materials that these choices offer for testing the durability of one candidate mirror system could easily involve the preparation and testing of more than 77,000 mirrors (Masterson 1983a).

However, because of the high performance requirements (see Chapter 2), the number of candidate combinations are not as great as it might seem. In addition, recent work on accelerated testing (see Chapter 4) has greatly reduced both the number of degradative parameters and the ranges of magnitude for study. Future research on silver/glass mirrors could focus on elucidating degradation mechanisms (discussed later in this chapter) and developing a relationship between the time for performance loss in accelerated testing and the time for comparable performance loss in real time testing (Masterson 1983b).

## Preparing Mirrors Using the Wet Chemical Electroless Process

The basic steps for preparing mirrors by the chemical process method consist of selecting and manufacturing the glass, processing the glass surface, sensitizing the glass surface, depositing the silver reflective layer, depositing the intervening copper layer, processing the copper surface, and backing the metallic surface, usually with a paint.

The "wet" or "electroless" chemical process used for metalizing silver mirrors consists basically of oxidation-reduction reactions. For example, silver is initially dissolved in the plating solution as an ammonia complex $Ag(NH_3)_2^+$. This complex reacts with inverted sugar in basic solutions to plate silver metal onto a substrate immersed in the solution. The words "wet" and "electroless" are frequently used to describe the chemical-process mirror because the glass surface is kept wet from polishing to painting and no electric current is used that could cause deposition, as is usually the case for plating metals from solutions.

The chemical components that are used to sensitize glass, to deposit silver and copper, and that are in a commercially used paint are shown in Figure 3-1, along with typical thicknesses of the various layers. The covalently bonded superstrate is in contact with the metallically bonded silver and copper layers, and these are bonded to the paint-backing layer. This section first considers the physics and chemistry involved in the step-by-step preparation of a mirror, then discusses the degradation reactions that occur or might occur at the various interfaces, and finally discusses the properties of both freshly prepared and degraded mirrors. Some recent research results will be appropriately included in each subsection.

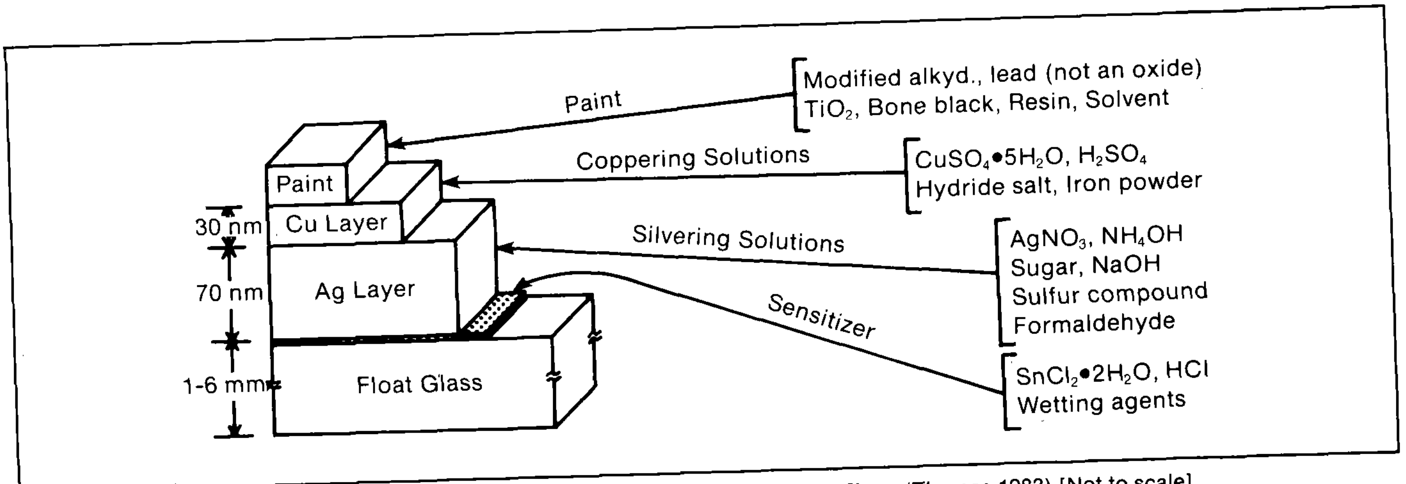


**Figure 3-1 Morphology and Chemical Components Used in a Typical Commercial Mirror** (Thomas 1983) [Not to scale]

## Mirror Preparation

**Glass.** The most economic method for preparing a high quality glass with a smooth, even surface is to float the molten glass on liquid tin with which it is insoluble and unreactive. Economy results because the glass is so uniform that the normal grinding and polishing steps can be eliminated from the manufacturing process. The glass manufactured by this process, which has an "air surface" and a "tinned surface," is called "float" glass. In 1958 a general composition of float glass was formulated, manufactured, and marketed (Schweig 1973). The glass composition is typically $SiO_2$, 72%; $Na_2O$, 14.3%; CaO, 8.2%; MgO, 3.5%; $Al_2O_3$, 1.3%; $K_2O$, 0.3%; $SO_2$, 0.3%; and $Fe_2O_3$, 0.1 wt %, which is the soda-lime silicate glass shown in Tables 2-2 and 2-3 (Chapter 2). All of the major glass manufacturers have licensed the float glass process from the patent holder, though each may have a slightly different composition of float glass constituents.

The next processing step for glass can vary widely among mirror manufacturers. In every case, the air surface of the glass is cleaned prior to sensitization; but in some cases the cleaning steps are numerous and the cleaning agents may be vastly different. Cleaning is necessary not only to remove dirt and grease but also to remove the hydroxylated silica gel layer on the glass surface. Mirrors made from freshly polished surfaces are known to have better metallic adhesion than those for which the cleaned glass is allowed to stand (Bomar 1981). The best explanation for this difference seems to be that the glass reacts with water to form an alkali-rich layer over the silica-rich layer (Hench 1982); the layer formed is presumably a hydrated alkali carbonate (Hench 1982) or a hydrated alkaline earth carbonate (Thomas 1983).

Polishing powders consist of metal compounds, usually metal oxides or proprietary mixtures of some or all of the following: oxides, hydroxides, carbonates, nitrates, and silicates. For many decades iron oxide, or a mixture of lead and zinc oxides, was the powder used in the polishing slurry. Today, the best polishing material is cerium oxide, $CeO_2$. The next best compound is zirconium oxide $ZrO_2$, which does not have the polishing performance of $CeO_2$, but is less expensive. Although each manufacturer has its own proprietary polishing process, the industry standard polishing material is "powder pack" (Lind 1979).

As implied above, experience has shown the manufacturer that the adhesion of the silver film and its optical properties depend upon the cleanliness of the glass surface before silvering. Classically, after polishing, a slurry of powdered chalk, mostly calcium carbonate and some ammonia, is used to clean the surface, though some manufacturers use inorganic detergents. In either case, all traces of the cleaning compound must be removed before sensitization. Some manufacturers polish and clean the glass surface at the same time by mixing zirconium or cerium oxides into the chalk slurries in proprietary mixtures. Hench (1982) reiterated the danger of assuming that glass is homogeneous. At times, phase separation, compositional segregation, devitrification, bubbles, or unreacted particles may result in accelerated degradative attack at interfaces. Surface abrasion, polishing relics, scratches, and pits can also cause accelerated attack (Sanders 1973). Concerning the penetration of tin into glass from the float-side, Colombin (1977) used ion etching and XPS to conclude that the tin concentration varies more rapidly in the first 100 nm than previously thought. In particular, a sharp tin concentration gradient occurs in the first 10 nm.

**Silver-to-glass bonding.** Several types of silver-to-glass bonding are possible, including ionic and covalent. Only the latter permits an adherent metallic layer of silver to be deposited.

**Sensitizing.** After processing the glass surface to prepare an impurity-free interface, the surface is sprayed with a solution of stannous chloride dihydrate, hydrochloric acid, and, in some cases, wetting agents. The wetting agents assure more complete wetting of the glass surface with the silvering solution.

According to Schweig (1973), "Stannous chloride is necessary for a rapidly deposited, strongly adherent, uniform film of silver." Though other more expensive sensitizers such as $PdCl_2$ have been found and many proprietary additives are included in the sensitizing solutions to improve the speed and uniformity of silver deposition, the excellent film adherence is due to the action of the stannous chloride. Stannous chloride can also be used to sensitize glass for plating Cu, Ni, or Co mirrors (Saranov 1968).

Recent studies (Pederson 1982 and Thomas 1983) have shown that upon thorough and prolonged rinsing of the glass surface after sensitization, all traces of chloride ion can be removed. Thus, the tin ion in some active form is deposited onto the glass surface and its interaction with the silver plating solution components causes the production of the interfacial adhesion layer which then acts as a nucleus for the deposition of the reflective silver layer.

Although stannous chloride has been used as a sensitizer for more than a century, it is the least understood step of chemical-process mirrors. Schweig (1973) provided the solution reaction

$$SnCl_2 + H_2O = Sn(OH)Cl + HCl \qquad (1)$$

and suggested that the sensitizer adsorbs onto glass to serve as a nucleation site for forming colloidal silver particles.

Evidence that tin chloride bonds to glass is shown in the XPS spectrum in Figure 3-2 (Lind 1979). Although Schweig (1973) did not suggest a bonding mechanism to the glass, he noted that oxidation occurs on standing; i.e.,

$$3\,SnCl_2 + H_2O + 1/2\,O_2 = SnCl_4 + 2\,Sn(OH)Cl \qquad (2)$$

and that only fresh stannous chloride solutions should be used.

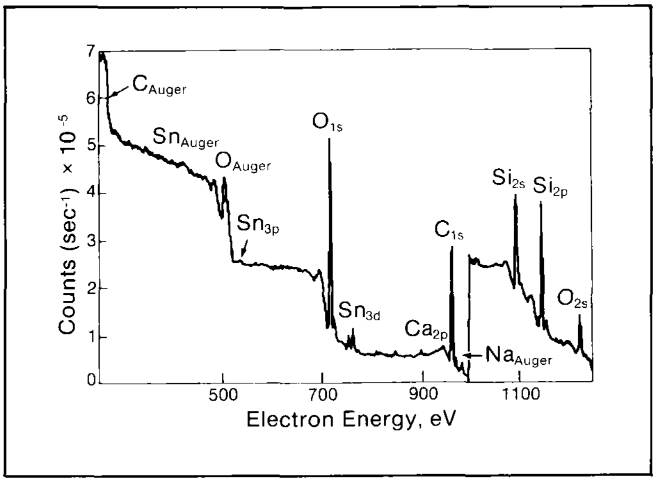
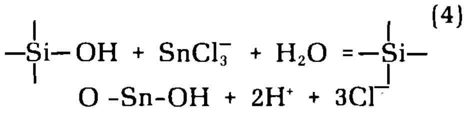


**Figure 3-2 ESCA Survey of the Unsputtered Air Surface of the Soda-Lime Silicate Float Glass** (Pederson and Thomas 1980)

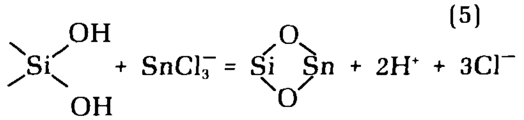
Work by deMinjer (1973) and Pederson (1982) attempted to explain the sensitization process by suggesting the sensitizer adsorbs by the reactions

$$SnCl_2 + Cl^- = SnCl_3^- \qquad (3)$$



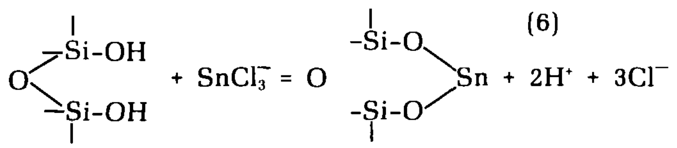
(4)

$$-Si-OH + SnCl_3^- + H_2O = -Si-O-Sn-OH + 2H^+ + 3Cl^-$$



(5)

and



(6)

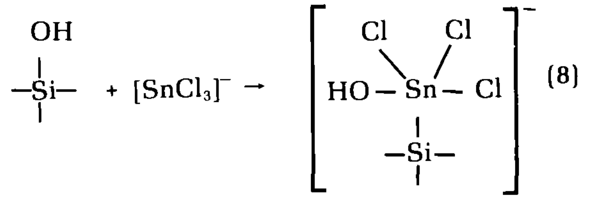
Similar reactions were suggested for $SnCl_4$ adsorption, but with two additional hydroxyl groups attached to each adsorbed tin species. According to Thomas (1983), $SnCl_2$ is, in reality, a chloride-bridged solid $(SnCl_2)_n$ that reacts with water (Cotton 1972).

In later efforts, Thomas (1983) explained the sensitization differently: The solid manufactured as stannous chloride is actually $SnCl_2{\cdot}2H_2O$, which is only slightly soluble in water. The real sensitizer, $[SnCl_3]^-$, is formed in an HCl solution,

$$SnCl_2{\cdot}2H_2O + HCl \rightarrow H^+ + [SnCl_3] + 2H_2O \qquad (7)$$

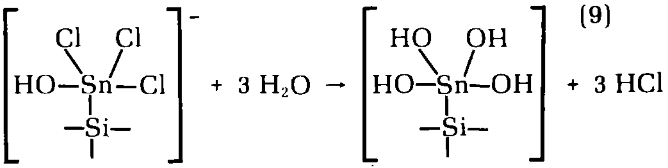
The mechanism by which $[SnCl_3]^-$ bonds to glass and then bonds silver to glass entails many steps involving insertion reactions, redox reactions, and detailed ligand exchange reactions. This proposed mechanism and all supporting references is discussed in detail in Thomas (1984).

Upon sensitization of glass, *it is found that* (1) *tin has* bonded to the surface and cannot be rinsed away (Pederson 1980, 1982; Schweig 1973; deMinjer 1973), (2) the ability of tin to bond to glass is affected by glass cleanliness and wettability (Daniel 1980; Mills 1980; Goggin 1982), and (3) the chloride ions disappear with vigorous rinsing (Pederson 1980, 1982; deMinjer 1973). Thomas' (1983) model for sensitization suggests that $[SnCl_3]^-$ initially inserts itself between the surface silicon to hydroxide bonds to form a five-coordinate tin complex on the glass surface



(8)

Upon formation of the tin complex, ligand exchange should be favored; in this way the chlorides may exchange readily with water or hydroxyl ligands during rinsing as illustrated in equation (9).



(9)

All the reported observations in the literature can be explained by reactions (7) through (9) and are supported by the XPS and AES data of Thomas (1983) and Pederson (1980, 1982) as well as by the radiotracer data of deMinjer (1973). A shift of 2.8 eV from Sn° in the XPS peaks of the Sn $3d_{5/2}$ and $3d_{3/2}$ doublet was reported by Thomas (1983), whereas only a 1.7 eV shift is expected from the ligands attached as given in equations (4) through (6). Thus, XPS data provide significant support for the number of ligands attached to Sn, as shown by equations (8) and (9). In using XPS to analyze Si-Sn alloys, Holm (1976) reported a chemical shift for the Sn 3d lines of about

1.6 eV between Sn metal and $SnO_2$. Pederson (1980, 1982) also reported differences of 1.6 to 1.8 eV for both $Sn^{+2}$ and $Sn^{+4}$ relative to Sn°. In these cases, no additional ligands are attached to increase the magnitude of the chemical shift to the 2.8 eV measured by Thomas (1983).

The Sn complex is restricted to the surface monolayer and only partially covers the available Si sites. The fractional coverage of Sn complexes on glass surfaces is estimated to be 0.2 (Thomas 1983), 0.1 to 0.5 (Pederson 1982; deMinjer 1973), and 0.17 ± 0.03 (Pitts 1984a). Low coverages are to be expected because of lateral electrostatic repulsions in the surface monolayer.

In other work, Feldstein (1972) reported improved effectiveness of the sensitizer by controlling its concentration. Jones (1972) found that repeated exposure and washing improved the effectiveness of $PdCl_2$ as well as $SnCl_2 \cdot 2\,H_2O$ before silver deposition. Buckwalter (1981) reported that contacting the glass with a solution of lanthanide rare earths, in addition to tin or palladium chloride sensitizer solutions, increased the resistance to delamination of the silver from glass in the presence of water. Kuznetsov (1975) improved the adhesion of silver to quartz by 3 to 4 times by depositing a 200 nm-thick porous $SiO_2$ film onto the quartz, using palladium chloride as a sensitizer, and heating to 100-300°C. Adhesion strengths improved from 53-58 $kg/cm^2$ to as high as 221 $kg/cm^2$.

**Silvering**. For silvering the sensitized glass, a silver nitrate solution and ammonia, which form a soluble $Ag(NH_3)_2^+$ complex, are invariably used (Schweig 1973). In the spray silvering technology currently in widespread use (see Chapter 5), formaldehyde and/or dextrose act as reducers to yield silver from the ionic form; sodium hydroxide raises the pH to accelerate the silver deposition rate, e.g.,

$$\begin{aligned} &12Ag(NH_3)_2OH + 6NaOH + C_6H_{12}O_6 \rightarrow \\ &12Ag + 6HCOONa + 12H_2O + 24NH_3 \end{aligned} \qquad (10)$$

$$\begin{aligned} &2Ag(NH_3)_2OH + NaOH + H_2CO \rightarrow \\ &2Ag + HCOONa + 2NH_4OH + 2NH_3 \end{aligned} \qquad (11)$$

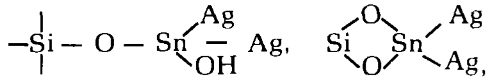
or other possible reactions (Schweig 1973).

Besides the silver nitrate salt and sugar components, other components make up the commercial spray silvering solution including formaldehyde, sodium hydroxide, ammonia, and a proprietary additive called a hardener that slows the deposition and increases the brilliance, density, strength, and uniformity of the reflective layer. In most cases the hardener is a thiosulphate salt. The other three additives are generally needed for the rapid deposition necessary for uniform films using a spray deposition of silvering components.

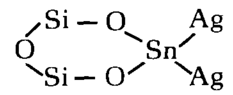
Since silver salts are not soluble in highly basic solutions, the silver ions must be complexed to ensure that silver does not precipitate as a metal oxide instead of as a metallic film. Finally, the formaldehyde is necessary for rapid deposition of the layer within the time span of the actual spraying. The silvering step is the most complex since the reducing solution, the caustic soda solution, and the complexed silver salt solution must be sprayed on from separate spray outlets and must not contact each other until they are mixed on top of the glass surface. In some cases, the silvering step is repeated to increase the thickness of the deposited film. A silver layer 70 nm thick is typically deposited in about one minute, so trapping impurities at the interface and in the film is a distinct possibility.

Before discussing the chemistry of silver plating, the acid-base chemistry of the glass should be considered. Penetration of silver into the glass substrate has been reported previously (Bastasz 1980; Buckwalter 1980; Pederson 1980 and 1982). When the sensitizer is sprayed onto the glass, the acidic solution probably protonates most of the surface silicate sites by exchanging $H^+$'s for $Na^+$, $K^+$, $Ca^{2+}$, and $Mg^{2+}$. When the silver solutions are applied, the highly basic solutions neutralize the acid and thus the silicate sites undergo ion exchange of their protons for $Na^+$, $Ag^+$, and $NH_4^+$. Since $Na^+$ and $NH_4^+$ are highly ionic, they will not bond as well as $Ag^+$ to these covalently bonded silicate sites. Thus, silver ions penetrate into the glass even as silver is plating onto the surface of the glass.

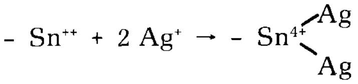
When other researchers applied the basic silver solution to sensitized glass without spraying the reducer so that the plating reaction could not take place (Pederson 1982; deMinjer 1973), they found that tin and silver both remain bound to the surface. A surface species was suggested by Pederson (1982) from XPS data whereby silver is bonded through the tin to the glass, with the Auger parameter data suggesting that silver is bonded covalently; i.e.,



and/or (12)



after undergoing an oxidation-reduction reaction,



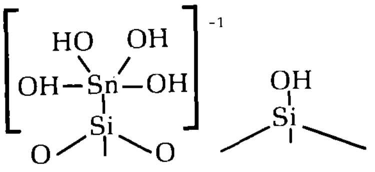
$$- Sn^{++} + 2\,Ag^+ \rightarrow - Sn^{4+}\!\begin{smallmatrix} \diagup Ag \\ \diagdown Ag \end{smallmatrix} \qquad (13)$$

These Auger parameter data should preclude simple ion exchange of silver as one of the possible mechanisms for silver bonding since ionically bonded silver ions must be involved in ion exchange.

The interpretation that silver is bonded through the tin to the surface is not supported by the isotopic work of deMinjer (1973) who showed that Pd could be bonded to the tin after the silvering step without any loss of silver from the surface. This result clearly suggests that after silver is bonded to the glass, tin is still separately bonded to the glass. In recent work, Pitts (1984b) confirmed that both Sn and Ag can be detected using XPS and ISS. The Ag signal is three times that for Sn, which is not possible by any of the bonding hypotheses shown in equation (12).

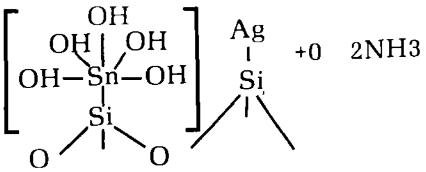
Thomas' (1983) model of this process suggests that $Ag^+$, the only Lewis acid in the plating solution, attacks the Sn-to-Si bond shown in equation (9), and leaves behind a covalent Ag-to-Si bond [equation (14)], which is also consistent with the Auger parameter data of Pederson (1982).

Before Ag $(NH_3)_2$ addition,



(14)

After Ag $(NH_3)_2$ addition,



Silver bonded to silicon has been detected using surface SEXAFS as the probe for silver that was vacuum deposited onto Si(111) single crystals (Stohr 1982). It is on this convalently bonded silver that the plating reaction would nucleate. Thomas' (1983) model suggests that upon reductive formation of the Ag-to-Si bond, the Sn complex becomes neutralized and attaches itself to an adjacent site which it previously could not occupy because of its electrostatic charge. Since the tin complex rebonds to the surface, the possible number of Ag-to-Si bonds is reduced by the number of sites occupied by the Sn. It has been observed (Daniel 1980) that the Ag-to-glass bond becomes stronger with time. This suggests that the tin may still sensitize Ag-to-Si bonds after forming the metallic Ag layer, possibly by reacting with $Ag^+$ bonded as surface silicates or trapped as impurities.

Once nucleation has taken place and an electron conductive layer is formed, the plating reaction should take place rapidly. Since the plating reaction is essentially electrode plating after the first surface layer has formed, impurities trapped in the bulk should not be as concentrated as impurities trapped at the Ag/glass interface. There could be a fairly large amount of plating solution constituents such as $H_2O$, $OH^-$, $Na^+$, $NH_4^+$, Sn complexes, etc., that are trapped in the first few atomic layers of the glass, depending upon the extent of porous "gel" layer formation on glass before plating (Goggin 1981).

The XPS spectrum of a silver surface after spraying, rinsing, and air drying shows the typical impurities C, O, S, and Cl from atmospheric exposure, but upon etching ~30 nm into the bulk, no significant levels of impurities could be found (spectrum 1, Figure 3-3). When the etching process is continued until reaching the silver/glass interface (~90 nm), evidence of Sn trapped at the interface was discovered (spectrum 2, Figure 3-3) that is consistent with the discussion in the preceding paragraph. In addition, dramatic increases in hydroxyl and carbon compounds were observed with SIMS (Thomas 1983). Components of the glass, such as iron, oxygen, calcium, and carbon, are evident in XPS and SIMS spectra. A contamination layer at the Ag/glass interface has been previously observed, and deuterium oxide experiments (Pederson 1980) suggest that this layer may extend 50 nm into the glass.

Shelby (1981) compared the crystallite sizes of both vapor-deposited and chemical-process silver films on silica. The latter were smaller, as deposited, whereas the former exhibited preferred orientations and were more uniform in thickness. The different durabilities observed for vapor- and chemically deposited mirrors led some researchers to suspect that differences in crystallite size and morphology conceivably affect the relative reactivity of the films.

Numerous investigations continue about the detailed composition or optimization of the silvering solution.

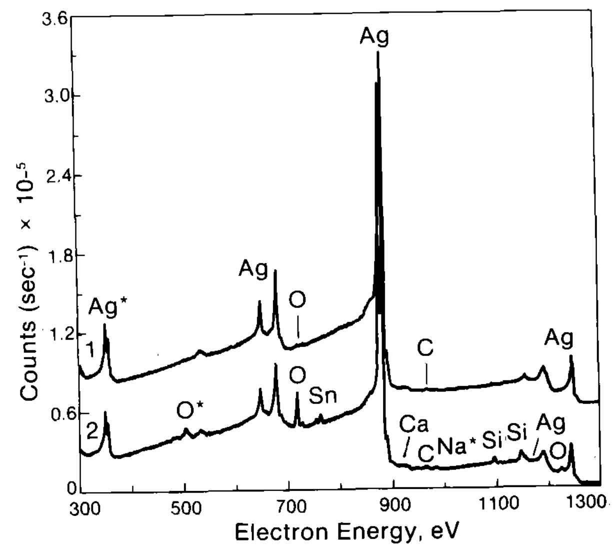


**Figure 3-3 XPS Survey Scan of the Elements Present in the Bulk of the Silver Layer (spectrum 1). XPS Survey Scan of the Elements Present in the Silver/Glass Interface Region (spectrum 2).** The asterisk indicates Auger signal (Thomas 1983)

In addition to those mentioned by Schweig (1973), recent patents or papers on improved silvering solutions include those by Filip (1969), Sivertz (1972), Ramanathan (1972), Morimoto (1974), Vaskelis (1975, 1976), Bahls (1976), Hepburn (1980), and Cottingham (1980). Karasek (1966) developed a solution to improve the uniformity of the silver layer.

Although the next processing step is coppering at room temperature, it is worth noting that any silver film on glass will agglomerate if heated to 100-150°C (Czanderna 1965; Lind 1979). The onset temperature for agglomeration is slightly lower in vacuum than in oxygen (Czanderna 1965).

**Backing with copper.** There are three methods of applying the copper backing layer. Electrolytic deposition and electroless pouring have almost been totally displaced by the spray techniques developed in the 1950s. The spray technique for copper deposition is also an electroless process and thus resembles the silver deposition step. The reducing solutions are totally different because of the desired rapid deposition in the spraying processes. To deposit copper rapidly, metal powders such as zinc or iron must be mixed into the coppering solutions since the electrochemical potentials are great enough for these metals to cause reduction. In some cases, extremely strong reducers such as calcium hydride are used to deposit the copper onto the silver film.

The only other chemicals added to the coppering solutions are acids such as sulfuric acid, since metal powders react faster in acidic solutions. In some processes, organic acids such as citric acid are added to the coppering solutions to improve the smoothness, evenness, and brilliance of the deposited copper layer. Pragmatically, an organic acid additive is not necessary since copper is used mostly as the backing layer and not as the reflective layer. A summary of the chemical compositions of various coppering solutions is also given by Schweig (1973).

After depositing a copper layer, which is usually one third to one half the thickness of the silver layer, strong jets of distilled water are needed to disperse the coppering solution from the copper surface and especially to remove all traces of the metal powder. After rinsing, the mirrors are usually dried on heated tables or by warming under infrared heaters before painting the copper surface.

At this point the ambient laboratory or household atmosphere has little effect on the copper-protected reflective layer. The copper-backed mirror thus exhibits a reasonable lifetime for indoor use. If a more extreme environment is encountered, such as a very humid bathroom, then more protection is needed. In these cases, the copper layer is protected by a kinetic barrier such as a layer of shellac or paint. These dense polymeric layers slow down the process of mirror degradation by limiting the pathways that the atmospheric reactants can take to reach the metallic layers, thus decreasing the exposed surface area.

Elements detected on the copper surface after stripping the paint include Fe and S; some authors (Pederson 1980; Mills 1980) have thought that the paint is the source of these impurities. However, Thomas (1983) prepared a Cu/Ag/glass mirror stack up to application of the paint step (Figure 3-4a); an AES analysis of the Cu surface (Figure 3-4b) showed that Fe and S were already present, as well as Ca, Na, C, Cl, and O, without contact to paint or primer. The likely source of sulfur is the plating solution ($CuSO_4$ and $H_2SO_4$). Powdered iron sprayed with the reducer solution is the logical source of iron; calcium hydride, the reduction accelerator, is the probable source of calcium. Sodium, chlorine, and carbon impurities are normally found on samples that are customarily processed. Analysis of multiple AES depth profiles into the copper layer indicate that the surface is composed mostly of oxide compounds.

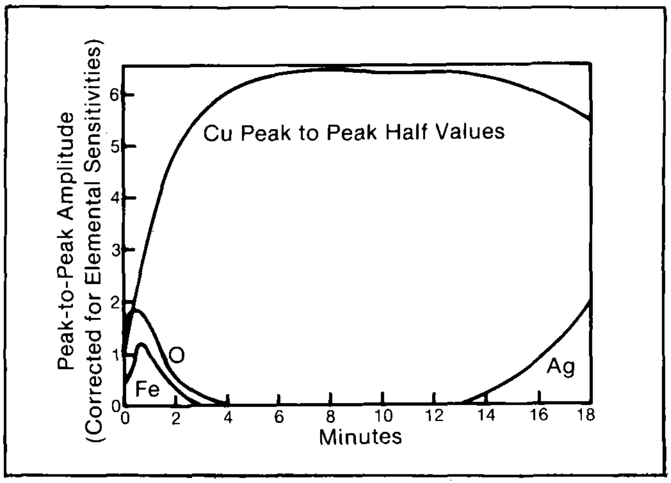


**Figure 3-4a Auger Electron Depth Profile Through the Copper Layer of a One Year Old Mirror after Removal of a Lacquer Backing with Acetone.** The profile has been corrected for elemental sensitivity factors as provided by Physical Electronics (Thomas 1983)

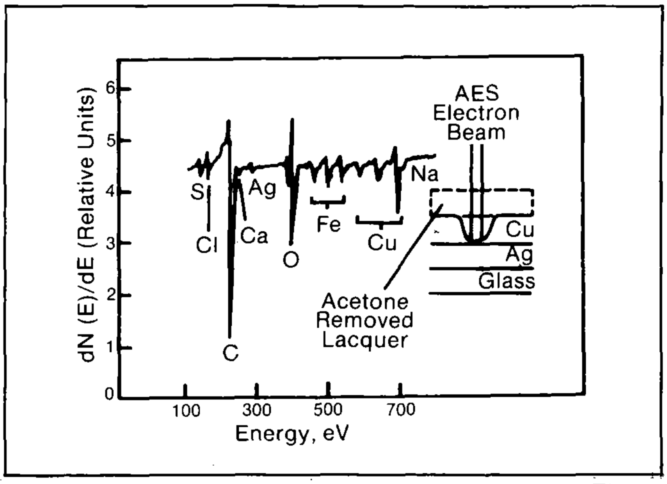


**Figure 3-4b Elements Present on Copper Surface (Zero Time) Shown Using an AES Scan** (Thomas 1983)

To learn more about the penetration of the oxide impurity-containing layer into the copper bulk with time, a mirror was made by replacing the paint with a lacquer to prevent any possibility of reactions with the inorganic components of commercial paint (Thomas 1983). The mirror remained in a laboratory environment for one year. After removing the lacquer with acetone, the sample was depth-profiled using AES; the profile of Fe, O, Cu and Ag each is shown in Figure 3-4b. In particular, the iron and oxygen impurities persist through the first one third of the copper layer, suggesting that a combination of iron and copper oxides are formed well into the copper film. Thus, the paint/copper oxide interface also consists of a paint/iron oxide interface.

**Ag/Cu interdiffusion.** The only direct evidence for a copper diffusion through silver at 20°C was reported by Thomas (1983) for a one-year old mirror. Pederson (1980) observed apparent interdiffusion, but the topography and morphology of his films caused doubt as to the certainty of interdiffusion. Nearly all Ag/Cu interdiffusion studies have been conducted above 450°C (Butrymonicz 1974).

The only studies on thin films of silver and copper that are close to room temperature were from 180°C to 220°C (Kunin 1969), 225°C to 500°C (Schoen 1979), and 327°C to 427°C (Gibson 1975). The latter work was for silver diffusion through epitaxial films of copper, while that of Schoen (1979) probed the grain boundary diffusion of silver through copper. James (1982) calculated the diffusion rates at 20°C based on diffusion data taken at higher temperatures and concluded that interdiffusion should be detectable in much less than a year. If copper does diffuse to the silver/glass interface and if silver diffuses to the copper/paint interface in significant amounts, then the mechanism of corrosive degradation of the metallization layers is more complicated than presently thought.

No evidence has been found for Sn diffusion into silver from the silver/glass interface (Thomas 1983; Pederson 1982). Furthermore, depth profiles by Thomas (1983) and Pederson (1980) through the metallization layers did not reveal impurities at the Ag/Cu interface. Occasional particles of Ca (presumably from $CaH_2$) and Fe were encountered in the copper layer by Thomas (198_).

**Paint layer.** After coppering, the nearly complete mirror is washed thoroughly with distilled or deionized water to remove all traces of solution and metal powder. Gjostein (1973) concluded from AES studies of metal surfaces that good paint adhesion depends critically on surface cleanliness, particularly with regard to residual hydrocarbon layers. The mirrors are dried, thus terminating the wet processing steps, and heated from the uncoated side with infrared to temperatures of typically 43°C to 65°C. The copper surface is then coated with a shellac or paints; all commercial mirrors are protected with paint.

The chemical composition of commercially available paints is a closely guarded secret; the constituents listed in Figure 3-1 were provided as a courtesy of the Peacock Laboratories. Most paints consist of a thinner, vehicle, pigment, and drier. Dake (1981) published a list of 25 commercially available backcoating and sealant materials. Some representative paints used to back glass/Ag/Cu mirrors documented in some typical patents include a mercaptoalkyl alkoxy Si compound (Viventi 1966), silicones (Gennari 1967), a resin containing bitumen and an epoxy resin (Makijima 1974), a moisture-resistant enamel (Nowotniak 1975), polymethyl-H-silozane in $CH_3CO$ (Minar 1975), polymeric quinoxaline derivatives (Sinclair 1975), universal paints (Gulf and Western 1976), an epoxy-alumina-polysulfide rubber-based protective coating (Beinarovich 1978), butadiene (Sakamoto 1979), acrylic co-polymers (Watanabe 1979), and benzotriazole (Furukawa 1981).

According to Schweig (1973), "Even the best paint is not considered good or durable enough for mirrors which are . . . used outside . . . . Impermeable and impenetrable backings are applied in these cases." One of three sheet materials is generally used for added protection. Thin sheets of metal such as lead, tin, or aluminum can be applied over the paint. Very dense, thick sheets of plastic could also be used to cover the backing paint. Finally, a second sheet of glass could be used to protect the metallic layers. In all of these cases, the edges of the stacks would have to be sealed from the atmosphere. Many other methods have been devised for protecting specific stack geometries, but economic and structural necessities must be considered when selecting the best protection of the reflective layer and its optical properties.

The components in the paint (Figure 3-1) appear relatively inert, but surface analysis data revealed that Cl and S are also present, as shown in Figure 3-5. The

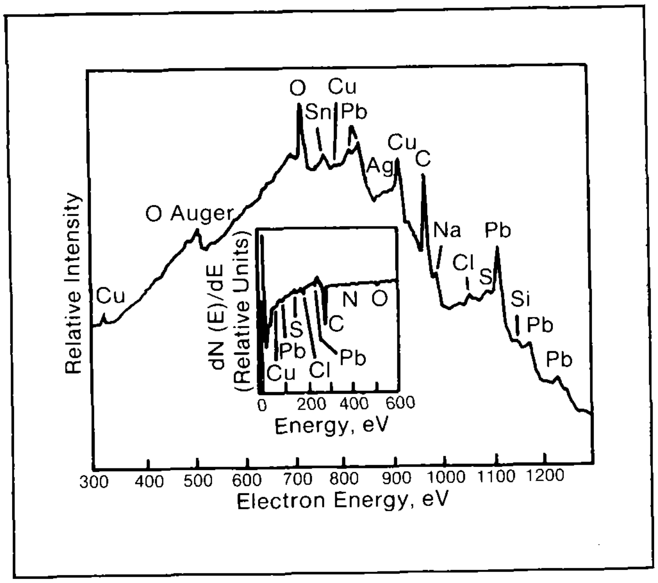


**Figure 3-5 XPS Survey Scan of Interfacial Residue on Mirror Paint After Adhesive Failure.** Inset is an AES of paint/copper surface (Thomas 1983)

influence of these elements on mirror durability will be discussed in the next section.

## Degradation Phenomena/Mechanisms

The physical properties of mirrors prepared by the chemical process were discussed in Chapter 2. The high reflectance (Table 2-5) can be improved by using different glasses (Figures 2-13 through 2-15). The physical properties of the glass, also presented in Chapter 2, may be properly chosen, but may change with time. Thus, the chemical and environmental properties (Table 2-1) are crucial to the lifetime of the completed mirror. Performance losses, some of which were mentioned in this chapter, result from reactions at the silver/glass interface; interdiffusion processes at the interfaces; permeation of the paint followed by corrosion of the metallic layers, particularly in the presence of water and halides; and agglomeration of silver, or pinholes left in the films during preparation. Other potential degradation may result from weathering and solarization of the glass, segregation of glass components that affect a change in the physical properties, UV degradation of paints, and mechanical abrasion of the paint.

In this section, reactions at interfaces and interdiffusion phenomena are discussed. Most of the understanding of the degradation mechanisms has resulted from reports or publications by Czanderna (1978), Lind (1979), Bastasz (1980), Buckwalter (1980), Burolla (1980), Daniel (1980), Mills (1980), Pederson (1980, 1982), Shelby (1980), Vitko (1982), Pitts (1984a, 1984b), and Thomas (1983). In all the preceding papers as well as that by Bomar (1981), water is identified as an essential agent for causing chemical degradation of the mirrors, but it is also indicated by some that other chemicals participate in, or at least catalyze, the reactions.

The various methods of surface analysis (Czanderna 1975) applied to solar energy materials (Czanderna 1981) have been extremely helpful for providing the data required to formulate the chemical degradative mechanisms proposed below. All of these reactions ultimately result in a decrease in the solar-weighted reflectance and thus contribute to increasing the life-cycle costs of solar thermal reflectors.

**Copper/paint**. Most paints are subject to UV photodegradation (Schissel 1980). Nevertheless, they are used to help preserve the mirror. The additives in commercially available paints are generally used to increase the density of the paint and thus retard the flow of atmospheric reactants to the metallic layers. An ideal paint would be very dense and strongly bonded to the metallic surface. Diffusion to the metallic layers before corrosion occurs would be time-consuming; the paint density would also retard the outward diffusion of corrosion products from the reaction area and further slow down corrosion reactions. Unfortunately, the paints actually used, which have been formulated for other applications (Bomar 1981), are especially porous to atmospheric gases, especially water vapor and oxygen. It is not surprising that Pb, Cu, and O have been detected at the copper/paint interface, but Fe, Ca, Cl, and S have also been identified (Thomas 1983; Pederson 1980). In field-degraded mirrors, the copper layer corrodes or actually disappears and precedes silver corrosion (Daniel 1980; Pederson 1980; Mills 1980). Copious amounts of chloride are also present. Based on this information, Thomas (198_) wrote the following reactions that can occur at the copper/paint interface with accumulated water and conducting paths for electrons

$$PbCl_2 + 2e^- \xrightarrow{\overset{\text{in}}{H_2O}} Pb + 2\,Cl^- \qquad (-0.268\text{ V}) \qquad (15)$$

and from the copper layer, trapped iron filings, and $CaH_2$, there are these following reactions

$$Cu \xrightarrow{\overset{\text{in}}{H_2O}} Cu^{++} + 2e^- \qquad (-0.337\text{ V}) \qquad (16)$$

$$Cu + Cl^- \xrightarrow{\overset{\text{in}}{H_2O}} CuCl + e^- \qquad (-0.137\text{ V}) \qquad (17)$$

$$O_2 + 2H_2O + 4e^- \xrightarrow{\overset{\text{in}}{H_2O}} 4OH^- \qquad (+0.401\text{ V}) \qquad (18)$$

$$O_2 + 2H_2O + 2Cu \xrightarrow{\overset{\text{in}}{H_2O}} 2Cu\,(OH)_2 \qquad (+0.77\text{ V}) \qquad (19)$$

$$Cu^{++} + e^- \xrightarrow{\overset{\text{in}}{H_2O}} Cu^+ \qquad (+0.153\text{ V}) \qquad (20)$$

$$Cu^{++} + Cl^- + e^- \xrightarrow{\overset{\text{in}}{H_2O}} CuCl \qquad (+0.538\text{ V}) \qquad (21)$$

$$2H^- \xrightarrow{\overset{\text{in}}{H_2O}} H_2 + 2e^- \qquad (+2.25\text{ V}) \qquad (22)$$

$$Fe \xrightarrow{\overset{\text{in}}{H_2O}} Fe^{++} + 2e^- \qquad (+0.44\text{ V}) \qquad (23)$$

$$Fe + S^{-2} \longrightarrow FeS + 2e^- \qquad (+0.95\text{ V}) \qquad (24)$$

$$Pb + S^{-2} \longrightarrow PbS + 2e^- \qquad (+0.93\text{ V}) \qquad (25)$$

$$2Cu + S^{-2} \longrightarrow Cu_2S + 2e^- \qquad (+0.89\text{ V}) \qquad (26)$$

$$Sn + S^{-2} \longrightarrow SnS + 2e^- \qquad (+0.87\text{ V}) \qquad (27)$$

The energy evolved from some of these half reactions is sufficient to break copper/paint adhesive bonds and produce corrosive reactions at the silver/glass interface (to be discussed later in this section). Chloride ions, which might accumulate from leaching of $PdCl_2$, aerosol contaminants or entrained sensitizer, are well-known depassivators of protective oxides.

The limited amount of surface analytical data obtainable from the highly insulating paint layers suggests that chloride from the paint may be one of the major problems in accelerating the corrosion of commercial mirrors (Pederson 1980; Thomas 1983). The XPS spectra in Figure 3-5, taken of the residues left on the paint after corrosion caused de-adhesion of the paint, provide only average elemental composition over the whole sample. The spectra show copious amounts of both lead and chlorine at this interface; AES analysis of striations left after edge attack of the metallic layer have shown them to be mostly areas of insoluble silver and copper (I) chlorides. These deposits may result from the precipitation of these slightly soluble compounds at the solid/liquid/air interface in a way similar to the formation of stalactites and stalagmites.

After corrosion caused delamination, AES depth profiles into the paint from the Cu/paint interface have shown great amounts of chlorine on the paint surface (inset Figure 3-5), but almost none could be found in the bulk of the paint. If lead chloride was a constituent of the paint, Thomas' (1983) inability to detect chlorine in the paint (bulk) probably resulted from leaching during exposure, which would concentrate chlorine at the copper/paint interface. Other authors have also reported that chlorine was present in degraded or corroded commercial mirrors (Pederson 1980; Mills 1980).

**Corrosion of silver and copper.** The oxidation of copper and silver in various environments is well known and included in many publications (Leidheiser 1974; Butts 1967), so the related chemical reactions will not be restated. For solar mirror applications, some procedure must be devised to exclude corrosive gases from reaching these two metals. The extensive corrosion detected in heliostats is well documented (Lind 1979; Daniel 1980, Mills 1980; Pederson 1980; Bomar 1981).

Vitko (1982), using vapor-deposited silver on float glass or vitreous silica and chemical-process mirrors stripped of paint and copper, found that pinholes formed in the silver films when immersed in boiling water (pH = 7.0), as long as the water contained oxygen. The overall dissolution reaction was given as

$$4Ag + O_2 + 4H^+ = 4Ag^+ + 2H_2O \qquad (28)$$

SEM photographs showed that the pinholes enlarge as a function of exposure (Figure 3-6) and that the topographical features are similar to those for corroded heliostat mirrors (Figure 3-7). In accelerated

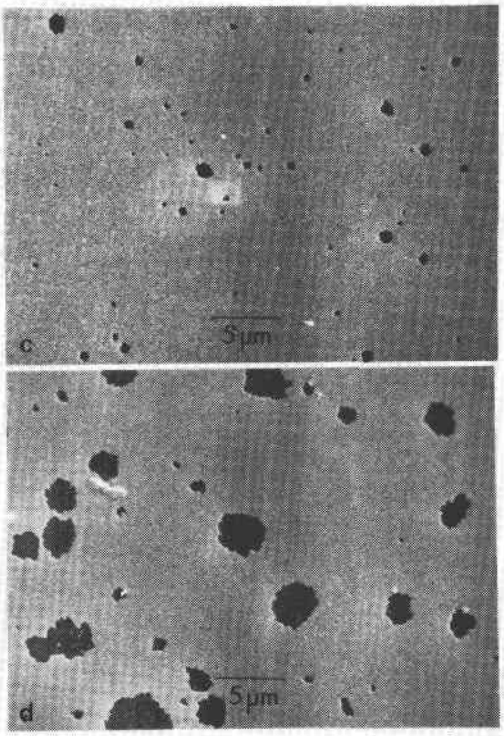


**Figure 3-6** Scanning Electron Micrographs of Silver Films on Float Glass Exposed to 1000 ml of Distilled Water at 90°C (Vitko 1982)

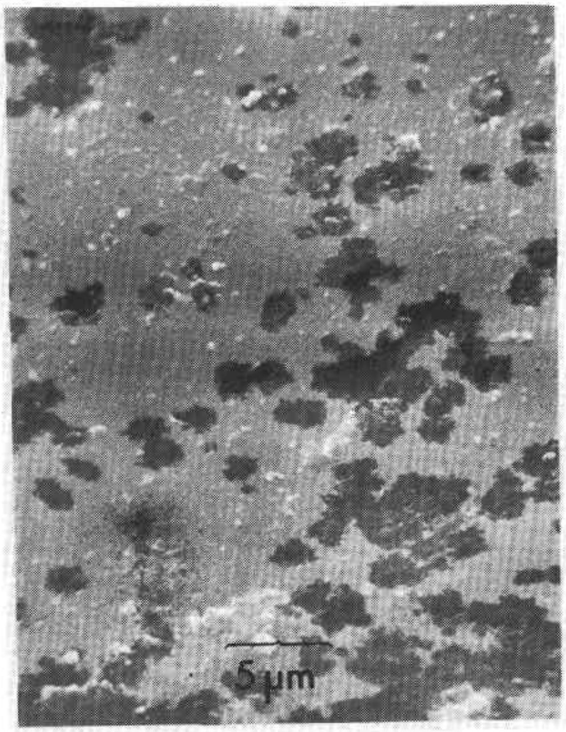


**Figure 3-7** Scanning Electron Micrograph of a Field-Corroded Mirror (Vitko 1982)

testing of complete mirrors, Coyle (1982) used moist HCl and $H_2S$ vapors to evaluate durability. Failure resulted in 3 to 90 hours in moist HCl and in 200 to 1200 hours in moist $H_2S$, depending on the manufacturer. Daniel (1980) found that degradation of silver occurs first where the copper backing has disappeared, presumably by an ion-forming reaction in which copper ions dissolve into a surrounding aqueous medium or the paint. Pederson (1980) also indicated that copper corrosion precedes that of silver. Mills (1980) interpreted her data as silver diffusion to the copper surface, but the exposure of silver might also have resulted from copper corrosion preceding that of silver. The corrosion products on degraded silver mirrors include Cl, S, C, and O (Czanderna 1978), O, Cl, Na, Ca, C, Sn, and S (Pederson 1980), and C, N, Cl, S, and O (Mills 1980).

Sharma (1978) measured the kinetics of corrosion for Cu, Ni, and Ag coupons in an air-conditioned office and non-air-conditioned basement for up to two years at 22°C. Silver tarnished linearly with time at 3 to 3.5 nm/month with S and Cl as major surface constituents (as AgCl and $Ag_2S$). The data for copper and nickel obeyed a parabolic growth law, and the major constituents detected were O and Cl. Data for Cu and Ni could be duplicated in only one year with an acceleration factor of 100 by using an environmental test chamber, but a correlation for silver corrosion could not be made.

Rice (1980, 1981) studied the indoor (1980) and atmospheric (1981) corrosion of copper and silver in which the concentrations of $SO_2$, $NO_2$, $NH_3$, $H_2S$, $S_8$, $CH_3SH$, $Cl_2$, and HCl were monitored. The corrosion products for indoor exposures were complex mixtures of hydroxides, carbonates, sulfates or sulfides, nitrates, and chlorides. Typical corrosion rates for silver at eight population centers in the United States ranged from 2.8 to 9.0 ng/cm$^2$-h for a 4380-hour period. This corresponds to about five atomic layers of product per day. In a typical mirror, the silver consists of about 230 atomic layers. The atmospheric studies (Rice 1981) were conducted in an environmental test facility in which the amount of $SO_2$, $NO_2$, $O_3$ $NH_3$, $H_2O$, $H_2S$, and HCl were controlled. The rate of copper corrosion is sensitive to the relative humidity, but the silver corrosion rate is not. The copper corrosion rate is influenced by $SO_2$, $H_2S$, $Cl_2$ HCl, and $O_3$. The rate of silver corrosion depends on $H_2S$, $Cl_2$, HCl, and $O_3$ concentrations. For silver, the rate of corrosion decreases in the following order: $H_2S > NO_2 > SO_2 \sim O_3 > Cl_2 > NH_3 > HCl$.

Franey (1981) showed that silver in an epoxy paste reacts rapidly with $H_2S$ to yield $Ag_2S$. Khrusch (1975) produced $Ag_2O$ in oxygen by the photostimulated oxidation of silver films. The wavelength of the photons ranged from 110 to 200 nm at 5 mW/cm$^2$ and 0.5 Å, so it is not known if similar oxidation will occur at solar wavelengths (>285 nm) and intensities (50-120 mW/cm$^2$).

**Silver/glass interface.** Corrosive degradation at the silver/glass interface will obviously result in a loss in reflectance for second-surface mirrors. Thomas (1983) identified Si, Ag, O, Na, K, Sn, and Cl at the silver/glass interface. There are three primary types of corrosion modes at this interface: (1) reactions that result from penetration of reactants through the copper and silver metallization, (2) reactions at the interface from trapped impurities at or near the interface, and (3) exchange reactions between silver and glass with diffusion of silver ions into the glass.

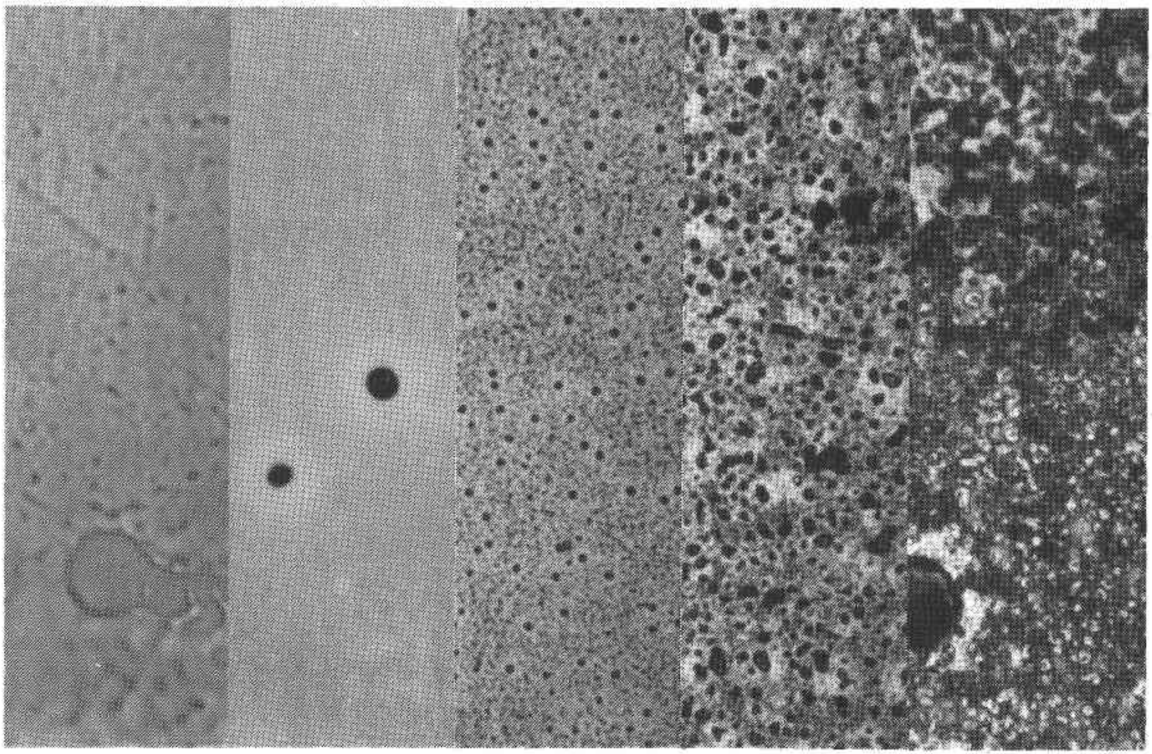
*Penetration through the metallization.* Several observations have been made that have led the observers to conclude that reactants penetrate to the silver/glass interface through the silver, copper, and paint layers. Dark nuclei, as observed visually, have been observed in heliostats deployed at Odeillo, France, Georgia Tech University, the Jet Propulsion Laboratory, and at the CTRF facility at Albuquerque, New Mexico (Bomar 1981; Burolla 1980). Burolla (1980) concluded that the black spots were pinholes formed in the metallization, as illustrated in Figures 3-6 and 3-7, probably by the mechanism proposed by Vitko (1982). However, dark solid phases are formed at this interface and can be seen through the glass by using optical microscopy (Gupta 1982).

These phenomena are illustrated in Figure 3-8, which shows photomicrographs taken through the glass of the same mirror before and after a two-week exposure to degradative parameters. The dark portions, developed at the silver/glass interface, apparently cause the reflectance losses. They are not pinholes but appear to be silver (or silver compound) agglomerates. The combinations of 80°C, $SO_2$, NO, $NO_2$, $Cl_2$(trace), $H_2O$, and UV apparently cause more visual degradation, but the measured optical degradation is not statistically significant (Masterson 1983b). Numerous other visual and optical data are available about corrosion products forming at the silver/glass interface (Lind 1980; Dake 1982; Masterson 1983a and 1983b).

Using surface analysis techniques to probe corrosion pits into the metallization, Pederson (1980) found copious amounts of Cl at the silver/glass interface; it was concluded that an interfacial reaction occurs after grain boundary diffusion of Cl to the interface. Thomas (1983) presented AES depth profiling data to show that copper diffuses through silver to the glass interface within 6 to 12 months. Thus, the visually observed dark products could be either copper or silver compounds formed at the interface.

*Possible reactions at the silver/glass interface.* With potential reactants that are at the silver/glass interface (Sn, Cl, O) or that are available from the near interface region (Ca, Na, K, Fe, Cu, Cl), several reactions can be proposed. Most importantly, Thomas (1984b) hypothesized

$$SnCl_3^- + 2e^- \rightarrow Sn + 3Cl^- \qquad (-0.3\ V) \qquad (29)$$



(a) Unexposed (b) T Only (c) UV plus T (d) Pollutants plus T (e) Pollutants, T, and UV

**Figure 3-8 Photomicrographs of Undegraded Mirror (a) and After Two Weeks of Exposure to Combinations of T, UV, Pollutants, and Relative Humidity** (Gupta 1982)

$\text{Si-Ag} + H_2O + Cl^- \rightarrow \text{Products} \qquad (-0.3\ V) \quad (30)$

$\text{Si-Ag (Interface)} \rightarrow \text{Si (surface)} + \text{Ag (metal)} \qquad (-0.8\ V) \quad (31)$

$Sn + 3OH^- \rightarrow HSnO_2^- + H_2O + 2e^- \qquad (0.91\ V) \quad (32)$

$O_2 + 2H_2O + 4e^- \rightarrow 4\ OH^- \qquad (0.4\ V) \quad (33)$

$\text{(Acid) } Si + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e^- \qquad (0.86\ V) \quad (34)$

$\text{(Base) } Si + 5OH^- \rightarrow SiO_3^{-2} + 3H_2O + 4e^- \qquad (1.70\ V) \quad (35)$

Although equations (16) through (35) are some of the possible half-reactions, it is essential to note that solubilities, corrosion products, and thus e.m.f.'s depend on the pH of the liquid water.

Although reactions (16) through (35) all could take place if the reactants are present, depending on the pH and other kinetic factors, only a select few actually contribute to the observed phenomena such as enhanced mirror degradation in aqueous media (Lind 1980; Bomar 1981; Vitko 1982), impurities detected (Pederson 1980; Thomas 1983), and debonding (Daniel 1980) at the silver/glass interface. For example, breaking the Ag-Si covalent bond requires about -0.8 V. Half reactions, both singular and multiple [e.g., reactions (21) and (23)] with a potential of +0.8 V or greater, could rupture the Ag-Si bond.

It is thought that strong adhesion at the silver/glass interface results primarily from forming Ag-Si bonds, but this hypothesis is not proven. Thomas (198_) emphasizes that a conductor is necessary for electron transport for half reactions occurring at the Cu/paint and silver/glass interfaces. The copper and silver metallizations obviously fulfill this need. Liquid $H_2O$ is necessary for ion transport. Some of the above reactions could be used to explain the improvement of adhesion with aging (Daniel 1980; Bomar 1981; Goggin 1981).

Thomas (1983) also reported that the glass interface is modified during the sensitizer application; i.e., a surface carbonate formed by reaction with carbon dioxide is reduced in concentration by the reaction

$$2\ H^+ + CaCO_3 \rightarrow Ca^{++} + H_2CO_3 \rightarrow Ca^{++} + H_2O + CO_2 \qquad (36)$$

In related studies, segregation of iron in the glass to the silver/glass interface was also reported (Thomas 1983). The implications of an enhanced iron concentration in this region are not known, but its presence may assist the observed cohesive failure in glass near the silver/glass interface.

*Diffusion of silver into glass.* Pederson (1980) published XPS depth profiles showing depletion of $Ca^{++}$ and $Na^{+}$ from 30 nm to 80 nm into the glass from the silver/glass interface (Figure 3-9). Evidence for silver ion diffusion into this zone was also presented by comparing depth profiles into glass and silver on silica. Daniel (1980) claimed that silver penetrates as deep as 500 nm into a glass reaction zone that is considerably enhanced by reactions with water. Exchange of $Ag^{+}$ with $Na^{+}$ in the glass was also reported by Buckwalter (1980) and $Ag^{+}$ diffusion into glass by Mills (1980).

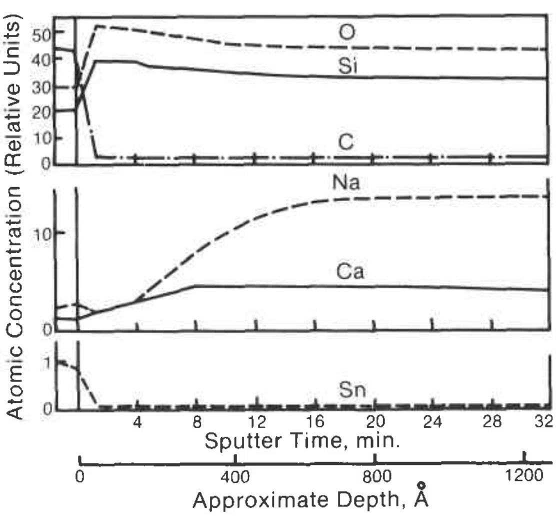


**Figure 3-9 ESCA Depth Profile of the Surface in Figure 3-2** (Pederson and Thomas 1980)

Bastasz (1980) found limited, if any, silver diffusion into glass, but his films were vacuum-deposited. The combination of all the above results suggests that water at or near the interface or trapped impurities may enhance the $Ag^{+}$ formation or diffusion. One of the macroscopic consequences of the ion exchange reaction zone into glass is that cohesive failure occurs through this region. Mills (1980) provided surface analytical data to support the phenomenological observation; i.e., SAM scans showed that Si was present on both sides of the silver/glass interface after forced delamination.

Exchange and diffusion of $Ag^{+}$ and $Na^{+}$ in glass has been studied extensively using molten salts and temperatures of 250°C to 600°C (Doremus 1968; Williams 1975; Kobayashi 1978; Shaisha 1981). Diffusion penetrations of up to 0.1 mm have been measured; Williams (1975) presented a diffusion model. Some interesting EPR techniques were employed by Kobayashi (1978) that could be applicable to the silver/glass mirror problem. Han (1978) used the radioactive isotopes $^{22}Na$ and $^{110}Ag$ to secure the diffusion coefficients $D_{Na}$, $D_{Ag}$, $D_o$, and $E_D$ at temperatures as low as 100°C for several glasses.

The aggregation and migration of ion-implanted silver in a lithia-alumina-silica glass were studied by Arnold (1977) using RBS. Colloidal aggregates were formed during implantation at room temperature and also during annealing up to 350°C.

Gotz (1972) used IR and microgravimetric analysis to measure the solubility of water in commercial float glass from 1200°C to 1470°C. Gottardi (1972) measured the kinetics of extracting $Na^{+}$ from float glass with $H_2O$ by using a nuclear reaction analysis technique. Concentration profiles for Sn and other components were also obtained.

**Glass weathering/solarization.** Solarization of glasses alters the optical properties by inducing chemical changes of the constituents in glass. Vitko (1980) discussed the magnitude of this effect and found a 2.5% improvement of the transmittance, presumably resulting from the conversion of $Fe^{+2}$ (solar absorbing) to $Fe^{+3}$ (nonsolar absorbing). Lind (1980) found that only minor changes occurred in the optical properties of glass after 40 years.

Weathering will result from compositional changes of the glass by attack from atmospheric constituents, primarily water vapor. In its simplest form (Higginbotham 1980), hydrolysis of the surface occurs by

$$\equiv\text{Si-O-Na} + H_2O \rightarrow \equiv\text{Si-OH} + Na^{+} + OH^{-} \qquad (37)$$

followed by, providing the leached alkali is not removed from the glass,

$$\equiv\text{Si-O-Si}\equiv + OH^{-} \rightarrow \equiv\text{Si-OH} + \equiv\text{Si-O}^{-} \qquad (38)$$

A more complete discussion of weathering is given by Hench (1982).

A recent bibliography on weathering was assembled by Godron (1976); the text is in French, but the 101 references, 20 tables, and several figures and reaction mechanisms are valuable assistance. An earlier review by Jelli (1974a) with 26 references is also in French. Isard (1981) compared weathered glass surfaces with leached ones and concluded that the surface reactions proceed by different mechanisms.

Hench (1982) emphasized the necessity of using surface analytical techniques such as AES, SIMS, NRA, XPS, IR, and secondary ion photoemission spectroscopy to monitor the changes in glass composition and to relate these to weathering phenomena. Examples of recent studies using AES on weathered glass surfaces are those by Chappell (1974), Gjostein (1973), and Shelby (1980b). The techniques of RBS (Della Mea 1978), XPS, XRF, ellipsometry, ionoluminenscence (Colombin 1976), XPS (Matsumoto 1981), and transmission electron microscopy (Doremus 1976) have also been employed to study surface compositional or particle size changes at or near glass surfaces.

Finally, Komppa (1978) found that glass-surface durability was greatly improved by storing glass for a few weeks before heat-treating it at 300°C. A hint that a vertically integrated mirror industry might be desirable could be gleaned from this comment and from those given in Bomar's (1981) document.

**Discussion of corrosion in the mirror system**. Segregation of glass components to the silver/glass interface (e.g., iron compounds), together with the formation of a gel layer, in time could weaken the glass structure at this interface. In fact, examination of different glasses, silvered by using several different methods and subjected to adhesion fracture tests at SERI and by others (Buckwalter 1980), revealed that cohesive failure of glass occurred instead of adhesive failure at the silver/glass interface.

Segregation of paint components to the copper-paint interface may initiate copper degradation, but none of the electrochemical reactions that could take place within the copper layer should be able to cause degradation reactions within the silver layer. Since the silver layer is also observed to undergo dissolution if one assumes a basic pH environment, two possibilities are presented. First, chloride from the paint lowers the potentials needed to cause silver to react, and this reaction will continue as a favored process until the chlorine is exhausted. Secondly, copper diffusion into the silver and then its reaction with oxygen at the silver surface and grain boundaries causes unreacted metallic silver to agglomerate. At elevated temperatures, increased oxygen absorption by metallic silver may enhance this degradation.

Thus, under basic pH conditions, the supply of oxygen and chlorine together, even though the chlorine quantity is limited, may account for the total corrosion or dissolution of the Ag/Cu metallic layer which occurs in accelerated tests within eight weeks (Masterson 1983b). To corrode silver under acidic conditions, only $O_2$ and $H_2O$ need be present (Vitko 1982). The paint delays direct attack on the metallic layer but may contribute to enhancing edge attack by providing $Cl^-$ ions. The diffusion of copper into the silver may be the rate-determining step in silver corrosion under basic pH conditions during accelerated testing.

The impurities observed to be trapped in the copper layer, at the copper/paint interface, and at the silver/glass interface, are factors in reducing mirror lifetime from a goal of 20 years. The variability of impurity levels may be the primary reason some mirrors fail long before others, even when made by the same manufacturer (Lind 1980; Pohlmân 1980; Masterson 1983a). For example, water trapped at the silver/glass interface can be converted by electrochemical reactions or ion exchange reactions to hydroxide ions which can then attack the glass. According to equation (9), reduction of tin chloride complexes at this interface will also release hydroxides to attack the glass. Calcium hydride and iron trapped in the copper layer can participate in reduction reactions as long as water or counter ions are available. A calcium hydride reaction with water releases enough energy to cause energetic side reactions in the glass that could affect silver-silicon bonds at the silver/glass interface. Thus, if the paint sealed out everything but water, even at the edges, degradation due to impurities could still take place as soon as the water diffuses to the metallic layers or interface regions.

**Dust**. The reflectance of mirrors is adversely affected by surface soiling, and generally the loss in performance increases with the amount of soil accumulated on the glass surface. The rate of dust accumulation depends on the site location, the stowed position of heliostats, mirror type, weather, etc. (Cuddihy 1980). Most importantly, the adhesion of dust to glass is a basic surface chemical reaction that has been studied only obliquely. Cuddihy (1980) indicated that the following criteria appear to be required for mirrors and photovoltaic cover plates: hard, smooth, hydrophobic, low-surface energy, and chemically free of sticky materials and water-soluble salts. Low-soiling environments or site locations should have low concentrations of organic vapors, frequent rains, low dew and relative humidity, and few dew cycles. The current evolving strategies include cleaning and washing; Morris (1980) discussed cleaning methods to test the feasibility of implementing the strategy. Measured reflectance losses resulting from dust accumulation have been reported for mirrors located in a variety of environments by Pettit (1978), Blackmon (1978), Morris (1980), and Roth (1980).

**Mechanical stresses**. Degradation in performance may result from various physical processes that are combined in this paragraph as mechanical stresses. The strength of glass can be changed by impact of sharp particles (Wiederhorn 1979a and 1979b) or by water vapor that alters the crack velocity growth from residual stresses in the glass (Zwissler 1981). In actual use, stresses will be induced in the glass by wind loadings on the heliostat, temperature extremes, and thermal cycling (Bomar 1981). Shrinkage of the paint may also produce stresses, so debonding at the silver/glass interface can result from a variety of mechanical stresses. Generally, the weakest part is not the zone near the silver/glass interface, but in the glass. The stress sensitivity of the glass/Ag/Cu multilayer stack is also indicated by attempts to use thick copper films which cause delamination at the silver/glass interface (Bomar 1981).

## Influence of Degradative Processes on the Properties of Mirrors

**Optical reflectance**. The most important aspect of a heliostat is the optical efficiency (see Chapter 2) that directly affects the energy gain of the central receiver. Optical losses can quickly limit the cost-effectiveness of a central receiver electrical generation system.

Optical losses can result from $Fe^{+2}$ absorption in the glass, defects in the glass introduced or excluded during processing, debonding, and dust accumulation. These losses seem to be "designed-in" from economic considerations. For example, low-iron float glass is less expensive than float glass with no iron present. The selection of float glass does not permit flexibility for minimizing manufacturing defects, nor does it provide a means of choosing a surface that is not reactive with dust. Furthermore, paints that can be applied to copper are numerous and inexpensive, but almost none can bond to silver with any durability. Thus, economics suggest using the inexpensive glass and leaving the copper layer intact but minimizing it.

Other losses in reflectance result from chemical processes in the multilayer stack. Scattering centers or pinholes develop at the silver/glass interface because of corrosion. Diffusion of silver into the glass may reduce the thickness to less than about 55 nm, which is the calculated uniform thickness needed to yield a 97% reflectance for a pure silver film. Interdiffusion of copper and silver may also change the reflectance from that of silver to that of a Ag/Cu "alloy." Impurities entrained at the silver/glass and copper/paint interfaces can result initially in debonding at the silver/glass interface, which is a consequence of the reactions, to produce optical losses. Finally, the entire metallization may be destroyed by corrosive reactions.

Because of the stacked makeup of the mirror, corrosive attack begins at the paint/copper interface and works toward the silver. If the mirror is free from pinholes, the progress of corrosion is restricted to the gradual movement of chemical reactions through the metallizations. Only after the silver is corroded so that its thickness is less than that needed for good reflectance does failure occur. Failure is seemingly sudden. Thus, many of the mirrors within a heliostat field that had been performing satisfactorily for years can fail precipitously within weeks or months of each other.

**Mechanical strength**. Various chemical reactions and physical processes can cause mechanical stresses that ultimately reduce the system performance. Obviously, stresses that cause failure in the glass are not desired, and these do not seem to be a serious problem. However, the glass near the silver/glass interface can easily become weakened by the corrosive reactions with the metallization, causing cracking not found in pure glasses. The shrinkage of paint can result in exposing the metallization to premature corrosion, or it can cause debonding at the silver/glass interface if adequate stress relief is not provided through the ductile metallization. A potential problem is the effect of weathering on the hail impact strength of the glass, but little information is available.

## Mirrors Made Using Vacuum Processes

The preparation, degradation, and influence of degradation on the properties of silver/glass mirrors made using vacuum processes have been studied only recently, compared with those described previously in this chapter. The preparation method is much less involved, and using vacuum offers better opportunities for securing a mirror with a 20-year lifetime. The basic steps for preparing mirrors by vacuum process methods consist of selecting the glass substrate, cleaning and processing its surface, silvering the glass, and applying a backing to protect the silver from the environment.

## Preparation of Mirrors in Vacuum

**Glass**. The criteria for selecting a glass for solar applications are the same as those discussed in Chapter 2. For vacuum processing, however, the glass thickness can be chosen to accommodate high-throughput vacuum technology. Thin glass with minimal losses from $Fe^{++}$ absorption (Figure 2-3 in Chapter 2) or Corning 7809 (Coyle 1981b), where iron is in the nonsolar absorbing ferric state, become options that are not as easily adapted to the chemical-process mirroring equipment.

The glass surface must have the gel layer removed and be cleaned prior to insertion into the vacuum chamber. Polishing steps similar to those previously described may be used, followed by using standard cleaning treatments for objects to be placed in a vacuum (Baouchi 1983). Borisova (1973) used radio frequency processes to remove the gel layer. After insertion into the vacuum chamber, sputter cleaning of the glass substrate may also be employed (Holland 1956). No systematic study of the influence of glass cleaning on the properties of vacuum-deposited silver mirrors for solar applications is known to be published.

When a suitable vacuum has been reached; e.g., ca. 0.1 Pa, the silver layer can be deposited by one of several methods. Those methods found in recent literature include sputtering, thermal evaporation, and ion plating.

**Silver deposition.** *Sputtering*. Sputtering is a process in which the material to be deposited is bombarded with energetic ions ($\sim$ 2 to 10 keV). Atoms from the target are ejected and deposited onto a substrate positioned properly for collecting them. Although Kienel (1981) did not prepare silver mirrors, he describes an automated cathode sputtering system that can be used for making mirrors 10 $m^2$ in size. He also cites a number of advantages of sputtering over thermal evaporation processes. Fan (1981) prepared glass/$TiO_2$/Ag/$TiO_2$ multilayers by an r.f. sputtering method. Since his objective was to secure partially transmitting multilayers, the silver layer was only 13 nm thick. The same method could be adapted easily for making mirrors.

Hartsough (1977) used planar magnetron sputtering at rates above 12 nm/s to prepare 100-nm thick aluminum films with reflectances as good as those made by thermal evaporation. Pitt (1981) used r.f. sputtering to prepare planar optical waveguides on microscope slides, but also prepared samples in which $Na^+$ ions in glass were replaced with $Ag^+$ using field-assisted diffusion. Thus, an alkali pre-depleted zone could be replaced with $Ag^+$ followed by silvering the glass to make a mirror rather than a waveguide.

Adams (1979) prepared co-sputtered films of silver and aluminum for reflector applications. The method could be adapted to preparing reflecting films of graded composition and desired properties. The reflectances of all the Ag/Al alloys were less than that of pure silver.

Carmichael (1975) described an apparatus for the continuous production of sputter-coated glass products, such as glass sheets. Typically, the glass could be ion-bombarded for cleaning before deposition of films. Multiple coatings could be applied by using vacuum locks between several chambers.

Jorgensen (1980) lists 25 mirrors that were prepared by sputtering 100 nm of silver onto soda-lime and Corning 7809 glasses. Different backing metals were used, as well as paint. The mirrors were subjected to salt spray and HCl acid-vapor accelerated tests. Masterson (1983b) also subjected sputter-deposited silver mirrors to accelerated testing at 80°C in 80% RH, with $SO_2$ and $NO_2$ pollutants, and with UV exposures.

*Thermal evaporation.* Vacuum evaporation of silver onto a substrate results from heating silver metal in a boat, basket, or other evaporant holder for deposition onto a substrate. The process is simple and excellent for laboratory work, but not as adaptable to production processes as sputtering. Films made by other processes are usually measured against evaporated films as the standard. Silver films with 97% solar-weighted reflectance have been routinely prepared (Call 1980).

*Ion plating.* With ion plating, the substrate is used as a target for stopping ions accelerated at a source. The material liberated from the source drifts to and coats the surface to be plated. Ion-plated silver mirrors were prepared in the following manner (Lind 1982): Ions were evaporated into an argon-defined r.f. plasma from a boat near ground potential. The glass substrate was biased at 500-700 V, and multilayer stacks were prepared with typical thicknesses of 100 nm of silver/100 nm of silver plus another metal and an overcoating metal alone (OMA) where the OMA thicknesses were 400 nm for Cr, 1000 nm for Ni, 1000 nm for 304 stainless steel, 1500 nm for Al, and 1500 nm for an Al (35%)/Cu (65%) alloy. Soda-lime silicate and Corning 0317 glasses were used as substrates. The reflectances were typically 89% to 91%. The mirrors were subjected to accelerated testing. Yoshihara (1977) also prepared ion-plated silver films on various substrates, but not on glass. Generally, the properties were comparable with those of r.f. sputtered films.

## Degradation of Mirrors Prepared in Vacuum

Several sputter-deposited silver mirrors subjected to salt spray and HCl accelerated degradation provided comparable durability to a chemical-process mirror used as a control (Jorgensen 1980). The (glass/silver/backing/paint) configurations that met acceptance are: 7809/silver/stainless 304/paint; 7809/silver/Inconel/paint; soda lime or 7809/silver/copper/paint; soda lime or 7809/silver/Mo/paint; and 7809 silver (chemical process)/copper/paint (control). Sputter-deposited silver mirrors did not survive accelerated tests nearly as well as the best chemical-process mirrors that were used as a control (Masterson 1983b). There were no accelerated tests of mirrors made by Lind (1982) or Masterson (1983a and 1983b) using thermal evaporation.

No standard-stack ion-plated mirror performed as well as the standard chemical-process mirrors, but glass/Ag/Cu/Ni (electroless)/paint mirrors showed promise of being more durable than the durability of the standard chemical-process mirror (Lind 1982).

## Influence of Degradation Processes on the Reflectance

No studies of the mechanisms of degradation have been conducted on mirrors made by vacuum processes. Solar-weighted reflectance is the only property used to measure the survivability in the three sets of accelerated tests (Jorgensen 1980; Lind 1982; Masterson 1983b). In all cases, reflectance decreases from its initial value as the silver corrodes in the environmental exposure or as scattering centers are formed at the silver/glass interface.

Hass (1975) used vacuum processes to prepare a multilayer stack of substrate/$Al_2O_3$/Ag/$Al_2O_3$/$SiO_x$, where the substrate glasses were silica, polished Cer-Vit, and fire-polished microscope slides. The $Al_2O_3$ and $SiO_x$ thicknesses were 30 nm and 100-200 nm, respectively. The original reflectances exceeded 95%; after passing a transparent tape adhesion test, the mirrors were tested at and survived a 195-hour exposure to moist $H_2S$ at 20-25°C without a measurable loss in reflectance.

## Mirrors Made Using Organometallic Solutions

The reaction that deposits silver from an organometallic solution is basically a thermally induced destructive oxidation-reduction reaction. At elevated temperatures of 200°C to 700°C, depending on the proprietary organometallic solution used, the organic ligands that complex the silver atoms or ions decompose. Since the decomposition products are usually volatile at elevated temperatures, they evaporate and metallic silver is left as a coating on the heated substrate. This process is in use but mainly for manufacturing films used as anti-glare, heat-reflecting, or decorative coatings. The organometallic process is slightly more expensive and gives slightly less reflective films than the electroless "wet" process.

## Mirror Preparation

**Glass**. As in the glass processing cases described above, the substrate is cleaned or polished. Advice for cleaning the substrate is often available from the manufacturer of the proprietary solution.

**Silvering**. Numerous manufacturers make organometallic silvering solutions; a recent listing is given by Schweig (1973). Although the exact composition is proprietary to each supplier, the solutions usually contain metal resinates or sulforesinates in organic solvents. For further details, a search of the patent literature is required. Langley (1974) published some background information on organometallic processing and included a complete literature review through 1965.

For silvering a cleaned glass substrate, the solution is sprayed or spun onto the surface by dropping the thick paste into the center of the rotating surface of the glass; the angular rotation of the substrate spreads the solution over the surface, which may or may not be heated at this stage. If it is at room temperature, the substrate is then heated to initiate the decomposition of the solution. Once the reaction has gone to completion, the substrate is cooled and the remaining steps of the manufacturing process are completed to obtain a finished mirror.

Using solutions and mirrors made by Englehard Corporation, reflectances of 85% to 93% were measured on Corning 7809 and 0371 glasses (Pitts 1984b). The silver thicknesses were 300-nm to 600-nm thick, which is 5-10 times more than is necessary to obtain the maximum reflectance of silver in a thin film.

**Protective backing**. The same options used for backing chemical-process mirrors are available for organometallic mirrors. Paints, lacquers, and enamels are frequently employed.

## Properties and Mirror Durability

The adhesion of organometallic mirrors is comparable to that for silver on sensitized glass. The limited data available suggest that the interfacial bonding of the silver to the glass is extensive and that the failure due to stress is always within the glass near the interface and not at the interface itself. Corrosion studies show that unbacked organometallic mirrors resist attack better than some backed vacuum-deposited mirrors. This probably results in part from the thickness of the film (up to 700 nm) as well as its strong interfacial bonding. The strong bonding is likely caused by depletion of oxygen from the glass surface during decomposition of the organometallic (Pitts 1984b); the reactive surface permits silver to form bonds with silicon from the glass, resulting in a strong interfacial bonding.

Accelerated testing of organometallic mirrors made with and without an adhesion promoter by the Engelhard Corporation was accomplished by Masterson (1983b). Their durability was shorter than for the chemical-process mirrors, but it is not known if the durability to accelerated degradation was a direct correlation to lifetime for normal use.

Research topics associated with organometallic mirrors include reflectance enhancement, minimizing the thickness of silver, and eliminating voids in the films (Pitts 1984b). The strong adhesion and simplicity of processing are attractive potential advantages.

## Mirrors Made Using Other Processes

In this section alternative silvering steps in a mirror preparation sequence will be cited. None of these is known to be in current widespread use, nor are any durability properties or degradation mechanisms known about them.

Electroplating silver from solutions is described in numerous textbooks on electrochemistry. It was replaced by the chemical process primarily for economic reasons (Schweig 1973). It is not known if a recently patented process for high speed electrodeposition will alter the economic factors (Rymwid 1981). No known chemical vapor deposition (CVD) process is known for depositing silver onto substrates (Schweig 1973). CVD processes exist for depositing Ni, Cr, As, and Al, but these all have lower solar-weighted hemispherical reflectances than silver.

Hamm (1977) patented a process in which a mixture of $KNO_3$, $NH_4OH$, $AgNO_3$, $CH_3CHO$, and water glass is heated from 195°C to 300°C in a mold. Maruno (1977) described a process for forming silver deposits from an $As_{15}S_{40}Ag_{45}$ glass by using a photosurface deposition technique; the process might be applicable for optical storage devices.

Ultraviolet laser-induced deposition of metal films has been used successfully for making Zn and Mg films on transparent substrates (Coombe 1980), and cobalt oxide on glass (Steen 1978). According to Steen (1978), the method has broad applicability for making metal and metal oxide films on substrates. The basic chemistry requires a thermally sensitive chemical to be blown onto the hot spot or pattern produced by the laser.

## Protective Coatings for Reflectors

Call (1980) presents a broad overview of reflector materials, including protective coatings, and the application of passive thin films for solar applications. Several recent papers have been published on specific coatings that are being studied for backing silver mirrors. These are all from the comprehensive summary of possible coatings (Dake 1981).

It seems obvious that the solution to silver corrosion is to exclude residues principally by isolating silver between impervious dielectric layers. Hence, it is no surprise that most efforts are directed toward depositing oxides such as $Al_2O_3$ (Davies 1971; Wille 1971; Adams 1972; Hass 1975), cuprous oxide (Franz 1976; Breininger 1982), and iron oxide (Franz 1976). Ebert (1982), taking a broader approach, has reactively sputtered $TiO_2$, BeO, $In_2O_3$, $SnO_2$, and $SiO_2$ onto glass substrates; his methods could be adapted to silver mirrors. Pearlstein (1979) deposited Rh onto silver to isolate it from reactants. Mattox (1980) reviewed briefly the various vacuum methods available for depositing coatings onto various substrates. Lebert (1980) favors sandwiching silver coatings between two glass panels whenever possible.

Recent papers dealing with organic coatings for copper or silver metals and a discussion of their performance include using benzotriazole on copper (Notoya 1979), plasma-polymerized organosilanes on silver (Bieg 1980), silicone resins on first-surface silver (Dennis 1980), and polymer-based ceramics for backing mirrors (Borisova 1975).

## Adhesion Enhancement

Adhesion at all interfaces in a multilayer stack is a natural requirement for durable mirrors. In addition to the above discussion about adhesion of silver to glass (e.g., role of silver-silicon bonds in chemical-process, vacuum-deposited, and organometallic mirrors), some recent specific studies were identified. Brewis (1967) discussed the surface properties associated with adhesion between metals. Larry (1975) used NiO to improve silver adhesion onto substrates and extended his work (1976) to include PbO, CaO, $Al_2O_3$, $B_2O_3$, $SiO_2$, and $Bi_2O_3$. The intended application of his efforts was toward conducting metallizations rather than preparing solar mirrors. Borisenko (1974) studied the effect of $H^+$ ion bombardment on the adhesion of silver films to glass.

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# Chapter 4

# Mirror Product Testing Procedures

## Introduction to Product Testing

The optical performance requirements for mirrors used as solar concentrators has been detailed in earlier chapters of this document. Briefly, reflectors used in solar concentrators should have a solar reflectance of at least 90% and, preferably, as close to 100% as possible. The mirrors must be highly specular so that the reflected beam of light reaches the solar thermal receiver's absorbing surface without meaningful loss due to scattering. In addition, in order to be cost-effective, these desirable optical properties should be maintained over a 20-30 year service life during which the component will be exposed to outdoor weathering conditions that are diverse and sometimes severe.

These requirements for solar concentrator applications are considerably more stringent than the performance requirements that the established domestic mirroring industry has had to meet in the past. The past performance requirements were directed toward mirrors used primarily for cosmetic and decorative purposes in an indoor environment. Visual appearance has been the primary concern and the basis for quality control and testing in the domestic mirror industry. Such test criteria are of questionable value for determining mirror performance and durability for the more demanding solar concentrator applications.

In general, a formal product testing program should have three fundamental objectives: (1) a near-term goal is to rank the performance of competing products in order to meet advertising or procurement requirements; (2) an intermediate goal is to develop a testing methodology for predicting the useful service life of solar concentrator mirrors used in various environmental regions in order that more reliable analyses of their cost-effectiveness and system economics can be performed; and (3) the third goal is to obtain a basic understanding of mirror degradation mechanisms so that the mechanisms can be passivated or designed out of the mirrors in order to obtain outstanding durability. A basic understanding of the degradation mechanisms provides the knowledge upon which more appropriate testing procedures can be developed. Also, limits on the reliability of such procedures can be set.

A thorough and complete testing program that would fulfill the needs embodied in these goals would proceed on several levels. The level giving the most reliable data is to expose mirrors and mirror specimens to natural weathering for many years at the intended solar installation sites. The obvious drawback is that sufficient data to meet the testing needs are not available for many years and probably not in time to influence choices of components for a particular installation. In addition, real-time, long-term testing is insufficient for the near-term goal of developing better mirrors. Long-term testing is most useful in validating degradation models and life-predictive methodologies based on the short-term accelerated or abbreviated tests.

Abbreviated tests expose mirror materials to natural weathering or controlled environments that simulate natural weathering. The appropriate mirror properties, such as reflectance and degradation products, are determined with a high degree of accuracy. The results are extrapolated to longer time periods using an appropriate model. The benefits of abbreviated testing are that data are collected over a short period of time and under exposure conditions that should cause degradation by mechanisms identical to those found in deployed mirrors. The difficulties are that, in general, sensitive and accurate characterizations must be made and the degradation model must be precise in order for the extrapolated lifetimes to be dependable.

In accelerated testing, a mirror or mirror specimen is subjected to exposure conditions that are more severe than those seen in a natural weathering environment. The benefit is that sufficient data to generate a substantial amount of degradation can be collected in a short period of time. This allows a more precise mathematical modeling of the degradation rates. The drawback of accelerated testing is that under severe exposure conditions, a different set of degradation mechanisms from those causing real-life failure may be invoked; although the mathematical model may be well defined, it may be highly inaccurate in determining service life for solar concentrator mirrors. Nevertheless, accelerated testing, because of the quick acquisition of data, is the preferred method of industry and research institutions for testing and developing mirrors and test methodologies. Only after the results from accelerated testing are found to correlate well with real-time, long-term, natural weathering, can one say that a reliable test methodology exists and that the degradation mechanisms are well understood.

## Existing Test Methodologies

The principal market for the domestic mirror industry is for cosmetic and decorative mirrors for which a successful product need only have good visual appearance and a 10-20 year lifetime in rather benign environments. High humidity and condensation does, however, occur often in bathrooms and has resulted in forming black spots and edge blackening. The industry standard for quality control testing is the salt spray test. In this test, mirrors are subjected to a fog of salt water (U.S. Government test DDM411 or ASTM B117). The fog condenses on the specimen and drips off.

Visual inspection of the degraded mirrors by trained individuals is used to measure the mirror performance qualitatively. Although this may serve for quality control and mirror comparisons, it is a poor substitute for quantitative measures of performance needed for solar concentrator engineering. The nation's largest organized consumer, the federal government, does apply specifications and standards for procurement activities. However, these standards (GGG-M-350a, DD-M-00411b, and MIL-STD-105) refer only to attributes such as appearance and construction and to the statistical procedures to be used in acceptance or rejection of products.

Another consumer of mirrors subjected to outdoor weathering characteristics is the automobile industry, whose primary concern is durability and appearance. High reflectance is not required. In fact, it has been found that somewhat lower reflectance, which provides contrast for the mirror in the ambient background, is desirable. Hence, modern automobile mirrors are metallized with chromium or nickel instead of silver. Apparently, the industry also uses a salt spray test to monitor product quality.

The German automobile industry has reportedly used both a salt spray (DIN 50021) and a test that uses alternating damp heat and sulfur dioxide vapors (DIN 50018) for chromium mirrors. The criteria for characterizing mirror degradation are not identified. It is interesting to note that before World War II, a substantial number of silvered glass mirrors were fabricated for use in the auto industry. Testing procedures and qualifications used at that time have not been determined by the authors. Test equipment and sophisticated analysis techniques such as those used in modern surface analysis and ultra-high vacuum technology were not available. The degradation problems, if they existed, were designed out of the system by switching to chromium metallization.

One application for solar reflectors that has received considerable testing is the thermal control of space vehicles. In this application, high solar reflectance was useful to reduce solar heating of spacecraft. In addition, high emittance was desirable to dissipate energy. Extensive testing (Marshall 1968; Hass 1970; Hollingsworth 1977; and Cunningham 1970) was performed on candidate materials in order to determine their suitability for such applications. The environments used to degrade the performance were high fluxes of extreme ultraviolet light and energetic proton and electron beams. For terrestrial applications, such causative agents are inappropriate. The data from the ultraviolet exposure of silvered fused silica are pertinent to testing of silver/glass mirrors and will be discussed later. During the mid-1960s, and in the space program, several ASTM standards for optical characterization of materials were developed.

## Testing Requirements for Solar Concentrators

Because of the unique requirements for solar concentrator mirrors, testing programs that have been established for other industry or consumer uses have been found inadequate. A more thorough and scientific approach to testing is necessary before lifetime predictive methodologies and advanced, more durable mirrors can be produced. Appropriate accelerated tests are required in order that data be obtained in a reasonable length of time; long-term natural weathering tests are necessary to validate degradation models in predictive methodologies.

A first step in an accelerated testing program is based on the best knowledge of the causative agents for degradation. The interactions that lead to mirror degradation and corrosion are probably of an electrochemical nature with physical diffusion through the thin films and interfaces of the mirror's structure. The causative agents may be internal in nature; that is, they may be produced by contaminants entrained during the mirroring process, electrochemical interaction with the paint-protective coatings, or from the basic electrochemical interaction of the various metal layers and glass surface. The causative agents may also be from external sources such as liquid or vapor forms of water, environmental pollutants, elevated temperature, ultraviolet light, or temperature cycling. Degradation may be, in fact, a combination of external and internal causative agents with external agents such as high temperature and water vapor accelerating the internal mechanisms.

## Characterization of Mirror Performance and Degradation

The fundamental performance parameter for solar mirrors is the specular solar reflectance. If the mirror maintains good specular reflectance, changes in other optical, physical, or mechanical properties are less important. In a formal testing program, however, any measurement that leads to elucidation of the degradation mechanisms, which provides an extremely sensitive measure of the onset of degradation, or which can be related easily to specular solar reflectance, is worthy of consideration.

Preferred characterization techniques are sensitive, nondestructive, and relatively inexpensive to perform. Optical reflectance measurements generally meet these requirements. Furthermore, they are directly related to the fundamental parameter of the solar reflectance. Several forms of reflectance measurements have been used to characterize mirror degradation. Diffuse reflectance measurements using integrating sphere reflectometers are sensitive in detecting early degradation. But because of low signal levels, they appear to offer little advantage over specular reflectance measurements. However, measurements of total integrated scatter using a Coblentz sphere could be performed simultaneously with the specular reflectance measurement and would seem to offer useful additional data on the characteristics of degraded mirrors. Table 4-1 summarizes the applicable reflectance techniques, their rationale, and the results of their application to the mirror degradation problem.

In contrast to the macroscopic measurements represented by the optical reflectance techniques, microscopic variations in the degraded mirror specimens have been scrutinzed in several studies. Several electron and ion microscopy techniques, together with the rationale for their use and some results, are summarized in Table 4-2.

Photomicroscopy is a valuable technique for observing mirror degradation. Its primary use is in viewing the degradation and enabling one to identify morphological changes in the various components of the mirror structure. Microscopy is also valuable for observing the light-scattering properties of degraded mirrors. However, the use of these techniques as quantitative measures of mirror degradation is limited because of difficulty in maintaining appropriate exposure and detection levels. The techniques are also too time consuming to be used extensively for quality assurance testing.

Optical photomicroscopy has been used qualitatively to characterize mirror degradation (Lind 1982a; Dake 1982; Masterson 1983a). The necessity to observe the silver/glass interface through the glass superstrate

**Table 4-1 Reflectance Techniques for Evaluating Loss in Mirror Performance**

| Techniques | Rationale | Limitations/Results |
|---|---|---|
| 1. Hemispherical reflectance | Search for surface plasmon effects in roughened silver films for 300- to 800-nm spectral scans | Time consuming for spectral scan. Revealed short wavelengths most sensitive. |
| 2. Hemispherical solar reflectance using portable reflectometer | Hemispherical reflectance is spectrally averaged | Fast, but not as accurate as 1 and 5. |
| 3. Surface enhanced Raman spectroscopy (SER) | Monitor small chemical changes in the silver/glass interface | Difficult to use; signals associated with agglomerated films were reported. |
| 4. Diffuse reflectance | Obtain spectral information sensitive to scattering centers | Not as sensitive as hemispherical reflectance when using typical integrating spheres. |
| 5. Spectral reflectance | Search for Bruggeman and Garnett roughening effects using 300-2500 nm spectral scans | Time consuming; same as 1; allows calculation of solar-weighted reflectance. |
| 6. Specular reflectance using portable reflectometer | Direct measure of the performance characteristic of greatest interest | Difficult to use consistently. Results comparable to other reflectance techniques. |
| 7. Differential laser scans | Monitor differences in reflectances at two laser frequencies to look for chemical or structural changes | Time consuming. Inconsistent correlation with 350-nm vs 650-nm sources. 1:$10^4$ sensitivity. |
| 8. Darkfield photography (100x) | Measure of light-scattering centers | Fast, permanent record. Definite trends that correlate to hemispherical reflectance. |
| 9. Photography (UV) | Monitor local regions of surface plasmon enhancement | Hard to do with conventional light sources; no enhanced regions. |

**Table 4-2 Results Using Surface Analysis Techniques for Evaluating Mirror Degradation**

| Technique | Results |
|---|---|
| Auger Electron Spectroscopy (AES) | Detected significant diffusion of Cu, Cl, and oxygen through the silver film to the glass interface. |
| Scanning Electron Microscopy (SEM) | Revealed agglomeration of silver in corroded areas of mirrors. |
| Ion Scattering Spectroscopy (ISS) | Elucidated the relative amounts of Ag and Sn bonded onto glass after sensitizing and silvering without reducers. |
| Secondary Ion Mass Spectroscopy (SIMS) | Provided first data that suggested Ag-Si bonds are adhesion for glass. |
| X-ray Photoelectron Spectroscopy (XPS) | Identified nature and density of silver/glass bonding sites in uncorroded mirrors and their dependency on preparation techniques. |

limits the magnification to 100x-200x. Nevertheless, the formation and growth of pinholes or other solid phases in the silver layer is readily observable and provides qualitative information on the nature and degree of degradation in the thin silver film. Both darkfield and lightfield illumination have been used. Figure 4-1 shows typical nuclei that formed during accelerated testing. Attempts to quantify the early stages of degradation by counting the density of light-scattering defects, or by determining the fractional area from which the light-scattering signal arises, suffered from the difficulty in reproducibly

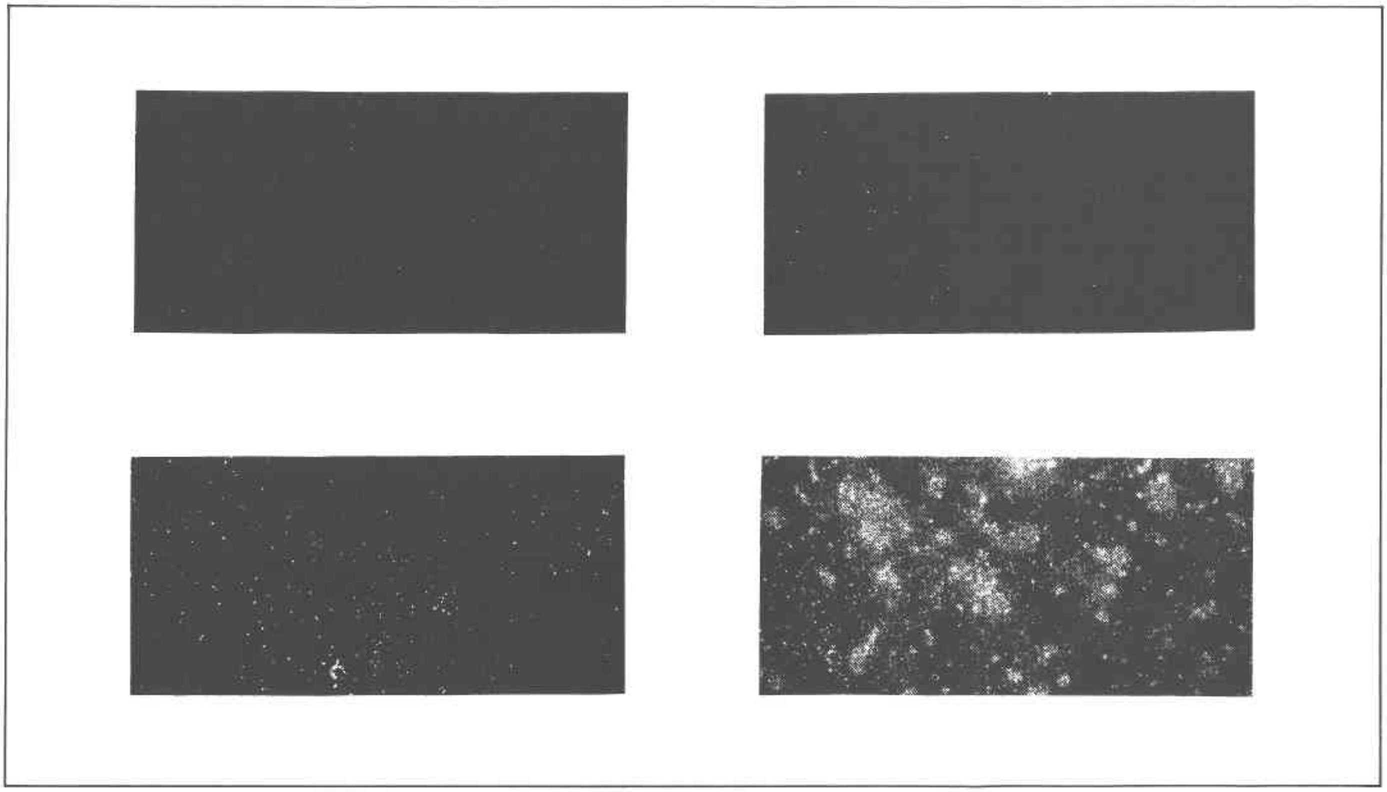

**Figure 4-1 Darkfield Photomicrographs (100x) of Degraded Commercial Mirror** [The exposure periods are as follows: (top, left) unexposed; (top right) after two weeks; (bottom left) after four weeks; (bottom right) after eight weeks.] (Masterson 1983b)

setting the gray scale. This is a threshold level for detection that is critically sensitive to instrument-operating temperatures and specimen illumination levels for commercially available microdensitometers and image analysis systems (Masterson 1983b).

Similar difficulties are experienced in the use of photographic film to quantify the nature and density of defects in the film as a function of exposure time to the degrading environment. The principal cause for this difficulty is the variation in film and exposure characteristics, which is apparently caused by poor control of shipping and storage conditions and times for the films. One further drawback of any attmept to quantify mirror degradation by photomicroscopy techniques is that the degradation in commercially produced silver/glass mirrors varies substantially from one location on a specimen to another, and within a few millimeters. Thus, great statistical uncertainties appear unavoidable.

The presence and quantification of light-scattering defects in mirror specimens can be more easily accomplished using sensitive diffuse reflectance measurements such as the total integrated scatter method described by Bennett (1978). The application of this method to quantifying degradation of mirrors for solar concentrators under accelerated exposure or natural weathering conditions would appear promising, but, as yet, it has not been attempted.

## Results of Exposure Testing

Various natural weathering and accelerated exposure tests have been performed in attempts to rank the durability of candidate silver mirrors and to assess their long-term performance in solar applications. Accelerated testing has been carried out in both liquid- and vapor-phase environments.

### Natural Weathering

Natural weathering tests are necessary to identify the degradation processes that should be accelerated during laboratory level durability studies. They are also necessary in order to provide long-term weathering data that can be correlated with short-term results in order to validate short-term testing and degradation models. Outdoor weathering tests were begun in the solar energy program by Honeywell (Rausch 1978) and by the Illinois Institute of Technology Research Institute (Gilligan 1979 and 1980) at various sites within the United States. Many of the materials were exposed at DSET Laboratories, Inc. near Phoenix, Arizona. DSET Laboratories is continuing the exposure and evaluation of several of the reflector materials included in the earlier studies.

In exposure tests, specimens of mirror materials are mounted on exposure racks and their reflectance is measured periodically. In the Honeywell experiments, specimens were also mounted at the focus of solar concentrator test facilities (ASTM E838-8) and exposed to solar radiation levels of eight times the natural exposure level. During such exposure, specimens accumulated total radiation amounts equal to 25 years of natural weathering. Modeling of the initial results for degradation in reflectance by Honeywell (Rausch 1980), using a modified Weibull function, was successful in describing the onset of degradation in reflectance.

Long-term exposure and carefully standardized optical measurements are necessary before this preliminary analysis can be verified adequately. Exposure tests for shorter periods of time have been conducted by McDonald-Douglas (Morris 1980) on test racks located at a number of sites selected for solar industrial process heat demonstration projects. Although degradation in the silver reflector layer was observed and measured, more significance in this study was placed on soiling and cleaning problems that were site specific. A common problem in many of the mirror degradation studies is a lack of standardization in the reflectance measurements, and thus, it is difficult to compare the results of the different experiments.

Another form of natural weathering tests, which is a good source of information, is the deployment of full-scale heliostat modules at a number of test sites and demonstration projects. Degradation observed in these modules provided the impetus for the laboratory degradation studies. It has been useful in establishing appropriate laboratory exposure and test procedures (Burolla 1980; Daniel 1980; and Shelby 1980). Degradation in these modules was severe in cases where liquid water was trapped in the structure. This observation and subsequent tests have led to a significantly better understanding of the role of water in the degradation process. Another important contribution of outdoor weathering programs is that specimens with long-term outdoor exposure are becoming available for detailed analysis and for comparison of degradation mechanisms to those observed in laboratory-accelerated tests.

### Liquid Phase Testing

Liquid phase testing of solar mirror materials has been conducted in several configurations. Specimens have been completely immersed in synthetic seawater (Pohlman 1980) and in deionized water; both, with and without dissolved oxygen (Vitko 1982). The latter tests were conducted at temperatures up to 90°C and produced pinhole formations similar to that observed in field-exposed mirrors except for an absence of agglomerated silver particles in the corroded spots (Figure 3-6 in Chapter 3). Degradation was substantial only when oxygen was dissolved in the water. This result is consistent with an earlier experiment where a cup, partially filled with water, was bonded to the back side of a mirror specimen which was then placed in a vertical frame (Burolla 1980). The results of this partial immersion indicated corrosion. Degradation was more severe when the ratio of the volume of air to volume of water was large than when the ratio was small. For large ratios, the amount of available oxygen is substantially higher.

Alternate immersion tests and salt spray exposures using techniques similar to that of many mirror manufacturers have also been used in laboratory studies of mirror degradation. These tests were done to help evaluate liquid cell electrochemical techniques for ranking the durability of commercially made silver mirrors (Pohlman 1980). The results of the electrochemical testing were encouraging since a good correlation in durability was obtained with rankings made using other tests. Furthermore, the electrochemical testing can be done in a few hours as compared to many days required for other accelerated lifetime testing methods or to many years required for real-time weathering studies.

In a reported test (Pohlman 1980), a scratch was made through the paint and metal layers so that the interfaces were exposed to the electrolyte in the cell; then the electrochemical potentials and corrosion currents associated with the metalizing layers were characterized. Since a field study of mirror degradation must also include the ability of the backing paint to protect the metalization from corrosion, additional studies to determine the permeability of the paint to water vapor and ionic transport would be necessary to supplement the electrochemical test before a realistic lifetime predictive methodology could be established. Nevertheless, the approach looks promising and would warrant further consideration in future studies of the mirror degradation process.

## Salt Spray Test

Standardized salt spray tests (ASTM B117-73) are used by the mirror industry (Bomar 1981) to assess the durability of developmental mirror systems and for quality control of production mirrors. Unfortunately, many of the results of these studies and the experience gained from such tests are considered proprietary by the various manufacturers and none of the work was found referenced in the literature survey. Qualitative information on degradation rates obtained from industry representatives, the results of the liquid- and vapor-phase exposure testing, and the degradation models proposed elsewhere in this report indicate that salt spray exposures are worthy of further study. This test has the necessary elements of high humidity, liquid phase water with substantial dissolved oxygen, and electrolytes. It has the potential to be used at elevated temperatures which makes it an attractive method for accurate accelerated testing of solar mirrors. Any future program to assess mirror degradation and predict mirror service life should give the salt spray test serious consideration for either direct application in the testing process or should modify it to more nearly meet the requirements of testing for solar mirror materials.

## Vapor Phase Test

Concern that liquid phase testing of solar mirror specimens might be too severe and that it does not realistically model the actual outdoor exposure conditions has led several researchers to conduct an accelerated exposure test where the mirror specimens are subjected to environments characterized by water and pollutants maintained in a vapor phase. Strong vapors of sulfuric acid and hydrochloric acid degraded mirrors quickly (Coyle 1982). Hydrochloric acid vapors were more effective in causing rapid degradation. The acid vapors attacked the backing paint protective layer on the mirror specimen with some diffusion of ions to the metalizing layers. Whether or not such a severe environment is appropriate for ranking mirror performance or predicting mirror lifetime is yet to be established. A similar test (DIN 50018), in which specimens are alternately subjected to high concentrations of sulphur dioxide and 100% humidity at 40°C, is reported to be used by some German auto makers for testing rearview mirrors. No further data on its use by the mirror industry or any test results were available.

In an effort to study the effects of the solar environment on mirror degradation more systematically, an extensive study associated with individual and multiple degrading agents was initiated under SERI's leadership (Masterson 1983a). In planning and coordinating this project, SERI was assisted by personnel from Sandia National Laboratories (SNL) and Pacific Northwest Laboratories (PNL). A considerable amount of laboratory experimental work and mirror characterization was conducted (Masterson 1983a; 1983b; Lind 1982a and 1982b; Dake 1982). In these studies, mirrors produced by several commercial mirroring companies were subjected to environments containing high levels of solar or ultraviolet radiation, $SO_2$ and $NO_x$ pollutant gases, relative humidity, mechanical stress, and elevated temperatures. These agents acted individually or in multiples of two, three, and four to test for synergistic acceleration of degradation. The results are detailed elsewhere (Masterson 1983a, 1983b; Dake 1982; Lind 1982a and 1982b) and will only be summarized here.

The most important results of these studies are that mechanical stress at levels close to those necessary for glass fracture, ultraviolet light at levels greater than 10 times those in the solar spectral irradiance below 310 nm, and pollutants at levels near 100 times the maximum allowed by EPA for one-hour human exposure caused little or no degradation in mirror specimens after exposure of up to eight weeks. There were also no synergistic effects observed where the exposure to these agents caused any degradation that was more rapid than the exposure to the high temperature and humidities alone.

In carefully controlled experiments (Masterson 1983a, 1983b; Lind 1982a, 1982b), eight weeks exposure to 80°C and relative humidity greater than 75% resulted in a degradation in hemispherical solar reflectance of up to 0.15 reflectance units in typical silver/glass mirrors (Figure 4-2). Degradation was accelerated at the high relative humidities where monolayers or greater of condensible water formed on the surfaces of specimens. It is suspected that corrosion rates were not humidity-dependent at lower relative humidities, but the verification of this hypothesis would require more data at the levels of relative humidities of interest.

One unexpected observation was that specimens exposed to the pollutant gases showed less degradation than when exposed to water vapor alone. Among several possible explanations for this, the most likely is that the nitrogen gas purged oxygen from the exposure environment and thus prevented any oxidation-reduction reactions, which may be responsible for much of the observed mirror degradation.

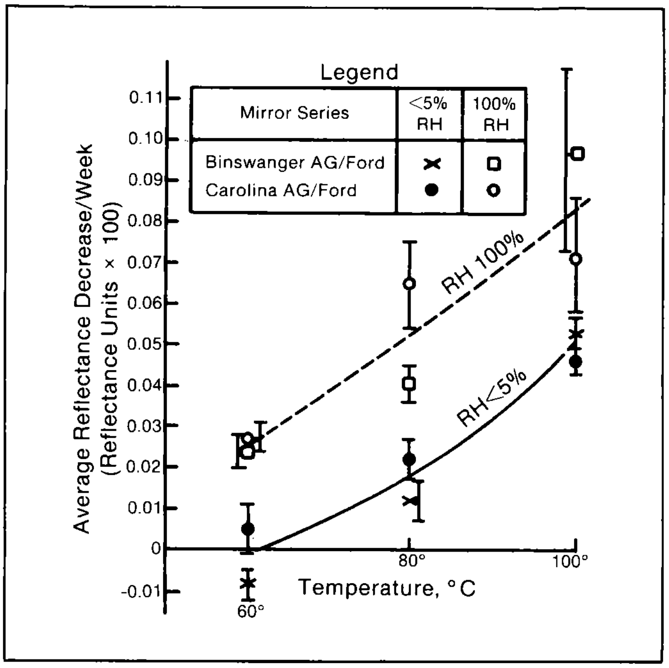

**Figure 4-2 Dependence of Degradation in Reflectance on Temperature for High and Low Relative Humidity Using Select, Quality Commercial Mirrors** (Masterson 1983b)

As part of this study, the ability of several optical characterization methods to detect early stages of degradation and to resolve differences statistically in degradation rates was also assessed. Many of the optical reflectance measurements used were sensitive in detecting mirror degradation. Statistical variations observed in most of the data appeared to arise from real differences in mirror degradation rates rather than from uncertainties in the optical measurements.

Mirror degradation rates appear to vary substantially across distances of only a few millimeters on the same mirror surface. For silver/glass mirrors, the spectral reflectance shows considerably more rapid degradation at wavelengths below 500 nm (Figure 4-3). A wavelength of approximately 400 nm would appear to be optimal for monitoring the degradation of both hemispherical and specular reflectance in silver/glass mirrors. A single measurement of specular reflectance at that wavelength combines degradation effects due to the scattering of light by roughening of the silver metal layer and increased absorptance caused by corrosion products and pinholes.

## High Temperature Exposures

One characteristic observed by photo and scanning microscopy of field-degraded mirror modules was the apparent agglomeration of silver into microscopic size particles in the center of the severely corroded areas (Shelby 1980). Since silver is known to agglomerate readily at temperatures above 100°C-150°C (Czanderna 1975; Presland 1972; Rhead 1963), several laboratories attempted to utilize high-temperature exposure as a mechanism for studying the durability of field-exposed mirrors and to develop appropriate lifetime testing methods (Shelby 1980; Dake 1982; Masterson 1983b).

In one study, exposure of a bare silver film in the ambient laboratory atmosphere at 150°C produced substantial agglomeration in a few hours. This is consistent with studies of silver agglomeration and was used to hypothesize that silver diffusion plays an important role in the degradation process. In the

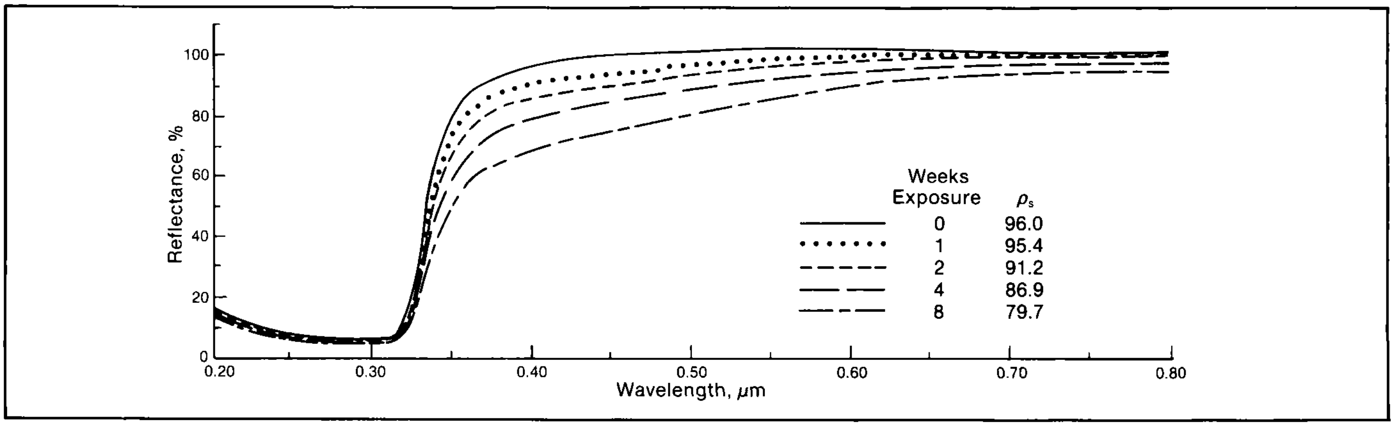

**Figure 4-3 Spectral Hemispherical Reflectance for Different Exposures of a Commercial Mirror** [Values for the exposure periods and the solar-weighted reflectance ($\rho_s$) are shown in the legend.] (Masterson and Lind 1983a)

SERI studies (Masterson 1983b), a commercially produced wet chemical-processed, silvered mirror was exposed to temperatures between 40°C and 200°C by inserting one end of the specimen into a laboratory furnace while the other end was cooled. Degradation was substantial at the high-temperature end of the specimen. Decreases in hemispherical reflectance at 400-nm wavelengths were measured along the mirror specimen and correlated to mirror temperature.

The data were used to produce an Arrhenius plot from which an activation energy for agglomeration in the silver film of approximately 30 kJ/mole was determined. This activation energy was only about one half of that previously measured, 69 kJ/mole (Presland 1972), for a bare film exposed to air. The reason for the extremely low activation energy is not completely understood, but it may be caused by the presence of impurities in the silver layer accumulated during the manufacturing process or by the thermal gradient along the 30-cm long specimen.

Since agglomeration is severe and takes place macroscopically at temperatures exceeding 90°C, it is concluded that all future accelerated weathering tests to determine mirror durability and mirror ranking should be performed at a temperature less than 80°C until studies can be made to demonstrate that no fundamental mechanistic changes occur above 80°C. Accordingly, systematic and carefully controlled high-temperature exposures and subsequent determination of the activation energies associated with the accompanying degradation may yield valuable insight and quantitative data on the degradation of commercially produced mirrors.

## Summary

Numerous testing procedures have been invoked over the past few years to assess the durability of silver/glass mirrors and to determine models for their degradation in the various exposure environments. The results, to date, indicate that the most important parameters to accelerate mirror degradation are elevated temperature, humidity (greater than 80% and high enough that condensible water is present on the back surface of the mirror), and an abundance of oxygen to participate in the oxidation-reduction reactions.

Spectral reflectance degrades most rapidly at the short wavelengths; near 400 nm (see Figure 4-3) for silver/glass.

In exposure to high humidity and high temperature, etching of the front surface of the glass superstrate is severe for some types of glass. When the purpose of the exposure is to test the stability of the optical properties of the metal reflecting layer, the glass surface must be protected from the corrosive environment.

Temperature cycling at high humidity causes severe edge corrosion and edge delamination in some specimens. However, this does not degrade the specular reflectance of the intact central portions of the specimens as quickly as the steady temperature condition. It appears that the length of time at high temperature is a critical factor in degradation.

Another finding from these controlled exposures is that specimens could be removed from the test chamber, characterized, and replaced without affecting the observed degradation rates. Also, simultaneous exposure to multiple environments indicated that the presence of ultraviolet light or typical gaseous pollutants does not significantly accelerate the observed degradation. There were no synergistic effects observed between the various exposure parameters; that is, the combined degradation rates were just the sums of the degradation rates observed for the individual parameters.

In these studies of mirror degradation, great variations in degradation rates were observed between specimens of a single mirror type and even between different areas of a single specimen. This appears to be caused by non-uniformity of thickness and composition of the various reflecting and protective layers that constitute a complete mirror. The non-uniformity is probably a consequence of the wet chemistry mirroring process as used by all commercial silver/glass mirroring companies. The consequence of this to accurate durability testing is that many specimens and measurements are needed to obtain results with high statistical precision.

No adequate testing scheme has been evolved for predicting mirror lifetime and durability. Accurate reproduction of all degradation phenomena observed in field-exposed mirrors has not been accomplished during accelerated laboratory testing. Nevertheless, substantial progress has been made in understanding many of the causes of degradation and in designing appropriate accelerated tests for determining mirror durability. Substantial work has yet to be done to obtain results for long-term, outdoor, accelerated exposures; to determine the rate equations for the degradation process; and to validate degradation models. Analytical techniques for characterizing the optical properties of degraded mirrors are now better defined. Surface analysis techniques to identify mirror corrosion products and interface interactions have been a useful tool in arriving at the present understanding of the causes of mirror degradation.

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# Chapter 5

# Solar Mirror Manufacturing Methods

The future use of solar energy for residential, commercial, and industrial applications depends to a large extent on the initial costs and the levelized costs of the total solar energy system. These costs, in turn, will depend upon the economy and efficiency of mass production of solar mirrors and reflectors. Solar mirrors and reflectors are manufactured mostly in either small quantities or in custom designs. The largest single quantity of solar mirrors manufactured by the glass and mirror industry so far has been the 93,000 $m^2$ (1,000,000 $ft^2$) of heliostats for the Solar One Solar Thermal Central Receiver Pilot Plant at Barstow, California.

The glass for the heliostats was manufactured by the Glass Division of the Ford Motor Company using a float glass process. The mirror preparation process was performed separately by Gardner Mirror Corp. under contract for Martin Marietta Aerospace Corp. This two-phase process is typical of the mirror industry today for glass mirrors; that is, typically, the mirror superstrate or substrate is manufactured by one plant and the preparation of the mirror surface is performed by another. Therefore, the mirror superstrate or substrate must be packed and shipped to a second facility to complete the fabrication. It is likely, however, that greater development of the solar industry will eventually necessitate the integration of the two manufacturing processes in order to achieve economy and efficiency.

The remainder of this chapter provides, first, a brief description of the float-glass process used by Ford Motor Company; second, a review of the mirror industry manufacturing process today; and, third, a projection of the solar mirror industry of the future.

The description of the float glass process is excerpted from a paper by Goodyear and Lindberg (1980). The presentation on the silver mirror fabrication process is from, *Heliostat Mirror Survey and Analysis*, prepared by Lind et al. (1979). The discussion of the solar mirror manufacturing plant of the future assumes that the superstrate/substrate fabrication will be performed in the same facility as the process for preparing the mirror reflecting surface. The discussion is excerpted from, *Preliminary Definition and Characterization of a Solar Industrial Process Heat Technology and Manufacturing Plant for the Year 2000*, by Prythero and Meyer (1979). The authors assume that parabolic trough collectors made with a thin glass substrate, a support structure, and a silvered reflector surface will represent a mass-produced solar collector in the year 2000.

## Float Glass Manufacturing Process

The float glass process was introduced by Pilkington Brothers of England in 1959 and has revolutionized the flat-glass industry. Until that time, quality glass was made by a plate process that included grinding and polishing the surfaces. This process is inherently slow, wasteful of raw materials, and requires a great investment in grinding and polishing equipment.

The manufacture of flat glass by the float process produces a continuous ribbon of high quality glass. The process consists of (1) weighing and mixing the proper ratio of raw material ingredients, (2) melting the batch raw materials in a high-temperature furnace, (3) forming the molten glass into a sheet by floating it on molten metal, (4) annealing the sheet, (5) cutting the glass to size, and (6) packing. Figure 5-1 is a schematic of the entire process.

The batching process involves weighing and blending the raw materials of sand, soda ash, limestone, dolomite, salt cake, crushed coal, and rouge into a homogenous mixture and delivering it to the melt furnace.

The melt furnace is a large refractory furnace capable of temperatures in the range of 1650°C. The furnace actually performs three functions. The initial phase melts the raw materials into a viscous liquid. Then, the melt proceeds through a refining zone allowing gaseous inclusions (bubbles), generated during the melting process, to escape from the molten glass. Finally, the molten glass enters a temperature-conditioning zone that stabilizes the glass at a desired viscosity.

Glass is formed into a sheet by flowing molten glass onto a bath of molten tin. A density differential between the glass and tin results in the glass "floating" on the tin and forming a continuous ribbon of glass with essentially flat, parallel and fire-polished surfaces. The glass ribbon is pulled along the bath of molten tin while simultaneously being cooled to a temperature at which it solidifies. Tin has a lower melting temperature than glass and remains molten throughout the process. A reducing atmosphere is necessary in the forming area to control the oxidation of the molten metal.

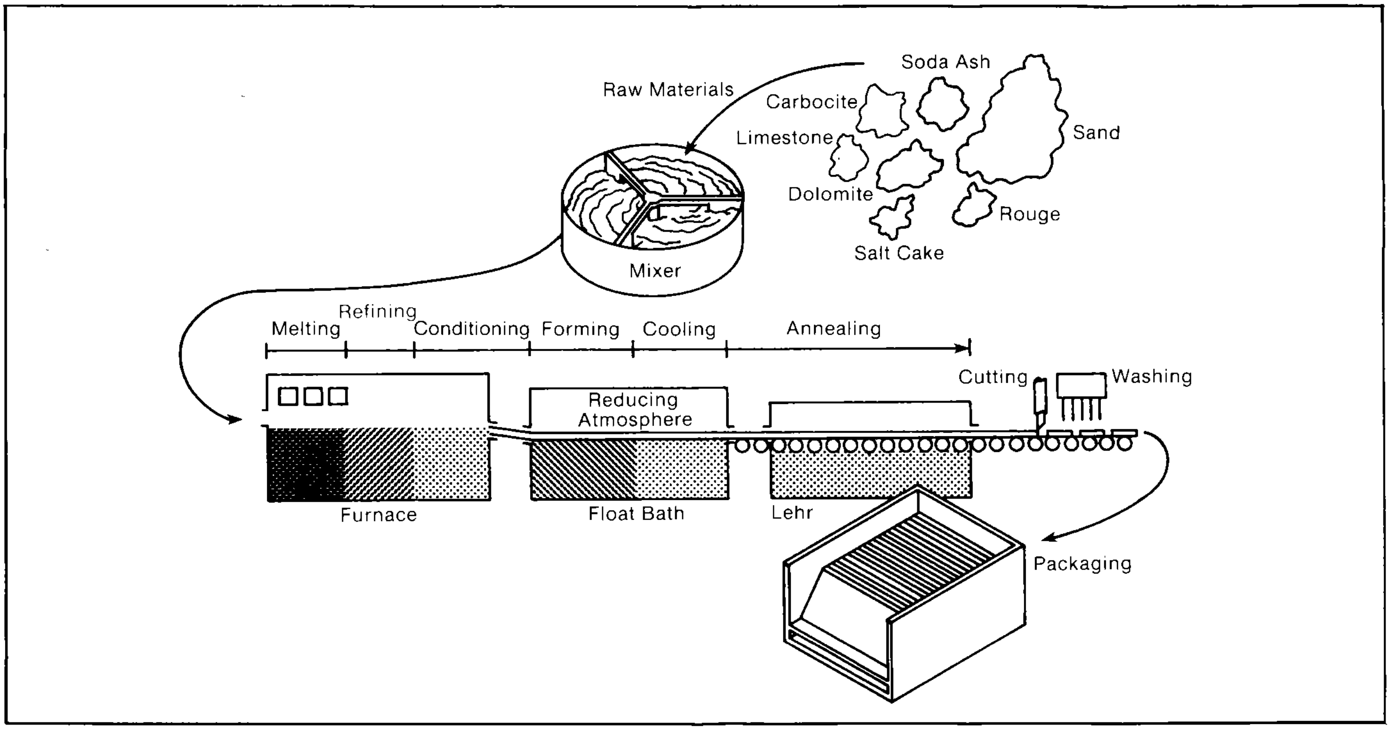

**Figure 5-1 Schematic Drawing of the Float Glass Manufacturing Process** (Lind et al. 1979)

It is possible to stretch the glass ribbon during the forming process to achieve the desired thickness before cooling to the point of solidification. The stretching process has been developed to a point that any thickness specification in the range of 1.5 mm to 12 mm can be met routinely.

The glass then proceeds continuously through the annealing lehr that alleviates stresses within the glass ribbon and further cools it to below 150°C. Then the glass ribbon is moved under a series of cutters that cut it "on-the-fly" to the desired size. After the cut sizes are conveyed through a washing operation, they are ready for packaging.

## Current Mirror Production Processes Overview

The evolution of mirror production techniques has been reviewed by Schweig (1973) who concluded that the generic chemical silvering solutions and reactions used today have been available since 1876. Significant advances have been made during that time in the solution constituents (variety and amount) to improve the film quality, deposition rates, and suitability for mass production. Early solutions required 2-5 minutes to deposit a silver layer and were suitable for batch production using stationary or rocking tables with the solution covering the glass.

Spray application was introduced in the 1920s, but slow deposition time still limited production. Speedy silver deposition became available in 1940 when Peacock introduced reducing solutions based on hydrazine and its related salts. Further reducing-solution improvements became available in the early 1960s when formaldehyde-dextrose solutions were patented. These solutions and a method for continuous processing became almost universal for domestic mirror production by the early 1970s.

The copper-deposition process has experienced a more pronounced change. Galvanic deposition techniques were used until the 1950s with early applications requiring mirror-dipping and later use allowing a conveyor belt motion. Patents filed in 1953 and 1954 introduced solutions for the spray application of copper employing copper sulfate solutions and metallic dust as a reducing agent. Variations on this generic approach are common today using iron filings. These solutions are suitable for use on a continuous-process production line.

Today the major chemical outlets market competitive forms of both the silver and copper solutions. The products are used interchangeably by the mirror manufacturing firms. Purchases are based on cost and a desire to avoid a dependence on only one supplier. Differences in chemical performance or process reliability are not mentioned by the coaters.

Modern mirroring production lines provide for continuous production and are based on a horizontal-moving conveyor system using turning rollers. Individual glass sheets are fed into the front of the system and no further handling occurs until the finished mirrors are removed from the line output. A typical production sequence is shown schematically in Figure 5-2. The primary steps are indicated in sequence from left to right.

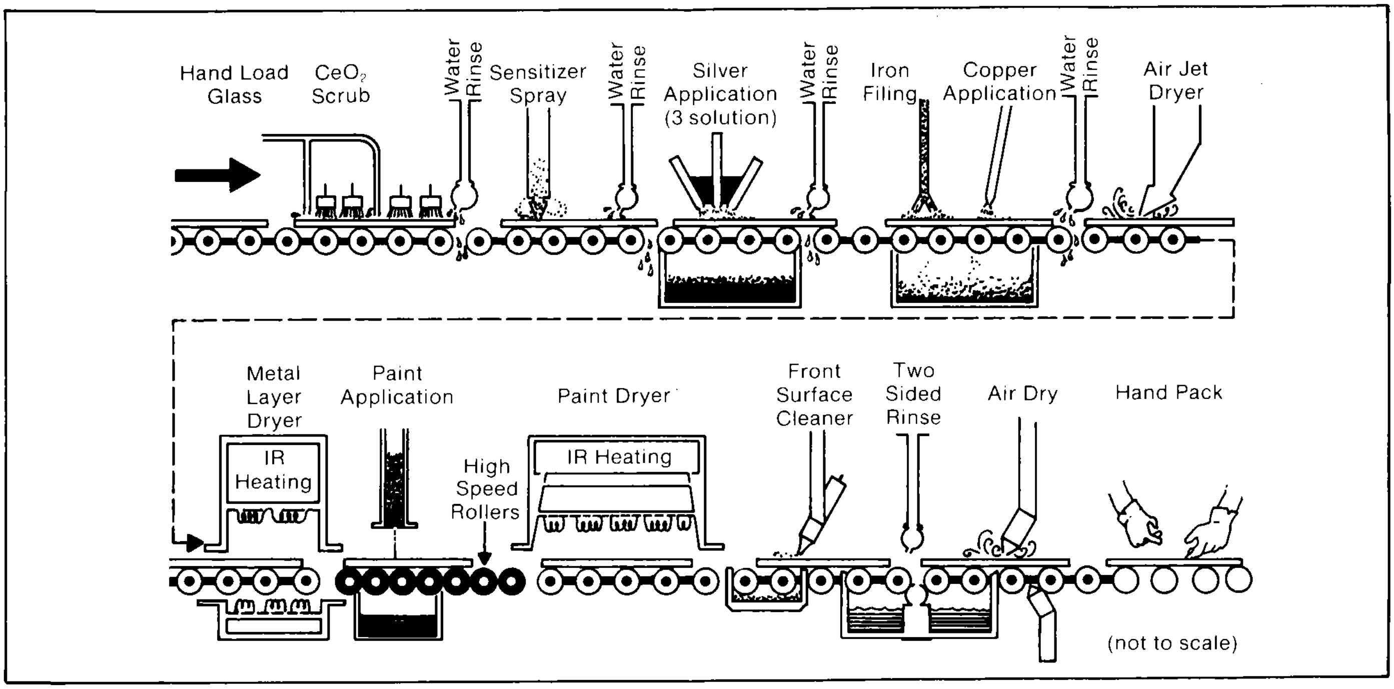

**Figure 5-2 Wet-Chemistry Mirror Production Sequence** (Lind et al. 1979)

Although all manufacturers visited during Lind's (1979) survey operated this generic sequence, there were notable differences in their production lines. Many of the differences were related to the age of equipment and the willingness demonstrated by the respective firms to upgrade their equipment.

The basic configuration and physical layout of the production line are determined at the time of the original equipment purchase. The design of the line is generally a variation of a design recommended by the equipment manufacturer and modified by the purchaser's technical and operating staff. A new line thus represents the current industry status as determined by the equipment supplier, yet the line will incorporate any advances or component preferences of the coaters, based on their own experience. This mode of operation allows the equipment manufacturer to benefit from many of the advances being made by their customers without having to perform all the development effort. This gain is then passed along to the current generation of customers.

## Conveyor System

The conveyor system is the most stable part of a production line. Most firms visited by Lind had upgraded selected areas of their equipment (scrubbers, dryers, paint applicator, etc.) but had maintained the conveyer system essentially as purchased. This allowed the modular improvement of equipment with minimum downtime and no building changes required to house a larger system. Most conveyor systems observed were fabricated from power and idler rollers. Other systems use flat belts, waffle-type belts, or cables covered with a resilient material that will survive the chemical environment and the production temperature sequence without degrading the mirror surface. Line widths ranged from 84 in. (2.1 m) to 130 in. (3.3 m). Most conveyor systems were in excess of 100 ft in length with the newer lines even longer. The trend to longer lines allows improved line speed and product throughput. Common line speeds were in the range of 9 ± 3 ft/min. (2.8 ± 0.9 m/min.). The size of sheets that can be handled with ease ranged up to 96 in. × 208 in. (2.4 m × 5.3 m).

## Glass Loading and Scrubbing

The production sequence begins with the transfer of individual glass sheets from shipping cases to the conveyor line. Small-to-moderate size stock is transferred to the line by hand with all personnel wearing gloves. Some firms have vacuum cup/mechanical handlers available for use with large sheets of glass. Care is taken to load float glass with its untinned (air) surface up to receive the mirror coatings. This is done because production experience has shown a higher probability of good mirror quality when the untinned surface is coated. Incorrect loading will increase the chances for poor visual performance and lower silver/glass adhesion.

It was also suggested that mirror quality could be improved by specifying that glass be paper-packed rather than powder-packed. These terms describe alternative techniques available to glass manufacturers to ensure the separation of adjacent glass sheets during shipment and storage. Failure to provide this separation can frequently result in adjacent sheets bonding to each other. Attempts to separate them can damage the surface of the glass.

Powder-pack is the industry standard and is accomplished by spraying a light powder coating on the glass sheet just before it is taken from the production line for packaging. Some powders contain adipic acid to reduce glass staining during shipment. Preliminary evidence indicates that standard glass cleaning procedures are not totally effective in removing the adipic acid from the surface. Related studies are now under way to determine if residual adipic acid is a possible source of degradation in finished mirrors.

An alternative packing method uses a sheet of paper between the surfaces of each adjacent sheet of glass. This prevents bonding and does not require the use of adipic acid. This does require additional labor and material for packaging and thus will generally cause an increase in cost. Also, the use of low grade packing paper may introduce similar problems associated with the acidity of the paper which remains from the milling process.

The mirror-coating procedure is a wet process from the initial glass cleaning until the deposition of the metal layers is completed. The top surface is not allowed to dry in order to minimize the detrimental effects that would result from the deposition of solution residues on the surface.

A typical glass-scrubbing unit is shown in Figure 5-3. The scrubber employs an abrasive slurry applied to the glass by small flow nozzles that move across the conveyor line transverse to the direction of glass motion. The transverse speed is coupled to the conveyor line speed to ensure that the surface is adequately cleaned. Cerium oxide slurry is the most commonly used abrasive. Wetting agents are generally added to the slurry to improve cleaning. Surface abrasion is accomplished by rotating brushes or pads that actually scrub the surface. The rotating brush assemblies oscillate back and forth across the glass to provide uniform cleaning. Municipal-grade water is used as the carrier for the abrasive slurry.

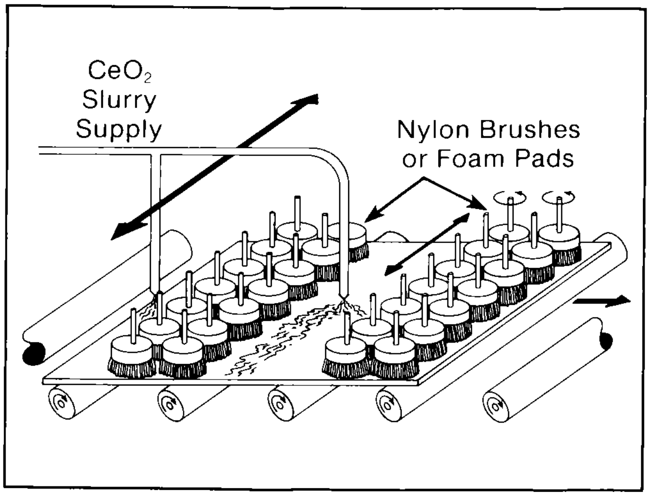

**Figure 5-3 Abrasive Glass-Scrubber Using Continuous Slurry Application and Oscillating Assemblies of Rotating Brushes** (Lind et al. 1979)

A related scrubbing mechanism is termed "blocking." This employs felt pads on heavy blocks that are moved back and forth across the glass surface. An abrasive slurry is used to enhance surface cleaning. Blocking has gone from the most common cleaning system to relatively little use because of damage to the glass surface from contaminants that become embedded in the felt pad. Blocking is being re-examined with new slurries to see if it can reduce problems associated with incomplete surface scrubbing.

The slurry residue is then rinsed from the surface using water nozzles directed against the direction of glass motion (Figure 5-4). This moves the residue toward the trailing edge of the glass where it finally drops into a recovery tray under the conveyor rollers. Incomplete removal of the cerium oxide slurry will generally result in a milky appearance of the deposited silver layer. The rinse water is deionized to prevent contamination of subsequent coating solutions and reduce the chances of staining or clouding the metal layers. The use of deionized water is continued from this step through the deposition of the copper layer. Significant differences were noted in the minimum resistivity values accepted by the different companies for their deionized water. The lowest value cited was 0.5 MΩ-cm, while others were an order of magnitude larger.

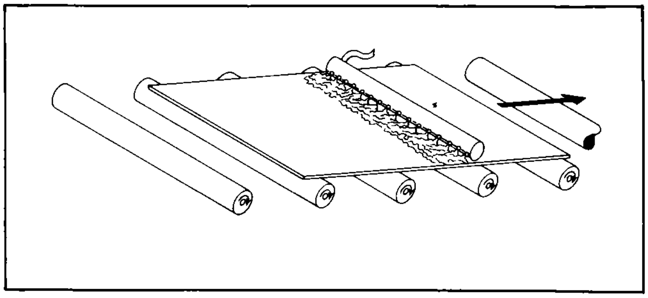

**Figure 5-4 Water-Rinse Mechanism Using Directed Water Spray to Rinse Process Residuals Off Rear Edge of Glass** (Lind et al. 1979)

## Sensitization and Silvering

The glass surface is then sprayed with a sensitizing solution that hastens the silver deposition rate and improves the silver/glass adhesion. The use of stannous chloride was first introduced in 1876, and it is still the most common sensitizer used for domestic mirror production, although palladium chloride is used occasionally. The sensitizer solution is sprayed onto the glass by a moving nozzle that oscillates back and forth across the conveyor line (similar to that used for $CeO_2$ as seen in Figure 5-3). Although the role of the sensitizer is not understood completely, it is thought that the resulting tin sites serve as nucleation centers for the silver-layer deposition process.

The sensitizer solution is then rinsed thoroughly from the surface using deionized water through a spray bar (Figure 5-4). Poor rinsing will cause a poor quality mirror. A light water spray is applied to the glass to maintain the moisture layer and facilitate the spread of the forthcoming silver solutions in a uniform layer on the glass.

The silvering chemicals are then sprayed onto the sensitized glass. The commonly used chemical systems consist of three distinct solutions: (1) silver, (2) caustic, and (3) reducer. The chemical reactions that result in the precipitation of a silver layer begin when the three solutions are mixed. This reaction is localized to the glass surface by using a spray applicator that simultaneously sprays the solutions at a common target point on the surface (Figure 5-5a). Mixture and initiation of the reaction occurs only on the surface of the glass.

All manufacturers use multiple sets of spray nozzles spaced along the direction of glass travel to renew the chemical solution periodically and produce a thicker layer of silver. The transverse spray assembly speed, conveyor speed, and nozzle spacings are selected to ensure that each region of the mirror is sprayed generally 6 to 12 times to provide the required film thickness and uniformity. This coverage is generally obtained with four or five sets of spray nozzles and a transverse nozzle speed that allows approximately 12 strokes/minute across the mirror line.

The most commonly used silvering chemical system utilizes formaldehyde and dextrose solutions as two of the separate component solutions. This system was commercially developed in the late 1960s and achieved general acceptance by the early 1970s. It has the advantages of being a fast chemical reaction (suitable for fast production rates) and being a highly efficient reaction for silver transfer from the solution to the glass. It is estimated that 85%-90% of the silver sprayed onto the glass deposits into the reflective layer. The process also provides improved silver/glass adhesion.

The chemical suppliers market the three component solutions in chemical concentrations that require 1:1:1 mixture on the glass. This is accomplished reliably by using metered pumping systems for each solution to reduce product variability and simplify the required production adjustments. The metered pumping systems provide an airless spray that reduces problems of overspray and chemical cross-talk from step to step. Production quality metered pumping systems can be purchased from at least one of the chemical supply houses.

The silvering solutions are rinsed thoroughly from the glass to terminate the silver reaction and to prevent the entry of residual silver solutions into the copper deposition portion of the line. Such chemical contamination is expected to degrade the quality of the copper layer.

## Copper Deposition and Drying

Copper deposition occurs next and commonly employs an iron filing/water slurry and a copper solution. The precipitation reaction begins as soon as the two solutions are mixed. The solutions are sprayed from an oscillating transverse nozzle system (Figure 5-5b). The surface is first sprayed with the iron slurry to allow it to spread across the silver layer before the copper is introduced. The copper solution is then sprayed simultaneously with another iron-filing slurry. All manufacturers use multiple sets of double nozzles to reach the desired copper thickness and film uniformity. An air sprayer is typically used for chemical application.

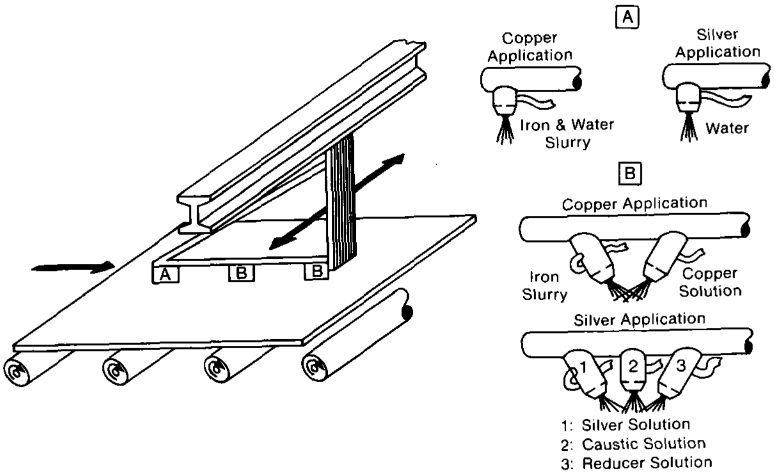

**Figure 5-5 Reciprocating Spray Chemical-Applicator for Wet-Chemistry Mirroring Solutions.** Specific nozzle arrangements are shown for a galvanic copper and a three-part silver process. The details A and B (on right) represent the nozzles placed at A and B on left of illustration. (Lind et al. 1979)

An alternative chemical system is now available for copper deposition that does not employ an iron-filing slurry. It has the potential advantage of reducing any copper layer defects that may be caused by the granular nature of the iron filings in the conventional process. This uses a metered pumping two-component application and airless spraying. The copper solutions are then rinsed completely from the glass with deionized water using a spray bar.

The deposition of the metal layers is now complete and the procedure ceases to be a water-based process. An air knife (Figure 5-6) is employed to remove water from the coated surface of the glass before attempts are made to drive residual water from the metal layers. Visual inspection of the surface, after the air jet dryer, revealed no evidence of standing water or stray droplets on the copper.

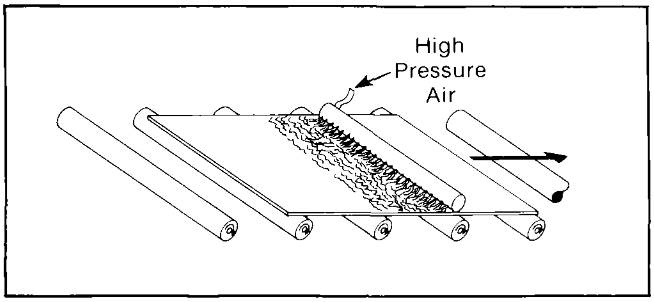

**Figure 5-6 Air-Jet Drying Station Using Directed Air Flow to Force Process Residuals Off Back Edge of Moving Glass Sheet** (Lind et al. 1979)

The mirror is then heated with infrared radiation from the uncoated glass side to cure the metal layers partially by driving residual water from them. Heating from the glass side raises the temperature of the entire mirror structure. Heating from the coated side would not heat the substrate effectively because of the reflective nature of the metal layers. This would tend to create significant thermal gradients within the mirror metallization that could degrade the final adhesion behavior of the metal layers. Heating from the glass side is also thought to drive the moisture away from the silver/glass interface rather than toward it.

The metal layer drying also reduces the chance of problems that could occur with the application of an oil-based paint on a wet surface. Dryers were observed that employed either resistively heated radiant ceramic cups or quartz tube heaters. The differences in these devices will impact operating costs, dryer box sizes, and maintenance requirements. No evidence was given to indicate preference for either type based on the curing mechanism as long as they raised the mirror temperature to the same level. Some manufacturers have suggested that optimal metal curing will occur when the layers are near 100°C (212°F). This is significantly higher than the typical values of 40°-55°C (110°-150°F) used in the industry today. The actual temperature used must be low enough to allow good paint adhesion in the next process step and should not initiate silver-to-glass debonding as shown by Masterson (1983) and Lind (1982).

## Back Painting

One paint application method predominately used for the production of quality domestic mirrors is the "curtain coater." It is seen in a cross-section view in Figure 5-7(A). A thin curtain of paint is created that flows continuously from the adjustable knife edge drain in the upper reservoir. As the mirror passes through the curtain, a uniform paint layer is deposited. Roll coaters [Figure 5-7(B)] are still used for some applications but are not preferred on the basis of product quality. The roll coater transfers paint

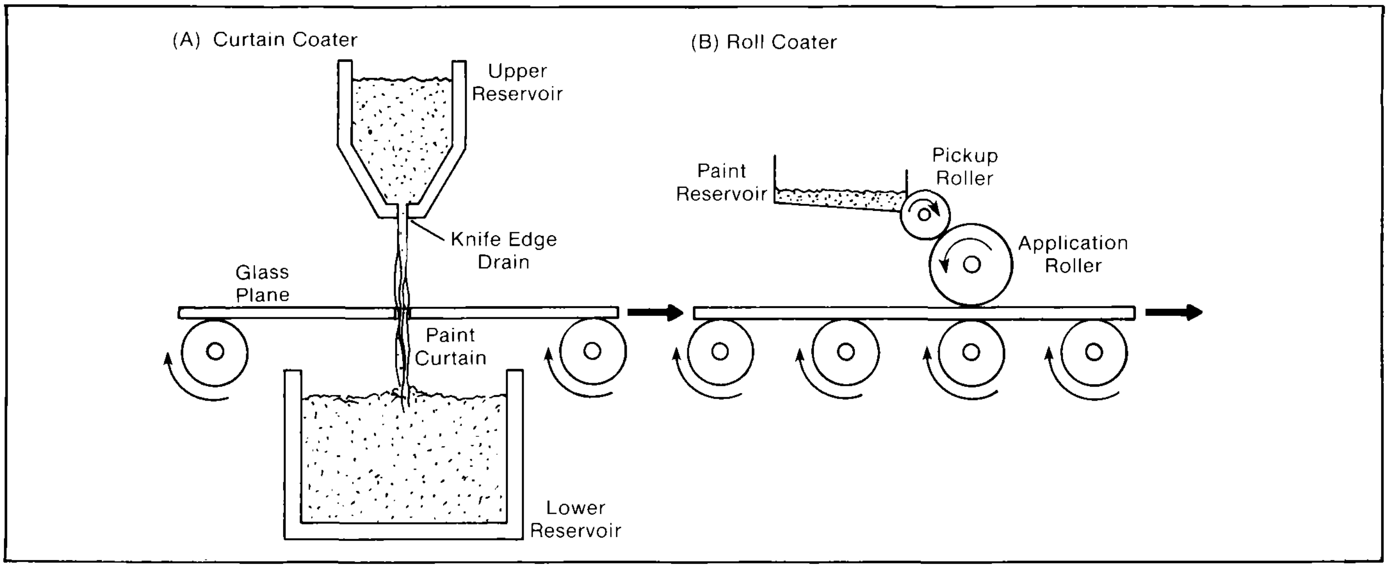

**Figure 5-7 Cross-Section View of Two Types of Paint Applicators** (Lind et al. 1979)

from a reservoir to the mirror with a series of roller-to-roller exchanges. This is similar to the ink transfer mechanisms used on many printing presses. Roll-coated mirrors tend to exhibit fairly non-uniform paint layers with corrugations seen in the paint that are reminiscent of the texture left by a household paint roller. Typical roll-coated paint exhibits a 50% thickness variation associated with the corrugated pattern.

Curtain-coater operation is further illustrated in Figure 5-8. Paint is pumped into the upper reservoir. The curtain then results from the gravitational feed of paint through the adjustable knife edge drain which allows the adjustment of both curtain uniformity across the line and the nominal curtain thickness. This type of feed system requires reasonable control on the paint viscosity and its particulate content. Most firms filter the paint supplied to the upper reservoir. A fixed wire is mounted at each end of the knife edge drain to serve as a guide for the end of the curtain. This prevents the breakup of the curtain ends that would normally occur. The edge wires extend into the lower paint recovery tray. The paint from the recovery tray is filtered and pumped back to the upper reservoir. Between mirror sheets the paint simply circulates through the system. When a mirror passes through the coater, most of the paint is intercepted by the mirror. This requires an automatic fill system for the reservoir in the standard production process.

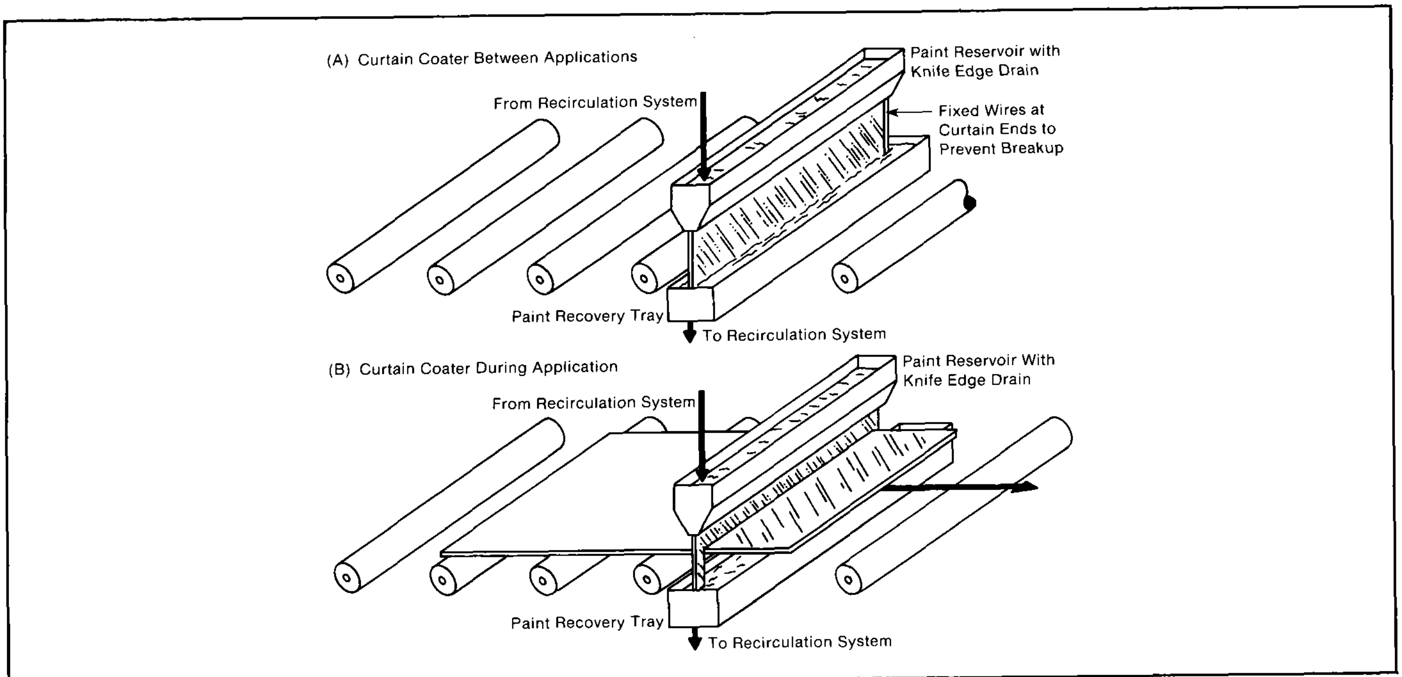

**Figure 5-8 Curtain-Coater Operation: (A) Between Applications, and (B) During Application** (Lind et al. 1979)

Practical implementation of a curtain coater also requires the use of a variable speed section in the glass conveyor system to achieve the paint layer thickness desired. This is required because the standard line speed would produce very thick paint films for easily controlled paint flow rates. The compromise solution uses practical paint flow rates and accelerated mirror transfer through the curtain coater. This is illustrated in Figure 5-9.

The variable speed rollers are accelerated when a pre-selected light beam is broken by the mirror's presence. The section continues at high speed long enough for the mirror to clear the paint curtain. The roller section then slows down to transfer out the painted mirror and to load the next mirror. The photo-detector location and high-speed operating time are selected on the basis of the mirror size being coated during a given production run. Typical speed changes required are from 6 to 8 ft/min (1.8-2.5 m/min) on most of the line to 18 ft/min (5.6 m/min) through the curtain coater.

The alternative paint application techniques not only affect the layer quality but also the painting costs. Spray painting (an early technique) required the use of approximately 10 gal/ft$^2$ (4.0 m$^3$/m$^2$) and additional paint was lost because of overspray problems. Roll coating generally is done at approximately 11 gal/ft$^2$ (3.6 m$^3$/m$^2$) to ensure that even the thin regions provide good mirror protection. But the curtain coater can provide good mirror protection at approximately 8 gal/ft$^2$ because of its excellent uniformity. The net effect of these differences in required thicknesses and paint wastage represent a significant difference in painting costs. Estimated costs per square foot (1976) were roughly $0.012, $0.015, and $0.024 for roll coating, curtain coating, and spraying, respectively.

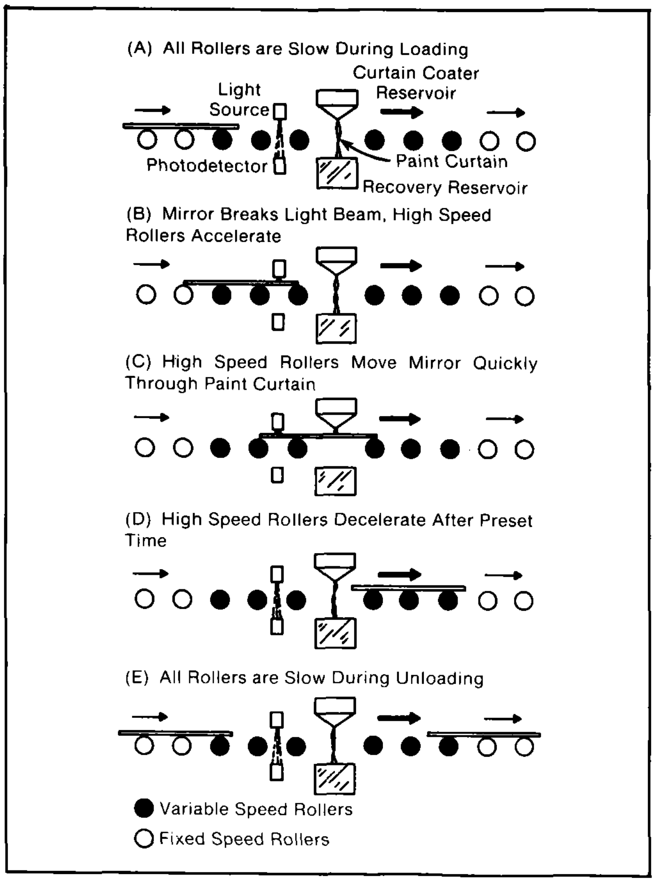

**Figure 5-9 Production Sequence for Variable-Speed Roller Section Associated with Curtain-Coater Operation** (Lind et al. 1979)

The mirror then passes through a vent hood that employs a circulating air sweep across the mirror to remove solvents from the paint before entering the paint dryer. The mirror temperature (residual from the metal dryer) and the forced air flow remove the bulk of the solvent. The use of preheated and ambient airflow for this "flash-off" process was observed. The fumes were exhausted from the production area.

## Final Drying, Cleaning and Packing

The painted mirror then passes through an infrared dryer to dry the paint to allow handling, packing, and storage. Typical baking times are several minutes, and temperatures are near 125°C (250°F). This is not intended to cure the paint fully. The ideal drying temperature depends on the paint formulation, and the paint manufacturer's recommendations should be heeded to provide optimum product quality. However, a practical temperature may be governed by the production line's capability to cool the finished mirror for final packing without thermally inducing breakage. Figure 5-10 shows the comparison between the typical production temperature profile and one designed for the supplier's recommendations.

The mirror then rolls across several rollers that carry a chemical solution to the uncoated glass surface, which removes any metal deposited by overspray. A variety of solutions are used but they fall into the generic category of aluminum desmutters.

Top and bottom surfaces of the mirror are then cleaned before removal from the conveyor. Rotating cylindrical brushes may be used to scrub the glass surface with the weight of the mirror holding the glass on the brush. Another approach employs a water spray. Both surfaces are then dried with air knife blowers. Most manufacturers then roll-stamp the back of the mirror with their name and the production date to allow product identification.

On-line product quality assurance is limited to visual inspection for pinholes and blemishes. Mirrors are turned over mechanically before attempting front surface inspection. Some firms employ front- and back-lighting with an observation point over the moving mirror. Others simply use overhead lights and observation from the perimeter of the production conveyor.

Removal from the conveyor system is done by hand for small and moderately size mirrors. Mechanical handlers are available at some firms for use with large mirrors. Mirrors are repacked in'the original glass-shipping crates. Small felt pads are applied to the front surface of the mirrors to prevent damage to the finished product during shipment.

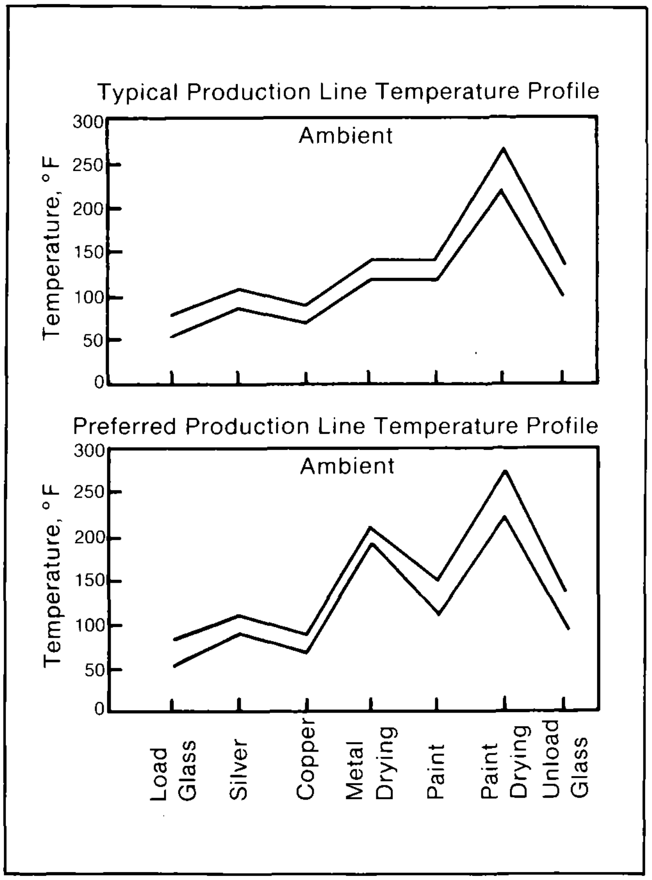

**Figure 5-10 Production-Line Temperature Profiles** (Lind et al. 1979)

The operating speed for the integrated production line must be selected to maximize the output volume while maintaining the product quality. The speed may be limited by

- Deposition times required for silver or copper.
- Desired glass temperature profile along the line.
- Power rating of infrared dryers.
- Component spacing.
- Heat capacity of the glass substrate (proportional to thickness).
- Glass handling rates for loading and unloading.

Several examples of these limitations should clarify the possible interactions. The use of thicker glass substrates will require the use of slower line speeds. The increased heat capacity of the glass will require longer times to heat and cool during the processing. Therefore, the speed must be reduced to maintain the same temperature profile along the line. Component spacing and required process times (e.g., silver spray-rinse separation and silver deposition time) may impose a maximum line speed compatible with maintaining product quality. Typical production line speeds vary from 7 ft/min to 12 ft/min for the different firms. The potential of reaching 18 ft/min with an optimized line configuration was mentioned.

## Manufacturing Plant in the Year 2000: An Overview

A plant manufacturing parabolic trough collectors would have to be a large operation to be profitable and to produce a well-priced unit. A plant producing a minimum size of 1 million ft$^2$ of collector may only be able to assemble the collectors, with most of the materials and components being manufactured elsewhere. The larger the plant, the more likely it is to conduct several manufacturing processes. A plant capable of producing 10 million ft$^2$ of collector would certainly contain several manufacturing operations.

It is likely that a plant producing parabolic trough collectors will also produce other types of solar collectors rather than the other components used in a solar system. For example, a plant can manufacture reflective mirrors for different concentrating collectors and heliostats. Since the same types of technologies are involved, it would make economic sense to manufacture similar items. A plant operation is more likely to manufacture similar products rather than products used in total solar systems that are dissimilar in construction.

The plant characterized in this study is considered to be a large capacity plant that manufactures parabolic trough collectors. It could easily add other types of line-focusing and point-focusing collectors to its production activity. A large operation would benefit from having most of the collector manufacturing conducted within the plant. For example, to manufacture parabolic trough support structures it would be advantageous to manufacture all specialty items within the factory to allow for a well-planned mass production process.

Based upon the actual design of the collector, it would require several different special components and materials. These include a glass reflector, sheet molding compound, black-chromed absorber tubes, sun-sensors and controls, and the tracking drive mechanism. All these items would require an expanded manufacturing operation unlike present solar manufacturing operations.

From an analysis of the manufacturing techniques required, it appears that the glass making, silvering, and mounting to a parabolic trough shape should be carried out in one continuous process to avoid excessive handling. There are two options available. One is to install a glass-making operation in the collector plant itself. The other is to make the parabolic trough, send it to a glass-and-silvering operation elsewhere, and then ship it back for final assembly. With present shipping procedures, it does not make sense to ship the glass to the collector plant once it is made, because of the potential for damage. Therefore, the solar plant in this study is characterized with a glass-making and silvering operation within the plant.

The manufacture of black-chromed absorber tubes could also be conducted in the solar plant. The principal reason for including the chroming operation is the volume of electroplating required. Other components that could be manufactured in the plant are the sun-sensing components and the control systems. The operation would consist mainly of assembling electronic components into specialized systems for use with the collectors.

Hence, the solar manufacturing plant is defined as manufacturing the glass, silvering it, and attaching it to a plant-manufactured trough. The absorber tubes would be black-chromed and installed in the fabricated collector unit. The electronic controls and sun-sensing devices could be assembled at the plant. The collector units would be assembled to the extent that shipping is practical; subsystems and components would be packaged with the collectors for distribution.

The only packaging of a "system" to be carried out at the plant would consist of the modular collector arrays with all appropriate components to make them functional. Additional specialty components needed for the complete solar system could also be packaged.

## Manufacturing/Assembly Processes for Major Components

**Reflective material.** The reflective material is a thin glass about 1.5 mm thick, which would be manufactured at the plant, silvered, and cold-pressed onto the parabolic trough structure in a continuous in-line process. This glass-manufacturing process is similar to other types of glass-making operations. It is energy intensive and requires a considerable amount of area for the kilns.

The process involves seven steps:

1. Receiving raw materials for glass.
2. Batch-mixing of the materials for firing.
3. Premelting, melting, and heat refining in a gas-fired tunnel kiln.
4. Forming by drawing the glass downward in a vertical fashion to obtain sheet glass (or by a fusion float-glass process).
5. Sending the sheets of glass through an annealing kiln (lehr) to reduce the glass temperature to room temperature.
6. Cutting the glass to appropriate lengths.
7. Finishing as necessary by trimming and polishing.

In subsequent operations, the glass is silvered and a protective coating is placed on the back. The silvering process involves several steps:

1. Cleaning of the glass.
2. Rinsing.
3. Sensitizing the surface with a tin solvent.
4. Rinsing.

5,6,7. Spraying (three stages) the silvering compounds on the glass.

8. Rinsing.
9. Copper plating the silver using a galvanic process.
10. Rinsing.
11. Drying.
12. Spraying a protective coating on the glass (possibly a plastic-based material).

Finally, the glass mirror is cold-pressed into the premade parabolic trough and bonded to the surface.

The glass-making operation would require a process line of about 100 ft to 150 ft in order for the process to be carried out in one operation. The silvering operation would require another 75 ft to 100 ft of process line.

**Parabolic trough support structure**. The manufacture of the parabolic trough would use a sheet-molding compound. This compound is a reinforced plastic containing resin, fillers, catalysts, thickeners, carriers for the thickeners, and reinforcement material. Once mixed, the sheet-molding compound is in the form of a dough-like mixture in sheet form. This material is placed in a matched-die molding machine.

The manufacturing process for making sheet-molding compound parabolic troughs involves a process ranging from mixing raw materials to trimming and inspection of a completed component:

1. Dry ingredients are mixed in a hopper equipped with an agitator.
2. The mixed compound is sent through a continuously mixing roto-feed extruder where the resins and catalysts are mixed with the dry material.
3. This material is sent to the sheeting equipment where glass fiber is chopped and forced into the resin. It is impregnated, compressed, and kneaded into a sheet about 0.1 in. thick, which is rolled up for use in the molding operation.
4. The sheets are cut to size for the shape of the parabolic trough mold.
5. The sheets are placed in the mold in sufficient quantity to achieve the proper thickness of plastic for the component.
6. The molding operation uses a match die molding machine in which heat and pressure are applied to the mold; heat at about 170°C with pressure of 500-1000 psia is required.
7. The trough is removed, trimmed, and inspected.

**Absorber assembly**. The absorber assembly consists of a steel tube that has been black-chromed, a plugged inner tube, a Pyrex glass outer tube with reflector coatings and appropriate gaskets, fastening devices, and support brackets. Most of the materials would be manufactured elsewhere and assembled at the plant. The black-chrome plating process is an optional manufacturing operation which would be carried out in the plant if the volume is sufficient.

The manufacturing operation associated with the absorber support bracket, bearing housing, and trough attachment assembly would require several operations. The operations include metal cutting, welding, drilling, machining, and fastening. Materials used would include steel tubing, angle and plate stock, bearing housings, and fastening devices.

The absorber tube would be pre-threaded and provided with appropriate fittings. Assembly of the gaskets and glass tube could be carried out at the factory or possibly performed at the job site.

The optional black-chroming process is an electroplating procedure involving 11 steps:

1. Sandblast the steel pipe to remove oxides and foreign materials.
2. Clean with an electrolytic chelating cleaner.
3. Acid dip.
4. Electrolytic chelating cleaner.
5. Acid dip.
6. Rinse
7. Nickel plate (dull).
8. Black chrome plate.
9. Water rinse.
10. Alcohol rinse.
11. Air drying.

This process uses a series of dipping tanks and electrolytic tanks and may require a process line of 50 ft to 60 ft.

**Collector support stand.** The collector support stand is fabricated from low-cost steel. This manufacturing operation involves a basic metal-working procedure. Steel tubing and plate are cut, drilled, machined, and welded to form the support stand. The stand consists of a mounting plate welded to the stand and the bearing house attached to the top end of the stand. The stand is cleaned, primed, and painted; then it is shipped to the job site where it is placed on concrete pads and the parabolic trough assembly is added.

**Tracking drive mechanism.** The hydraulic-action tracking drive mechanism consists of components such as actuators, piping, pumps, and control equipment, which would be assembled in the factory. It is not anticipated that machining would take place to build any parts of the hydraulic drive in the plant. However, the double-acting actuators might be constructed in this plant.

The hydraulic components would be placed on mounting brackets attached to the parabolic trough assembly and the support stand. As many of the components as possible would be attached to the collector units in order to minimize on-site assembly operations.

**Sun-sensing device and control system.** The sun-sensing device and control system could be manufactured in the plant. If built by another manufacturer, the components could be shipped to the factory or delivered to the job site for attachment. Using the solar heating and cooling industry as a basis, it would seem that the electronic control firms rather than the collector manufacturer would be the most likely supplier of these components. However, if these components are produced by this factory, it would be an assembly operation. The operation would include obtaining microprocessors, electronic parts, switches, and components from electronic firms. The control systems and heat-flux sensing devices would be assembled according to the requirements of the collector tracking specifications. This operation would be a labor-intensive, bench-top assembly operation.

**Piping couplings.** The collector array modules will require adequate coupling to the heat-transfer fluid manifold network of the collector array, which necessitates the use of either flexible or swivel-jointed couplings to allow for the movement of the collectors. Since these special couplings are manufactured by other industries, the solar manufacturer would purchase these units and attach them to the collector system.

## Activities of the Solar Manufacturing Plant

The solar manufacturing plant would carry out several major activities including receiving, warehousing, metal working, electroplating, glass making, silvering, plastic forming, assembly and fabrication, painting and finishing, packaging, and shipping. Subsidiary activities indirectly related to the manufacturing process would include management, water treatment, air quality control, and solid waste disposal.

Many operations in the manufacturing plant require that processes be placed in line with each other to reduce excessive handling and additional space requirements. It will be necessary to have the glass-making and silvering operations together and they will require the most space in the manufacturing plant. Many other operations would have to accommodate these operations. For example, the attachment of the glass mirror to the parabolic trough must occur at the end of the silvering process. Other operations such as plastic forming and the assembly of the electronic controls can be carried out in remote areas of the factory. They need not be integrated into the production flow of the collector assembly.

## General Description of the Manufacturing Plant

The manufacturing operations described in this study would require that the plant be located in an area zoned for heavy industry in a community or county, mainly because of the glass-making and electroplating operations. If these processes were not included, the plant could be considered a light industry.

The plant's internal configuration and physical appearance would not be unusual. However, air pollution control equipment and a water treatment plant would be evident as additions to the building. Minimal outside area would be required for the plant. Protected storage areas for the glass raw materials may be required.

Externally, the plant should change considerably compared to current configurations. Assuming the existence of a large solar system plant in the year 2000 implies that the use of solar energy will be significant. It is probable that the plant itself will use solar power extensively. The types of solar systems or elements could include hybrid passive and active space heating or cooling, high-temperature process heat for either preheating or direct process heat for the kiln operations, and wind power or photovoltaics for electricity. Cogeneration concepts might be integrated into plant operations for additional electric power generation.

In urban settings it is unlikely that biomass could be used as a back-up energy source. Passive energy conservation techniques; for example, trees or structures in strategic wind-breaking or sun-shading locations, the use of earth berms or subterranean construction, and absorbing or reflecting external wall surfaces, should be evident. Also, the plant configuration and orientation could maximize the availability of insolation.

It would be preferable to have access to a railroad and to a major highway. Because of the large quantities of materials required for glass making, it would be beneficial to locate the factory near these sources of raw material.

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