SAND79-8225
Unlimited Release

Weathering of Low Iron Float and CGW-0317 Glasses

J. E. Shelby, J. Vitko

Prepared by Sandia Laboratories, Albuquerque, New Mexico 87115
and Livermore, California 94550 for the United States Department
of Energy under Contract DE-AC04-76DP00789.

Printed May 1979

Sandia Laboratories

SF 2900 Q(7-73)

Issued by Sandia Laboratories, operated for the United States Department of Energy by Sandia Corporation.

SAND79-8225
Unlimited Release
Printed May 1979

WEATHERING OF LOW IRON FLOAT AND CGW-0317 GLASSES

J. E. Shelby, Applied Physics Division 8342
J. Vitko, Applied Physics Division 8342
Sandia Laboratories, Livermore

Abstract

A simple accelerated weathering test was used to evaluate the <u>relative</u> weatherability of glasses which are being considered for use in solar heliostats. Glasses were exposed to 98-100% humidity at temperatures ranging from 40 to 80°C for periods of one to four weeks. Under these conditions, low-iron float glass exhibits severe surface corrosion, which occurs predominantly on the tin poor surface. This result indicates that silvering the tin-poor surface will increase the weatherability of mirrors made from this glass. CGW-0317 fusion glass exhibits no detectable signs of surface corrosion.

Introduction

Present designs for central solar power systems utilize very large (> 60,000 m^2) areas of second surface glass mirrors. Any glass used in such applications must endure many years of severe environmental exposure. Most common glasses undergo a series of changes in their surface properties, henceforth referred to as weathering, during such exposure[1]. Although weathering rarely results in significant removal of material from the surface of common commercial glasses, it does frequently result in the deposition of leach products on the weathered surface. If these deposits have an effect on the solar transmission of the glass, weathering could result in a serious degradation in the efficiency of such a power plant.

Two glasses are now considered to be the prime candidates for solar mirror applications: low iron float glass and CGW-0317 glass (frequently referred to as "fusion glass"). Both of these glasses contain large quantities of sodium. Since the leaching of sodium from the surface of glasses by interdiffusion with protons (as supplied by water) is known to be one of the primary weathering mechanisms[2], it appears that these glasses may be somewhat more susceptible to weathering than many other glasses. If this is indeed the case, neither of these glasses may prove acceptable for solar applications.

This paper reports the results of accelerated weathering tests for several glasses of interest to solar programs, with special emphasis on low iron float and CGW-0317 glasses. Low iron float glass has been found to exhibit serious weathering effects under certain conditions. CGW-0317 glass has not been found to exhibit similar effects under any of the test conditions of the present study.

Experimental Procedure

Most of the accelerated weathering studies were carried out in a controlled temperature-humidity chamber. Rectangles of each glass (2.5 x 1.5 cm) were cut from large sheets. These specimens were held at the edges by plastic holders so that the faces were in a vertical position. Under these conditions, the water which condensed on the glass surface tended to run off in a manner similar to that which would occur in the field when the heliostats were in an operating position. The holders were placed on a stainless steel shelf in the test chamber which was already at the desired condition. All exposures were made at 98-100% humidity and at temperatures ranging from 40 to 80°C for one to four weeks.

Several tests were made in plastic bottles which contained a small amount of distilled water. The specimens were suspended above the water by threads. The bottles were sealed and placed in a water bath at the desired temperature. This test was done such that the humidity was constant at 100% throughout the test. The times and temperatures used were similar to those used in the chamber tests.

The post-test specimens were examined visually, their specular transmission and reflection spectra were measured with a Cary-17I spectrometer, and their surfaces were examined by ESCA. (The ESCA spectra were measured by A. West and M. W. Clift - 8315.) Control specimens cut from the same sheets were also examined by each of these techniques.

Results

The results of the accelerated weathering tests are dramatically evident in Figure 1. The three soda-lime-silica glasses (labeled LIF for low iron float, SIF for standard iron float, and SHEET for standard sheet, or window, glass) exhibited severe surface corrosion, whereas the other glasses show no visible effects. The CGW-0317 glass (labeled 317) exhibited no visible signs of surface corrosion. Specimens of Pyrex® and vitreous silica (T-08), which are both noted for outstanding chemical durability[3], were included for comparison purposes. Neither of these glasses exhibited any sign of surface damage.

The results shown in Figure 1 were obtained for a 29 day exposure at 75°C. The corrosion of the float glasses was significantly greater on one surface than on the other. A second set of specimens were run at 50°C for one week. In that test, the low iron float glass (only the low iron float and CGW-0317 glasses were included in most of the tests) distinctly showed more corrosion on one surface than on the other. As would be expected, the degree of corrosion was much less than was observed for the considerably longer exposure at 75°C. The CGW-0317 glass, again, exhibited no sign of surface corrosion.

A similar test was performed for the low iron float glass by a different method. A test specimen was placed in a plastic bottle so that it was suspended above a small amount of water. This bottle was immersed in a water bath at 60°C for one week. Since the bottle was sealed, this procedure should provide a 100% humidity atmosphere. The test was included to eliminate any possible contamination from the test chamber used in the other tests. The results were qualitatively identical to those obtained in the temperature-humidity chamber.

A final series of specimens were run in the temperature-humidity chamber at 70°C and 98% humidity. All of the specimens were placed in the chamber at the same time. One set (consisting of a low iron float specimen, a CGW-0317 specimen, and a vitreous silica specimen) was removed after one week. The remaining sets of specimens were removed at one week intervals over a period of four weeks. The low iron float specimens exhibited a continuous increase in the degree of surface corrosion as determined by visual examination. Neither of the other two glasses exhibited any visually detectable corrosion.

Figure 2 shows the absorption spectra of the series of low iron float glasses exposed in the temperature-humidity chamber at 70°C. The transmittance (ratio of transmitted to incident flux) of those specimens exposed for 2 or more weeks is severely reduced in the visible and ultraviolet regions, with a lesser effect in the infrared region. Surprisingly, the onset of weathering is characterized by an improvement in the transmittance of the specimen. This is evident in Figure 2 for the "one-week" specimen. There is a definite improvement in transmittance in the region around 1000 nm, i.e., in the same spectral region as the Fe^{2+} absorption band. Comparison of the specular reflectance of the weathered sample with that of 'as-received' samples (Figure 3) suggests that this improvement results from the formation of an anti-reflection coating on the tin-poor surface. Figure 4 compares the experimental reflectance with that calculated by assuming a uniform film of index n and thickness d. A 'best fit' was obtained for $n = 1.25$ and $d = 1900$ A. These values are in good agreement with the values determined by ellipsometry ($n \simeq 1.2$, $d = 2000$ A) and interferometry ($d = 2000$ A). [The ellipsometry measurements were performed by P. D. Thatcher (2552) and the interferometry by B. D. Schneneman (8123).] The rather low index of refraction obtained by these procedures may indicate a porous film. Heating the sample to a temperature near the transition region of this glass (500-600°C) removes the anti-reflection film and results in a transmittance very nearly that of the as-received samples.

As stated earlier, the low iron float glass exhibited considerably more corrosion on one surface than on the other. Examination of a series of these glasses by ESCA revealed that the corroded surface was the tin-free face (see

Figure 5). In each case, the corroded face also showed a considerable depletion in the sodium concentration. These results suggest that the basic corrosion mechanism is indeed a sodium-proton interdiffusion. They also suggest that the presence of tin in the glass surface (as a result of the manufacturing process[4]) somewhat improves the chemical durability of the glass. This observation leads to the obvious suggestion that the durability of low iron float glass mirrors could be improved by applying the reflective coating to the tin-free surface. (It should be mentioned that this surface is not completely tin-free. Some tin is deposited from the vapor on this surface during manufacture. However, the concentration of tin on this surface appears to be no more than 10 to 20% of that on the surface exposed directly to the bath[4].)

Discussion

The corrosion of glass surfaces has been discussed in detail in a recent review article.[2] In general, the corrosion process can be most readily discussed by considering the changes which occur in the surface composition as a function of time. The stages in the corrosion process are shown in Figure 6 (this figure is taken from Reference 2). The first phase consists of the selective leaching of sodium from the near surface region of the glass. This process results in the formation of a layer of different composition than that of the bulk glass. In many cases, the layer is much more durable than the bulk glass and hence serves as a protective film to prevent further corrosion (Figure 6A). This is the case for soda-lime-silica glasses (such as the low iron float glass) when immersed in a large quantity of water or when the leachant is quickly removed from contact with the glass surface, as is usually the case for rain. However, if the leachant is allowed to remain on the glass surface in the presence of a very small quantity of water, as when water condenses to form a thin film, the pH of the solution in contact with the glass surface increases rapidly. As the pH begins to increase, the silica protective film begins to undergo congruent dissolution with nearly equal loss of both sodium and silica (Figure 6B). Since the corrosion rates are approximately equal for all components of the glass, the protective film is removed and the glass undergoes rapid corrosion at a rate determined by the bulk composition of the glass (Figure 6C).

A slightly different corrosion process can occur in aluminosilicate glasses[2,5] such as CGW-0317. In this case, a two-layer film can be formed on the glass surface (Figure 6D). The outer layer is usually an Al_2O_3-SiO_2 binary glass which has better corrosion resistance than the silica-rich layer developed on the surface of a soda-lime-silica glass. This layer is formed by precipitation of an alumino-silicate complex onto the glass surface when the Al^{3+} concentration in the solution exceeds some minimum value. Since the formation of this protective layer is determined by the concentration of aluminum in the solution, a thin layer of solution actually promotes the formation of the protective film. This layer also serves to slow the leaching of sodium from the glass surface, which in turn slows the rate of increase of the pH of the solution. This process aids in reducing the weathering rate of the glass, since even the alumino-silicate film is soluble in a sufficiently high pH.

As noted earlier, the weathering of low iron float glass appears to be dependent upon the tin content of the surface of the glass. The surface of the glass which was in contact with the tin bath during manufacturing has a tin oxide content of 1.5-2.0 wt. % for a depth of at least 10 microns[4]. The other surface of the glass also has a small tin oxide content due to vapor deposition of tin during manufacturing. However, the tin concentration in this surface has been reported[4] to be only about 0.1 wt. % and to extend for considerably less distance into the glass. These relative values are in good agreement with the results of the ESCA measurements of the present study which indicate that the tin-poor side of the specimens has between 8 and 13% of content of the tin-rich side. The ESCA measurements also firmly establish that the tin-poor side of the low iron float glass exhibits considerably more weathering than does the tin-rich side. Although the exact mechanism for this improvement in the durability of the tin-rich side is not known, the general principles discussed earlier imply that the tin oxide causes a decrease in the rate of sodium leaching and/or results in the formation of a more durable protective film. In any case, it would appear to be advantageous to utilize this effect to produce more durable mirrors by mirroring the tin-poor surface if possible. In effect, this procedure would create a protective film of silver/copper/paint over the less durable surface of the glass, while simultaneously only exposing the more durable surface of the glass to the elements.

It is also possible that consideration should be given to the possibility of improving the weatherability of the low iron float glass by one of the techniques commonly used in industry for container glasses. These glasses are quite similar to float glass in bulk composition. They are known to be poor in durability for many of the liquids for which they are commonly used. Frequently, they are treated with SO_2 gas to remove alkali ions from the near surface region of the glass[6]. The sulfur dioxide reacts with the sodium oxide in the glass to form sodium sulfate, which can be easily dissolved from the glass surface. Other techniques involve treating the glass surface with volatile fluorine-containing compounds[6] such as 1, 1-difluoroethane, or by depositing a thin film of tin on the surface[4].

One other factor should be considered in discussing the weathering of these glasses. Adams[7] has indicated that the permanence of the weathered coating is different for the two glasses discussed here. He reported that the corrosion film can be removed from the CGW-0317 glass, by washing whereas the film cannot be removed readily from typical soda-lime-silica glass such as the low iron float glass. This result is consistent with our findings that the corrosion film on the float glass is quite difficult to remove. Since we have been unable to produce a significant corrosion film on the CGW-0317 glass, we cannot state whether or not a similar film on that glass can be removed by washing. If this contention is indeed correct, the CGW-0317 glass would offer considerable advantage over the float glass, even if both glasses formed a corrosion film at equal rates.

Conclusions

1. Low iron float glass readily forms a weathering film on the tin-poor surface upon exposure to elevated temperature-humidity conditions. This film can be severely detrimental to the optical properties of the glass. This film is extremely difficult to remove once it has been allowed to accumulate to the point where degradation of the optical properties of the glass has occurred.
2. CGW-0317 glass, or "fusion glass," does not appear to form a similar weathering film. If such a film does in fact occur, it does not significantly affect the optical properties of the glass.

3. Since the weathering of low iron float glass is considerably worse on the tin-poor surface, it is recommended that any mirrors made from this glass be silvered on the tin-poor surface. Furthermore, since it has been observed that the weathering products can be at least partially removed

from this glass if they are removed before a significant time period has elapsed, mirrors made from low iron float glass should be cleaned more frequently than may be required just for the removal of accumulated dust.

References

1. H. V. Walters and P. B. Adams, "Effects of Humidity on the Weathering of Glass," J. Non-Cryst. Solids 19, 183-99 (1975).

2. L. L. Hench and D. E. Clark, "Physical Chemistry of Glass Surfaces," J. Non-Cryst. Solids 28, 83-105 (1978).

3. R. H. Doremus, Glass Science, John Wiley & Sons, Inc., New York (1973).

4. J. H. Sieger, "Chemical Characteristics of Float Glass Surfaces," J. Non-Cryst. Solids 19, 213-20 (1975).

5. M. F. Dilmore, D. E. Clark, and L. L. Hench, "Aqueous Corrosion of Lithia-Alumina-Silicate Glasses," Am. Ceram. Soc. Bulletin 57, 1040-44 (1978).

6. P. R. Anderson, F. R. Bacon, and B. W. Byrum, "Effect of Surface Treatments on the Chemical Durability and Surface Composition of Soda-Lime Glass Bottles," J. Non-Cryst. Solids 19, 251-62 (1975).

7. P. B. Adams, personal communication dated November 1, 1978.

Figure Captions

1. Effect of a 29 day exposure at 75°C and 98% relative humidity on the appearance of a variety of glasses. The three obviously corroded specimens are low iron float (LIF), standard iron float (SIF), and normal sheet glass (SHEET). Fusion glass, or CGW-0317 (317) exhibits no sign of surface degradation. Specimens of Pyrex®, vitreous silica (T-08) and CGW-7806 (circular specimen) were included for comparison purposes.

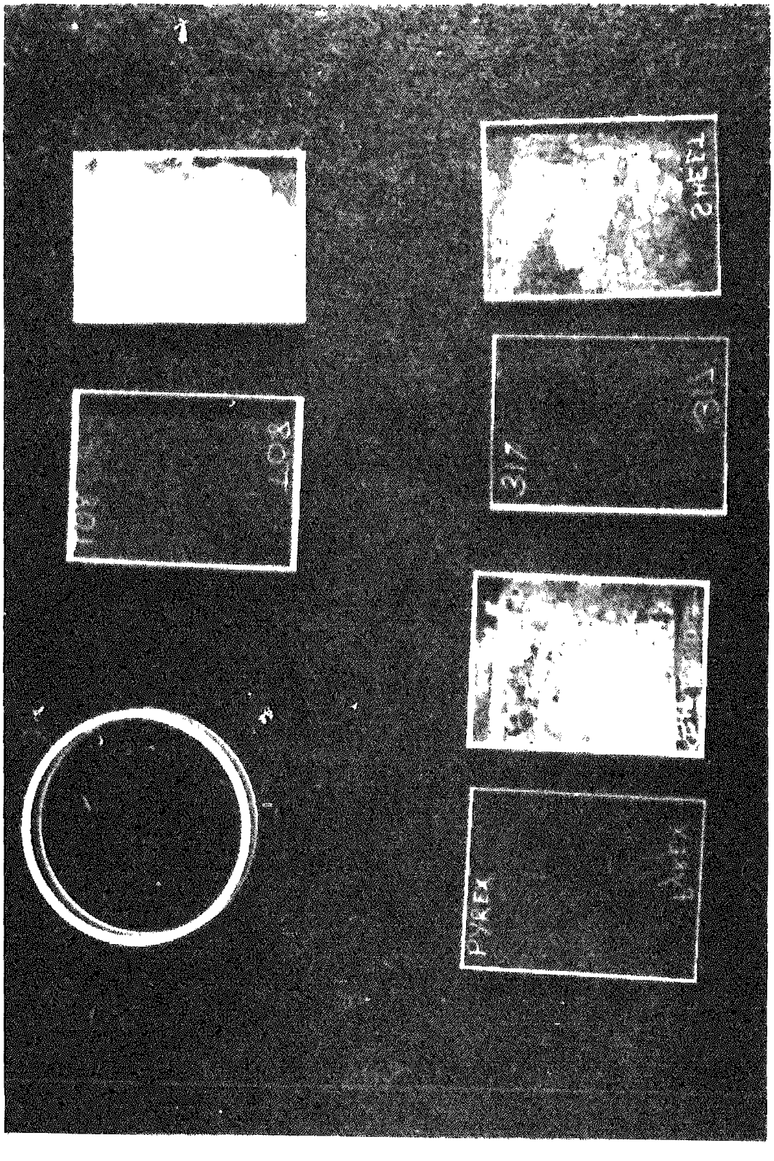
2. Effect of treatment time on the optical density of weathered low iron float glass.

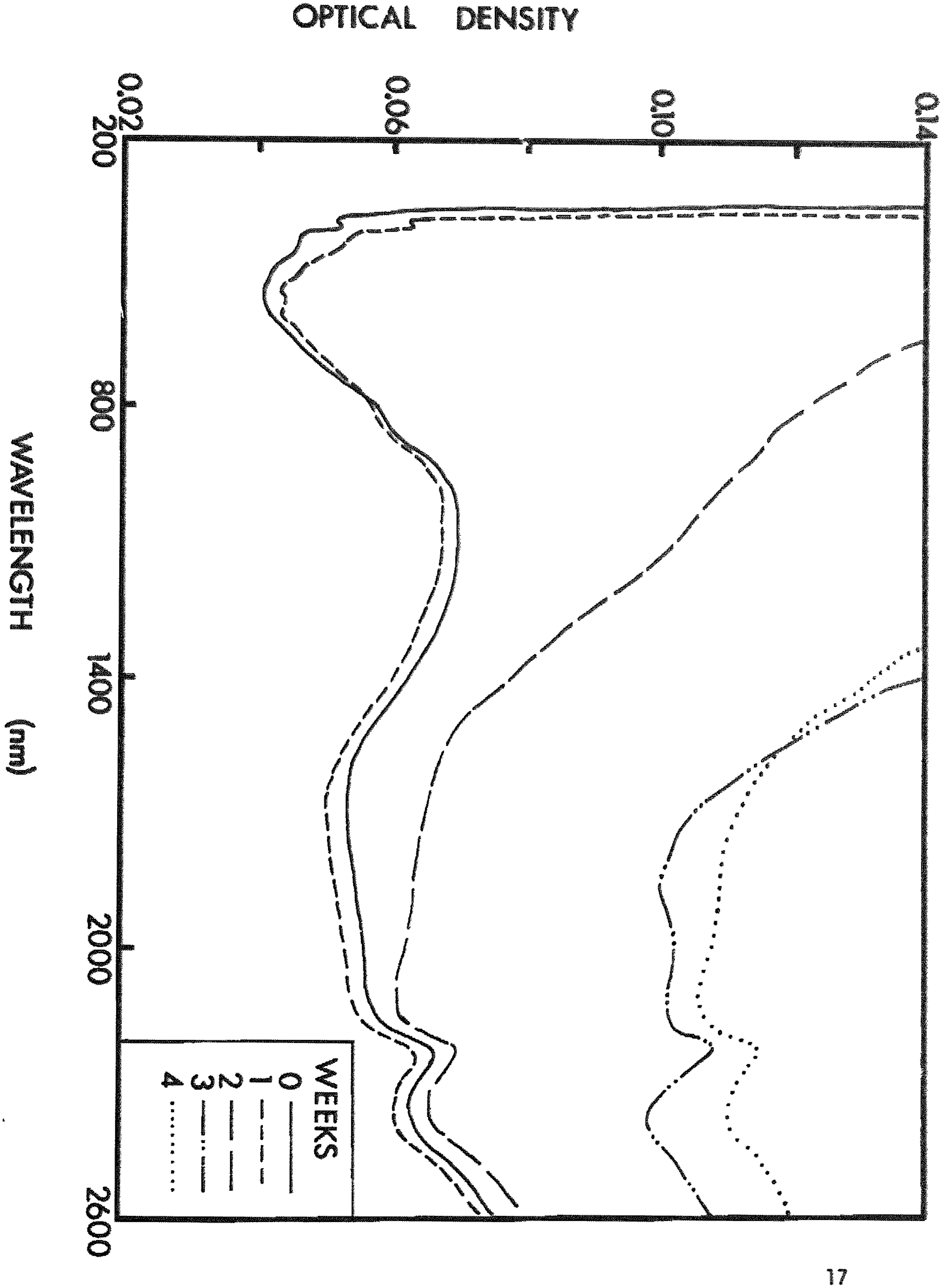
3. Comparison of the specular reflectance of a slightly weathered low iron float glass with that of an as-received sample.

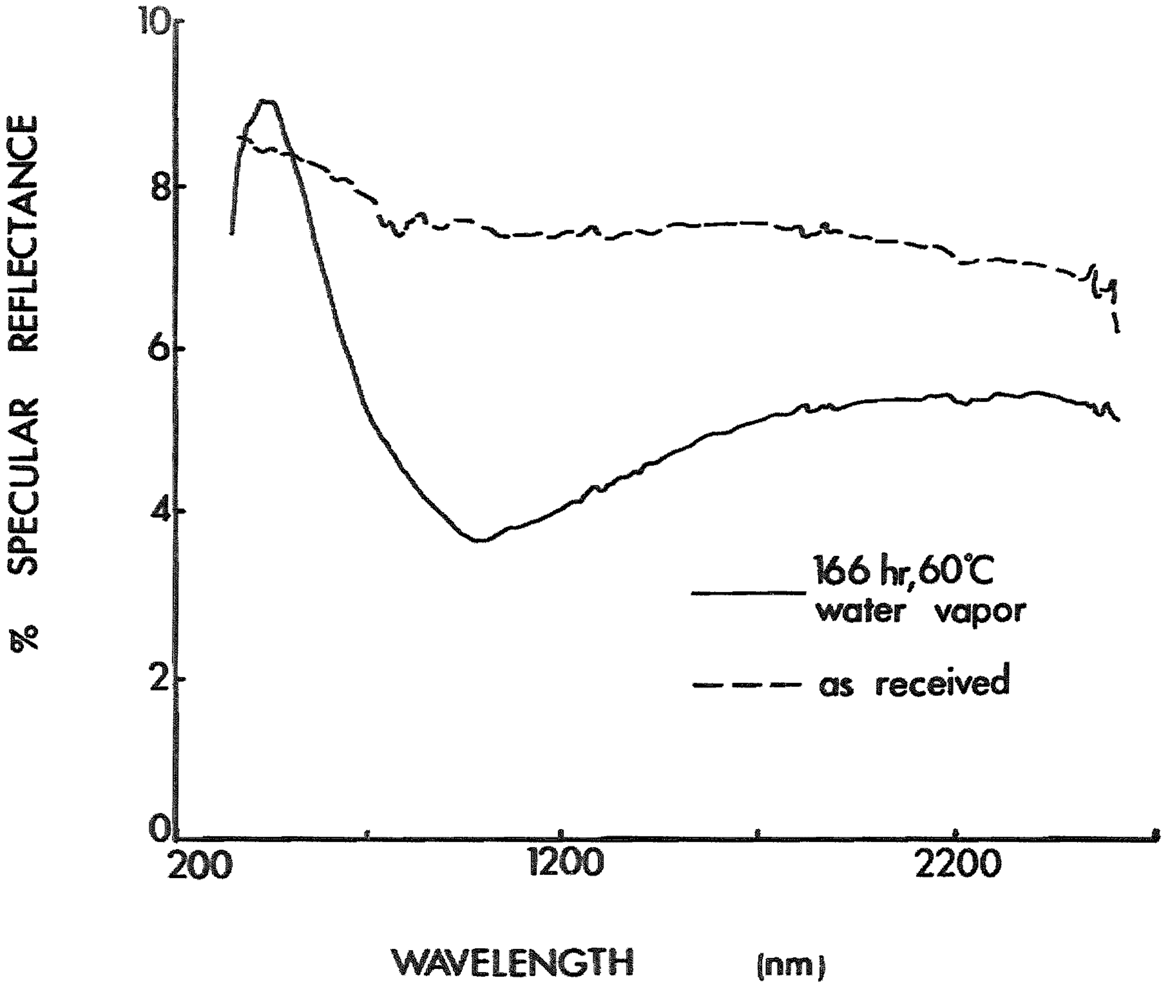
4. Comparison of the measured reflectance of a slightly weathered sample with that calculated by assuming formation of a uniform film of index n and thickness d.

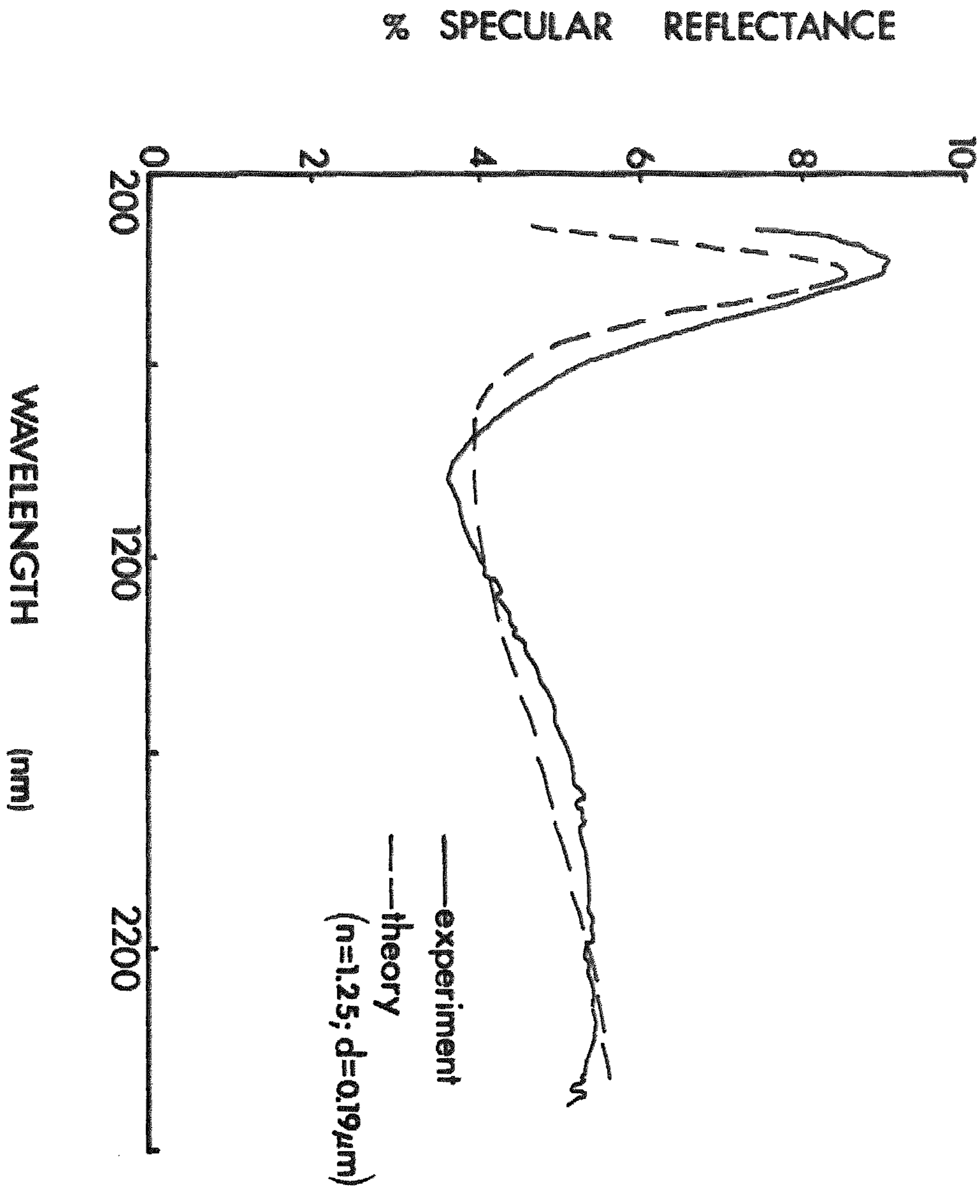
5. ESCA spectra for the heavily-corroded (lower curve) and slighly-corroded (upper curve) surfaces of low iron float glass. Note the presence of both tin and sodium in the upper spectrum.

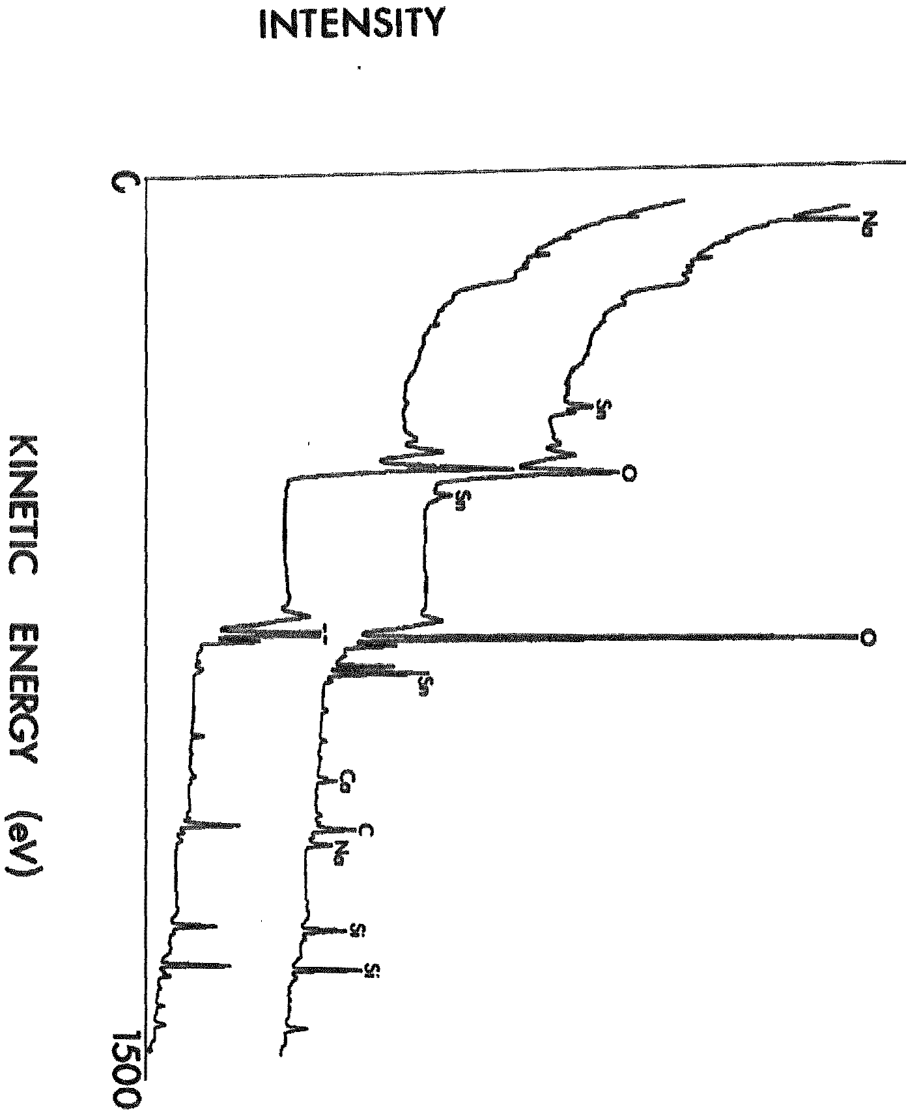
6. Idealized corrosion stages in the weathering of glass.

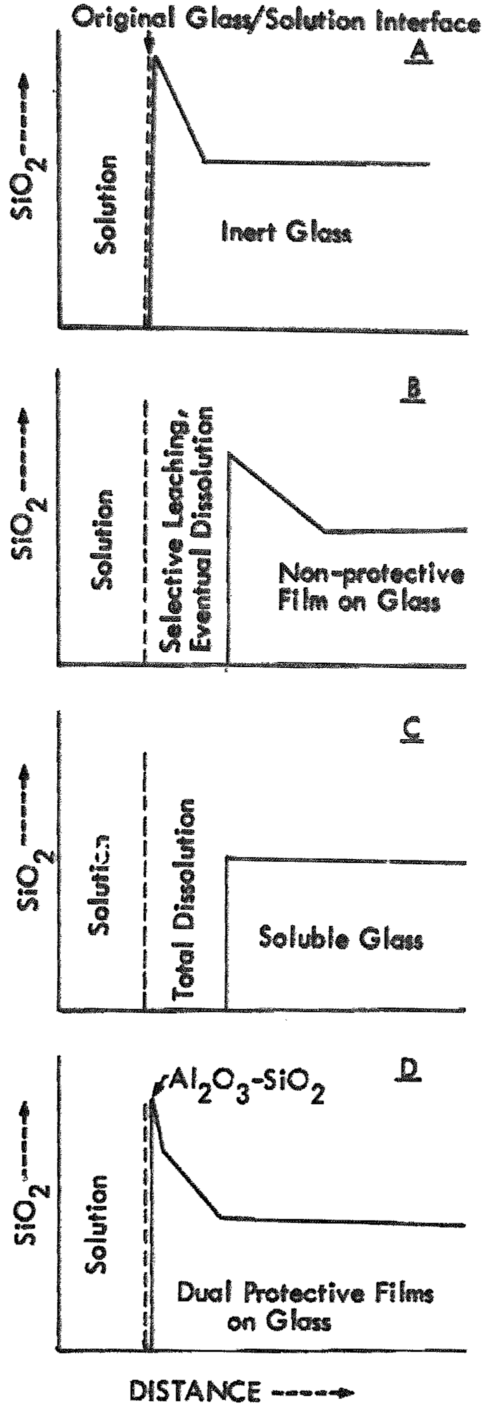

SHELL
317
317
PYREX
PYREX
108
108


OPTICAL DENSITY
0.02
0.06
0.10
0.14
WAVELENGTH (nm)
200
800
1400
2000
2600
WEEKS
0
1
2
3
4


% SPECULAR REFLECTANCE
10
8
6
4
2
0
200
1200
2200
WAVELENGTH (nm)
166 hr, 60°C water vapor
as received


% SPECULAR REFLECTANCE
0
2
4
6
8
10
200
1200
2200
WAVELENGTH (nm)
—experiment
– – theory (n=1.25; d=0.19μm)


INTENSITY
KINETIC ENERGY (eV)
0
1500
Na
Sn
O
Sn
Ti
O
Sn
Ca
C
Na
Si
Si


Original Glass/Solution Interface
A
SiO_2 ---->
Solution
Inert Glass
B
SiO_2 ---->
Solution
Selective Leaching, Eventual Dissolution
Non-protective Film on Glass
C
SiO_2 ---->
Solution
Total Dissolution
Soluble Glass
D
SiO_2 ---->
Al_2O_3-SiO_2
Solution
Dual Protective Films on Glass
DISTANCE ---->

ACKNOWLEDGMENT

Accelerated weathering tests were made by W. L. Smith (8342). Optical spectra were measured by R. D. Gay (8342). ESCA measurements were made by M. W. Clift and A. West (8315). The ellipsometry measurements were performed by P. D. Thatcher (2552) and the interferometry by B. D. Schoeneman (8123). Specimens were supplied by C. L. Mavis (8451).

INITIAL DISTRIBUTION

J. C. King, 2300
P. D. Thacher, 2552
G. E. Brandvold, 4710
V. L. Dugan, 4720
J. F. Banas, 4722
H. J. Saxton, 5840
R. B. Pettit, 5842
F. P. Gerstle, 5844
R. J. Eagan, 5845
E. K. Beauchamp, 5846
T. B. Cook, 8000
W. J. Spencer, 8100
A. N. Blackwell, 8200
B. F. Murphey, 8300
D. M. Schuster, 8310
D. R. Adolphson, 8312
R. W. Mar, 8313
W. R. Hoover, 8314
D. K. Ottesen, 8315
B. E. Mills, 8315
L. A. West, 8315
J. C. Swearengen, 8316
T. S. Gold, 8320
W. Bauer, 8340
W. D. Wilson, 8341
P. L. Mattern, 8342
J. E. Shelby, 8342 (5)
J. Vitko, 8342 (5)
D. L. Hartley, 8350
L. Gutierrez, 8400
H. R. Sheppard, 8424
  ATTN: V. P. Burolla
R. C. Wayne, 8450
R. L. Bridges, 8451
T. D. Brumleve, 8451
W. G. Wilson, 8451
T. A. Dellin, 8451
C. L. Mavis, 8451
A. C. Skinrood, 8452
J. J. Bartel, 8452
J. D. Gilson, 8453
Publications and Public Information Division, 8265, for TIC (2)
F. J. Cupps, 8265/Technical Library Processes Division, 3141
Technical Library Processes Division, 3141 (2)
Library and Security Classification Division, 8266-2 (3)