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EFFECTS OF SIMULATED SOLAR RADIATION ON THE TRANSMISSION OF MAGNESIUM FLUORIDE AND CRYOLITE THIN FILMS

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INTRODUCTION

In radiation testing of candidate optical materials for the Earth Radiation Budget (ERB) experiment on Nimbus-F, it was observed that two interference filters exhibited far too much ultraviolet degradation for use in the solar channels of the instrument (reference 1). The degradation took place after 1100 equivalent sun-hours (ESH) at 2.0 solar constants using an unfiltered xenon lamp. The filters were made with fused silica substrates and had protective covers, also of silica. The first multilayer filter was composed of layers of aluminum and cryolite with a thorium fluoride overcoat; the multilayer of the second filter was composed of layers of silver and cryolite with no overcoat.

Control samples of the fused silica submitted to radiation testing along with the filters showed moderate degradation (2 to 10 percent loss in transmission) in the 200- to 400-nm wavelength region, but not enough to account for the losses exhibited by the filters. One filter was peaked at 265 nm with a 65-nm bandwidth, and the other was peaked at 395 nm with a bandwidth of 115 nm.

The optical properties of cryolite films have been very fully investigated by Dell (reference 2). Cryolite has a lower refractive index than magnesium fluoride, and is more efficient in suppressing reflection from glass surfaces, particularly glasses of low index. Maclead (reference 3) and Hermansen (reference 4) describe in detail the evaporation and deposition of cryolite thin films. Bourg (reference 5) has studied the optical properties of thin cryolite films as a function of the pressure prevailing in the chamber during deposition. Ennos (reference 6) has studied stresses induced by vapor deposition of cryolite by observing the bending of a thin silica strip as it becomes coated. No mention was found in the literature, however, regarding the resistance of cryolite coatings to ultraviolet radiation, and this lack, plus the degradation of the ERB filters, prompted the present work.

Thin films of cryolite and magnesium fluoride were deposited on 2.54 by 2.54 cm square pieces of good quality, fused silica substrates. These substrates were cut from a single piece of silica 2.54 by 7.62 cm in size and 0.1570 ± 0.0003 cm in thickness. The substrates were exposed to simulated solar radiation along with an uncoated control square. Degradation observed in the cryolite coating indicates that loss in transmission of the ERB filters was due to degradation of the cryolite used in the filter multilayer constructions. The good

performance of magnesium fluoride relative to cryolite indicates that it is a better choice of material in thin film multilayer constructions for applications in an ultraviolet-rich radiation environment.

SAMPLE PREPARATION

Prior to coating, the three substrates were cleaned with hot water and tri-sodium phosphate and rinsed with distilled water and then ethanol. Cryolite powder and granular, optical-grade magnesium fluoride were used to coat two of the substrates. Emission spectrographic analyses of these materials for traces of contamination are given in table 1. These materials were vapor-deposited onto the substrates using a Veeco Ve-400 vacuum station. Film thickness was monitored with a Sloan quartz-crystal microbalance, model DTM-3. One substrate was coated with 250 ± 5 nm of cryolite (Na_3AlF_6), and the other substrate was coated with 244 ± 5 nm of magnesium fluoride (MgF_2).

Table 1
Emission Spectrographic Analysis of Materials Used
in Film Construction

Cryolite Powder		Magnesium Fluoride Granuals	
Element	Percent by Weight	Element	Percent by Weight
Ca	0.01 to 0.1	Ca	0.01 to 0.1
Mg	0.01 to 0.1	Si	0.01 to 0.1
Si	0.01 to 0.1	Fe	0.001 to 0.01
Fe	0.01 to 0.1		
Cu	0.001 to 0.01		
Mn	0.0001 to 0.001		

RADIATION TESTING

The samples were irradiated in a vac-ion system at 1.33×10^{-5} N/m^2 with a Spectrolab X-25 filtered xenon, square-beam solar simulator. The samples were maintained at room temperature during testing by mounting them on a water-cooled, stainless steel block. The bulkhead which seals the vacuum chamber has windows of sapphire. This bulkhead was placed over the array of samples. The spectrum of the simulator at 1.0 solar constant prior to starting the irradiation is shown in figure 1. The samples were irradiated at a starting intensity of about 2.0 solar constants. Due to degradation of the xenon lamp and contamination of the X-25 optics, which are open to the atmosphere, the spectrum and intensity of the radiation changed during the test. These changes were noted, however, and accounted for in the exposure calculations, along with attenuation due to the sapphire windows. The value of the solar constant was taken to be 135.3 mW/cm^2 (reference 7).

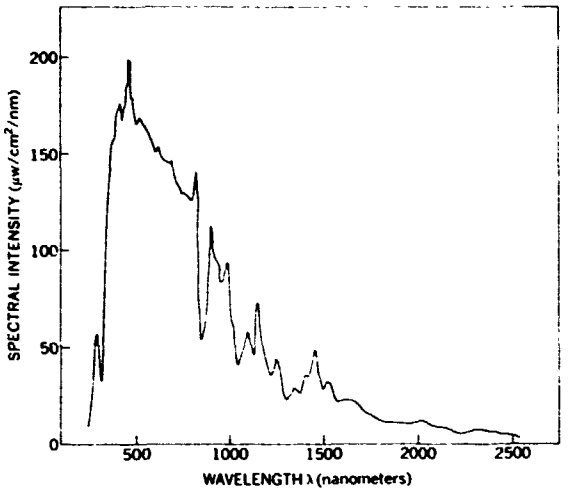

Figure 1. Solar simulator spectrum at one solar constant prior to testing.

OPTICAL EVALUATION

The optical spectral transmissions of the samples were measured with a Beckman DK-1A recording spectrophotometer. Between 3400 and 700 nm, a Beckman 3333 tungsten source was used with a lead sulfide detector (air reference) and a scan time of 3 minutes. Between 700 to 350 nm the same tungsten source was used with a photomultiplier detector (1X sensitivity, air reference) and a scan time of 30 minutes. In the ultraviolet region, between 360 and 190 nm, a hydrogen source was used with the photomultiplier detector (20X sensitivity, air reference) and a scan time of 3 minutes. Transmission measurements were made before irradiation and after 175.5, 448.1, 837.8, and 1126 equivalent sun-hours (ESH) of exposure. The transmission measurements were made within 8 hours after removal from the vacuum chamber. The samples were also monitored visually during the testing and were photographed.

RESULTS

The cryolite-coated sample is the only sample that showed any visible change. This sample, after 1126 ESH of exposure and illuminated with a spotlight, is shown in figure 2. The cryolite coating was almost invisible before testing except around a 0.32- by 0.32-cm area near an edge of the plate where the sample was held during evaporation. This area was not coated, and when the sample was held at a grazing angle to the light, the uncoated area was observable. During irradiation, however, a round, matt-textured, translucent section developed in the area exposed by the circular sapphire window over the sample. Microscopic examination of the sample showed that the cryolite crazed in some areas in the exposure circle. In the exposed circular area the coating was easily rubbed off with a wooden probe and was powdery. The unexposed periphery was not crazed and the cryolite

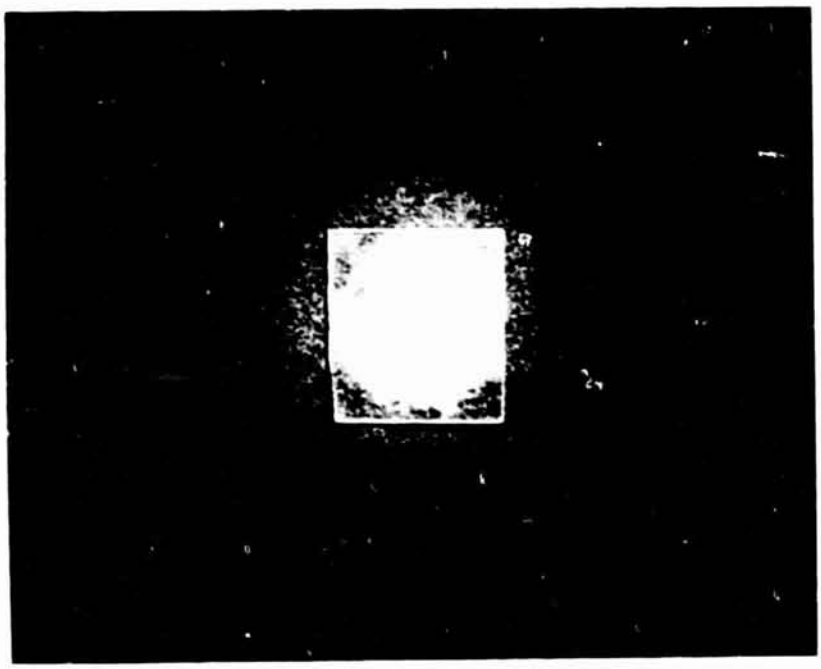

Figure 2. Matt-textured translucent area that developed on the cryolite-coated sample during 1126 equivalent sun-hours of exposure.

could not be rubbed off with a wooden probe, but could be removed with a steel probe. Visible effects in the cryolite were apparent after as little as 175.5 ESH.

Figure 3 shows the transmission of the uncoated control sample before irradiation and after 175.5, 448.1, 837.8, and 1126 ESH of exposure. A transmission loss is observed mostly in the ultraviolet between 200 and 400 nm. This loss ranged from about 9 percent at 200 nm to 2 percent at 400 nm after 1126 ESH.

Figure 3. Transmission of fused silica control before irradiation and after 175.5, 448.1, 837.8, and 1126 ESH.

Figure 4 shows the transmission of the cryolite-coated sample before irradiation and after 175.5, 448.1, and 837.8 ESH. The cryolite coating was visibly altered by the radiation and showed large decreases in transmission with increasing radiation exposure. After 1126 ESH of exposure the coating had crazed and sections of it began to curl. The sample was rubbed accidentally after this exposure and some of the coating was smudged off, showing it had lost mechanical integrity. After 837.8 ESH the transmission decreased by 48 percent at 270 nm.

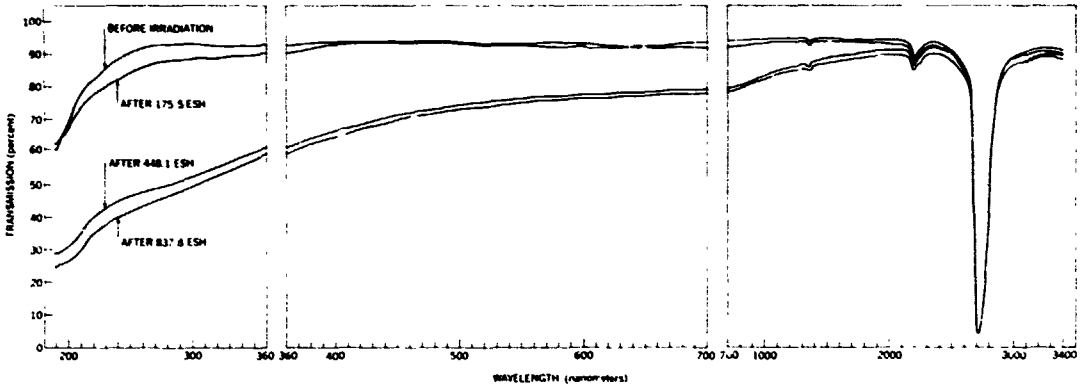

Figure 4. Transmission of cryolite-coated sample before irradiation and after 175.5, 448.1, and 837.8 ESH.

Figure 5 shows the transmission of the magnesium-fluoride-coated sample before irradiation and after 448.1, 837.8, and 1126 ESH of exposure. The loss in transmission is comparable to that observed for the fused silica substrate alone. At 200 and 400 nm, the transmission decreased 9 and 2.5 percent, respectively. There was no visual evidence of damage to the coating.

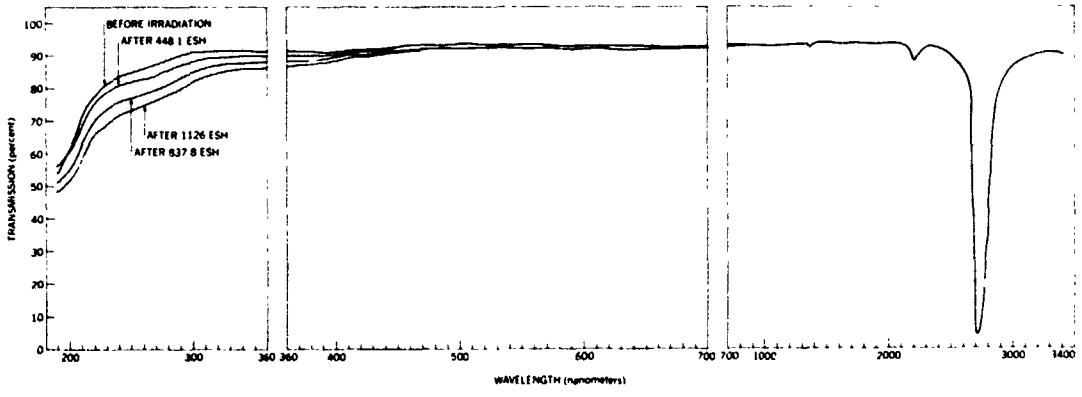

Figure 5. Transmission of magnesium-fluoride-coated sample before irradiation and after 448.1, 837.8, and 1126 ESH.

CONCLUSIONS

The results of this study indicate that cryolite is seriously affected by as little as 448.1 ESH of exposure to radiation with a spectrum closely approximating that of the sun. The results also indicate that magnesium fluoride has excellent solar radiation resistance. The index of refraction of magnesium fluoride is 1.38 compared to 1.35 for cryolite. Although cryolite has a slightly lower index than magnesium fluoride, which makes it a better blooming material for most low index glasses, it is softer and not as adherent after solar irradiation as magnesium fluoride.

Degradation observed in the cryolite coating indicates that loss in transmission of the interference filters tested in reference 1 was due to degradation of the cryolite used in the filter multilayer constructions. The good performance of magnesium fluoride relative to cryolite indicates that it is a better choice of material in thin film multilayer constructions for applications in an ultraviolet-rich environment.

ACKNOWLEDGMENTS

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