SERI/RR-255-1630

September 1982

Status Report on Testing of Advanced Mirrors

Gary Jorgensen

Solar Energy Research Institute
A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

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

Printed in the United States of America
Available from:
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price:
Microfiche $3.00
Printed Copy $4.00

NOTICE

SERI/RR-255-1630
UC Categories: 62e, 63e

Status Report on Testing of Advanced Mirrors

Gary Jorgensen

September 1982

Prepared Under Task No. 1089.00
WPA No. 117-81

Solar Energy Research Institute
A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

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

FOREWORD

This report documents the progress through September 1981 of a research project to study the durability of several types of advanced mirrors to accelerated degradation in salt spray and HCl vapors. The experimental work was carried out at SERI, although 21 of 27 mirror types tested were prepared for SERI by an external source. This report was prepared by Gary Jorgensen.

P. Schissel, Task Leader

Approved for

SOLAR ENERGY RESEARCH INSTITUTE

Gordon E. Gross, P.E., Chief
Materials Research Branch

Barry L. Butler, Manager
Solar Thermal and Materials Research Division

SERI

SUMMARY

This status report summarizes the Advanced Mirror Screening tests performed under the auspices of the Materials General Research Task during FY 1981. The objective of this work was to obtain data indicative of the durability and corrosion resistance of a number of candidate advanced mirror samples subjected to several environmental parameters. Different glass substrates were used and several back protection processes were employed. The extent of degradation was characterized by a variety of optical tests as well as by visual inspection.

SERI

TABLE OF CONTENTS

SERI

LIST OF FIGURES

LIST OF TABLES

SERI

SECTION 1.0

INTRODUCTION

The most commonly used mirrors for solar applications have been made from wet-process silvered glass, backed with a protective paint. These mirrors, largely of the household variety, were not specifically designed to withstand the cycling of temperature and humidity, together with exposure to direct sunlight and atmospheric pollutants expected during use in a solar collector. There is strong evidence that such reflective materials suffer severe degradation under weathering conditions [1,2]. The back coating of paint not only adds expense to the final mirror, but is suspected of adding inorganic impurities which are capable of initiating unwanted corrosion reactions. These, in turn, can cause delamination and corrosion of the metallic reflective layer [3]. For these reasons, alternative mirror concepts were considered. The feasibility of using sputtered back coatings which could be used after sputter-depositing the reflective layer was the primary subject of the work reported in this paper.

SECTION 2.0

EXPERIMENTAL PROCEDURES

2.1 SOURCES OF MIRRORS

Mirror samples prepared in-house and by outside sources were included in the test program. Twenty-one mirrors were provided by Donnelly Mirrors, Inc., of Holland, Mich. (samples #1-21 in Table 2-1). Seven different metallic protective overcoats were tried to improve the corrosion resistance of these samples. In each case a 100-nm layer of silver followed by a 50-nm overcoat was deposited by a reactive sputtering technique. An oxygen atmosphere was maintained to enhance adhesion to the glass substrates. As indicated in Table 2-1, some samples received a Mir-O-Cron® paint backing in addition to the metallic overcoat. Sample #22 was prepared using a wet chemistry process by Falconer Glass Industries, Inc., and had a protective paint backing. Sample #23 was prepared by an in-house wet chemistry process, but no back protection was provided. The final four samples (samples #24-27) were also produced in-house using a sputtering deposition process. A 2.5-5.0-nm layer of Inconel was sputter deposited in an argon atmosphere onto several glass substrates. This initial layer was intended to improve the adhesion of the silver reflective layer to the glass without adversely affecting optical performance. A silver layer of 100 nm was then followed by an Inconel protective backing of 25 nm thick.

2.2 MIRROR TESTING

All mirror specimens were subjected to two environments to accelerate degradation; these consisted of salt spray and an HCl acid vapor. Three mirrors

Table 2-1. Advanced Mirror Samples

Sample (#)	Glass Substrate	Protective Overcoat	Deposition Process	Paint	Supplier
1	Soda Lime	Titanium	Sputtered	Yes	Donnelly Mirrors, Inc.
2	Corning 7809	Titanium	Sputtered	Yes	Donnelly Mirrors, Inc.
3	Soda Lime	Stainless Steel 304	Sputtered	Yes	Donnelly Mirrors, Inc.
4	Corning 7809	Stainless Steel 304	Sputtered	Yes	Donnelly Mirrors, Inc.
5	Soda Lime	Inconel 600	Sputtered	Yes	Donnelly Mirrors, Inc.
6	Corning 7809	Inconel 600	Sputtered	Yes	Donnelly Mirrors, Inc.
7	Soda Lime	Copper	Sputtered	Yes	Donnelly Mirrors, Inc.
8	Corning 7809	Copper	Sputtered	Yes	Donnelly Mirrors, Inc.
9	Soda Lime	Molybdenum	Sputtered	Yes	Donnelly Mirrors, Inc.
10	Corning 7809	Molybdenum	Sputtered	Yes	Donnelly Mirrors, Inc.
11	Soda Lime	Hastelloy	Sputtered	Yes	Donnelly Mirrors, Inc.
12	Corning 7809	Hastelloy	Sputtered	Yes	Donnelly Mirrors, Inc.
13	Soda Lime	Chrome	Sputtered	Yes	Donnelly Mirrors, Inc.
14	Corning 7809	Chrome	Sputtered	Yes	Donnelly Mirrors, Inc.
15	Corning 7809	Stainless Steel 304	Sputtered	No	Donnelly Mirrors, Inc.
16	Corning 7809	Chrome	Sputtered	No	Donnelly Mirrors, Inc.
17	Corning 7809	Inconel 700	Sputtered	No	Donnelly Mirrors, Inc.
18	Corning 7809	Titanium	Sputtered	No	Donnelly Mirrors, Inc.
19	Corning 7809	Copper	Sputtered	No	Donnelly Mirrors, Inc.
20	Corning 7809	Hastelloy	Sputtered	No	Donnelly Mirrors, Inc.
21	Corning 7809	Molybdenum	Sputtered	No	Donnelly Mirrors, Inc.
22	Corning 7809	None	Wet chemistry	Yes	Falconer Glass, Inc.
23	Float	None	Wet chemistry	No	SERI
24	Corning 7809	Inconel 600	Sputtered	No	SERI
25	Corning 0317	Inconel 600	Sputtered	No	SERI
26	Soda Lime	Inconel 600	Sputtered	No	SERI
27	Quartz	Inconel 600	Sputtered	No	SERI

(each two inches square) were cut from each of samples #1-14 and #22-27, and three one-inch square mirrors were cut from each of samples 15-21. A 1-cm diagonal scratch was then scribed across the protective backing of each mirror specimen to provide an additional edge-type site for corrosion attack. Following initial characterization, these were then exposed to a synthetic sea water (salt spray) corrosion test developed in-house [4]. Specimens were removed and measured at 24-, 48-, and 72-h intervals.
Another mirror specimen from each sample was prepared as described above (without the 1-cm scratch) and used for the HCl acid vapor test [5]. Mirrors were initially characterized and then periodically inspected on a subjective pass/fail criteria. A mirror with visible degradation was considered to have failed. Specimens #22-27 were also optically remeasured after six hours of exposure.

In an effort to quantify the level of degradation experienced by the various mirror samples, several characterization procedures were used. The first provided a subjective visual estimate of the extent of corrosion. For the salt spray test, each criterion listed in Table 2-2 was ranked on a scale of 0 to 10, with 0 meaning no degradation, 1 = 10%, 2 = 20%, and so forth. A mirror specimen was defined as having failed when the sum of the corrosion criteria scores exceeded 4.9. A mirror was considered to have failed the HCl test if more than ten visible degradation spots were evident or if attack proceeded more than 10 mm inward from an edge.

Reflectance measurements were performed in an attempt to compare the extent of corrosion to optical degradation. Normal hemispherical reflectance was measured in a manner comparable to the recently proposed ASTM standard method [6]. This provided a tabulation of solar weighted reflectance as a function of exposure time. Recent in-house studies have suggested that the reflectance spectrum of silver mirrors is sensitive to degradation effects at a wavelength of 400 nm [1]. Accordingly, the reflectance value in this spectral region of the various mirror specimens was also compiled. Finally, parallel in-house work with other mirrors indicated a correlation between the formation of light scattering centers and degradation processes. A diffuse reflectance measurement device (Fig. 2-1) was used to gather light scattering data comparable to data reported in Ref. 1. For the advanced mirror studies, the beam expander shown in Fig. 2-1 was omitted to accomodate the reduced specimen size.

Table 2-2. Salt Spray Corrosion Criteria

Criterion	Property	Description
1	Undercutting	Coating lifts up around the edges
2	Condition of paint	Flexible, brittle, cracked, etc.
3	Extent of corrosion	Fraction of area or perimeter attacked
4	Edge	Corrosion near edges
5	Pitting	Pinhole cavitation on coated surface
6	Corrosion product	Color of corrosion
7	Coating disappearance	Percent of coating totally removed

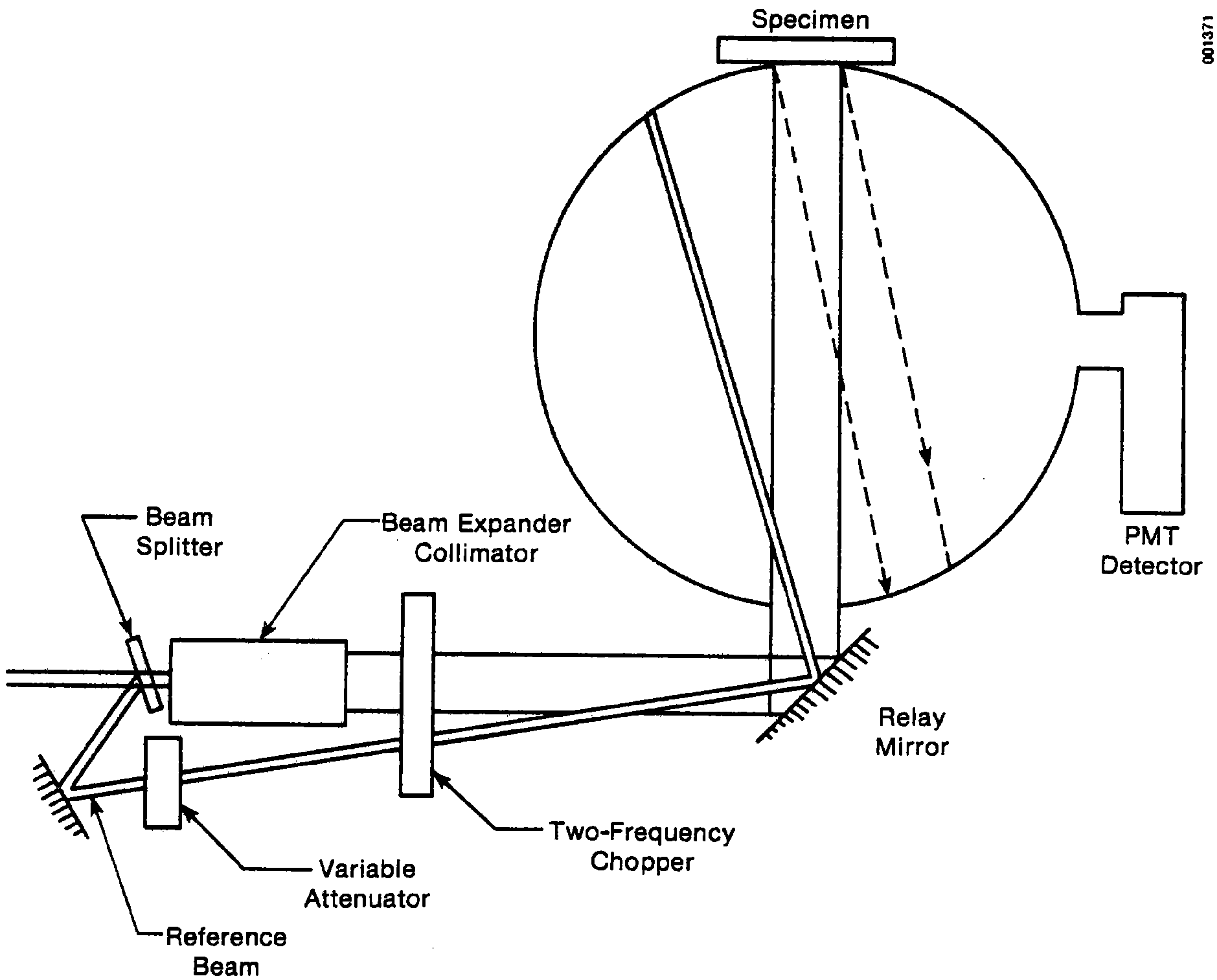

Figure 2-1. Schematic Diagram of an Optical System with An Integrating Sphere Used for Light Scattering Measurements

SERI

SECTION 3.0

RESULTS AND DISCUSSION

Optical measurements provided little useful information about salt spray degradation rates. Table 3-1 presents the initial (nonexposed) solar weighted normal hemispherical reflectances (ρ_s) of the mirror specimens. The sums of the residual reflectance values are also given in column 3 $\{\Sigma\Delta = 2\,\rho_s\,(t=0) - [\rho_s(t=24h) + \rho_s(t=48h)]\}$. The reflectance values of the

Table 3-1. Optical Data Following Salt Spray and HCl Tests

Sample (No.)	$\rho_s(t = 0)$	$\Sigma\Delta$	Salt Spray Pass/Fail Score	HCl Time to Failure (h)
1	84.5	-0.03	7	22*
2	86.5	-3.75	7	22*
3	83.0	-2.04	5	>31* (P)
4	85.5	-0.57	4 (P)	22*
5	83.8	-6.09	18	22*
6	88.0	0.55	4 (P)	22*
7	84.8	2.04	0 (P)	29
8	87.6	5.20	0 (P)	22*
9	85.3	-1.32	4 (P)	>31 (P)
10	87.3	0.31	3 (P)	>31 (P)
11	82.0	-8.61	5	22
12	85.2	-3.77	8	>31 (P)
13	88.7	5.47	7	>31 (P)
14	89.1	3.70	7	>31 (P)
15	87.2	≠	7	22*
16	86.7	≠	7	22*
17	87.7	≠	7	22*
18	87.8	76.56	10	22*
19	87.4	-4.22	16	22*
20	87.9	77.59	11	22*
21	88.1	≠	16	22*
22	82.4	-8.62	0 (P)	>31 (P)
23	66.8	4.47	18	22
24	47.1	-15.06	3 (P)	6*
25	38.4	-6.09	3 (P)	6*
26	34.6	-4.35	4 (P)	6*
27	45.2	-1.05	2 (P)	6*

≠Delaminated; no coating.
*Initial inspection.
ρ is the solar weighted normal hemispherical reflectance.
$\Sigma\Delta$ residual reflectance (see text).
P indicates the mirror passed the criteria established for durability.

nonexposed Donnelly mirrors (samples #1-21) should be a function of the type of glass substrate only and independent of the type of protective backing. A variance of roughly 4% in the data for nonexposed mirrors can then be compared with the $\Sigma\Delta$'s to evaluate the significance of optical degradation with time. As is evident, the variations of the reflectance measurements with exposure time are generally within the measurement error determined by the nonexposed specimens. Exceptions are samples #18, 20, and 23, as well as the in-house Inconel/Silver/Inconel samples (#24-27). The first set of exceptions is displayed in Fig. 3-1. Samples #18 and 20 are of the unpainted Donnelly series (15-21). Most of these mirrors degraded so rapidly, usually by delamination of the metallic coating, that optical measurements could not be made after the initial (t = 0) measurement. Of those which were measurable, a substantial decrease in reflectance accompanied by corrosion failure is apparent in Fig. 3-1 for samples #18 and 20. Only sample #19, the copper backed mirror, did not experience appreciable degradation. No trend is readily apparent with Sample #23, the wet chemistry process mirror.

Figure 3-2 shows the reflectance increases after exposure of the Inconel/Silver/Inconel samples to salt spray. This effect is believed to be due to oxidation of the initial Inconel layer. Oxidation would tend to transform the Inconel, normally an absorbing metal and hence a poor reflector, to a more "transparent" oxide, thus enhancing reflectance by the silver.

The other optical characterization methods of reflectance at 400 nm and diffuse reflectance did not correlate with salt spray exposure any better than the ρ_s measurements.

Fortunately, a fair amount of useful information can be obtained from the subjective visual inspection and classification of the degraded mirrors. These results are listed below:

1. The painted Donnelly mirrors with molybdenum, copper, and stainless steel backings withstood salt spray corrosion very well. In particular, the copper backed mirrors (samples #7 and 8) showed no signs of deterioration (Table 3-1).
2. None of the unpainted Donnelly mirrors survived either the salt spray or the HCl corrosion tests, suggesting that paint at least delays corrosive attack by reactive vapors.
3. The only samples to survive both the salt spray and HCl tests were #9 and #10, the molybdenum backed Donnelly mirrors, and #22, the Falconer mirror. Sample #22 was especially inert to the salt spray test, although the solar weighted reflectance was roughly 5% lower than that of the molybdenum backed mirrors (Table 3-1).
4. In general, the HCl test proved to be too severe for these samples, particularly the unpainted, metallic backed variety. As indicated in Table 3-1, the majority of mirrors subjected to this test had failed by the time they were first inspected for corrosion. Paint inhibited this effect to some extent but did not significantly deter degradation.
5. Although the low initial reflectance of the in-house Inconel/Silver/Inconel samples precludes their use as solar mirrors, they survived the salt spray test well. This offers hope for Inconel backed mirrors that use a different substance than Inconel that will serve as the initial adhesion-enhancing layer but will not compromise reflectance.

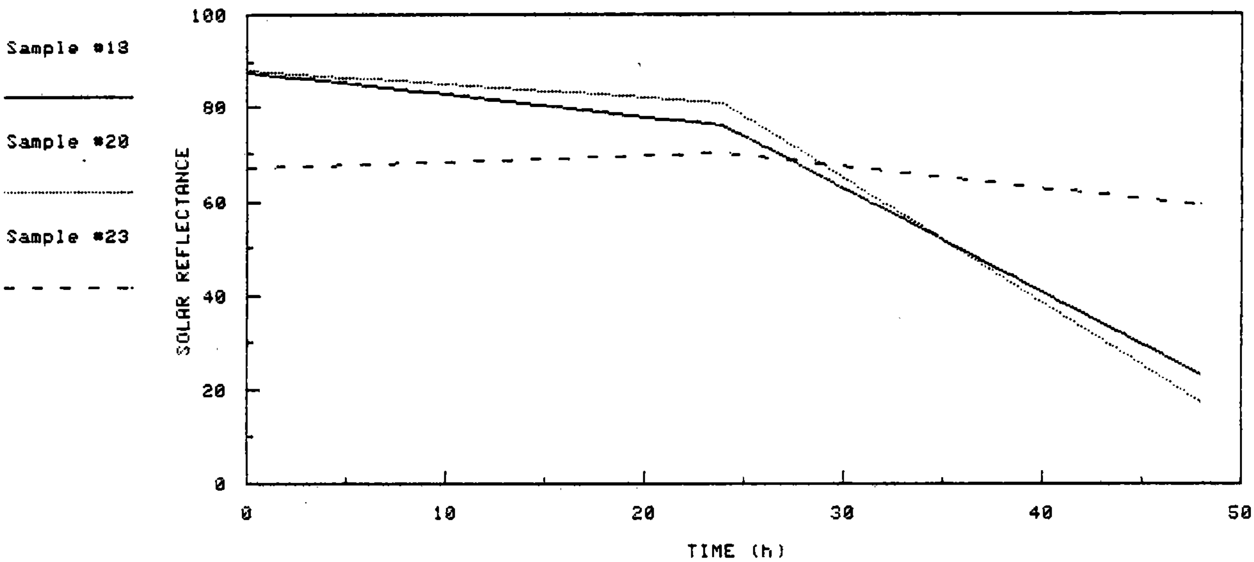

Figure 3-1. Degradation of Solar Reflectance Due to Salt Spray Exposure for Samples Having Large Variance (Δ)

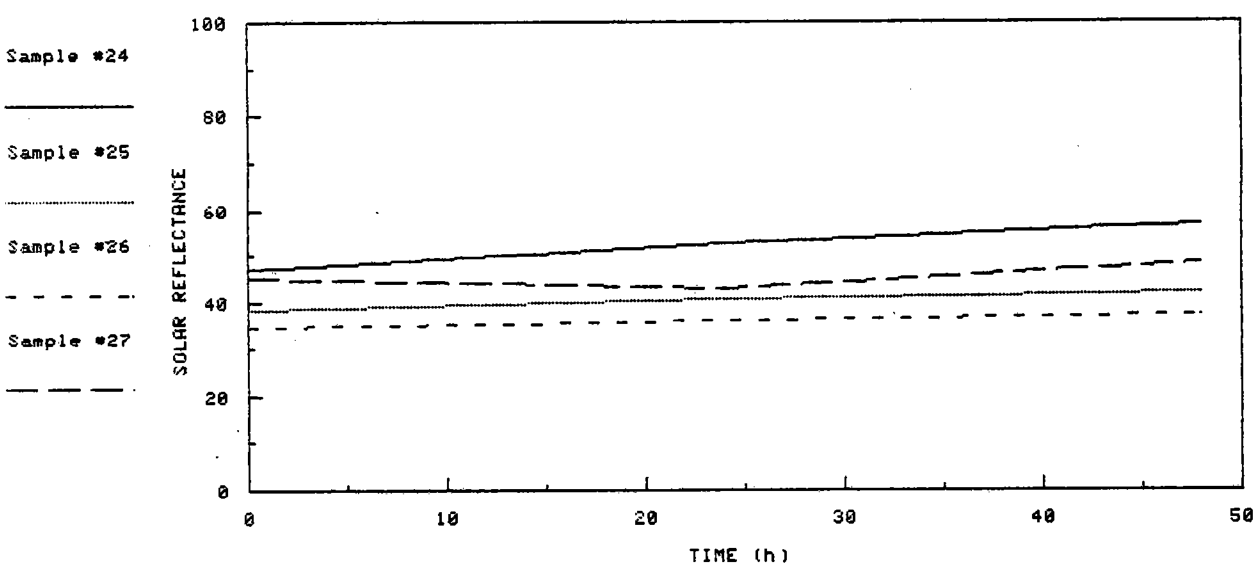

Figure 3-2. Increase of Solar Reflectance After Salt Spray Exposure of Inconel/Silver/Inconel Samples

SERI

SECTION 4.0

CONCLUSIONS

Most of the unpainted advanced mirror candidates were unable to withstand the salt spray and acid vapor tests. A notable exception was the Inconel backed samples. Mirrors with a non-Inconel adhesion-enhancing layer (between the silver and the glass) which incorporate an Inconel protective backing should be further pursued.

The HCl acid vapor test was too severe. A more realistic (in terms of expected levels and composition of pollutant) and more systematically controlled test of advanced mirror candidates should be performed.

A statistically designed method for accelerated degradation testing of advanced mirrors is warranted, similar to the MATM (Matrix Approach for Testing Mirrors) described in Refs. 1 and 2.

SECTION 5.0

REFERENCES

1. Masterson, K. D.; Lind, M. A. 1982. Matrix Approach for Testing Mirrors--Part 1. SERI/TR-255-1504. Golden, CO: Solar Energy Research Institute.

2. Masterson, K. D., et al. (to be published). Matrix Approach for Testing Mirrors--Part 2. SERI/TR-255-1627. Golden, CO: Solar Energy Research Institute.

3. Thomas, T. M.; Pitts, J. R.; Czanderna, A. W. "Surface Analysis of Commercially Made Mirrors." Submitted for publication in Applications of Surface Science.

4. Pohlman, S. L.; Russell, P. M. 1980 . "Corrosion Resistance and Electrochemical Evaluation of Silver Mirrors." Solar Energy Materials. Vol. 3: pp. 203-212.

5. Coyle, R. T. 1981 (Oct.). "Durability of Silver-Glass Mirrors in Moist Acid Vapors." SERI/TP-631-623. Golden, CO: Solar Energy Research Institute.

6. "Standard Test Method for Solar Absorptance, Reflectance, and Transmittance of Materials Using Integrating Spheres." This proposed practice of Committee E44 (committee document number 136) is a draft under development. A copy of the latest edition of the draft is available from ASTM Information Center, 1916 Race Street, Philadelphia, Pennsylvania 19103.