

SERI/TP-631-623
Preprint

Durability of Silver-Glass Mirrors in Moist Acid Vapors

R. T. Coyle
J. M. Barrett
P. J. Call

October 1981

Prepared under Task No. 1003.00
WPA No. 281-81

Solar Energy Research Institute

A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

Prepared for the
U.S. Department of Energy
Contract No. EG-77-C-01-4042

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Abstract

The durability of glass second-surface mirrors is a major concern in the outdoor environment where they are used in solar energy applications. A simple durability test using moist HCl, H₂S and SO₂ vapors on 22 different types of mirrors was found to correlate well with experience on mirrors outdoors and with the expected durability of the mirrors. The mechanism of mirror failure was investigated, and it was found that pores and other defects in the protective paint of the mirror are probably the sites at which failure begins for most commercial mirrors.

Acknowledgments

We would like to acknowledge the assistance of Rita Goggin in preparing mirror samples, in monitoring some of the mirror degradation experiments, and in conducting the adhesion experiments. Manuel Gutierrez assisted in the scanning electron microscopy.

1. Introduction

Glass second-surface mirrors for solar energy applications must maintain their high performance for periods as long as 20-30 years to be economically attractive. However, there are strong indications from the early experience with solar concentrators that this lifetime will not be easily achieved. The 0.1-m^2 mirrors in service at the 1 MW_{th} solar furnace at Odeillo, France, have suffered silver corrosion on 50% of the total reflective area after ten years of service. Prototype mirrors for heliostats developed in the Department of Energy Solar Thermal Power Program have shown numerous dark spots after less than one year's testing outdoors at Livermore, Calif. [1].

The mirrors used in these solar applications are of the same type found in homes and commercial buildings. Figure 1 is a schematic diagram of the structure for this type of mirror--detailed discussions of the materials and processes appear in Lind et al. [2] and Schweig [3]. The silver and copper layers are applied by electroless deposition and the protective paint is deposited by curtain coating. All of these processes are done on a continuous mirroring line. It is important to emphasize that the present choice of materials for mirrors is made to produce cost-competitive mirrors for indoor use and not specifically to perform well in solar energy applications. For example, the paint has been formulated to be pigment-rich, thus porous and brittle when cured, to allow for rapid drying on production mirroring lines and to allow for easy breaking of mirrors into desired sizes after the paint has been applied. Optimization for solar applications might include the application of a second nonporous coating and standardization of sizes, thus eliminating the need for breaking the mirrors.

Most mirrors are currently made with the goal of surviving a 20% NaCl salt-spray test which is run for 150 h at 35°C [4]; this test is the most widely used accelerated degradation test in the mirror industry. There are strong indications from early solar installations that this test is not a good predictor of mirror performance for outdoor applications. In addition, for quality control purposes, it would be advantageous to have an accelerated degradation test that would take substantially less than 150 h to give a good indication of mirror quality.

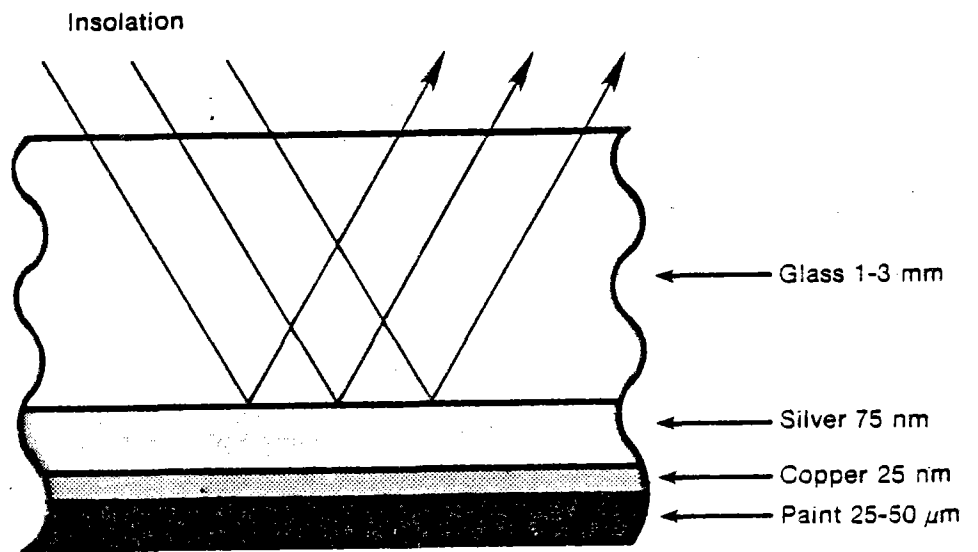


Figure 1. Schematic Diagram of the Structure of Typical Mass-Produced Silver Mirrors

In seeking an alternative accelerated degradation test that would be appropriate for mirrors used outdoors in solar applications, it was found that moisture, sulfides, and chlorides are most frequently cited in the literature as the cause for mirror failure. H_2S has been cited as the source of the sulphur [5], and both Dahms [6] and Warner [7] have described the use of tests with H_2S gas and high relative humidity to judge the effectiveness of coatings for protecting silver from degradation. Quack [8] has reported the use of HCl gas in testing the degradation of silver. In this paper we report an acid-vapor accelerated-degradation test where HCl or H_2S gas is used in a high relative humidity atmosphere to test the degradation resistance of mirrors. Most of the emphasis in this work was placed on the HCl test because it caused degradation that was more than an order of magnitude faster than for H_2S . Some experiments were conducted using SO_2 as the corrosive vapor. However, the results of these tests were similar to those with H_2S , and the SO_2 system was not extensively explored.

2. Experimental Procedures

The Acid Vapor Mirror Degradation test was conducted by placing samples of mirrors in a 2.5 L desiccator and introducing 20 ml of an aqueous reagent that generated the desired corrosive vapor. Either concentrated hydrochloric acid (12 M) or concentrated aqueous hydrogen sulfide* (0.044 M) was used to provide an HCl or H₂S vapor environment, respectively. The test was conducted at 25°C, and the desiccator was opened periodically to inspect the mirrors for degradation. The desiccator was recharged with reagent after each inspection.

2.1 Sample Preparation

Samples of mirrors to be tested were cut into 4 cm × 4 cm coupons and the paint side was lightly degreased with acetone. Mirrors were visually inspected for obvious defects in the paint prior to the start of testing. Elimination of the degreasing step by avoiding direct handling of the mirror edges and backing after fabrication would be preferable. The mirrors tested in this work had an unknown handling history.

2.2 Introduction of Mirrors and Reagent

Eight to twelve mirrors were placed in the desiccator for each test. The mirrors were supported in the desiccator by a polyethylene sample support which rested on the flange of the desiccator base. Mirrors were placed edgewise into slots of the sample support, as shown in Fig. 2, so that they tilted about 30° from the vertical with the glass side up.

After introducing the mirrors, the lid was placed on the desiccator and left slightly ajar, as shown in Fig. 2, so that the reagent could be pipetted into a Pyrex or Nalgene dish at the bottom of the desiccator without touching the mirrors. This step took about 15 seconds, after which the desiccator lid was

*Anderson Laboratories, Inc., P.O. Box 8429, Ft. Worth, Tex. 76112.

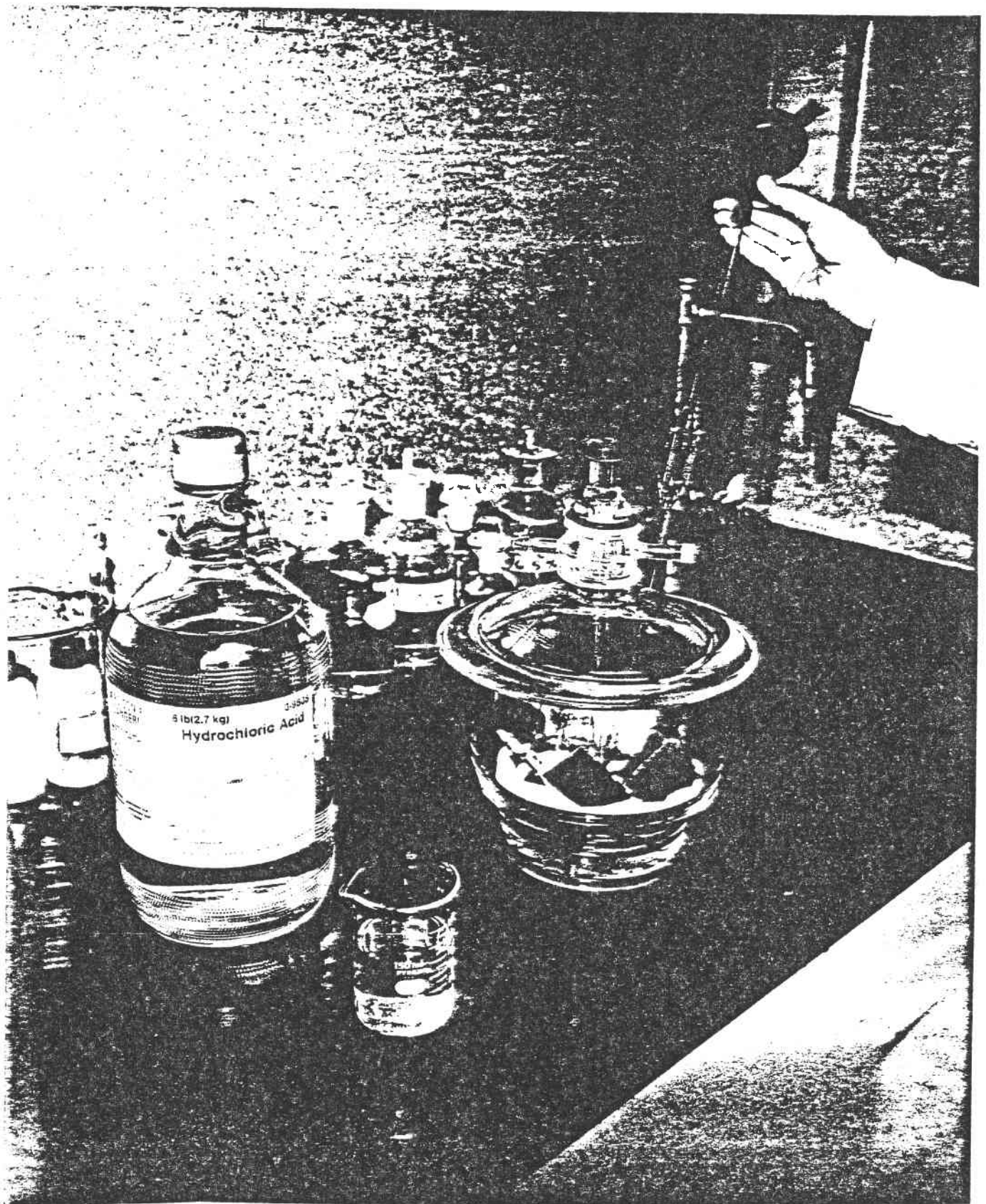


Figure 2. Desiccator with Mirrors Showing a Top Charging Septum and a Side Septum for Gas Sampling. The Pipetting Method of Charging with Reagent is Shown

closed. The lid seal was maintained using stopcock grease.* An alternative method was tested for introducing the reagent into the chamber. It involved injecting the reagent through the septum on the vertical spout shown in Fig. 2. No difference was detected in the desiccator vapor concentration for these two techniques. (See Sec. 3.)

2.3 Sample Inspection

Samples were removed for inspection at least once a week. To avoid a serious decline of the vapor concentration in the desiccator a fresh charge of reagent was used when the samples were subsequently replaced in the desiccator for continued testing. The sample mirrors were wiped before inspection with a lint-free cloth to remove dust particles, moisture, and a white film that formed on the glass surface during testing. Each sample was then inspected by viewing a diffuse uniform white light source in the mirror, a technique which allows defects to be seen more readily.

2.4 Failure Criteria

A mirror was considered to have failed if a 4 cm × 4 cm piece showed ten or more degradation spots—visible to the unaided eye as shown in Fig. 3A—or if the attack in from the edge of the mirror sample exceeded 10 mm along more than half of the exposed edge (Fig. 3B). Other rarely observed failure modes (such as hazing or wrinkling of the entire reflector surface) are mentioned in Sec. 4 along with more details on the common failure modes.

*Dow Corning, Midland, Mich., 48640.

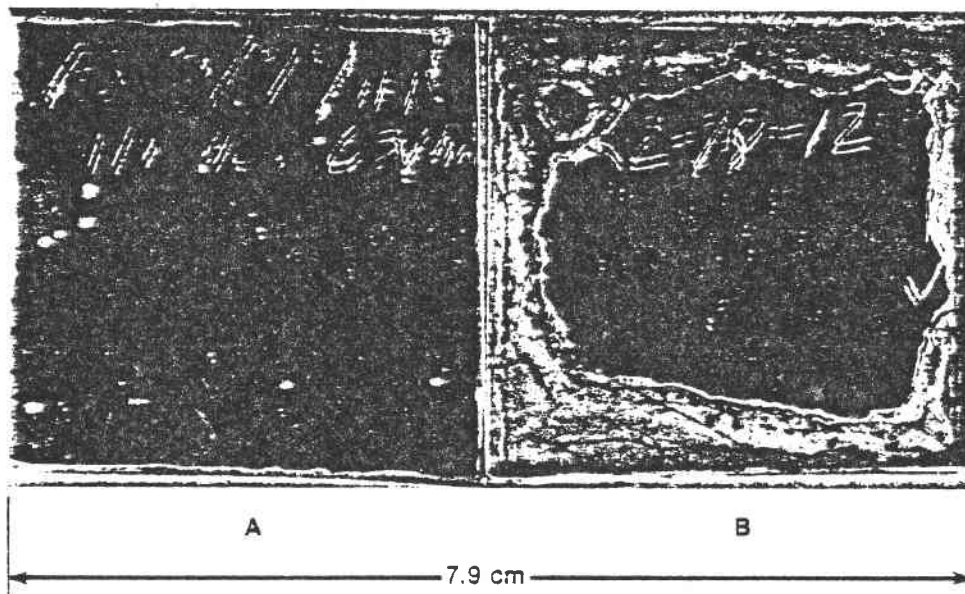


Figure 3. Examples of Mirror Failure:

A. Spotting

B. Interfacial, note the reduction of interfacial failure by edge sealant used on the right side

2.5 Adhesion Testing

Tests of the pull strength of the mirror stack were done using an adherence tester* to pull 2.5 mm diameter aluminum studs. The studs were bonded to the paint on the mirror by using a cyanoacrylate adhesive.** A good bond between the cyanoacrylate and aluminum was obtained by stripping the precoated studs--supplied by the manufacturer of the adherence tester--to take advantage of the already cleaned aluminum surface. The surface of the mirror paint was lightly cleaned with acetone prior to bonding.

2.6 Time-Lapse Photography

A time-lapse photographic record was obtained of the simultaneous attack by HCl vapor on four different mirror samples. Samples were chosen to represent a wide range of degradation resistance (mirrors #8, #16, #19, and #22 from Table 1). The samples were sealed together in a square array with silicone adhesive. Using a teflon gasket, the array was securely fastened to a plastic receptacle containing concentrated HCl, as shown in Fig. 4. This positioning resulted in exposure of the painted surface to the moist HCl vapor, and allowed viewing and photographic documentation of the resultant degradation from above the reflection surface. The mirror samples were illuminated through the edge of the glass sheet by fiber optic light sources so that light scattering from the silver surface revealed defects. The progress of the degradation was recorded every 16 minutes with an automatically timed camera.

*Sebastian I Adherence Tester from the Quad Group, Santa Barbara, Calif.

**Eastman 910.

Table 1. Description of the mirrors evaluated and results of molar acid vapor tests.

Mirror Number	Mirror Manufacturer	Description	Mirror durability in moist H ₂ S Vapor				Mirror durability in moist H ₂ S Vapor			
			Failure Time (h)	Failure Mode	Interfacial Failure (mm)	Comments	Failure Time (h)	Failure Mode	Interfacial Failure (mm)	Comments
1	Hiltem	Protective glass sheet bonded to the paint using white polymer.	90	None	1	Protected by sheet glass; 4 mm interfacial failure along broken sample edge.	1200	None	0.25	
2	Schott	Paint protected with yellow rubber.	90	None	6	Condensation beaded on rubber protective coating.	---	---	---	
3	Hinsinger	Paint protected with white polymer layer.	90	None	7	Edge sealer reduced interfacial failure to 1 mm in places.	1200	None	0.75	Saw 0.1 mm diameter spots causing mottled appearance under microscope.
4	Hinsinger	Paint protected with white polymer layer.	90	None	7	White polymer backing turned pink. Edge sealer reduced interfacial failure.	1200	None	0.75	Saw 0.1 mm diameter spots causing mottled appearance under microscope.
5	Hinsinger		30	Spotting	5		1200	None	1	Saw 0.1 mm diameter spots causing mottled appearance under microscope.
6	Stueclair	Mirroring on Corning Code 0317 glass. ^a	75	Spotting	4		1200	None	0.75	Several black spots on mirror.
7	Schott	Schott Code 8270 glass, b	20(4) ^c	Spotting	2	Condensation beaded on the paint.	1200	None	1	Several 0.5 mm diameter red spots.
8	Falcomer	Corning Code 7809 glass, c	12(10) ^d	Interfacial	10	Spotting proceeded in from edge.	---	---	---	
9	Hiltem	Metallization protected by primer, top coat and inlay.	12	Spotting	3	Condensation beaded on the protective coating, outer coating delaminated.	1200	None	2.5	Many 0.05 mm red spots seen under microscope.
10	Hiltem	Metallization protected by primer and top coat.	12	Spotting	8	Condensation beaded on the protective coating.	1200	None	2	A few 0.05 mm red spots seen under microscope.
11	Carolina	Mirroring on Corning Code 0317 glass.	10(11)	Interfacial	10		250(31) ^e	Spotting	---	
12	Laboratory Mirror	Commercial mirroring process glass cleaned with solvent. Corning Code 0211 glass.	9	Spotting	6		200	Spotting	---	
13	Schott	Paint protected by clear rubber.	6	Spotting	2	Condensation beaded on the protective coating.	---	---	---	
14	Schott Perichlor		6	Spotting	3	Condensation beaded on the paint.	---	---	---	
15	Schott Spiegel Glass	Green paint.	5	Spotting	2	Condensation beaded on the paint.	---	---	---	
16	Hochstein		5(12) ^f	Spotting	2		400	Spotting	0.5	Toned completely black between 150 and 300 h.
17	Laboratory Mirror	Made with commercial chemicals and paint.	4(5) ^g	Silver Mottled	---	Glass was hand scrubbed.	250	Spotting	0.5	One sample covered with grey-green 0.25 mm diameter spots, other one undegraded.
18	Laboratory Mirror	Made with commercial chemicals and paint.	1	Spotting	---	Condensation beaded on the paint.	900	Spotting	1.5	Black spots steadily developed from 5 to 300 h.
19	Reo Age	An inexpensive commercial mirror with an copper metallization and unbacked paint.	2(10) ^h	Spotting	0.5	Tested two lots of mirrors from same manufacturer, both had the same degradation behavior.	100(7) ⁱ	Spotting	0.5	Black spots steadily developed from 5 to 300 h.
20	Laboratory Mirror	Made with commercial chemicals and paint.	1.5	Silver Mottled	---		100	Spotting	0.5	Black spots steadily developed from 5 to 300 h.
21	Experimental Mirror	Commercial mirror with only primer of the top coat paint of 400.	---	---	---		10	Spotting	---	
22	Hochstein	Commercial mirror used in first generation backscatter.	1(12) ^j	Spotting	---		4(11) ^k	Spotting	---	

^a An oxidized Hitec glass.

^b An oxidized Hitec glass.

^c An aluminum borosilicate glass.

^d An oxidized Hitec glass.

^e Number of mirrors tested in brackets, otherwise two were tested.

^f Sample probably failed too quickly to see interfacial failure.

Viewing and Photography
to Monitor Degradation

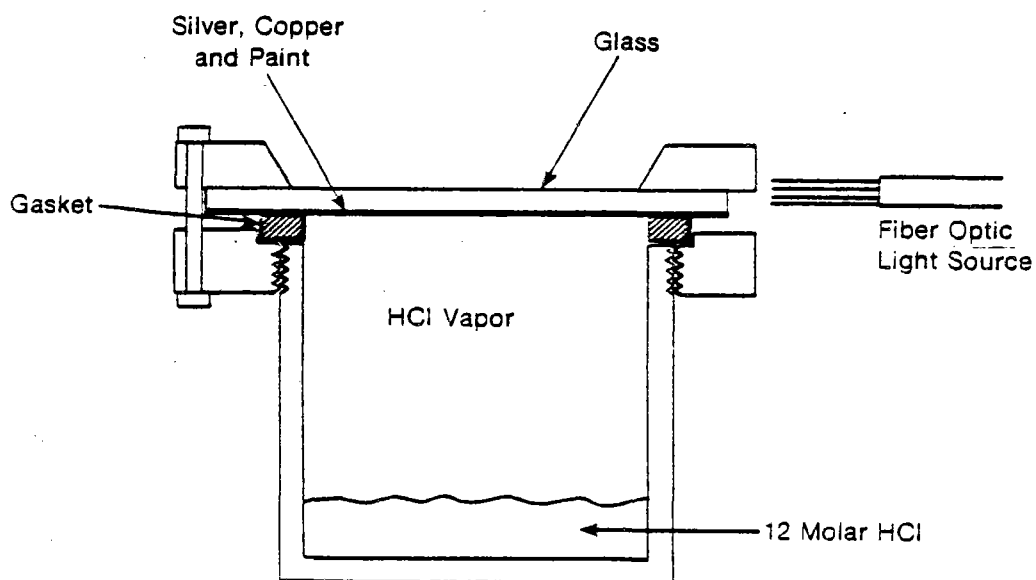


Figure 4. Test Chamber for Time-Lapse Optical Studies of Mirror Degradation

3. Evaluation of the Test Procedures

The concentration of the corrosive vapor in a desiccator during a test was quantitatively determined and the sensitivity of vapor concentration to variables in the test procedure was evaluated in a series of experiments. The major variables studied were temperature (20°C and 30°C), the presence or absence of mirrors, and the concentration of the reagent. Before adding reagent, all desiccators were brought to the test temperature in a constant-temperature water bath, where they remained during the experiment. The desiccator was charged with reagent as described in Sec. 2. All vapor samples were withdrawn through a teflon septum in one of the spouts in the desiccator lid (see Fig. 2).

3.1 HCl(g) Determination: Analytical Methods

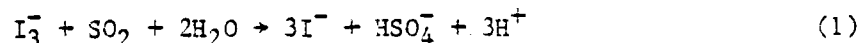
At logarithmic time intervals, the HCl vapor concentration in the desiccator was determined using a technique described in detail by Thompson et al. [9]-- the vapor was generated by aqueous HCl reagent that was pipetted into the desiccator as described in Sec. 2. The technique consisted of withdrawing 5 ml of 0.5 M sodium acetate into a 10-ml, gas-tight syringe. Then, through the septum in the desiccator lid, 5 ml of vapor were withdrawn from the desiccator into the solution. The mixture was thoroughly agitated, then injected into a sealed serum bottle containing 45 ml of 0.5 M sodium acetate. Before each sampling of the vapor the syringe was thoroughly rinsed with a sodium acetate solution to free any residual HCl which had adsorbed onto the glass surface. Subsequently, the syringe was washed with deionized water and with acetone to permit rapid drying.

The chloride ion concentration in solution was measured with a chloride ion selective electrode.* Stock 0.5 M $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$ was used as the electrode filling solution to minimize drift and equilibration time. The electrode was calibrated by analyzing aqueous HCl diluted volumetrically with stock sodium acetate solution.** Using the ideal gas relationship, it was determined that 1 ppm $[\text{Cl}^-]$ in solution was equivalent to 0.6 volume percent HCl in the vapor phase.

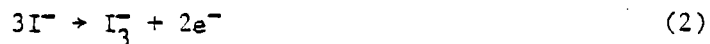
3.2 $\text{H}_2\text{S}(\text{g})$ Determination: Analytical Methods

Oxidative microcoulometry [10] was used to determine the concentration of H_2S vapor in a desiccator. H_2S reagent was pipetted into the desiccator as described in Sec. 2. The concentration of the H_2S reagent was measured using an ion selective electrode method for testing sulfur concentrations.† At logarithmic time intervals, aliquots of vapor were withdrawn into an empty, gas-tight syringe. The samples were then injected for analysis into a combustion tube maintained at 800°C and having a flowing stream of gas containing 80% oxygen and 20% argon, which converted the sulfide to sulfur dioxide.

The sulfur dioxide flowed into a titration cell where it reacted quantitatively with triiodide ion in an electrolyte solution according to the reaction:



Triiodide consumed during the titration was replaced coulometrically by the following half reaction:



*ORION Microprocessor Ionalyzer 901 with ORION Model 96-17 Chloride Ion Selective Electrode.

**SPEX Industries, Metuchen, N.J. 08540.

†ORION Model 94-16 Sulfide Ion Selective Electrode.

The number of coulombs required to replace the triiodide is a measure of the amount of sulfide that was present in the original sample [11].

3.3 The Influence of Acid Vapor Concentration and Experimental Factors on Mirror Degradation Times

The concentration of HCl vapor as a function of time after the introduction of hydrochloric acid into a desiccator is shown in Fig. 5. The two lines in the upper part of the figure depict the results for desiccators containing 12 M reagent, at 20°C and 30°C, and containing no mirrors. The lines in the lower part of the figure are for experiments with no mirrors at 20°C where the starting reagent concentration was 10 M and 9 M. The results for the experiments run at 20°C with 12 M reagent are about 40% lower than the results for 30°C and 12 M reagent. A reduction in the concentration of the hydrochloric acid reagent from 12 M to 10 M resulted in nearly an order of magnitude drop in the concentration of HCl vapor in the desiccator, while 9 M resulted in a drop by another factor of 3.

Also included in the figure are results for desiccators containing 10 mirrors where 12 M reagent was used and the test temperatures were 20°C and 30°C. The figure shows that without mirrors in the range from 30 min to 10⁴ min (7 days) the vapor concentration was in the range 10 ± 5 vol %. The presence of the mirrors caused the concentration of HCl vapor to be on the low end of this range for times greater than 300 min.

Experiments were performed to determine the sensitivity of mirror degradation times to the desiccator temperature and to the concentration of HCl reagent. Results are shown in Table 2. Four pieces each of mirrors 22, 16, and 8 were placed in a desiccator for each experiment (see Sec. 4 for mirror descriptions). Three desiccators were used; one at 30°C using 12 M HCl, one at 22°C with 12 M HCl, and one at 22°C using 10 M HCl. The failure times of the mirrors under these conditions were observed. It was found that there was very little difference between the failure times at 30°C and at 22°C for a

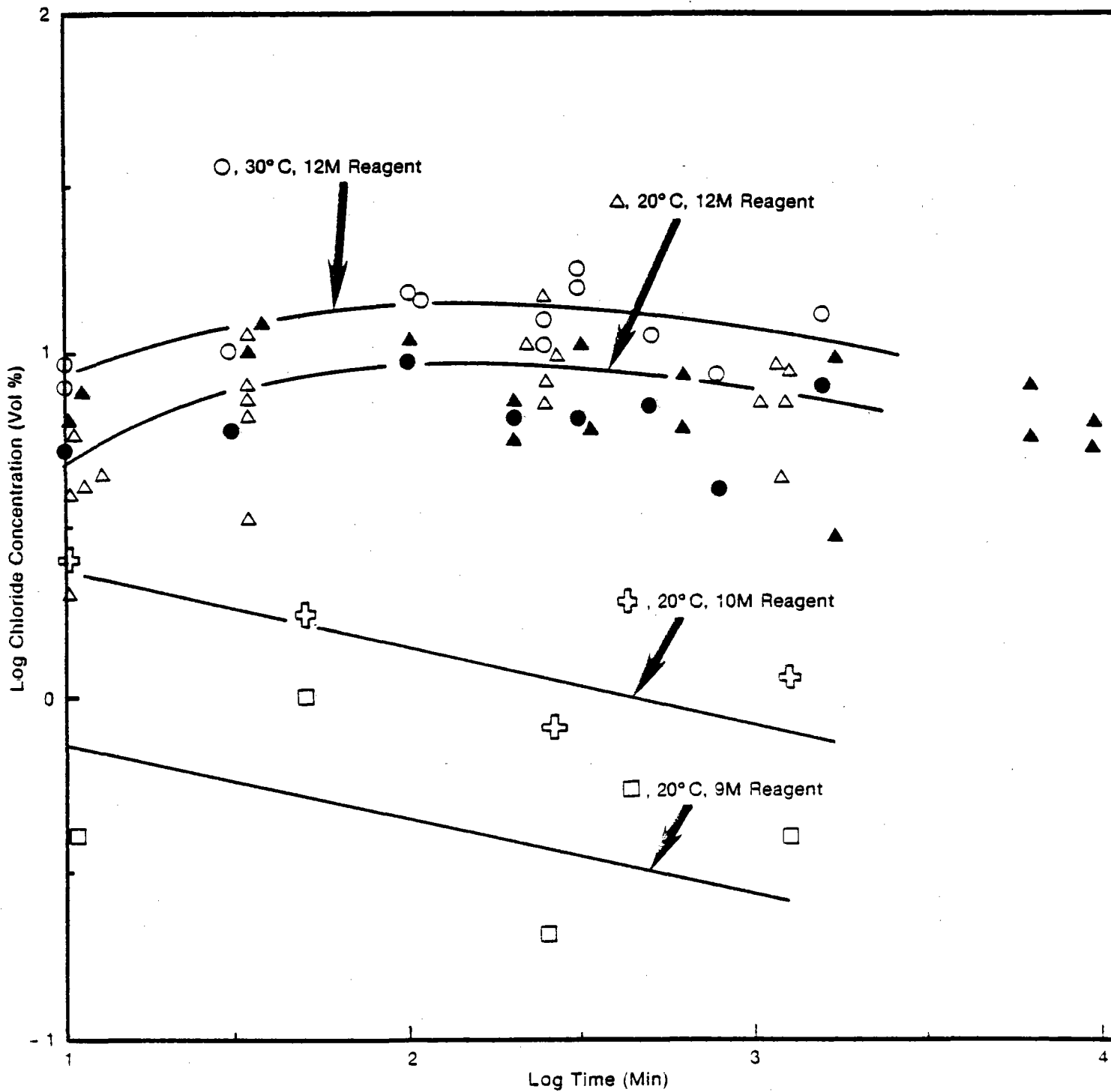


Figure 5. HCl Vapor Concentration in a Desiccator with No Mirrors as a Function of Temperature and Concentration of HCl Reagent; the Influence of the Mirrors is Shown by ●(30°C, 12-M Reagent, 10 Mirrors) and △ (20°C, 12-M Reagent, 10 Mirrors)

Table 2. Failure Time of Mirrors in Moist HCl At
22°C Vs. 30°C and 12 M HCl Vs. 10 M HCl

Mirror no.	30°C/12 M HCl	22°C/12 M HCl	22°C/10 M HCl
8	12 hr	12 hr	20 hr
16	5	5	10
22	~ 1	~ 1	~ 1

desiccator charged with 12 M HCl. However, the failure times for the mirrors tested at 22°C with 10 M HCl showed longer time to failure by about a factor of two, except for mirror 22--it is difficult to get accurate times for failures that occur in an hour or less. These results indicate that at temperatures between 22° and 30°C, the failure times for the 12 M HCl are quite insensitive to temperature and to the ~ 40% higher HCl(g) concentration associated with the higher temperature. Thus, it is estimated that for concentrations of HCl(g) in the range 10 ± 5 vol % and temperatures of $26 \pm 4^\circ\text{C}$, failure times are affected by less than 25% from one desiccator experiment to the next.

A number of other experiments were done using the moist HCl vapor test to explore the sensitivity of the vapor concentration to the factors encountered in the test. The factors considered were amount and surface area and amount of silicone stopcock grease exposed to the interior of the desiccator, the substitution of a polyethylene mirror holder for a glass holder, the surface area of the HCl solution, the method (top charging with closed desiccator lid versus pipette, see Fig. 2) of introducing the HCl solution, and the position of the sidearm with the gas-sampling septum (in contact with or isolated from the desiccator throughout an experiment). None of these factors was found to have an effect on the concentration of HCl vapor as a function of time within the desiccator.

Results similar to the 12 M HCl data of Fig. 4 were seen for the studies of H₂S vapor concentration at 25°C using 0.04 M reagent. The major difference between the H₂S and HCl results was a peak concentration of about 0.9 vol % for H₂S versus about 15 vol % for HCl. As in the HCl vapor concentration experiments, there was a noticeably lower H₂S concentration at about 10⁴ min when mirrors were present. However, in the range of time from 10 min to 10⁴ min, the H₂S vapor concentration was in the range 0.6 ± 0.3 vol %.

4. Results and Discussion

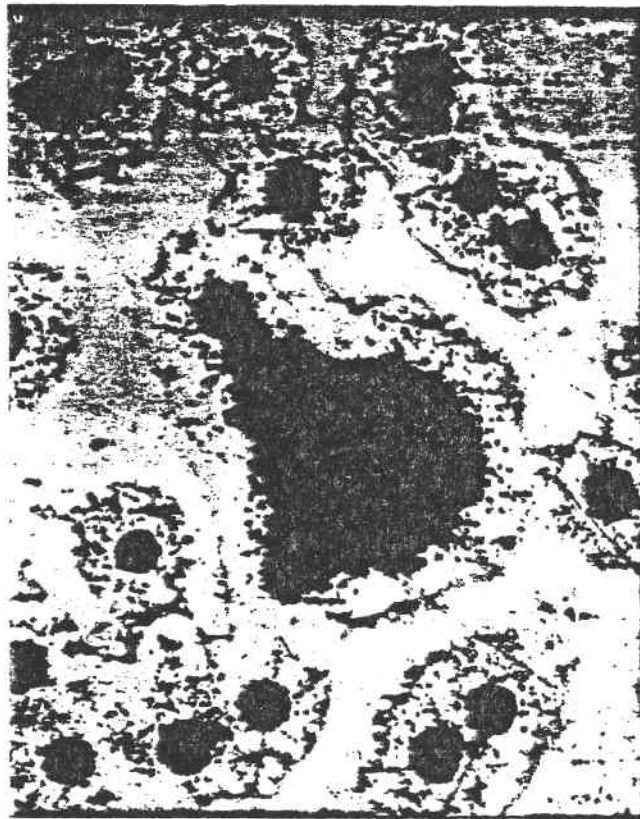
Accelerated degradation tests on 22 different glass second-surface mirrors were done at room temperature using corrosive vapors (HCl and H₂S) in an environment with high relative humidity. Most of the mirrors were made using commercial processes [2] on soda-lime-silicate float glass.

Table 1 gives a description of each mirror that was tested, indicating deviations from either the standard commercial process outlined in the introduction or from the mirror structure shown in Fig. 1. The listing of mirrors in the table is in the order of decreasing durability as judged by the moist HCl vapor test. The most durable mirrors have a protective layer of glass or polymer in addition to the mirror paint. The table also shows that the use of glasses other than soda-lime-silicate float glass for the superstrate results in mirrors of comparable durability (note mirrors 6-9).

4.1 Tests with Moist HCl Vapor

The results of tests in moist HCl are also shown in Table 1. Information on the time to failure and the failure mode is given in the table, along with the amount of interfacial failure (or when the test was terminated) and comments on the test results.

The most common failure mode observed in this work was that of spotting (Fig. 3A) similar to the mode of failure observed by Shelby and coworkers [12]. This mode of failure was characterized by the simultaneous appearance of spots which are typically black to the unaided eye. Sometimes a general haze on the mirror surface was observed. When this phenomenon was observed under a microscope, numerous tiny spots were seen (Fig. 6). The mirror often had failed already (10 visible black spots) at the time hazing occurred. However, the occurrence of a haze alone would also have been judged as a mirror failure. Still another failure mode resulted from wrinkling of the silver across the entire mirror surface without initial discoloration. An interfacial failure mode is like that shown in Fig. 3B; it starts at the



0.4mm

Figure 6. Early Stages of Spot Formation for Mirror #19 in Moist HCl Vapor for 90 Minutes

outside edge of the mirror and progressively works inward. This mode was usually limited to a small distance in from the edge of the mirror and is called edge spoilage in the mirror industry. In some cases large areas of the mirror fail by this mode before any spotting occurs.

Visual observation of the size and number of spots and the degree of edge encroachment on mirrors exposed to the H_2S or HCl tests can be made quantitative with care and appropriate training. However, two techniques have been explored since the conclusion of the exposure experiments described in this paper. They are diffuse reflectance measurements and image analysis of photomicrographs with 1X and 100X magnification. The photomicrographs are prepared in a dark field geometry so that only light scattered outside of the specular cone is observed. Quantitative data on the distribution of defects at the silver/glass interface, including size, shape, and number, are recorded using an image analyzer. This requires the establishment of a gray scale threshold for the light scattering intensity. Changes in incident light intensity and detector sensitivity (e.g., film speed) must be considered in order to make the technique truly quantitative.

In the diffuse scattering experiment a monochromatic beam of light is incident on the mirror surface through ports in an integrating sphere. The specular component of the reflected light exits through another aperture in the sphere, whereas scattered light appears as background intensity within the sphere and is detected at an angle far from the specular angle. To be truly representative of the mirror surface, the collimated incident beam must be expanded to approximately the entire mirror surface. The diffuse reflectance of unstressed mirrors is very low, offering the opportunity to detect an emerging signal as the acid vapor test progresses. Both of these techniques can yield a numerical value for mirror degradation as a function of time.

The tests shown in Table 1 were conducted for up to 90 h, and most of the mirrors failed in this time. These results are to be compared with the salt-spray test, the test used most commonly by the mirror industry to judge mirror degradation resistance, in which a selection of these mirrors shows few failures after test times of up to 300 h.

After 90 h, the surviving mirrors were the ones that were expected to be the most durable because they all had protective layers in addition to the standard layer of paint. Mirror #1 with a layer of sheet glass bonded to the paint showed the greatest durability because there was minimal interfacial failure--a similar double glass mirror has been used on heliostats at the Central Receiver Test Facility for over four years outdoors at Albuquerque, N. Mex., with no mirror failures. With this mirror, it was found that the factory-prepared edge showed 1 mm of interfacial failure although the broken edge of the sample showed 4 mm. This test is representative of the general experience that edges where the mirror has been broken have inferior degradation resistance.

The importance of the edge preparation in reducing interfacial failure is further demonstrated in Fig. 3B. Here an edge sealing solution has been applied along the right-hand edge of mirror #4 and the amount of interfacial failure has been substantially reduced. The use of edge sealer in mirror #3 was also effective. However, some edges that were sealed showed little improvement over ones that were unsealed.

Mirror #22 in the table showed the poorest durability in these tests. This mirror was made by the manufacturer to duplicate the mirrors proposed for use in the first-generation heliostats, which started showing signs of black spots after less than a year of outdoor exposure in Livermore, Calif. Table 1 shows that the majority of the least durable mirrors were made in the laboratory or were inexpensive (as with #19) or unfinished (as with #21). From present field experience mirror #22 appears to have lower durability than is usually experienced in outdoor solar applications. Another mirror from this same manufacturer, #16, was found to have substantially higher durability.

Most of the standard mirrors with a single coat of commercial mirror paint were found to have intermediate durability. These mirrors, #5 through #16 (except #12), showed a variation in failure time from 5 to 30 h.

Beaded condensation was observed on many of the paints and polymer backings behind the paint. This was seen with mirror #2 and with mirror #18, as well

as with a number of mirrors of intermediate durability. This condensation indicates that a number of the paints and polymer backings may have been chosen to be hydrophobic, with the objective of preventing moisture from penetrating to the metallization. The range of durability exhibited by mirrors with these hydrophobic coatings probably reflects differences in coating porosity which governs access by corrosive agents and moisture to the metallization.

The results in Table 1 indicate that testing in moist HCl provides a reasonable ranking of the durability of mirrors. Mirrors whose durabilities were expected to be high (those with glass or polymer backings) were found by the tests to be very durable. Mirror #22, which demonstrated low durability in actual outdoor tests, and mirrors that were expected to show poor durability due to the fabrication method (#19 and #21) were found by the test to be of low durability. The standard commercial mirrors, such as numbers 5 through 11 and 13 through 16, were found to be of intermediate durability, as expected.

4.2 Tests with Moist H₂S Vapor

HCl(g) would probably not be encountered in the vicinity of most solar installations, but H₂S(g) is widespread naturally [13], and tests with this gas were done to see if failure rankings were the same as with HCl(g).

The results of mirror durability tests in moist H₂S vapor are also shown in Table 1. Most of these mirrors tested in H₂S(g) were tested separately in HCl(g). It is seen by comparing the failure times for the two gases that mirrors degrade one to two orders of magnitude more slowly in the moist H₂S vapor than in the moist HCl vapor. However, the failure rankings of the mirrors are remarkably similar. The most notable exception was mirror #18, which had a much longer failure time in H₂S(g) than would have been anticipated on the basis of the moist HCl test.

4.3 Mechanisms of Degradation

The visual observation of the formation of spots during failure indicates that failure occurs at localized sites on the mirror surface rather than uniformly over the entire surface of the mirror. This conclusion was confirmed by reflectance* measurements on mirror #19 where the solar-weighted specular reflectance was unchanged after failure in the H₂S test. (The 10 or more spots that were defined to constitute mirror failure did not create enough damage to affect reflectance significantly.)

A scanning electron micrograph of the paint of mirror #16 prior to testing is shown in Fig. 7. It is seen that there are large pores which extend into the surface of the paint. This indicates that the reason for the formation of spotting during degradation may be the ready penetration of moisture and corrosive gases through defects in the paint to the metallization. Figure 8 shows an optical micrograph of an area where the paint has been pulled away in an adhesion test. Some areas, such as the upper right where the paint has been completely peeled away, appear to be locations where the paint did not properly wet the metallization during manufacturing, thus providing a site where the metallization could be readily attacked.

Measurements are shown in Fig. 9 of the tensile pull strength of a typical paint/copper/silver/glass stack (mirror #6) as a function of time at 65°C and 100% relative humidity. Ten to twelve pulls were done at each aging time, and the results for the cohesive failures in the paint are presented in the figure. All of the initial failures in this figure were cohesive failures within the paint. However, after 10 days, 7 of the 11 failures were due to loss of adhesion at the paint/copper interface (presumably due to moisture penetration) and at about the same low value (< 0.1 MPa) as most of the cohesive failures in the paint. There were 4 adhesive failures in 12 tests after 1 day of aging and 2 in 11 after 3 days.

*Mobile Solar Reflectometer Model MS 251 Gier-Dunkle Instruments, Inc.



Figure 7. Scanning Electron Micrograph of the Paint on Mirror #16

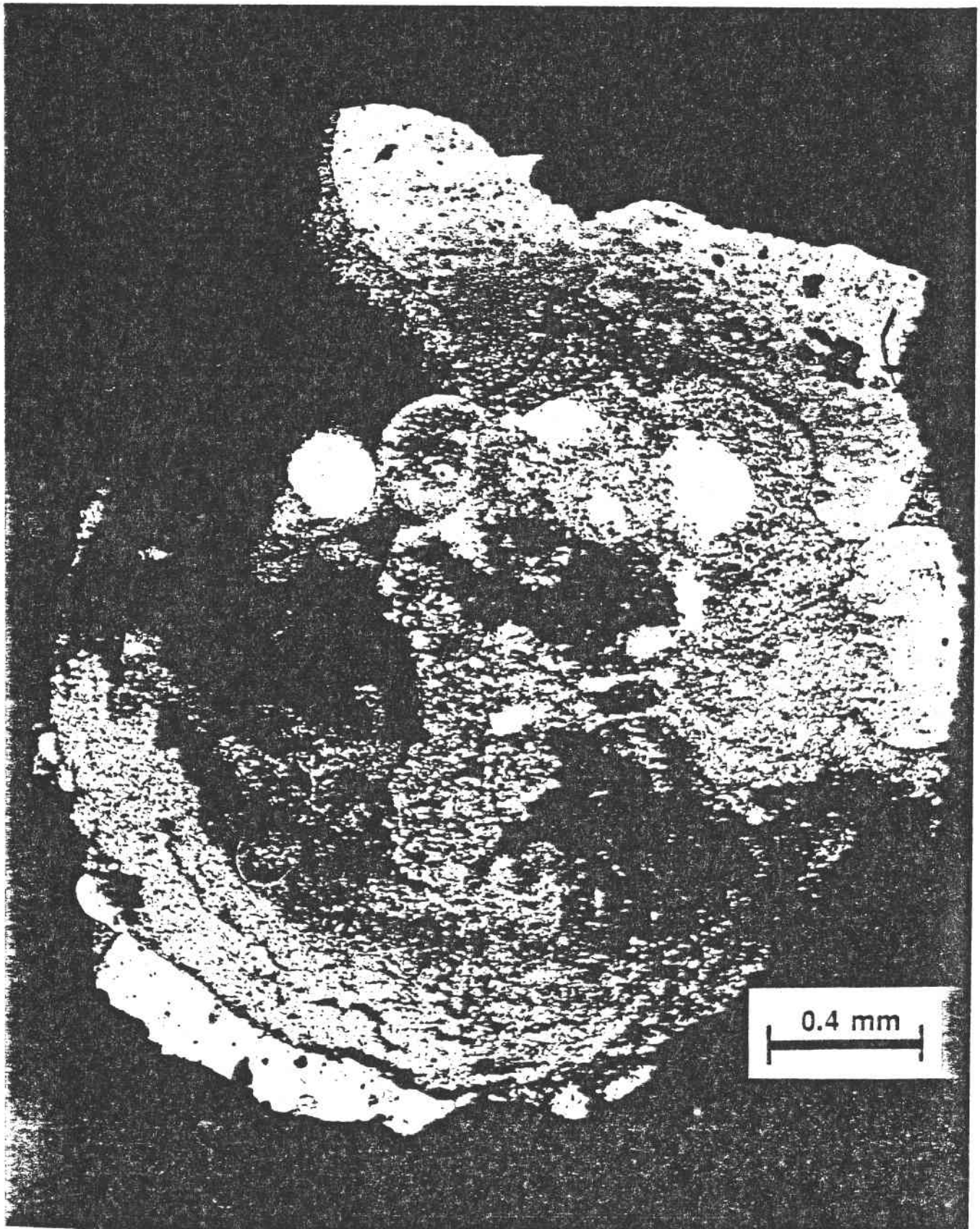


Figure 8. Optical Micrograph of Paint/Copper Interface Showing Nonwetted Areas

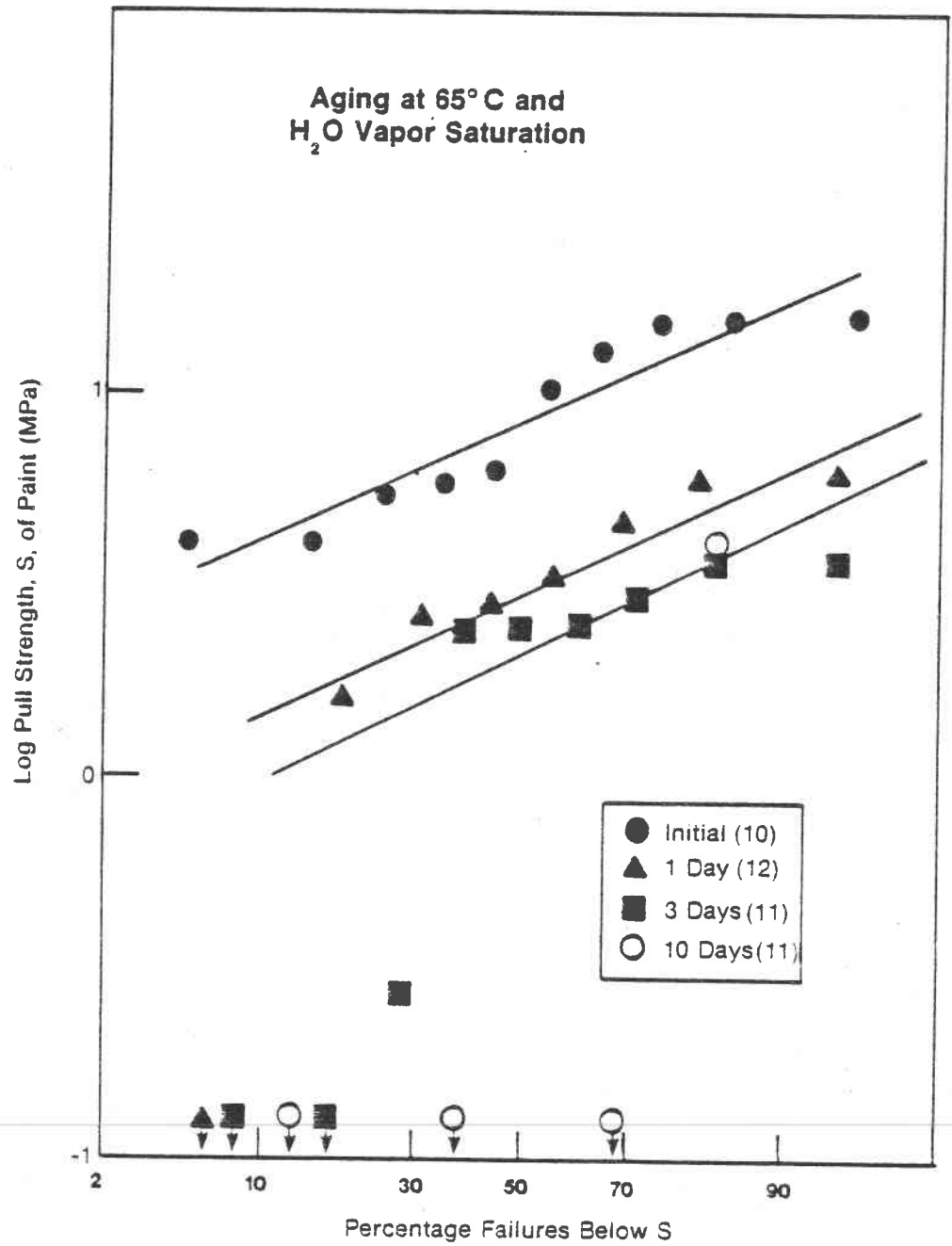


Figure 9. Log Normal Plot of Pull Strength of the Paint on Mirror #6 as a Function of Aging at 65°C and H₂O Vapor Saturation; the Number of Pulls at Each Time is Given in Parentheses in the Key to Symbols

This selective reduction of the adhesion at the copper/paint interface is consistent with the idea of pores in the paint that lead to spot failures much more quickly in some areas than in others. These results indicate that for a typical paint, penetration of moisture to the interface occurs much more quickly (≤ 24 h) at some spots on the surface than others (> 240 h). This test also indicates that the moisture that penetrates into the paint layer softens the paint and degrades its cohesive strength. This loss of cohesion and adhesion occurred in mirrors where water beaded up on the paint, as well as where water wet the paint.

The results of the time-lapse photographic study of the HCl-induced degradation of four different mirrors are shown in Fig. 10. This figure shows how spotting suddenly occurs for mirrors #22 and #19. For mirror #16 it shows an interfacial failure in which the degraded region sweeps across the mirror. This interfacial failure is probably different from that seen in the desiccator tests, because in the latter tests the edge of the mirror was exposed while in the former all mirror edges were covered--two edges were covered with silicone to hold the mirrors together and two with the teflon gasket that pressed against the back of the mirror to prevent leakage of HCl(g). The gasket appears to be the initiation site for the failure of mirror #16. The normal mode of failure for this mirror is spotting, as shown in Table 2. Mirror #8 in the figure failed by a combination of the spotting and interfacial modes. Spotting was observed over a wide area at the front of the interfacial failure; a similar mode of failure was observed in the desiccator tests. (The light scattering that appears in the initial photograph of the sequence is due to dust on the mirror surface which caused double images.)

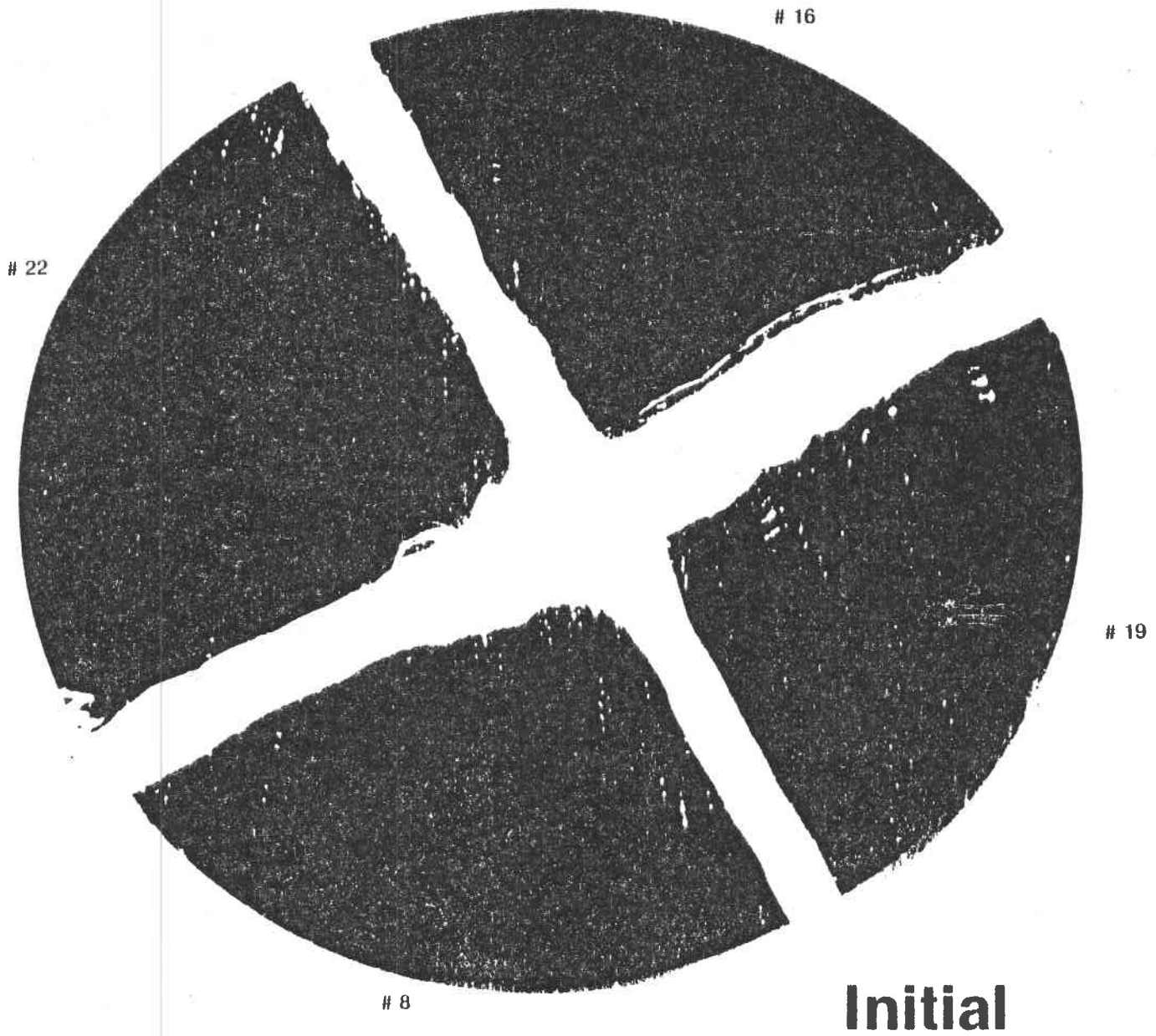
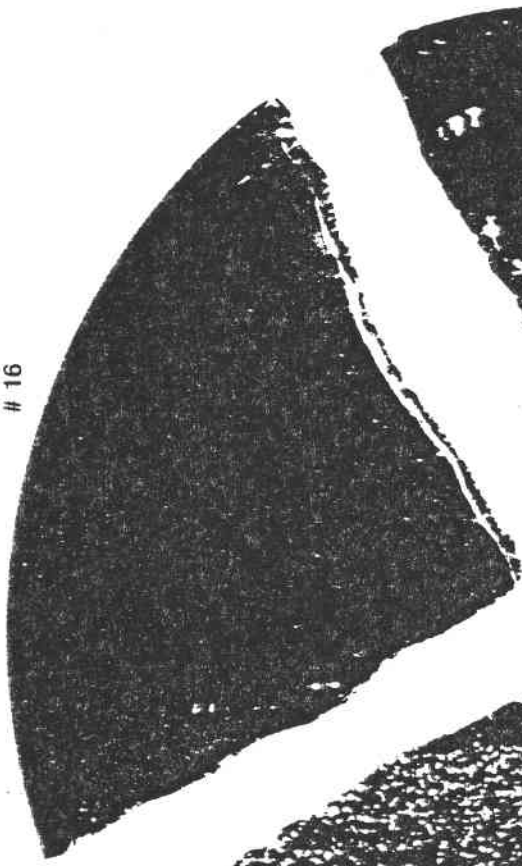
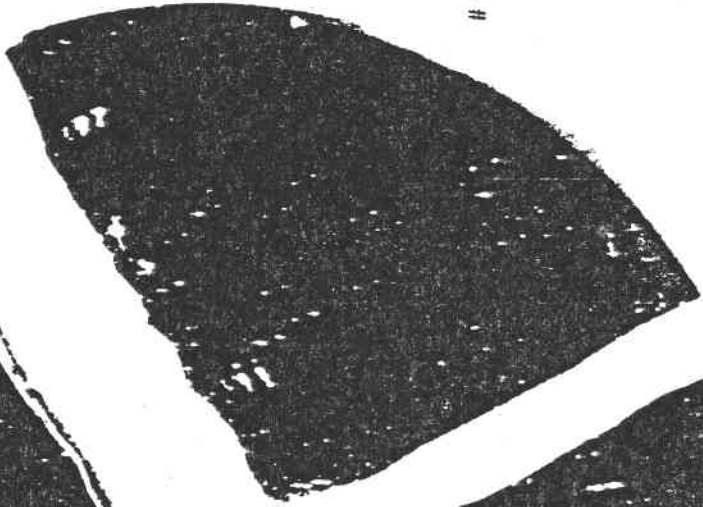


Figure 10. Elapsed Time Photographs of the HCl-Induced Degradation of Mirrors Studied in the Test Chamber of Fig. 5; the Mirrors Under Study are Identified on the Photographs

16



19



96 min.

8



22



16



19

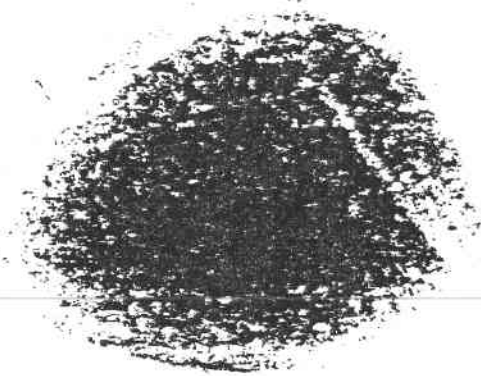


592 min.

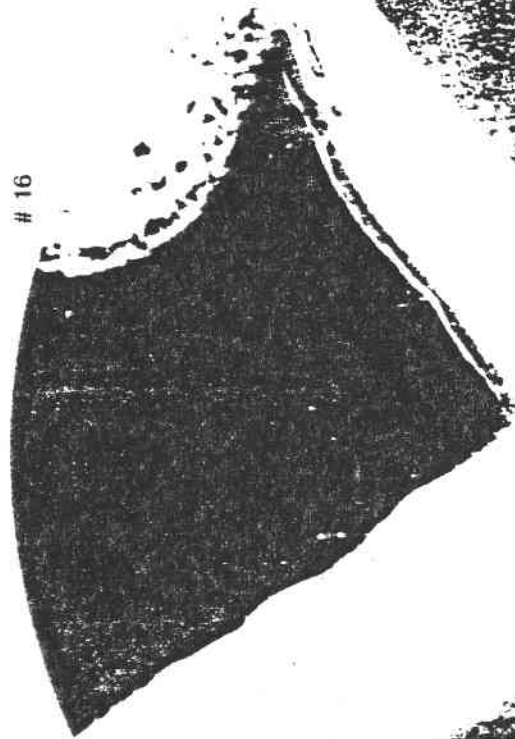
8



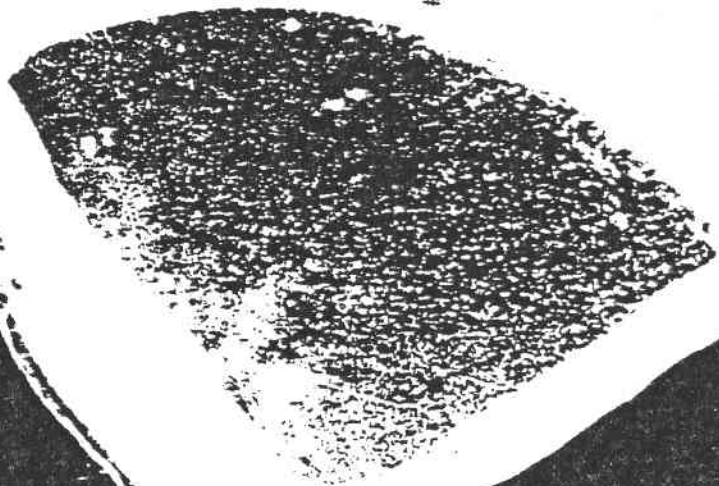
22



16



19



736 min.

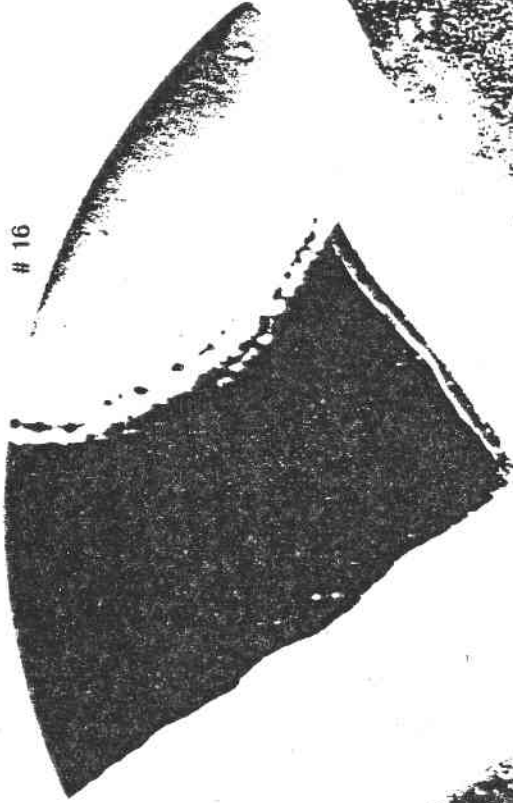
8



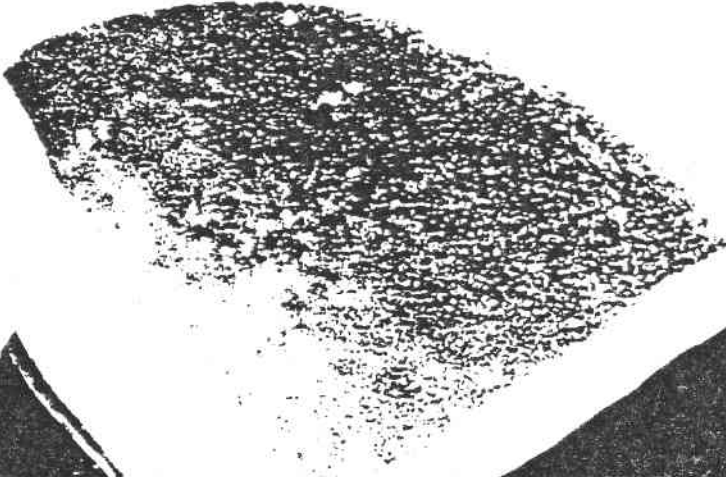
22



16



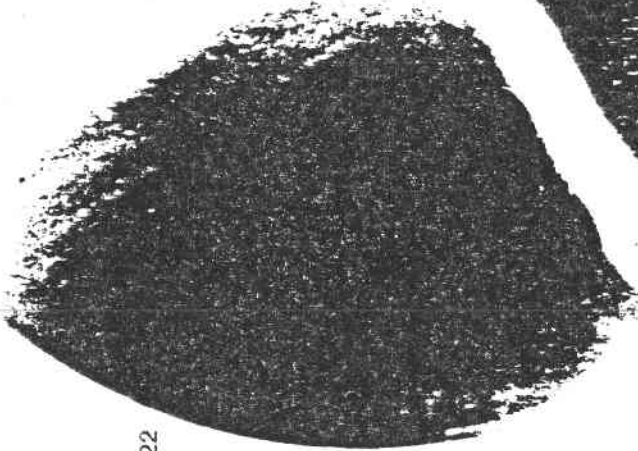
19



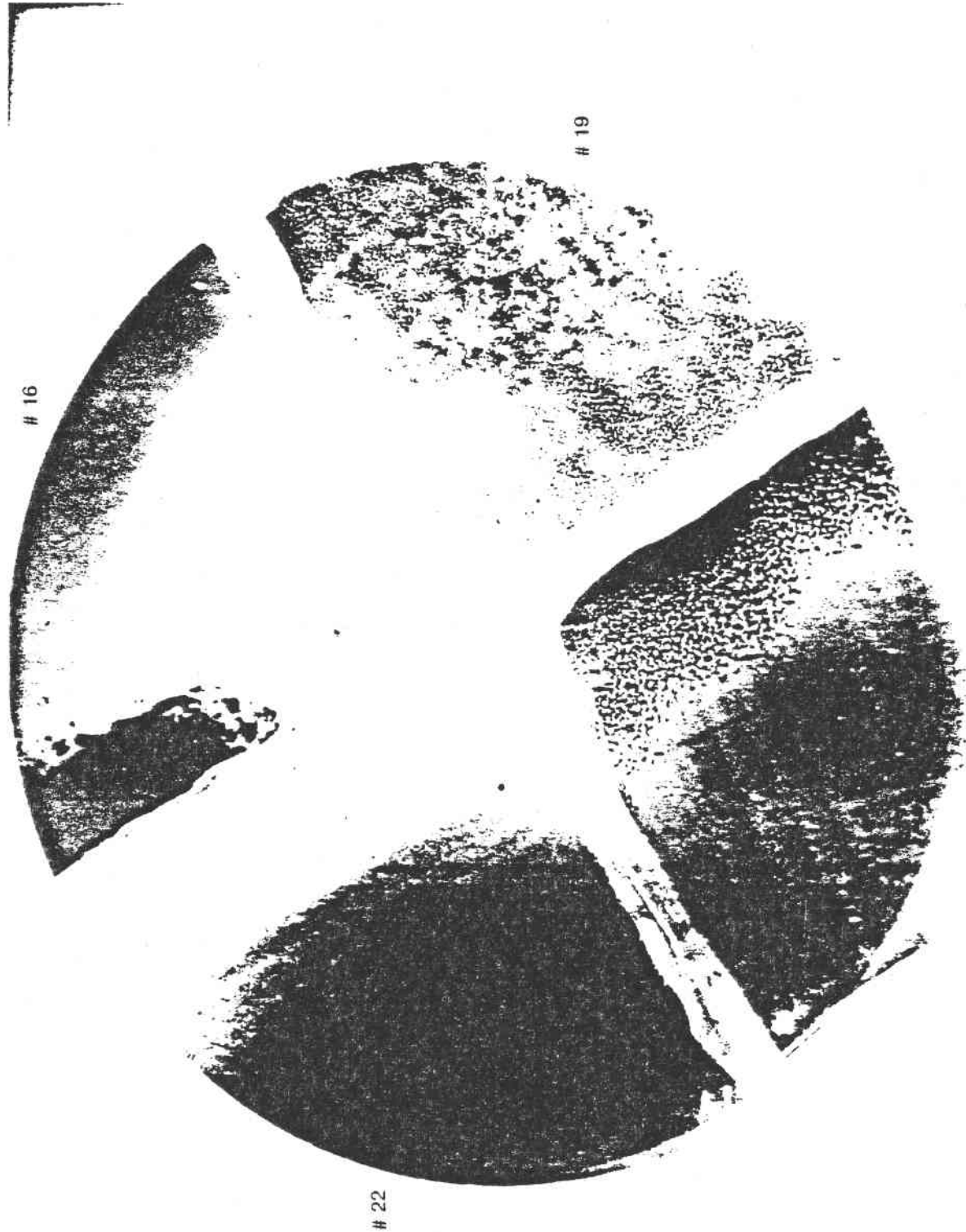
8



22



928 min.



1456 min.

5. Conclusions

It appears that the time required for silver/glass mirror systems to fail in accelerated moist HCl and H₂S tests is determined by the quality of the protective layer. Defects in the form of pores or poor paint/metal adhesion can lead to failure. Tests with commercial mirrors indicate that defects in the protective layer, rather than its general permeability, nearly always dominate the initial degradation. Application of a nonporous layer to the mirror paint can therefore result in much improved durability.

A simple, reproducible, and rapid test of the protective quality of mirror-backing layers has been developed. The ranking of degradation resistance is in agreement with practical experience with solar mirrors and is consistent with expectations for the mirrors tested.

REFERENCES

- [1] V. P. Burolla, *Solar Energy Materials* 3 (1980) 117.
- [2] M. A. Lind, C. Q. Buckwalter, J. L. Daniel, J. S. Hartman, M. J. Thomas, and L. R. Pederson, *Pacific Northwest Laboratory Report PNL3194* (September 1978) Chap. 1.
- [3] B. Schweig, "Mirrors," Pelham Books, London (1973).
- [4] Interim Federal Specification DD-M-004110 (65A-F55) (April 5, 1968) (available from the General Services Administration).
- [5] A. Butts, and C. D. Cox, "Silver: Economics, Metallurgy and Use." D. Van Nostrand Co., Inc. (1967).
- [6] W. Dahms, U.S. Patent 3,649,373 (14 Mar. 1972).
- [7] P. F. Warner, U.S. Patent 3,846,139 (5 Nov. 1974).
- [8] A. Quack, *Appl. Polymer Symp.* 23 (1974) 45.
- [9] C. R. Thompson, et al., *Historiska Och Litteraturhistoriska Studies* 12 (3) (1975) 253.
- [10] ASTM Standard D3246-76.
- [11] R. E. Dickerson, H. B. Gray, G. P. Haight, *Chemical Principles*, 2nd Ed. (W. A. Benjamin, Inc., 1974) Chap. 18.
- [12] J. E. Shelby, J. Vitko, and R. L. Farrow, *Solar Energy Materials*, 3 (1980) 185.
- [13] H. W. Georgii, *Atm. Environ.* 12 (1973) 681.