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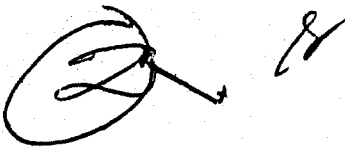
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RAIN EROSION RESISTANT AR COATINGS FOR ZnS WINDOWS

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10 MAY 1980

TECHNICAL REPORT AFWAL-TR-80-4059
Final Report for the period January 1978 to January 1980

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- o High transmittance over the wavelength range of interest.
- o Extreme durability and rain erosion resistance.
- o High-temperature (200°C) stability.
- o Coating uniformity over sizes up to 14in x 20in.

Zinc sulfide (ZnS) is currently being used as a window material for Forward Looking Infrared (FLIR) thermal imaging sensors such as those incorporated in the PAVE TACK pod and the IR Maverick Missile.

This report describes the successful development of FLIR (8.0 to 12.0µm) and multispectral (0.5 to 0.9, 1.06 and 8.0 and 12.0µm) wavelength antireflection coatings which can be applied to large ZnS windows and meet above requirements.

Various optical design methods are described; the measured spectral properties of various coatings before and after rain erosion test are discussed; the results of various durability tests for each coating types are analyzed; and the selection process for large window coating designs together with the necessary fabrication process are discussed.

Eight different rain erosion resistant coating systems were successfully designed and fabricated. One of these designs was selected for coating the two large window test samples of ZnS which were delivered to the Air Force for further testing.

PREFACE

This document is the Final Report for the Rain Erosion Resistant AR Coatings for ZnS Windows Program. This report was prepared under Contract No. F33615-77-C-5056 for the Air Force Systems Command and covers the period of January 1978 to January 1980. The report describes the successful development of FLIR (8.0 to 12.0 μm) and multispectral (0.5 to 0.9, 1.06 and 8.0 to 12.0 μm) wavelength antireflection coatings which can be applied to large ZnS windows and operate at high performance under severe environmental conditions.

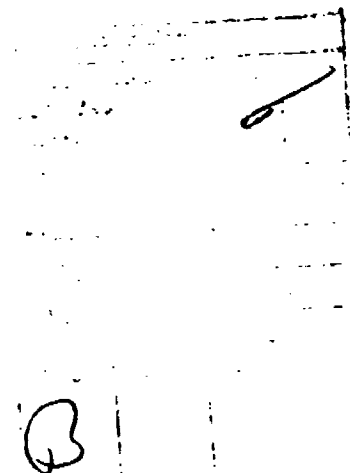


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SECTION I

INTRODUCTION

IR transmitting window materials are being developed for imaging electro-optical sensor systems intended for use on high performance aircraft such as F-4, F-15, F-16, A-10, F-18 and F-111. These windows require a broad band anti-reflective coating which must possess the following properties:

- o High transmittance over the wavelength range of interest.
- o Extreme durability and rain erosion resistance.
- o High-temperature (200°C) stability.
- o Coating uniformity over sizes up to 14" x 20".

Zinc sulfide (ZnS) is currently being used as a window material for Forward Looking Infrared (FLIR) thermal imaging sensors such as those incorporated in the PAVE TACK pod and the IR Maverick Missile.

Same current generation infrared sensors utilize ZnS windows, anti-reflection coated to provide maximum transmission in the 8.0 to 12.0 μ m region. The addition of target designation and range finding capability to such systems imposes further window coating requirements at 1.06 μ m and in the visible LLTV region (0.5 to 0.9 μ m) and necessitates the development of multispectral anti-reflectance coatings which can survive exposure to high speed raindrop impingement. In addition to the rain erosion, such coatings must also exhibit extremely high durability to withstand aerodynamic heating without any performance degradation.

Since the feasibility of depositing truly rain erosion resistant coatings for the 8 to 12 μ m region was demonstrated (Report Number AFML-TR-77-8) under Government Contract No. F-33615-76-C-5039, the initial objective of this program was to develop a process for uniform deposition of high optical

quality rain erosion resistant coatings on ZnS window blanks up to 14 inches by 20 inches. However during the initial phase of the program, it was found that the above rain erosion coating used NdF_3 and even though it passes the rain erosion test (1 inch/hour simulated rain fall, 1.8mm diameter drops, exposure time of 20 minutes at 470 mph and 78° impact angle), there were transmission losses of approximately 10% after the rain erosion test.

This transmission loss was attributed to the internal fracturing in ZnS itself⁽¹⁾. However if coatings of ZnSe/NdF_3 are removed from the substrate by polishing after the rain erosion testing, it can be shown that the loss of transmission due to internal fracturing in ZnS is only 2% to 3%. The rest of the loss is primarily due to chemical decomposition of the NdF_3 material caused by the effects of water absorbed in the coating material. This unexpected problem necessitated the investigation of new coating materials, and the development of processes to fabricate coatings which can pass rain erosion tests and not lose transmission by more than 2% to 3%. The materials investigated on this program were various fluorides (ThF_4 , CeF_3 , YF_3 , PrF_3 and LaF_3) as low refractive index materials and ZnSe as the high refractive index material. Two approaches, double layer and quarter-quarter, were utilized for designing the infrared AR coating. The multispectral AR coatings were designed using multi-layer stepgraded index coating as an approximation to an inhomogeneous film.

This report describes the successful development of FLIR (8.0 to $12.0\mu\text{m}$) and multispectral (0.5 to 0.9, 1.06 and 8.0 to $12.0\mu\text{m}$) wavelengths antireflection coatings which can be applied to large ZnS windows. Various optical design methods used during the program are reviewed in Section II of the report and the process and function techniques developed for the coatings are described in Section III. The measured spectral properties of various coatings before and after rain erosion tests are discussed in Section IV together with the results of durability tests (adherence, hardness, abrasion, humidity, salt fog, etc.) for each of the coating types. The selection process of the coating design for coating the large window samples is discussed in Section V together with the fabrication process. The optical properties of coating on large windows are also given in this section. Section VI describes the conclusion and recommendations made.

(1) Honeywell Inc., Erosion Resistance AR Coatings for IR Windows, AFML-TR-77-8, 1977.

All of the samples were tested for rain erosion tests at Air Force facilities. The results are discussed in Appendix A.

As a result of this investigation, eight different rain erosion resistant coating systems were successfully designed and fabricated. One of these designs was selected for coating the two large window test samples of ZnS which were delivered to the Air Force for further testing.

SECTION II

ANTIREFLECTION COATING DESIGNS

2.1 INTRODUCTION

The objective of this program is to optimize the design and fabricate two different antireflective coating designs. The requirement for the first antireflective coating design using ZnS as the window material, is 95% minimum transmission over an 8 to 12 μ m wavelength band. The requirement for the second antireflective coating design is 95% minimum transmission at LLLTV (0.5 to 0.9 μ m), laser (1.06 μ m) and FLIR (8 to 12 μ m) wavelengths. Since the transmission of coated windows not only depends upon the coating design but also on the substrate material, it is necessary first to discuss the optical properties of the ZnS window material before attempting to optimize antireflection coating designs for it. This section therefore first describes the optical properties of the chemical vapor deposited ZnS manufactured by Raytheon Company. The subsequent paragraphs describe the various techniques used for designing AR coatings and the selection process used for the coating materials.

2.2 VISIBLE/NIR/IR OPTICAL PROPERTIES OF ZnS WINDOW MATERIAL

The transmission spectrum of an uncoated ZnS window material shows large losses in the visible and NIR regions (Figure 2-1) together with moderate loss at wavelengths greater than 10.0 μ m (Figure 2-2). In the uncoated state, window losses are due to: (1) intrinsic absorption characterized by an absorption coefficient $\alpha(\lambda)$ cm^{-1} , and (2) due to Fresnel reflection losses at each window surface given by

$$R = \left[\frac{n(\lambda) - 1}{n(\lambda) + 1} \right]^2 \quad (1)$$

where $n(\lambda)$ is the refractive index of the material. The spectral curves in Figure 2-1 show the effect of these two loss mechanisms on the window

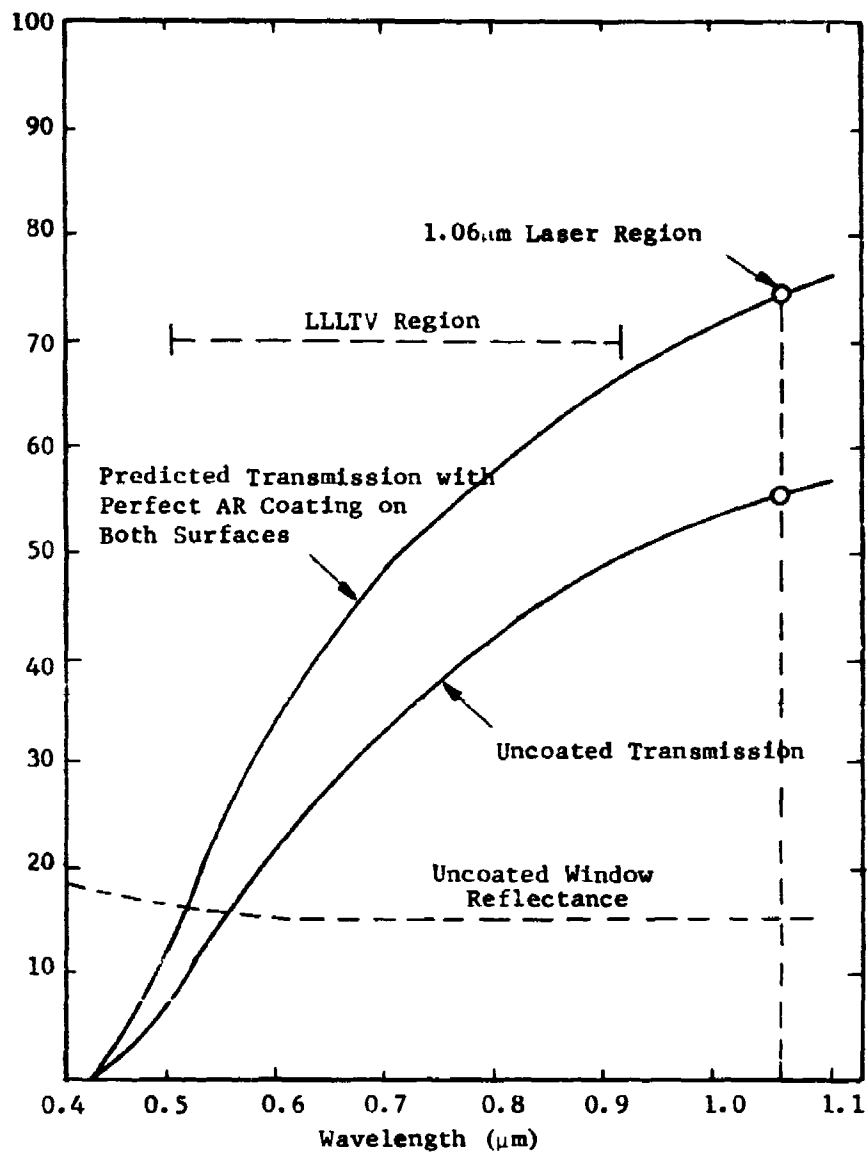


Figure 2-1. Optical Transmission of an Uncoated Zinc Sulphide Window Sample (0.2" Thick) Showing Large Intrinsic Absorption in the Visible and NIR Regions. Reflection Losses Account for ~ 18% for Surface in this Region

transmission in the visible and NIR regions, and indicate that even a perfect antireflection coating on both surfaces cannot cause the window transmission to be the required 95% value in the 0.5 to 0.9 μ m region or at 1.06 μ m. Similarly, increased absorption beyond 10.0 μ m (Figure 2-2) limits the transmission of a perfectly antireflection coated window to less than 95%. Figures 2-1 and 2-2 indicate the transmission of a typical ZnS substrate, although it should be noted that large variations occur from substrate to substrate. The magnitude of this variation is discussed in detail in Section 5.2.1. The variation of window absorption with wavelength and the limited bandwidth of antireflection coatings must also be considered when optimizing window transmission. This variation in the transmission of the uncoated window, the absorption in the window material and the limited bandwidth nature of antireflection coatings must be taken into consideration in designing the coatings to provide reduced reflection losses.

2.3 INFRARED COATING DESIGNS

The simplest antireflective coating design consists of a single-layer coating with a refractive index satisfying the following equation:

$$n = \sqrt{n_o n_s} \quad (2)$$

where n_o is the refractive index of the incident medium and n_s (= 2.21 at 10 μ m for ZnS) is the refractive index of the substrate. The optical thickness of the layer must be an odd multiple of a quarter wave at the design wavelength. Thus a single layer of material with an index of 1.45 and of mechanical thickness $t = 1.68\mu$ m would produce zero reflectance at $\lambda = 10\mu$ m. However the increase in reflectance with λ as we move away from 10 μ m will be too large and will not meet the requirements of the program. A broader region of wavelength over which the reflectance is low can be achieved either by using double-layer antireflection coatings with adjustable film thicknesses, or by using quarter-quarter design with inner layer synthesized from the high and low index materials in the form of a Herpin equivalent layer⁽²⁾. These two approaches are discussed in detail in the following paragraphs.

(2)

A. Herpin, Compt. rend. 225, 182 (1947).

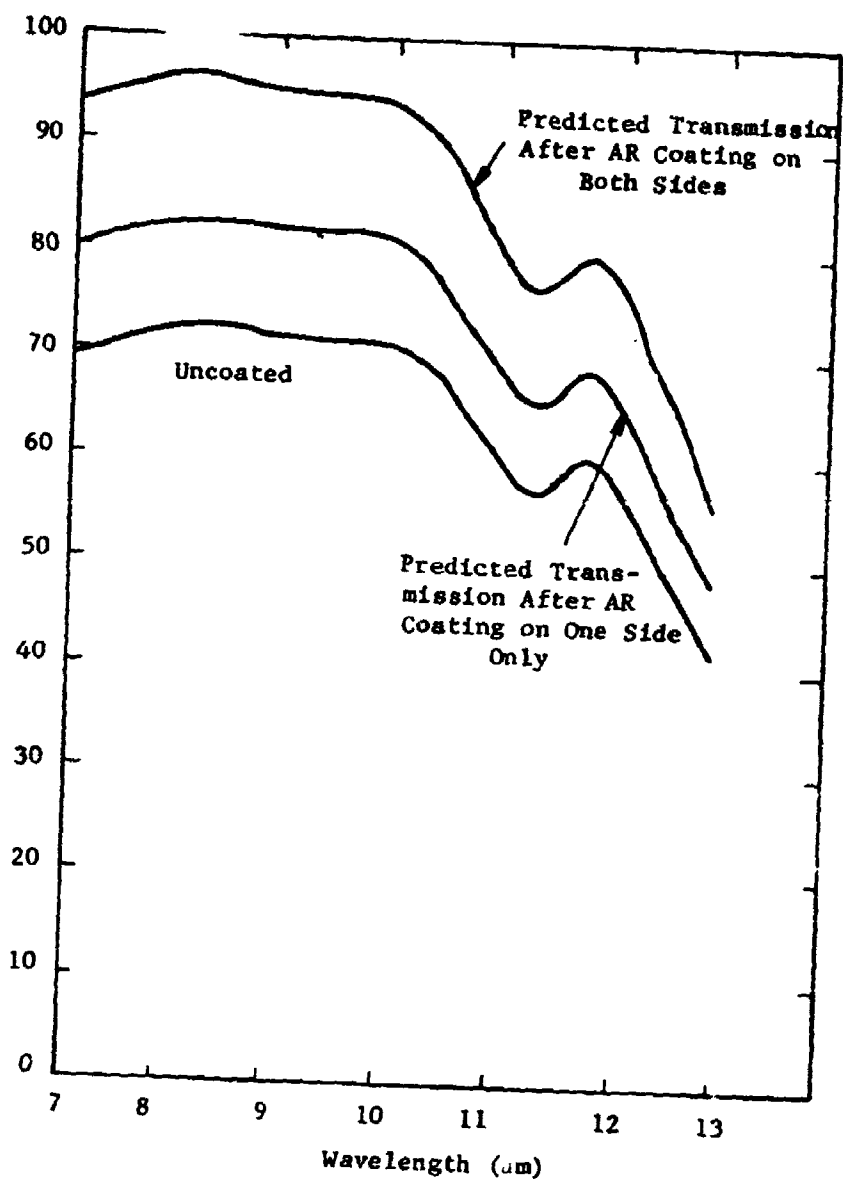


Figure 2-2. Optical Transmission of an Uncoated ZnS (0.2" Thick) Showing Increased Absorption at Wavelength Greater Than 10μm

2.3.1 Double-layer Coating Design Using Adjustable Film Thickness

If n_1 and n_2 are the refractive indices of the outer and inner layers, respectively, the zero reflectance can be obtained if:

$$\tan^2 \psi_1 = \frac{n_1^2 (n_s - n_o) (n_2^2 - n_o n_s)}{(n_1^2 n_s - n_2^2 n_o) (n_o n_s - n_1^2)} \quad (3)$$

$$\tan^2 \psi_2 = \frac{n_2^2 (n_s - n_o) (n_o n_s - n_1^2)}{(n_1^2 n_s - n_2^2 n_o) (n_2^2 - n_o n_s)} \quad (4)$$

where

$$\psi_1 = \frac{2\pi n_1 d_1}{\lambda}$$

and

$$\psi_2 = \frac{2\pi n_2 d_2}{\lambda}$$

d_1 and d_2 are the mechanical thicknesses of outer and inner layers

The above equations (only true for normal incidence) first derived by Schuster⁽³⁾ are illustrated by means of the very useful Schuster diagram (Figure 2-3). In this diagram n_2 is plotted as a function of n_1 with $n_o = 1$ (air) and $n_s = 2.21$. The diagram illustrates the range of indices n_1 and n_2 for which ψ_1 and ψ_2 from Equations (3) and (4) are real, and for which zero reflectance is possible on a Zinc Sulfide substrate. The shaded areas are the regions where zero reflectance can be obtained with real values of ψ_1 and ψ_2 . Outside of the shaded regions zero reflectance is not possible although the reflectance can be quite low⁽⁴⁾. The horizontal and vertical boundaries are graphs of $n_2^2 = n_o n_s$ and $n_1^2 = n_o n_s$, respectively, which correspond to single quarter-wave antireflection coating. The diagonal boundary is a plot of the equation $n_1^2 n_s = n_2^2 n_o$, which corresponds to a quarter-quarter coating, producing zero reflectance. Coatings corresponding to the dashed curve, given by $n_1 n_2 = n_o n_s$, have layers of equal thickness which in general are not integral multiples of one-quarter wavelength thickness.

(3) H. Schuster, Ann. Phys. (6) 4, 352 (1949).

(4) H. Schroeder, Z. Angew. Phys. 3, 53 (1951).

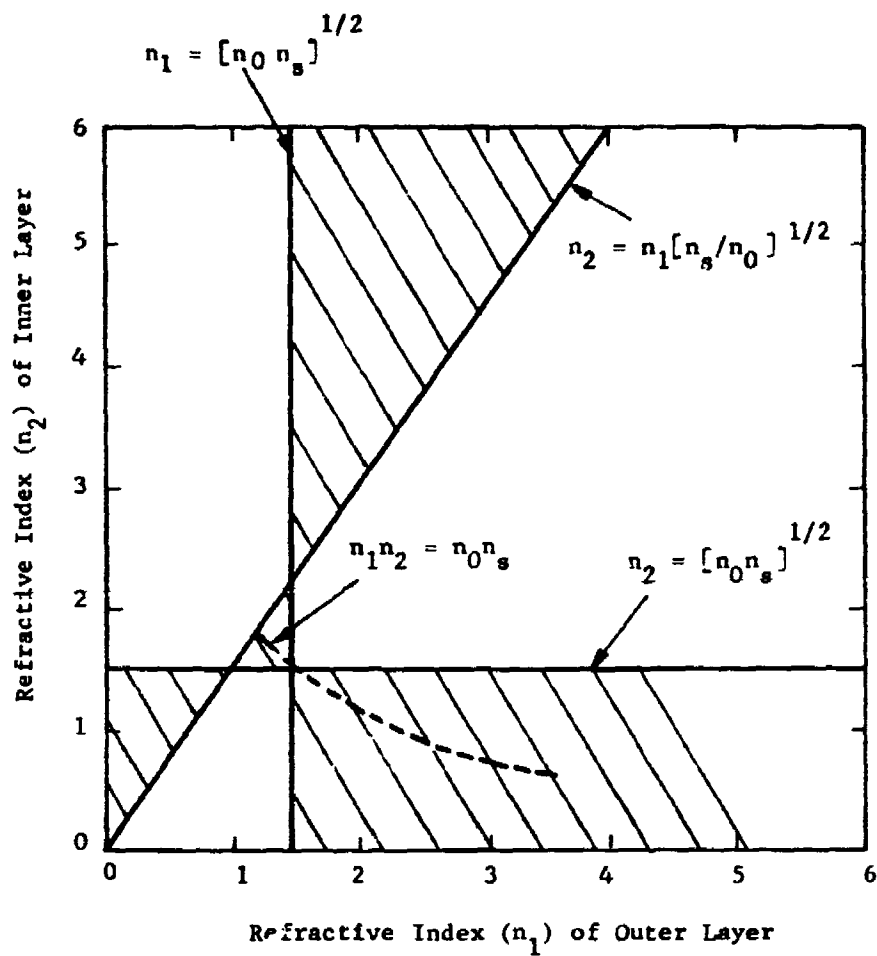


Figure 2-3. Schuster Diagram for Double-Layer AR Coatings on ZnS

Thus, from the Schuster diagram the acceptable ranges of indices for double layer AR coatings on ZnS are 1.0-1.6 for n_1 and 1.5 - 2.4 for n_2 . The coating designs based on this conclusion are discussed in Section 2.5.

2.3.2 Quarter-Quarter Coating Design Utilizing a Herpin Equivalent Index Inner Layer

The other coating design utilizing two films, each of quarter wave optical thickness for zero reflectance, can be understood given the following considerations. An important film construction which gives zero reflectance is

$$n_1^2 n_s = n_2^2 n_o \quad (5)$$

and

$$\psi_1 = \psi_2 = (2m - 1) \frac{\pi}{2}, \quad m = 1, 2, 3 \dots$$

or

$$n_1 d_1 = n_2 d_2 = (2m - 1) \frac{\lambda}{4} \quad (6)$$

Thus each layer is of an odd multiple of quarter wavelength thickness.

In designing the AR coating on this principle, usually, the outer layer is chosen from the durability and refractive index point of view (the lower the index of the outer layer, the better the transmission). The refractive index of the inner layer is then calculated from Equation (5). In practice, the calculated value of the inner layer is such that no known material with that refractive index exists. In such a case, a synthesized layer from low and high index materials in the form of a Herpin equivalent layer is constructed to achieve the required index. This technique has been utilized for some of the coating designs on this program. Also, when the outer layer is chosen to be ThF_4 , a very thin protective overcoat of CeF_3 is needed, as shown experimentally, to increase the durability of the coatings.

2.4 VISIBLE/NIR/IR COATING DESIGNS

The multispectral AR coating was designed using a multilayer step-graded index coating as an approximation to an inhomogeneous film⁽⁵⁾. This method considers a step-function approximation to a graded index film, i.e., a film whose refractive index decreases monotonically in relatively small steps from the index available. The most commonly used step-functions in the designing of multilayer AR coatings are linear and exponential functions. This means that the index of the layer decreases linearly or exponentially from the substrate side to the air side. During the initial computer phase of the design, it was found that an exponentially graded index film system provides slightly better antireflecting properties than the linearly graded index film system as applied to the present program requirement. Hence exponentially graded films were used throughout this program. Theoretical calculations have been carried out for 5 and 10 layer (each quarter wave in the visible region) exponentially graded films with MgF_2 as the outermost layer. The results are plotted in Figure 2-4. In order to achieve low reflectance in the 8 to $12\mu\text{m}$ region, the thickness of the last layer was adjusted so that the total thickness of the layer becomes a quarter wave at some wavelength between 8 to $12\mu\text{m}$. The reflectance versus wavelength results, as plotted in Figure 2-4, show that the additional mechanical complexity of a 10 layer design is not warranted in terms of decreased integrated reflectivity when compared to the 5-layer design. For this reason 5 layer designs were chosen for all multispectral antireflection coatings during the remainder of the program. Since the mechanically thinner design reduces the effect of intrinsic film stresses at the film/substrate boundary, an additional advantage of the 5 layer design is improved durability. The use of a multilayer graded index coating requires refractive indices for the intermediate layers for which coatings are not available. Thus these layers need to be synthesized using Herpin equivalent layers constructed from the highest and lowest available refractive indices chosen from real thin film materials.

(5)

J. Cox and G. Hass, Phys. of Thin Films, 2, 239 (1964).

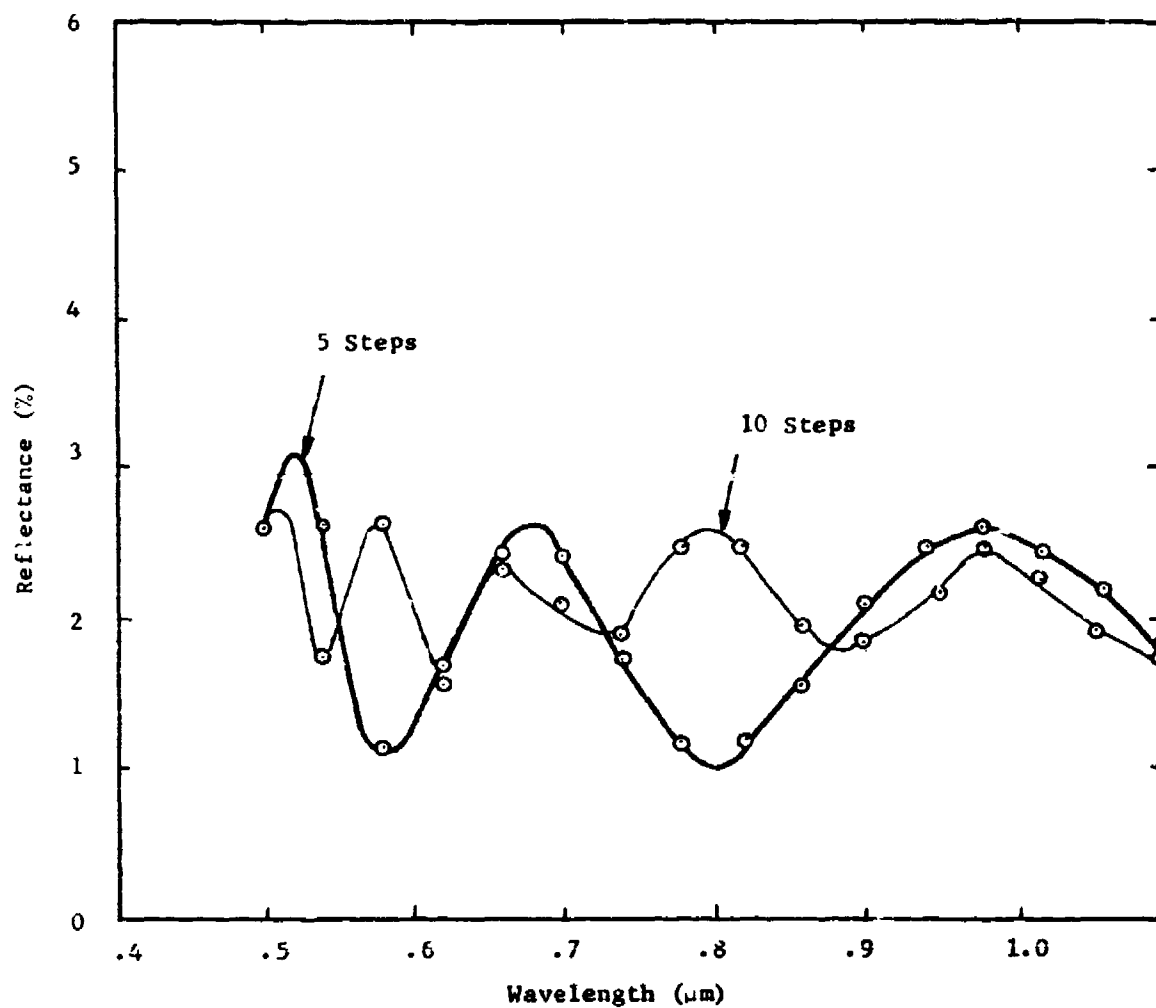


Figure 2-4. Comparison Between Theoretical Reflectances of 5 and 10 Steps Exponentially Graded Film Systems (In Both Cases MgF_2 is the Outermost Layer)

2.5 SELECTION OF MATERIALS AND VARIOUS COATING DESIGNS

A literature search was made on a large variety of coating materials based on qualifying refractive indices. ZnSe was chosen as the high index material because of its known ability to adhere to a ZnS substrate. The low index materials were chosen on the basis of durability as well as the ease with which they can be deposited in combination with ZnSe. All of the materials except Praseodymium Fluoride (PrF_3) deposited were compatible with ZnSe. In some designs Cerium Fluoride was used as a protective overcoat. All of the designs fabricated are listed in Table 2-1.

2.6 THEORETICAL REFLECTIVITIES OF VARIOUS DESIGNS

Theoretical reflectivities of various coating designs fabricated under this program are shown in Figures 2-5 to 2-15. From these curves, it is evident that the program goal of less than 1% reflectivity at all wavelengths cannot be met either for double layer coatings or multilayer coatings. However, using a quarter-quarter design, a theoretical reflectivity of less than 1% at all wavelengths between 8 to 12 μm can be obtained with the exception of the ZnSe/ CeF_3 design.

The next section (Section III) describes the coating fabrication facilities. The spectral transmission and reflectance measurements of the coatings based on the above theoretical design are described in Section IV.

TABLE 2-1. VARIOUS COATING DESIGNS

TYPE OF COATING	TYPE OF DESIGN	COATING DESIGN
Infrared	Double Layer	ZnSe/NdF_3 $\text{ZnSe/NdF}_3/\text{CeF}_3^*$ ZnSe/PrF_3 ZnSe/LaF_3 ZnSe/YF_3 ZnSe/CeF_3
	Quarter-Quarter	$\text{ZnSe/YF}_3/\text{ZnSe/YF}_3$ $\text{ZnSe/LaF}_3/\text{ZnSe/LaF}_3$ $\text{ZnSe/CeF}_3/\text{ZnSe/CeF}_3$ $\text{ZnSe/ThF}_4/\text{ZnSe/ThF}_4/\text{CeF}_3^*$
Visible/NIR/IR	Multilayer	$(\text{ZnSe/ThF}_4)^5$ $(\text{ZnSe/ThF}_4)^5\text{MgF}_2$ $(\text{ZnSe/ThF}_4)^5\text{CeF}_3^*$ $(\text{ZnSe/YF}_3)^5$

CeF_3 is used as protective overcoat.

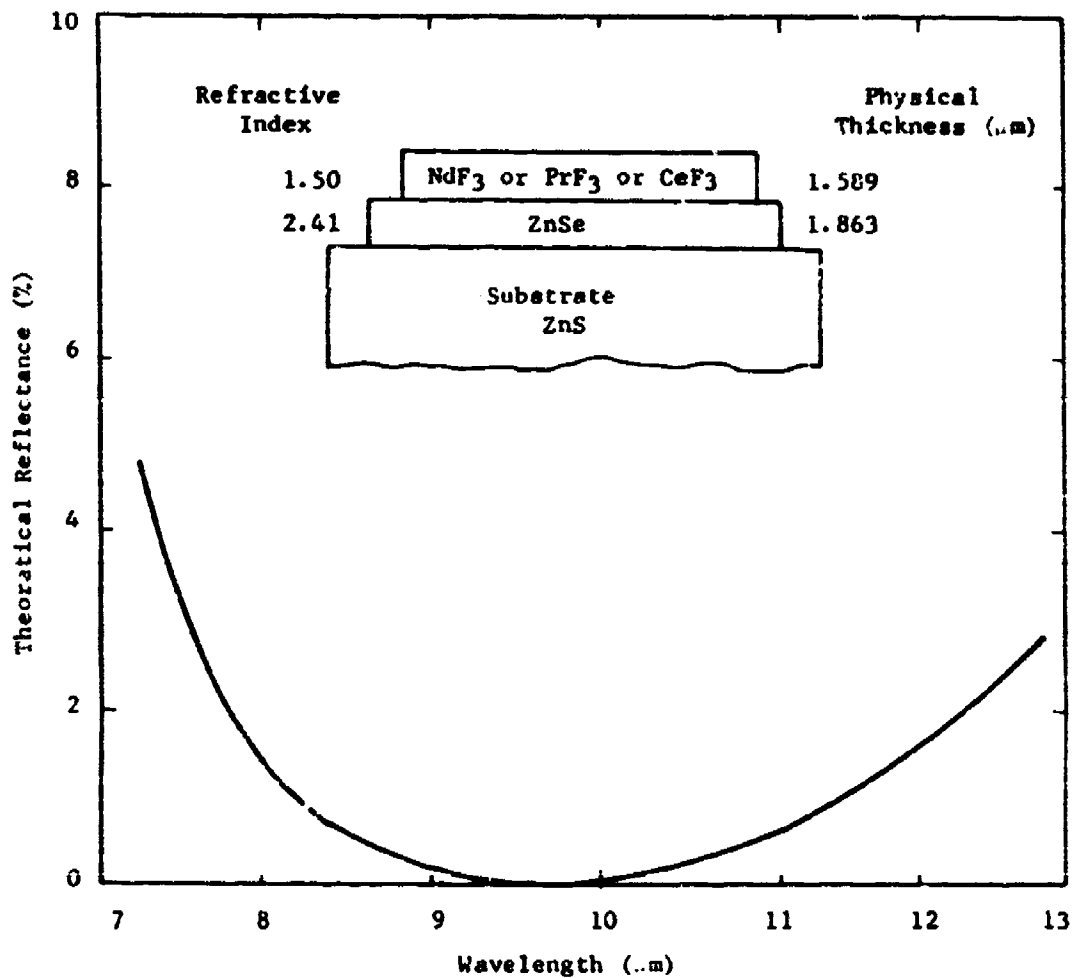


Figure 7-5. Theoretical Reflectivity Curve of Double Layer Design

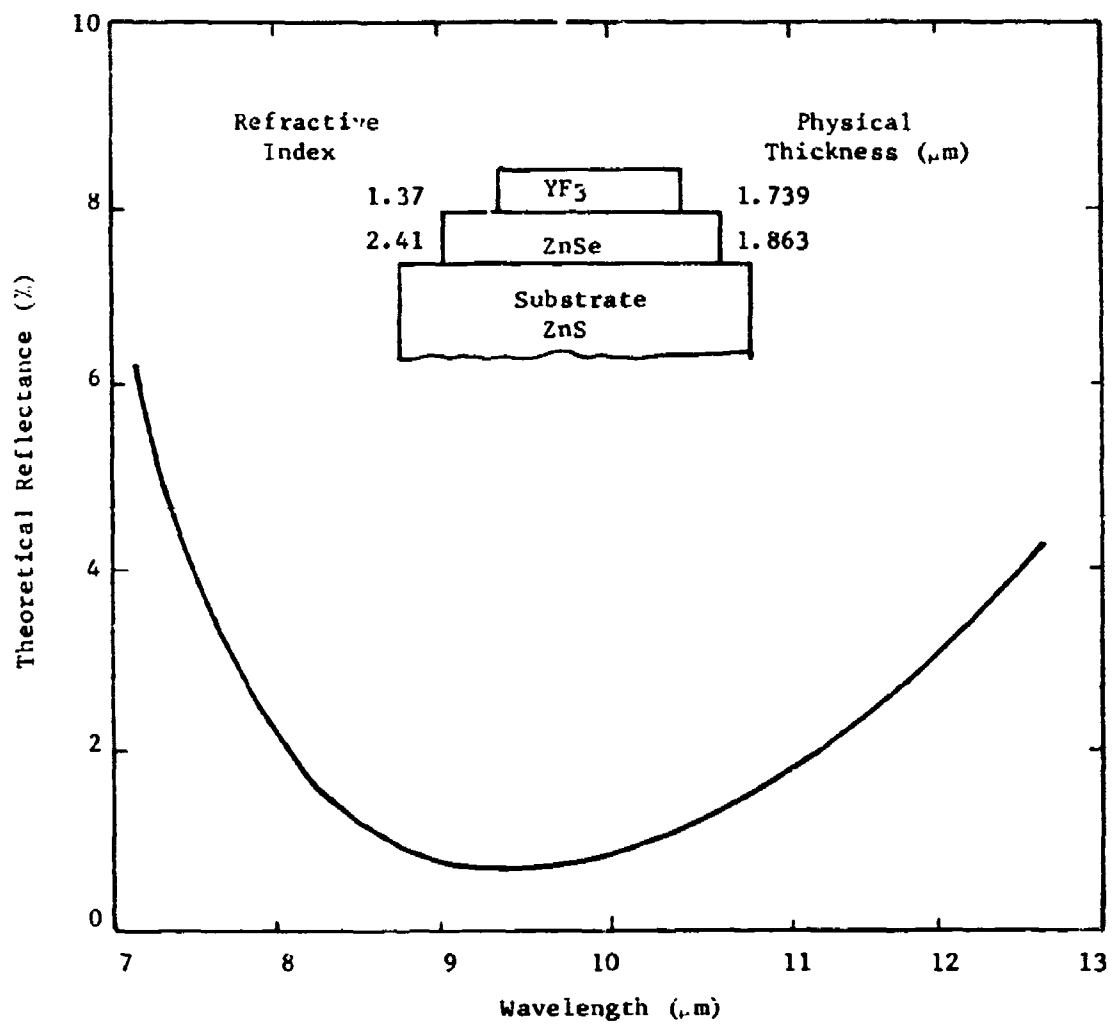


Figure 2-6. Theoretical Reflectivity Curve of Double Layer Design

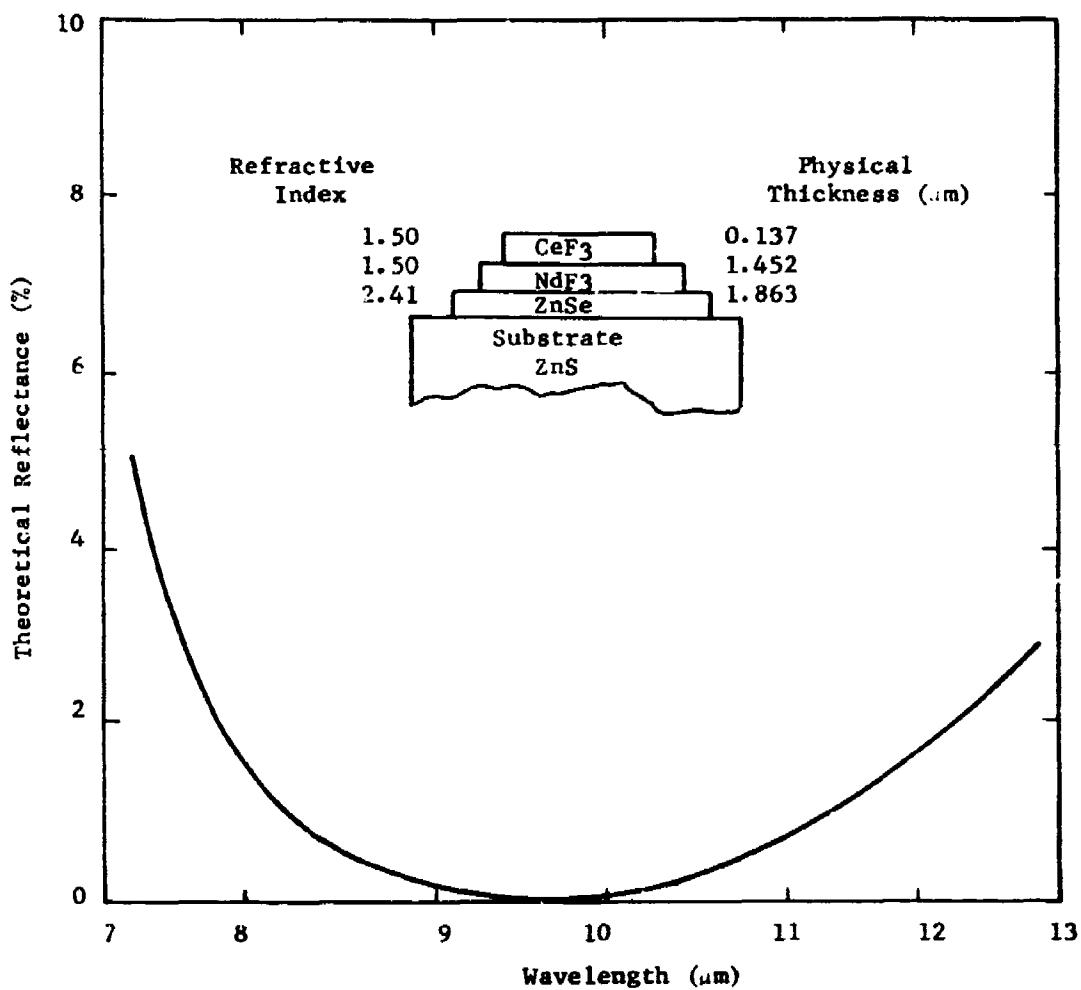


Figure 2-7. Theoretical Reflectivity Curve of Double Layer Design
(CeF₃ is Used for Protection)

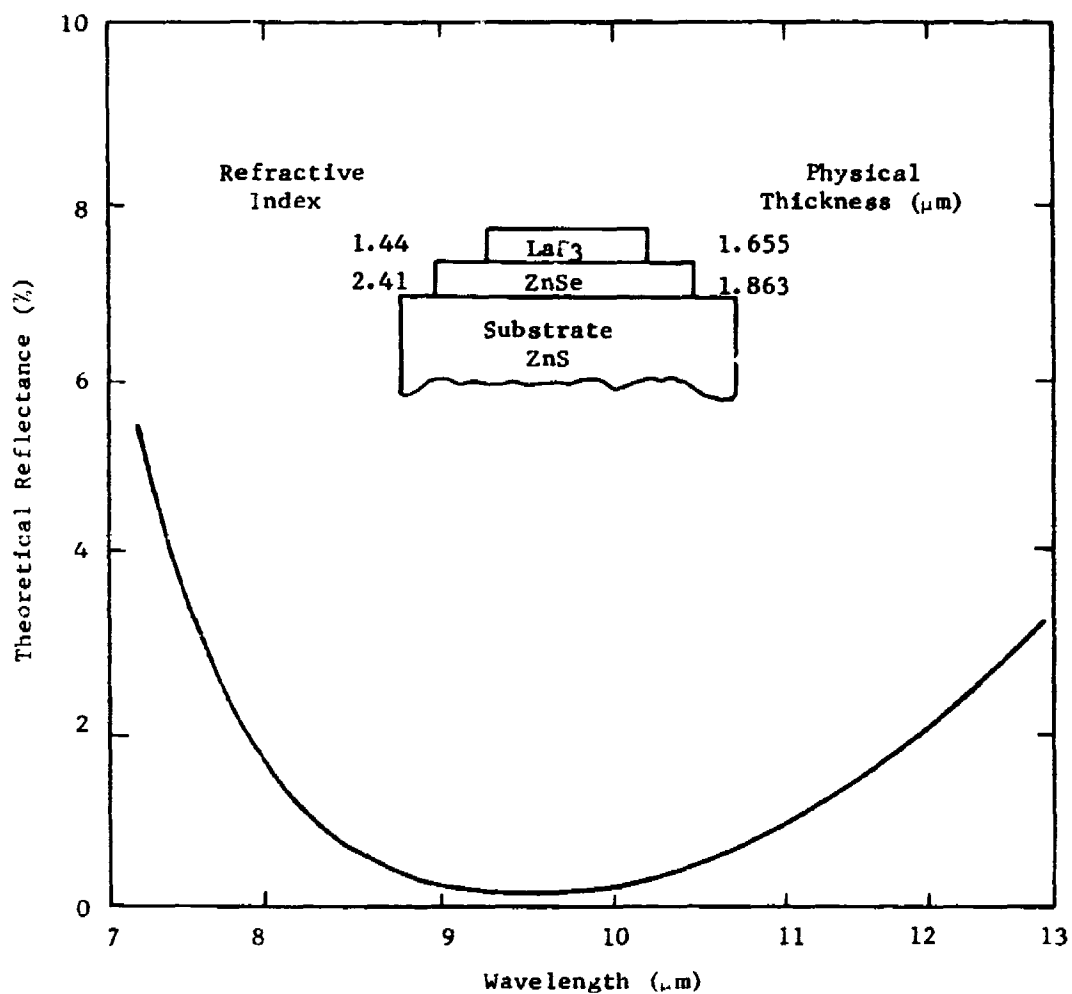


Figure 2.8. Theoretical Reflectivity Curve of Double Layer Design

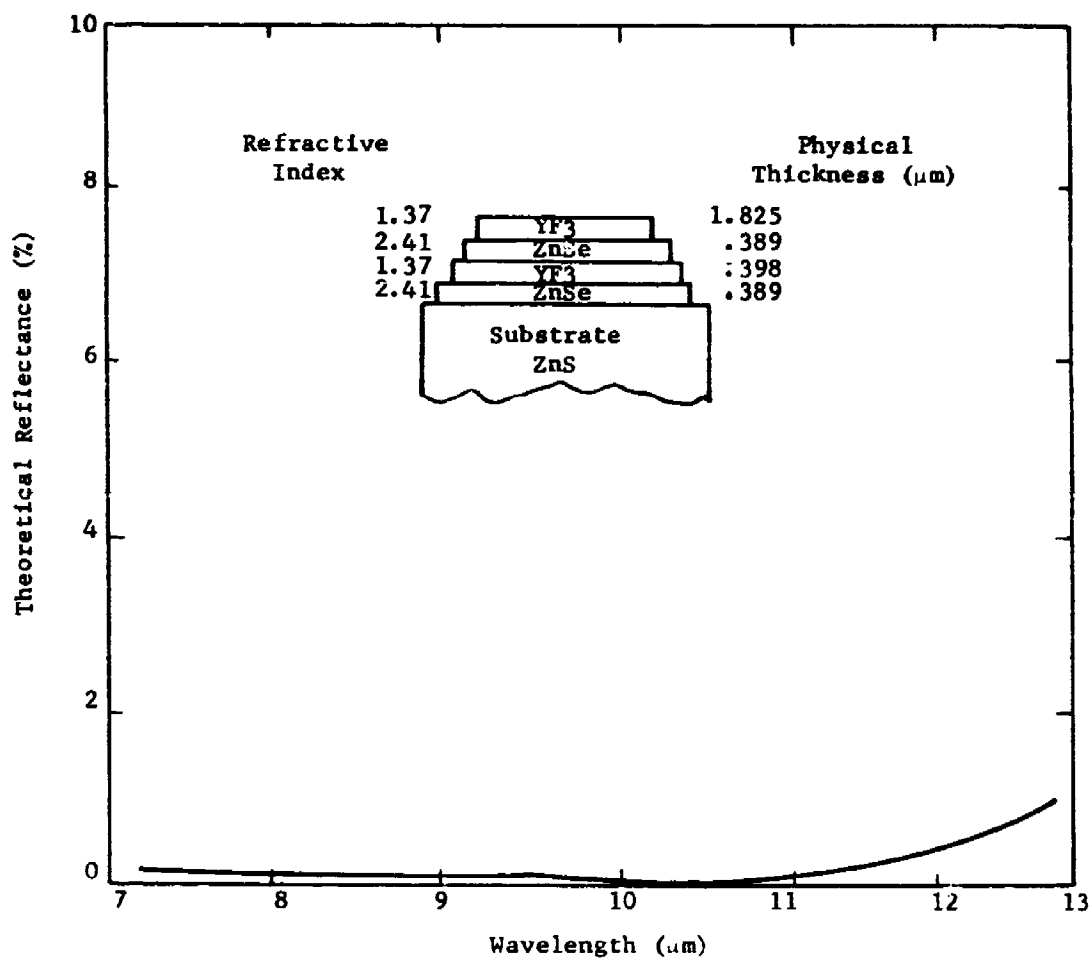


Figure 2-9. Theoretical Reflectivity Curve of Quarter-Quarter Coating

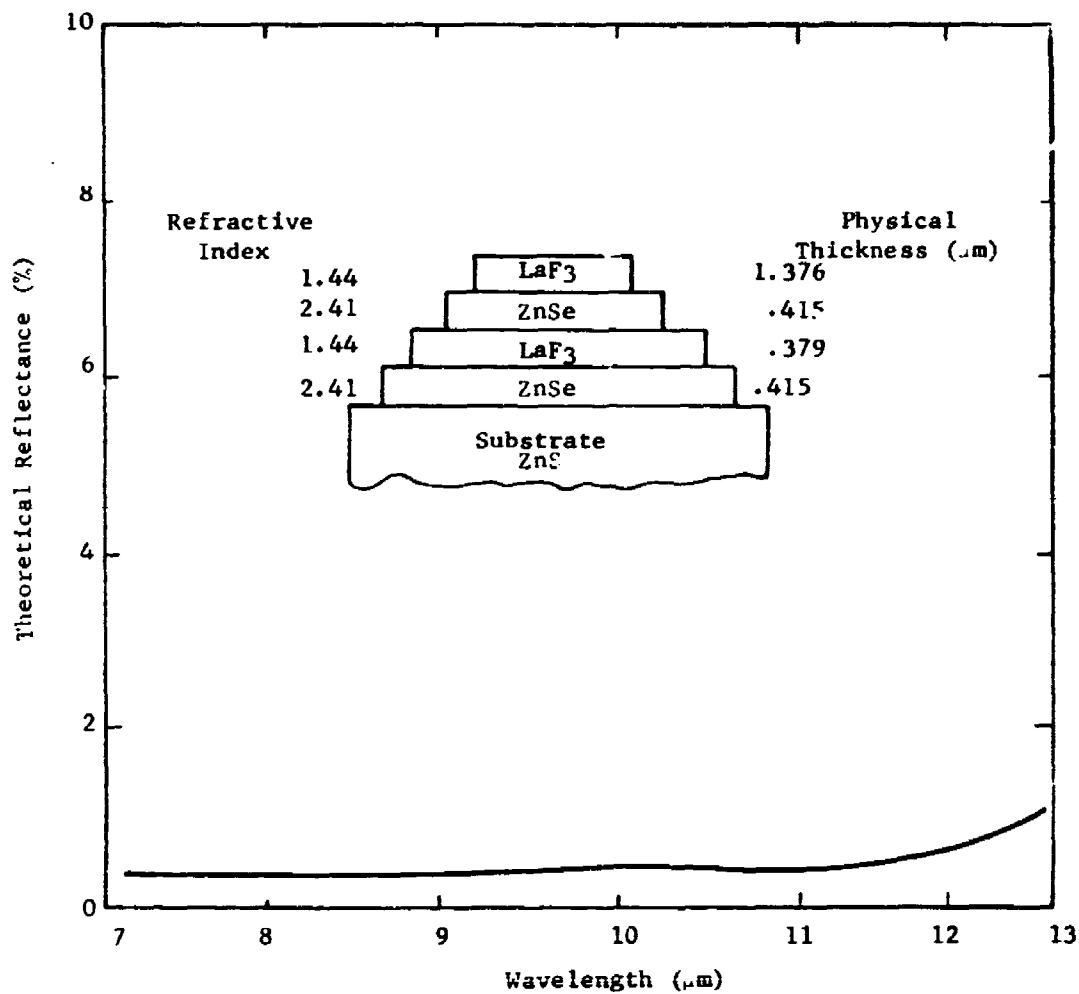


Figure 2-10. Theoretical Reflectivity Curve of Quarter-Quarter Design

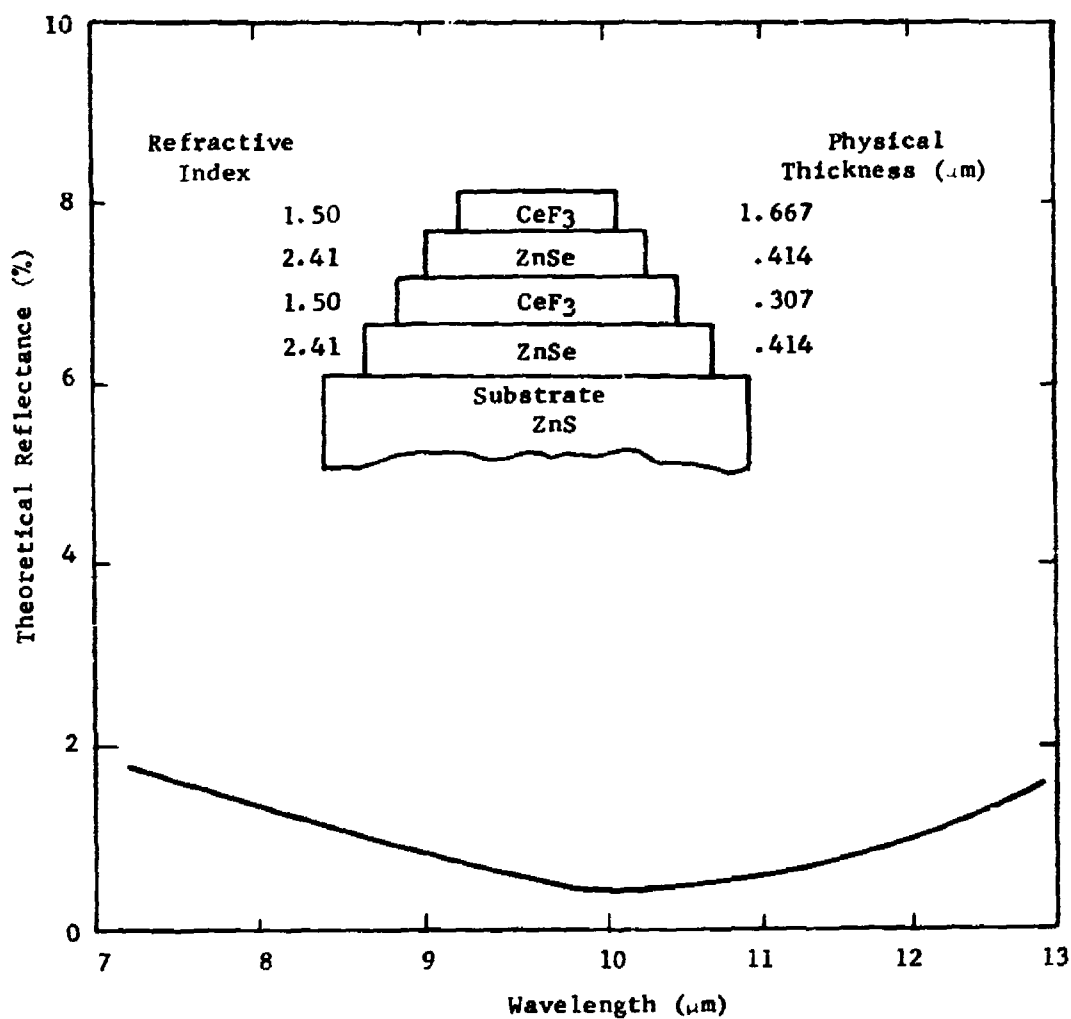


Figure 2-11. Theoretical Reflectivity Curve of Quarter-Quarter Design

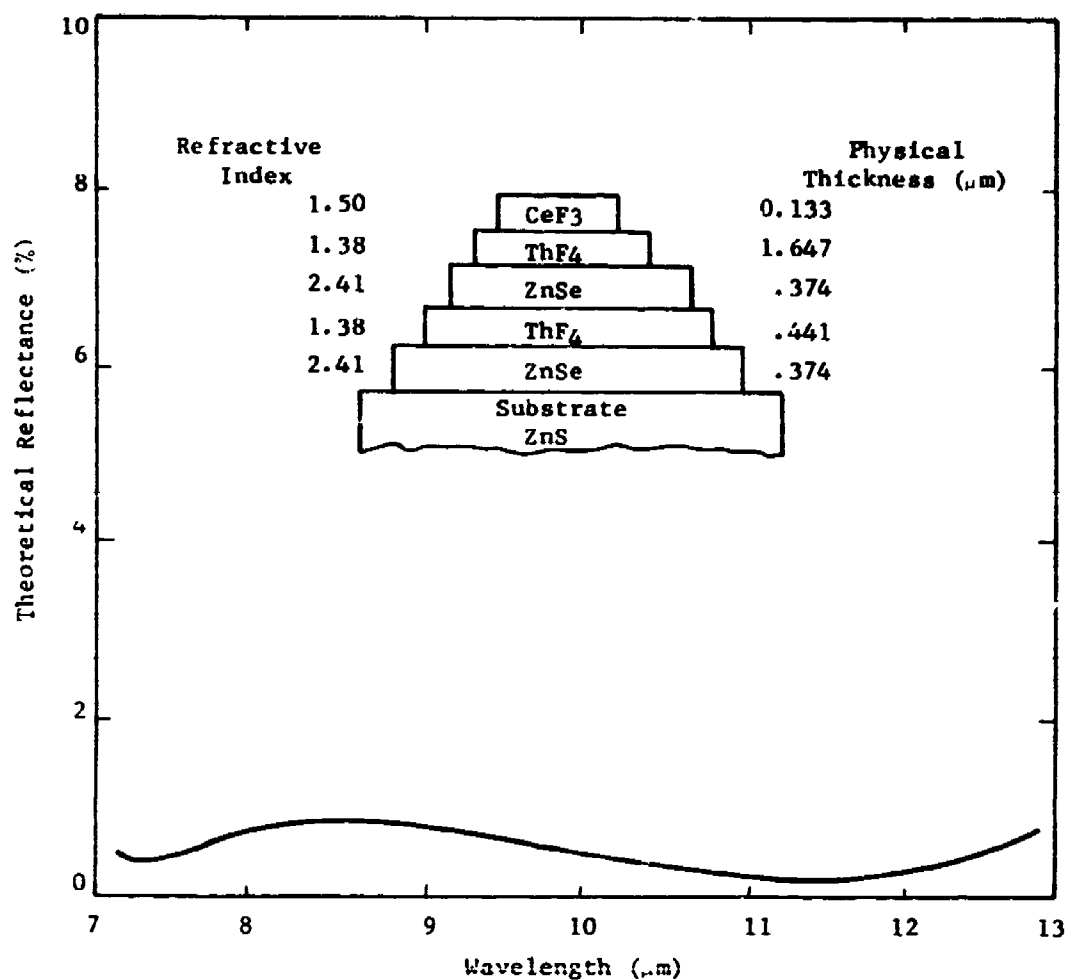


Figure 2-12. Theoretical Reflectivity Curve of Quarter-Quarter Design (CeF₃ is a Protective Overcoat)

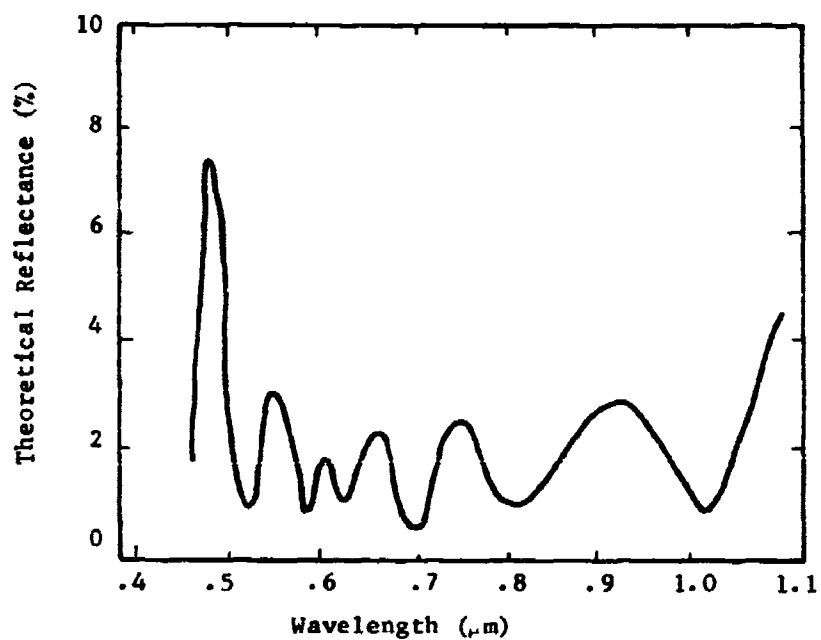
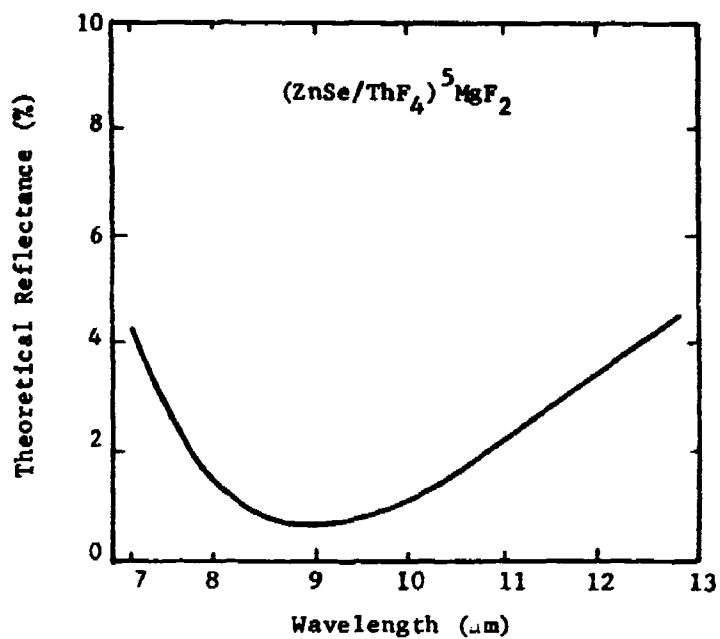


Figure 2-13. Theoretical Reflectivity of VIS/NIR/IR Coating with MgF_2 Protective Overcoat

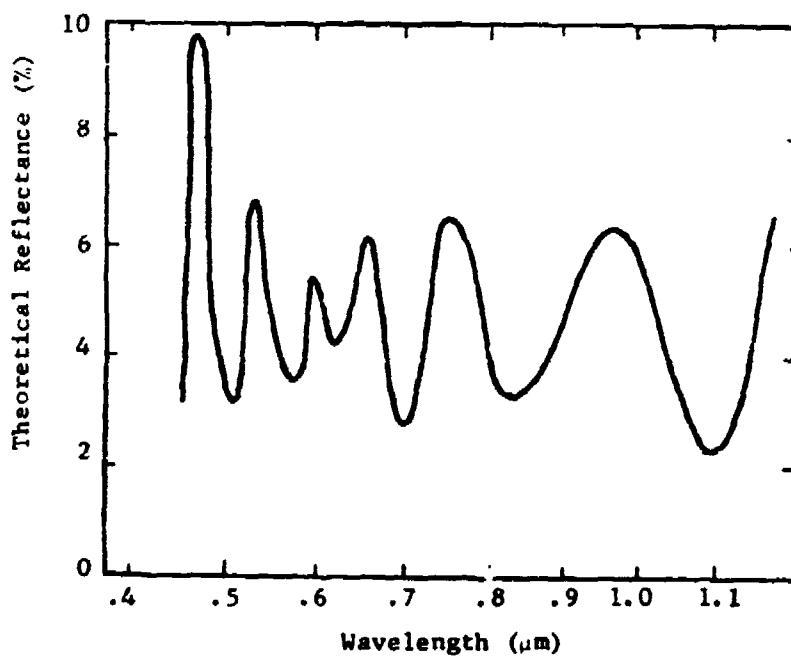
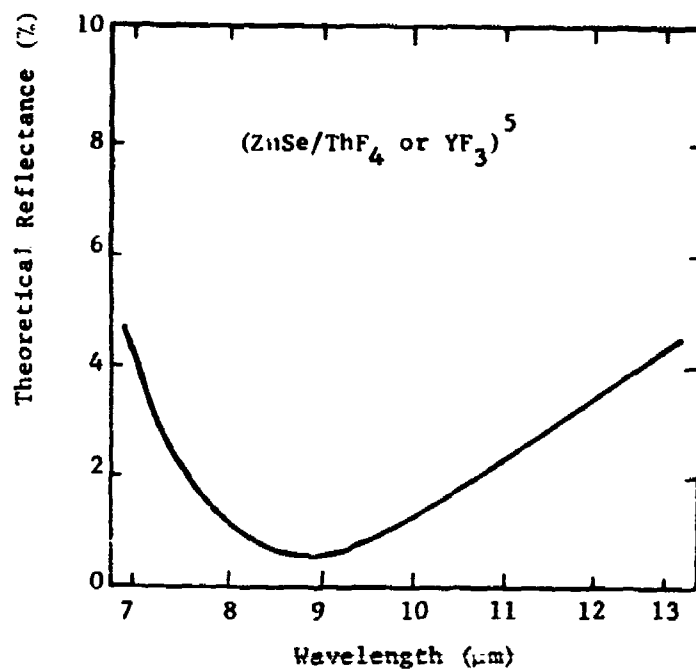


Figure 2-14. Theoretical Reflectivity of VIS/NIR/IR Coating with No Protective Overcoat

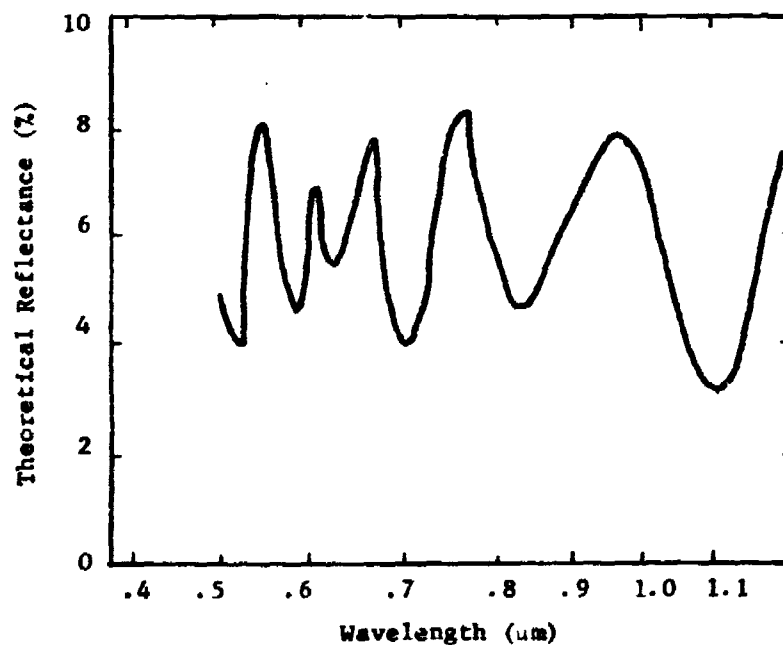
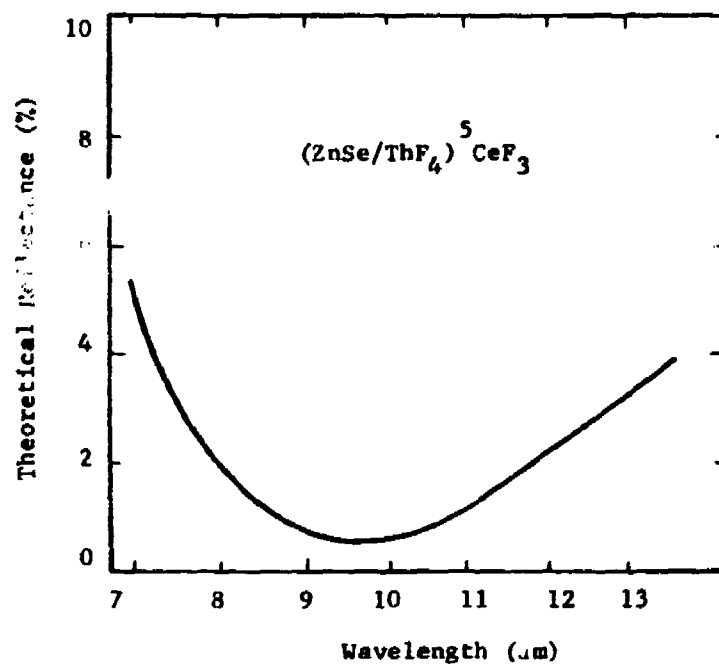


Figure 2-15. Theoretical Reflectivity of VIS/NIR/IR Coating with CeF_3 as Protective Overcoat

SECTION III

COATING FABRICATION

3.1 INTRODUCTION

This section briefly describes the actual substrate and coating deposition procedures and also includes a brief description of the coating chambers and their associated apparatus.

3.2 SUBSTRATE FABRICATION

ZnS substrates (1.5" x 0.5" x 0.2") were fabricated from Raytheon ZnS blanks. The cutting and polishing were done at Perkin-Elmer. The surfaces of the substrates were prepared using conventional polishing techniques. The substrates met the following specifications.

- o Flatness: 1λ in visible
- o Scratch to Dig Ratio: 60/40
- o Bevel: 0.75mm

The larger ZnS windows (2.0" x 2.0" x 0.5") were also cut and polished from Raytheon ZnS blanks. They were polished to the same specification as small ZnS substrates.

3.3 COATING CHAMBERS

All of the optical coatings for this program were done in a 36-inch and a 56-inch box-type vacuum evaporation system. Figures 3-1 and 3-2 show photographs of the two chambers utilized in this program. Table 3-1 shows the type of vacuum system and control systems used for these chambers.

The optical monitoring system used in both evaporation systems allows separate monitoring of each film in a dielectric stack by means of a multiple monitor slide head. The combination of this technique and the ability to monitor at any wavelength in the 0.3μm to 2.5μm region allows monitoring of the optical film thickness to accuracies of one-half % or better.

TABLE 3-1. SUMMARY OF THE FEATURES OF PERKIN-ELMER
HIGH VACUUM EVAPORATION SYSTEM

50-INCH VACUUM CHAMBER	56-INCH VACUUM CHAMBER
• High vacuum pumping systems by the use of a 5300 liter/sec. diffusion pump with a liquid nitrogen trap.	• High vacuum selective pumping systems by the use of a 1550 liter/sec. ion pump operated in conjunction with liquid nitrogen condensation panels and a large titanium gettering system.
• Multipocket electron gun source.	• Dual multipocket electron gun source.
• Resistance evaporation source.	• Multiple resistance evaporation sources.
• Calrod heater blanket to attain substrate temperatures up to 400°C.	• Calrod heater blanket and quartz iodine heater lamps to attain substrate temperatures up to 400°C.
• Dual crystal rate monitors to control source evaporation rate.	• Multiple crystal rate monitors to control the source evaporation rate.
• A temperature monitoring system with five thermocouple to measure temperature at five different positions.	• A digital thermocouple temperature monitoring system (five thermocouples) capable of measuring temperatures on substrates while it is rotating during deposition.
• Optical thickness monitor which uses a white light/monochromator system and synchronously modulated detection system.	• Optical thickness monitor which uses a white light/monochromator system and synchronously demodulated detection system. • Capability of accommodating substrates up to 40 inches in diameter.

3.4 COATING FABRICATION PARAMETERS

Major parameters of the coating's preparation are discussed in the following subsections:

3.4.1 Surface Cleaning of Substrates

The substrates were first rinsed in deionized water, then scrubbed with cotton and orvis detergent. After scrubbing, the substrates were again rinsed with deionized water and then flushed with isopropyl alcohol. After flushing, the substrates were left to dry in a clean bench class 100 environment.

3.4.2 Purity of Source Materials for Vacuum Deposition

All of the materials used for deposition during this program were obtained from either CERAC, Incorporated, or Research Chemicals and were 99.9% or better in purity.

3.4.3 Pre-Deposition Cleaning of Substrates

Substrates were cleaned in a vacuum before coating deposition by the use of glow discharge. The typical time for glow discharge was 15 minutes.

3.4.4 Pressure During Deposition

The typical pressure range for a various coating deposition runs was 1.0 to 5.0×10^{-6} torr.

3.4.5 Deposition Rates

The materials were deposited either by electron gun or by resistant heating of a platinum boat. Typical deposition rates were $12 \pm 5 \text{ \AA/sec}$.

3.4.6 Substrates Temperature

All the samples for rain erosion test were coated at 350 to 375°C substrate temperatures.

3.5 POST-ANNEALING OF COATED SAMPLES

After deposition of coating and cool down of the chamber, the substrates were taken out from the chamber and placed in a stainless steel post annealing fixture. This fixture is capable of accommodating twenty-four (1.5" x 0.5" x 0.2") or six (2" x 2") ZnS pieces and can be maintained in a furnace at a temperature of 200°C with dry nitrogen flowing through it. All of the coated pieces were postannealed at 200°C for 2 hours in a dry nitrogen atmosphere.

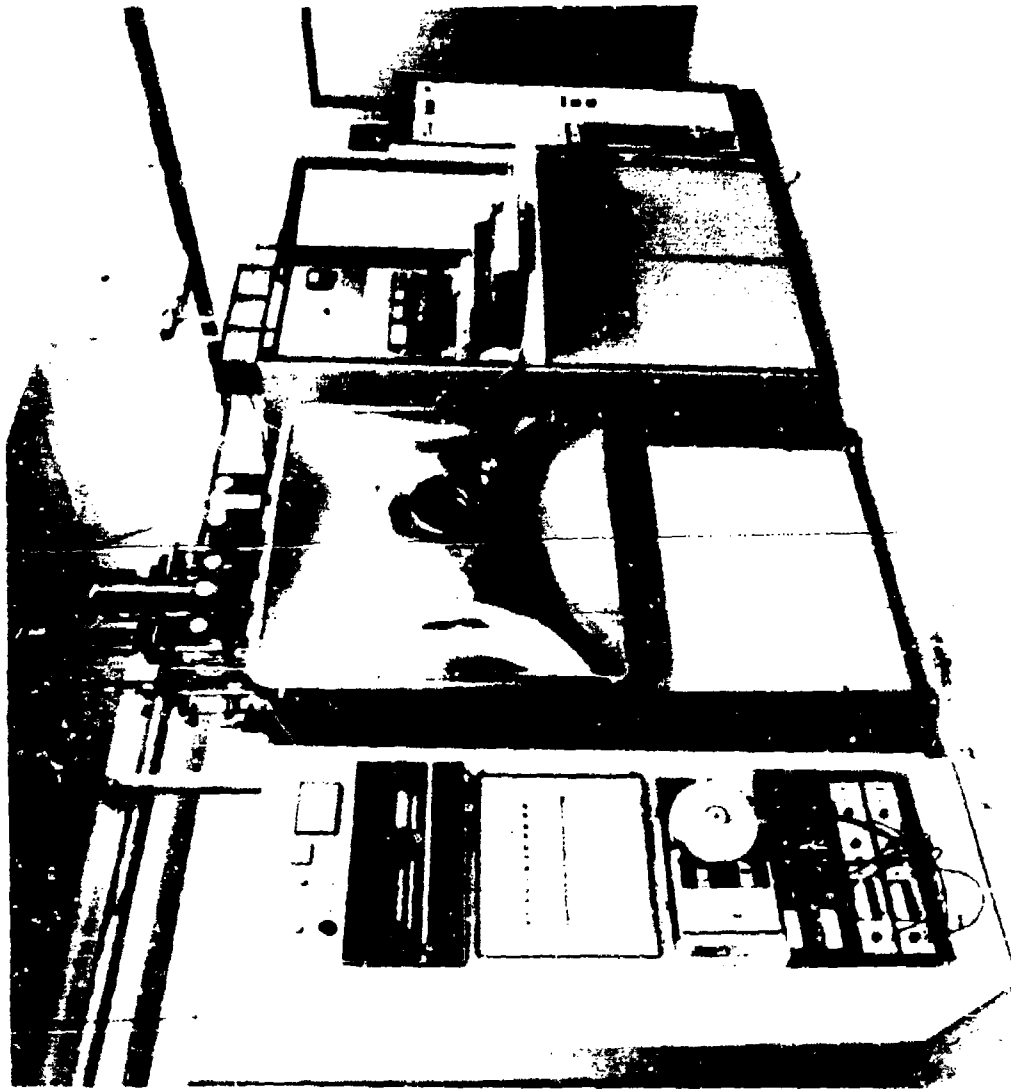


Figure 3-1. 36" High Vacuum Evaporation System

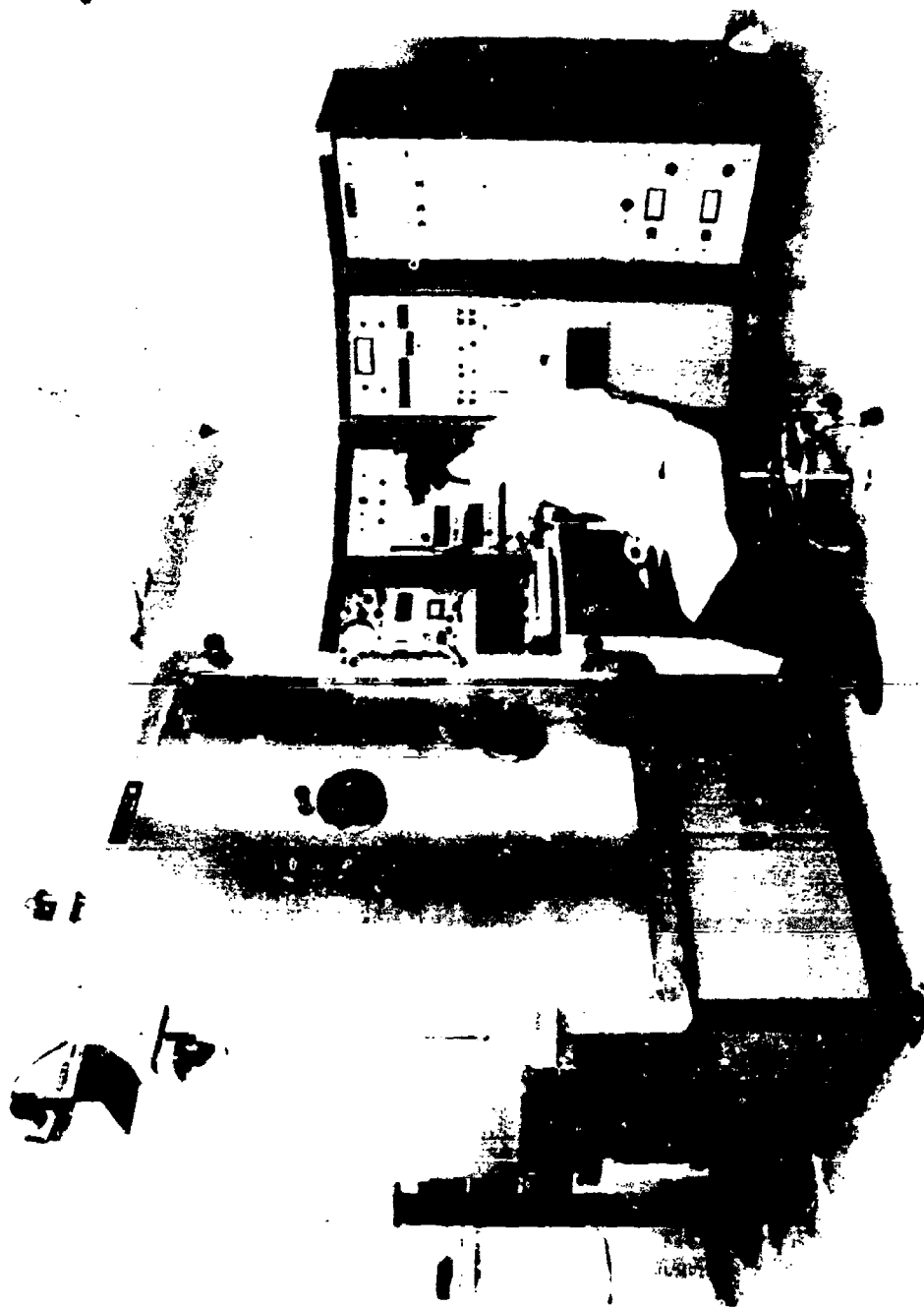


Figure 3-2. 56" High Vacuum Evaporation System

SECTION IV

RESULTS OF COATING FABRICATION

4.1 INTRODUCTION

This chapter presents the results of various measurements conducted on the optical coatings fabricated, based on the theoretical designs outlined in Section II. Spectral measurements, transmission and reflectance on the samples were made before and after the rain erosion test. The actual rain-erosion test was conducted at Air Force facilities and is described in Appendix A. However, the results of the test are summarized in this Section. In addition to the spectral data, durability tests which include adhesion, hardness, abrasion, solubility, salt fog and humidity tests, conducted at Perkin-Elmer, are also included. All substrates used were the test samples of ZnS of dimensions 1.5" x 0.5" and 0.2" thick.

4.2 SPECTRAL MEASUREMENTS

Transmission and reflection measurements in infrared were performed on the Perkin-Elmer spectrophotometer models #180 and #580D. The visible and near infrared measurements on visible/NIR/IR coatings were performed on Hitachi Model #323. The results of spectral measurements on the uncoated substrates and substrates coated with various types of coatings are described below.

4.2.1 Uncoated Substrate

The optical transmission of randomly picked uncoated substrates were measured in visible and infrared and is shown in Figure 4-1. A large variation in visible and near infrared transmission (up to 12% at 1.06 μ m) was found from piece to piece. A much smaller variation among pieces was found in infrared. A maximum variation of 2% in transmission was found among pieces at 10 μ m.

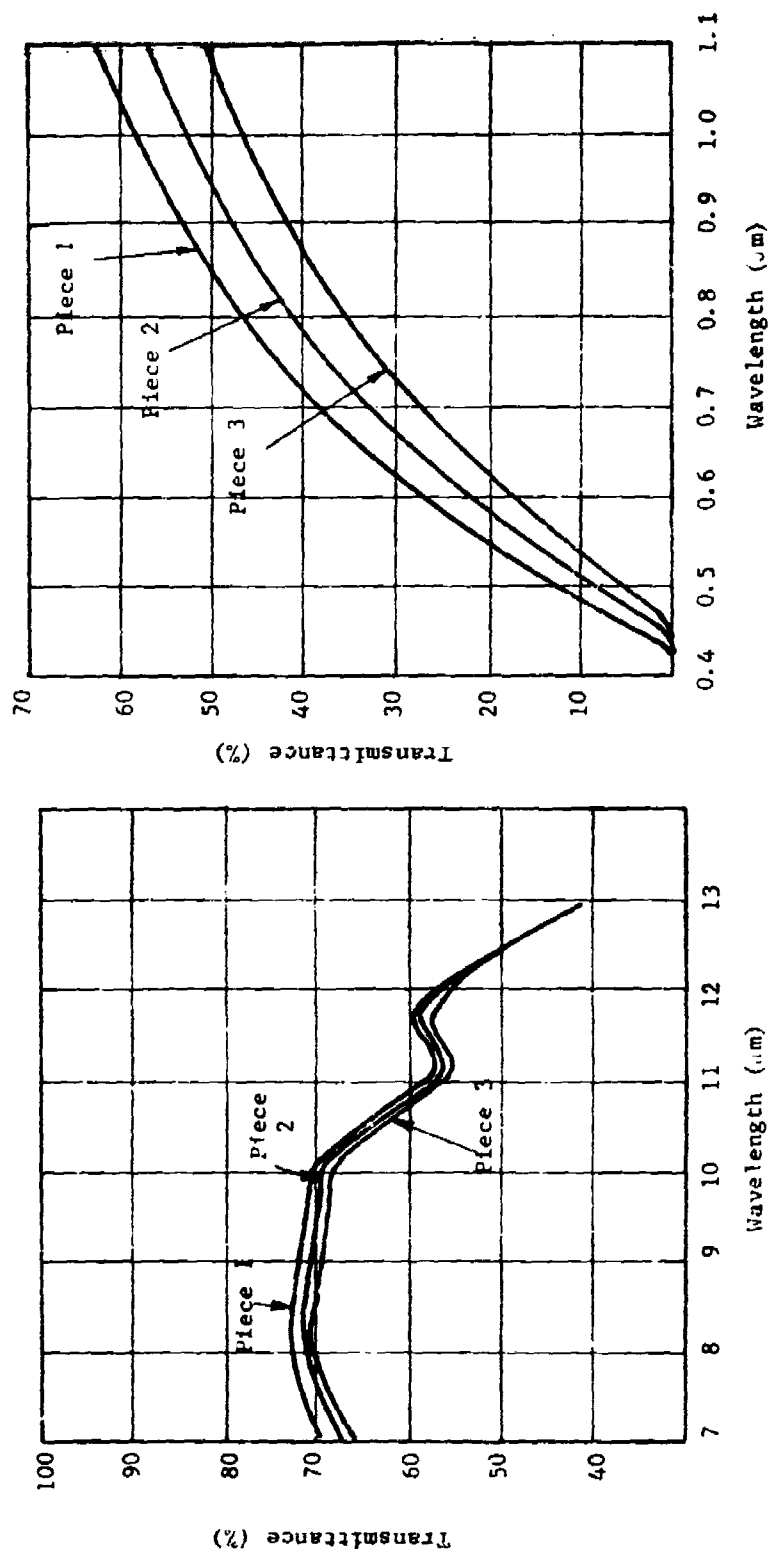


Figure 4-1. Transmission Through Various 0.2" Thick ZnS Substrates. All Have Surface Finish with Scratch to Dig Ratio Better Than 60/40

The effect of the rain erosion test (1-inch/hour rainfall, 1.8mm drop size, 470 mph drop impact velocity, 90° impact angle and 20 minute exposure time) on the visible and infrared transmission of an uncoated substrate is shown in Figure 4-2. A much larger transmission drop was observed in visible and near-infrared as compared to far infrared wavelengths. The transmission loss, due to cracks produced by the rain erosion test, was 9% at 1.06 μ m compared to 2.5% at 10 μ m.

The transmission of an uncoated ZnS piece was also measured at 200°C in infrared and is shown in Figure 4-3 together with the transmission at room temperature. No significant variation in transmission was observed for the two temperatures. The visible/NIR transmission could not be measured at 200°C as the substrate-heater housing would not fit into the small sample compartment of the Hitachi spectrophotometer.

4.2.2 Infrared Coatings

The effects of the rain erosion test on the transmission of infrared coatings are summarized below. (Details are discussed in Appendix A.)

- a) Double Layer Coating: Large transmission losses were observed on coatings containing NdF₃ as indicated in Figures 4-4 and 4-5. This transmission loss was attributed to absorption in the complex compound formed by the chemical reaction of NdF₃ and water. Double layer coatings of ZnSe/YF₃, ZnSe/LaF₃ and ZnSe/CeF₃ did not lose much transmission. The losses on these coatings were within those of uncoated substrates. The losses were due to cracks in substrates produced by the rain drop impact.
- b) Quarter-Quarter Coating: All the quarter-quarter coatings passed the rain erosion test with transmission losses comparable to or less than the losses of uncoated substrates. Losses in the various coatings are indicated in Figures 4-9 through 4-12. These coatings were much broader than double layer coatings, as indicated by their reflectance curve. Samples of coating ZnSe/ThF₄/ZnSe/ThF₄/CeF₃ were tested for various rain erosion tests. On each test, no

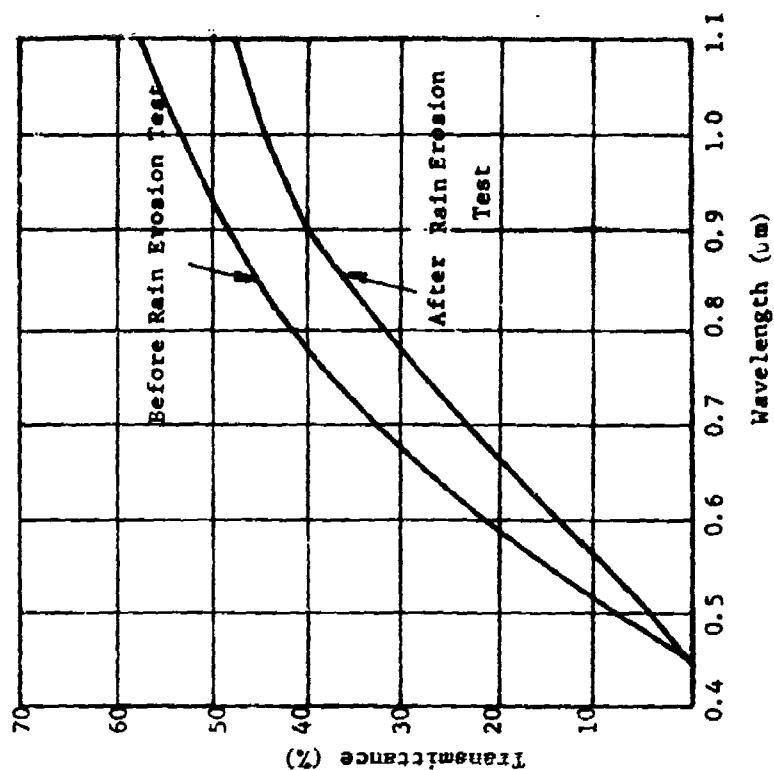
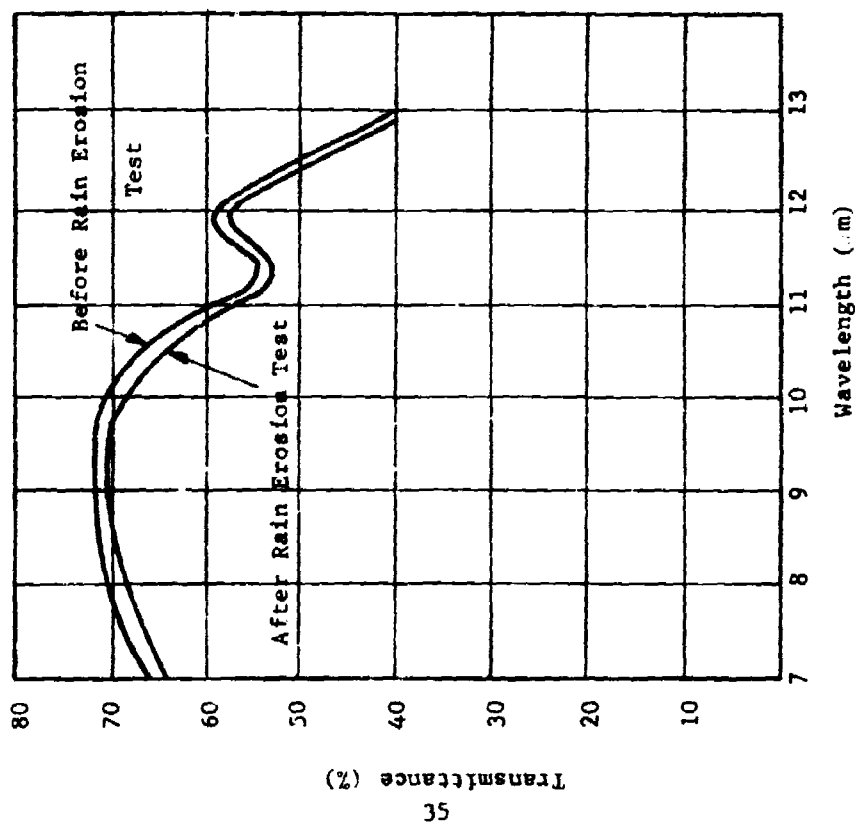


Figure 4-2. Transmission of 0.2" Thick Uncoated ZnS Piece Before and After Rain Erosion Test

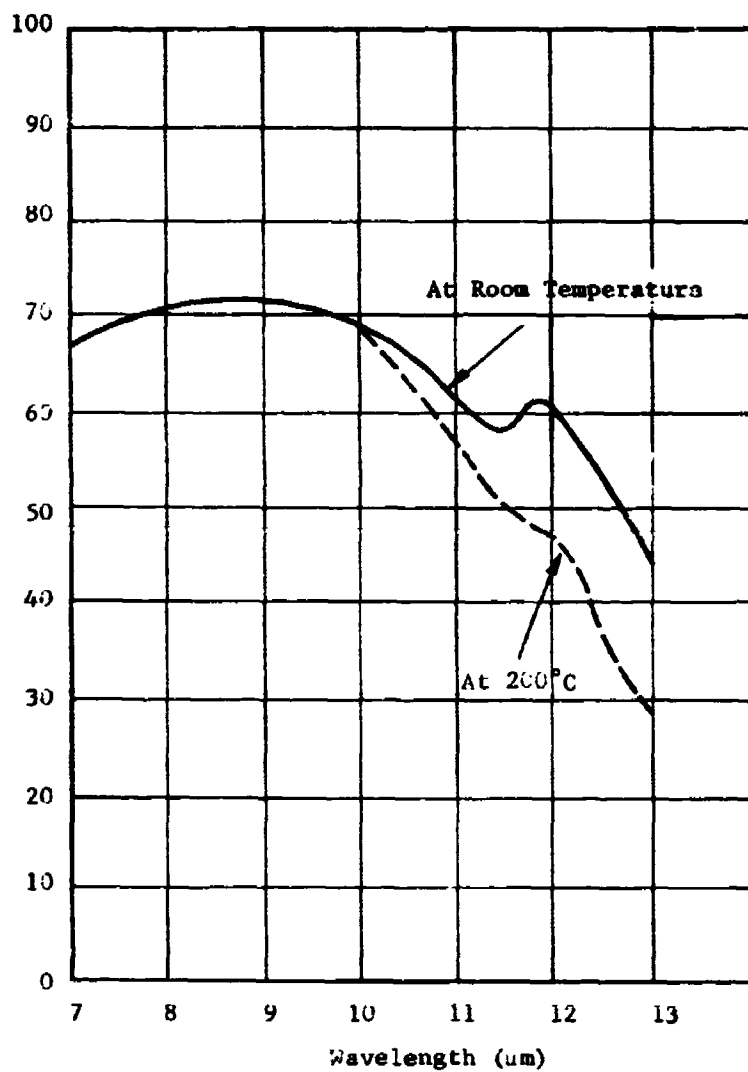
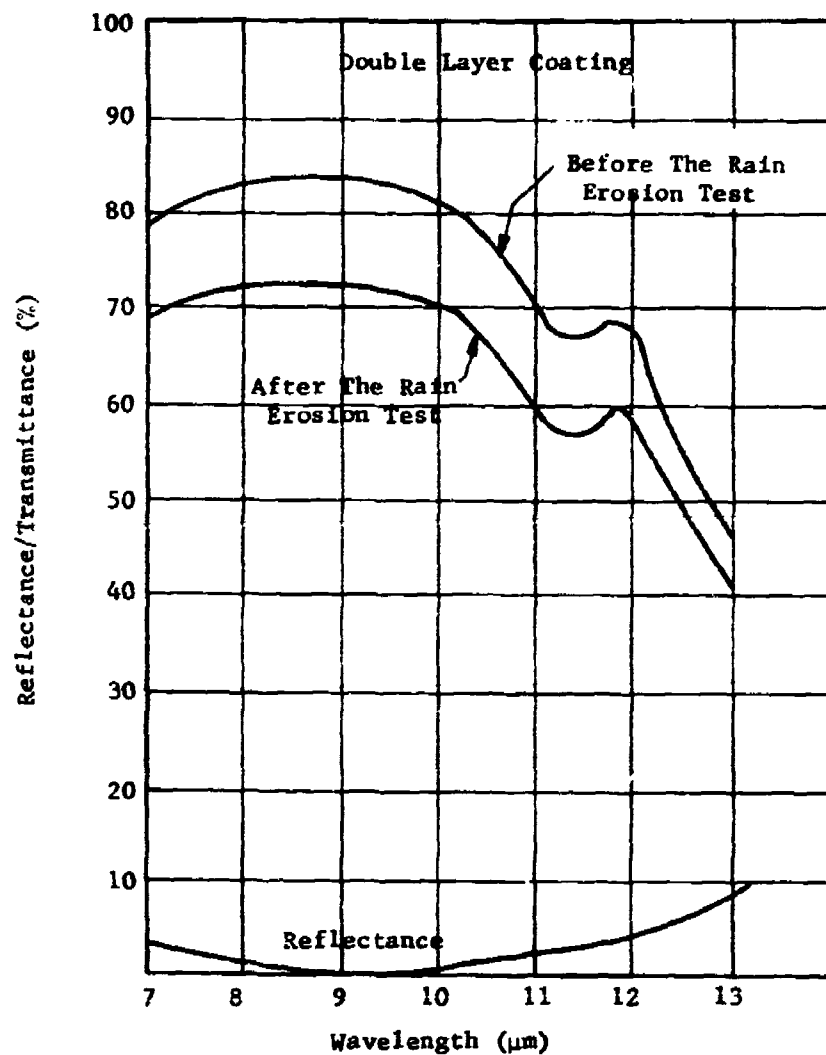
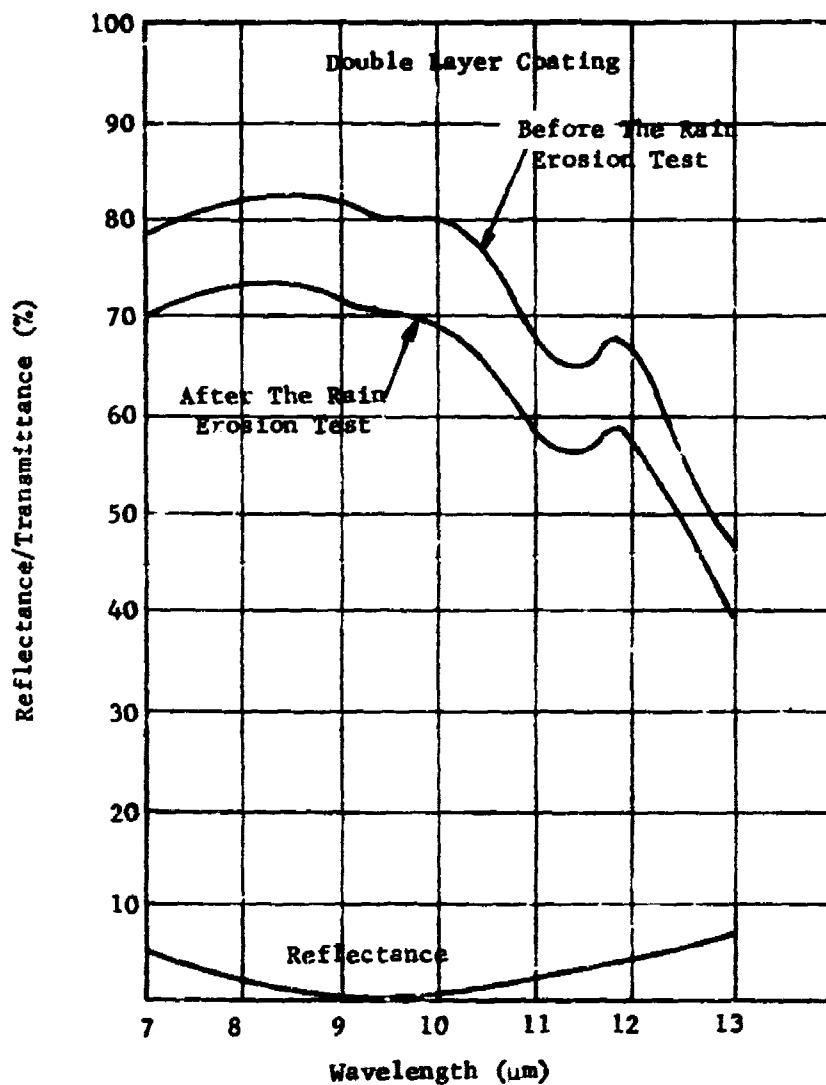


Figure 4-3. Transmission of Uncoated 0.2" Thick ZnS Piece at Room Temperature and 200°C



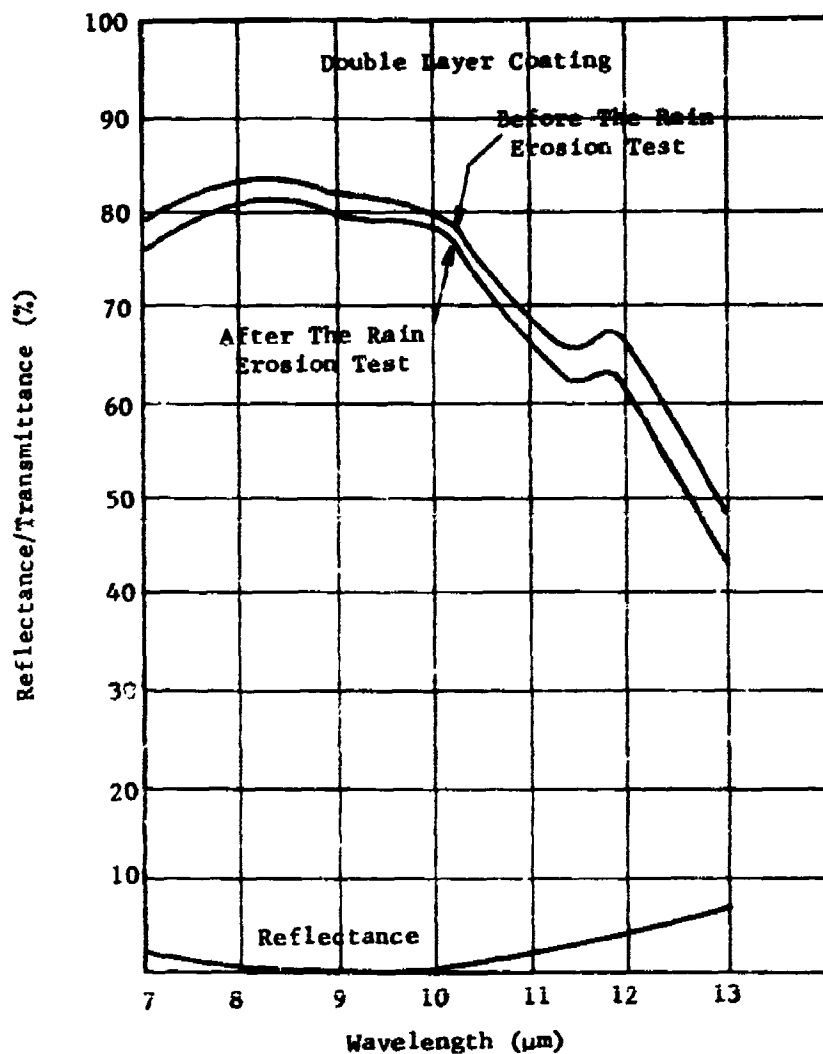
Rain Erosion Test Parameter: 1 Inch/Hour Rainfall, 1.8mm Drop Size, Impact Velocity 470 mph, Impact Angle 78°, Exposure Time 30 Minutes.

Figure 4-4. Transmission Before and After Rain Erosion Testing of ZnS Piece (AFML #9023) Coated on One Side with ZnSe/NdF₃. Reflectance of the Coating is Also Given.



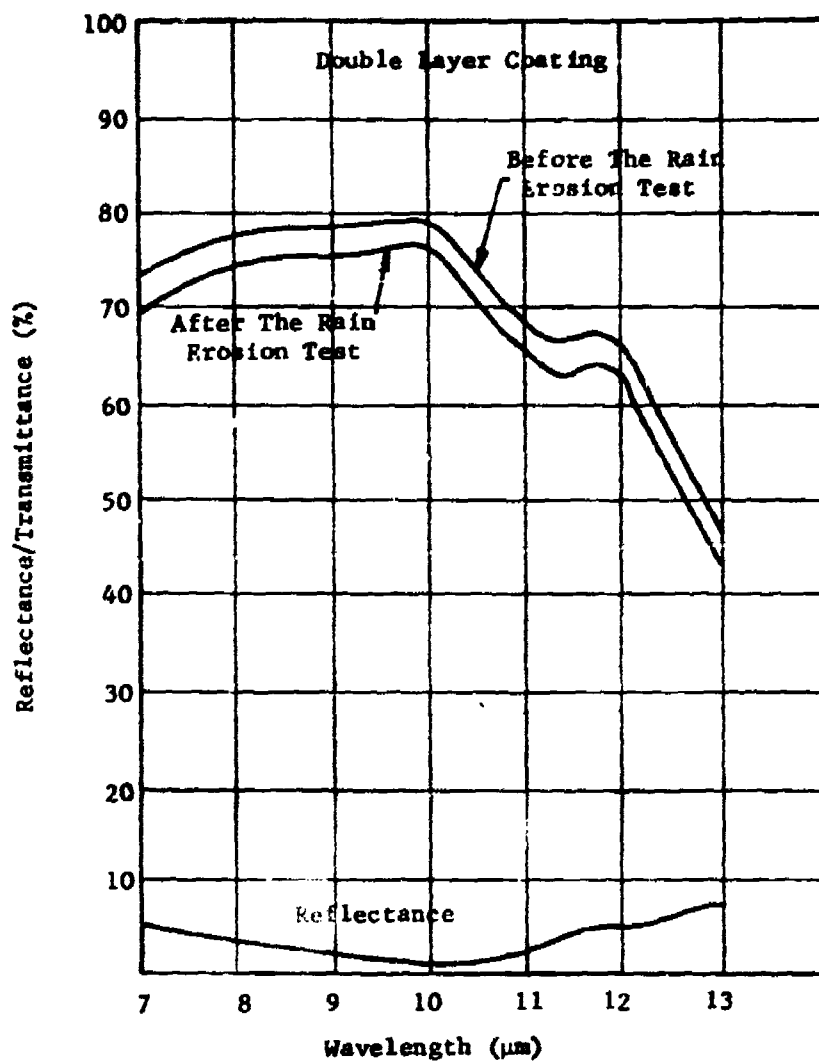
Rain Erosion Test Parameter: 1 Inch/Hour Rainfall, 1.8mm Drop Size, Impact Velocity 470 mph, Impact Angle 90°, Exposure Time 20 Minutes.

Figure 4-5. Transmission Before and After Rain Erosion Testing of ZnS Piece (AFML #9123) Coated on One Side with ZnSe/NdF₃. Reflectance of the Coating is Also Given.



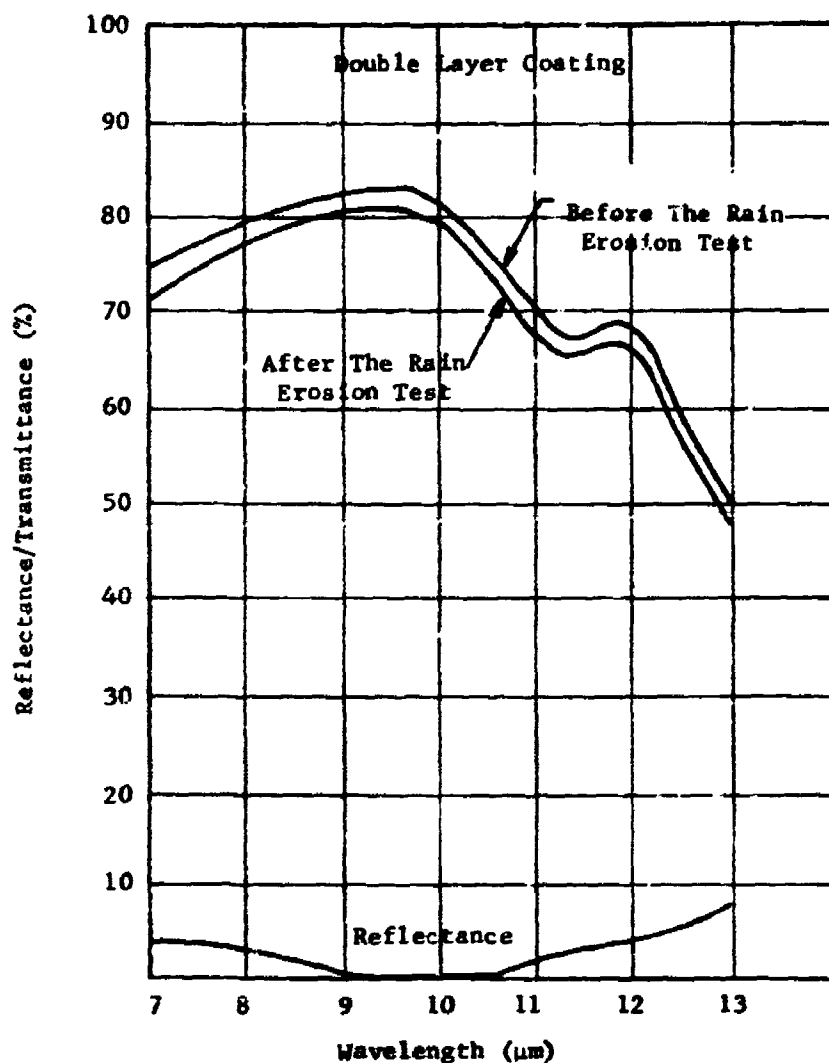
Rain Erosion Test Parameter: 1 Inch/Hour Rainfall, 1.8mm Drop Size, Impact Velocity 470 mph, Impact Angle 90°, Exposure Time 20 Minutes.

Figure 4-6. Transmission Before and After Rain Erosion Testing of ZnS Piece (AFML #9602) Coated on One Side with ZnSe/YF₃. Reflectance of the Coating is Also Given.



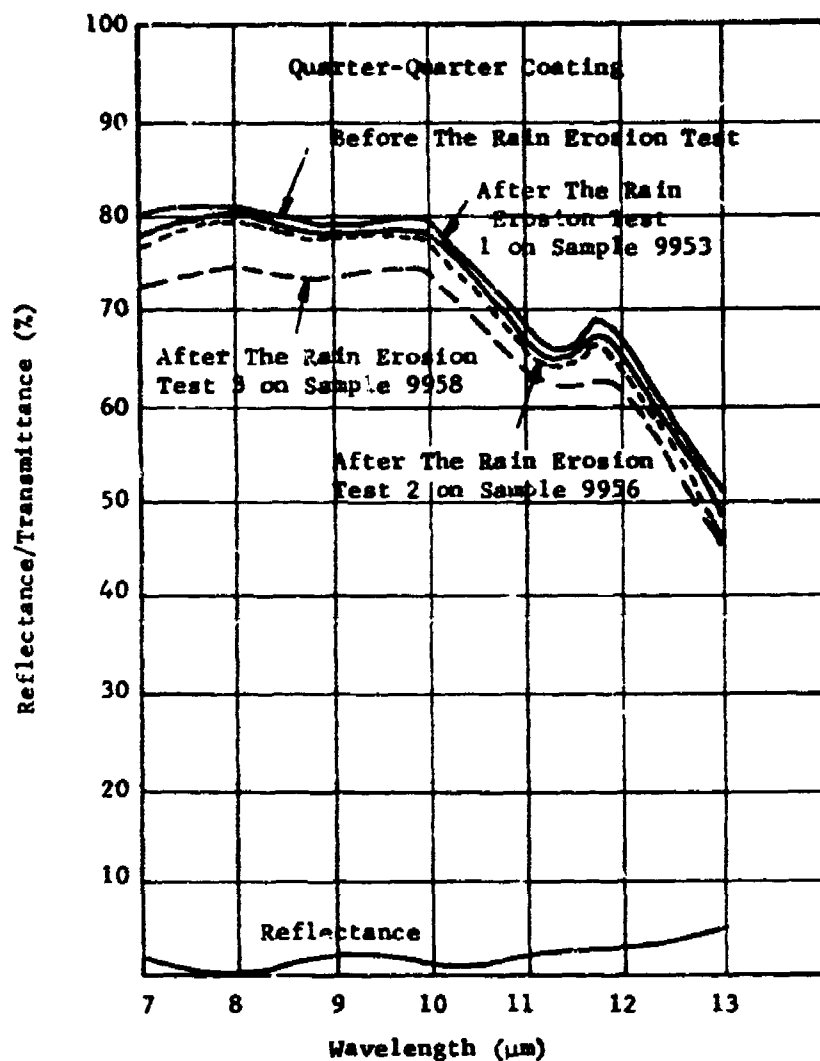
Rain Erosion Test Parameter: 1 Inch/Hour Rainfall, 1.8mm Drop Size, Impact Velocity 470 mph, Impact Angle 90°, Exposure Time 20 Minutes.

Figure 4-7. Transmission Before and After Rain Erosion Testing of ZnS Piece (AFML #9605) Coated on One Side with ZnSe/LaF₃. Reflectance of the Coating is Also Given.



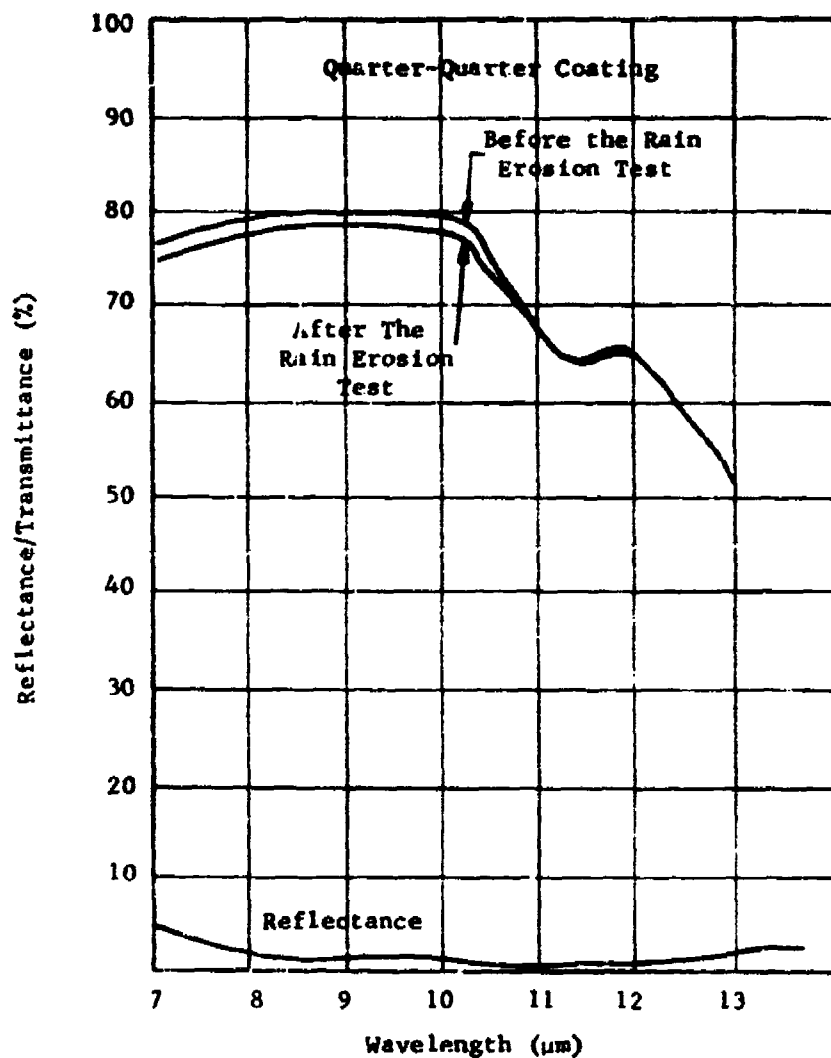
Rain Erosion Test Parameter: 1 Inch/Hour Rainfall, 1.8mm Drop Size, Impact Velocity 470 mph, Impact Angle 90° , Exposure Time 20 Minutes.

Figure 4-8. Transmission Before and After Rain Erosion Testing of ZnS Piece (AFML #9607) Coated on One Side with ZnSe/CeF₃. Reflectance of the Coating is Also Given.



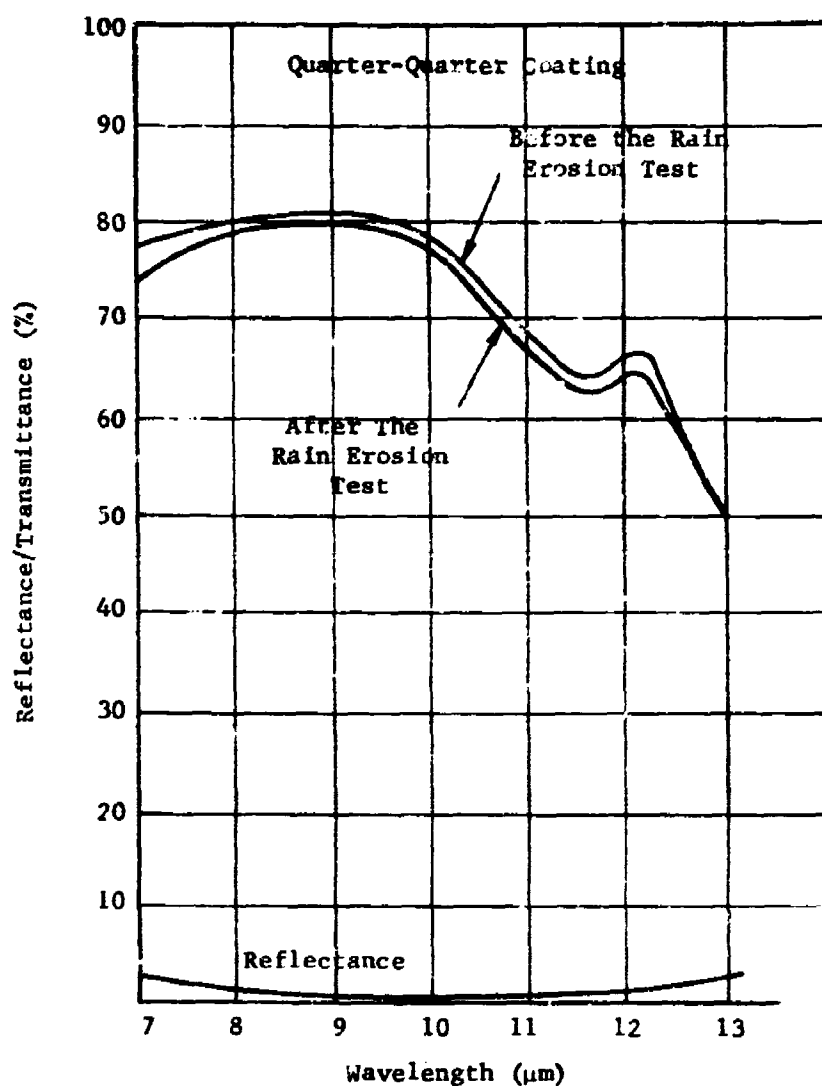
RAIN EROSION TEST PARAMETERS					
Test #	Rate of Rainfall Inch/Hour	Drop Size MM	Impact Velocity MPH	Impact Angle	Exposure Time Minutes
1	1.0	1.8	470	90°	20
2	1.0	1.8	575	90°	5
3	0.4	0.7	682	90°	1

Figure 4-9. Transmission After Various Rain Erosion Tests on ZnS Pieces Coated with ZnSe/ThF₄/ZnSe/ThF₄/CeF₃. Transmittance and Reflectance Before the Rain Erosion Test is Also Given.



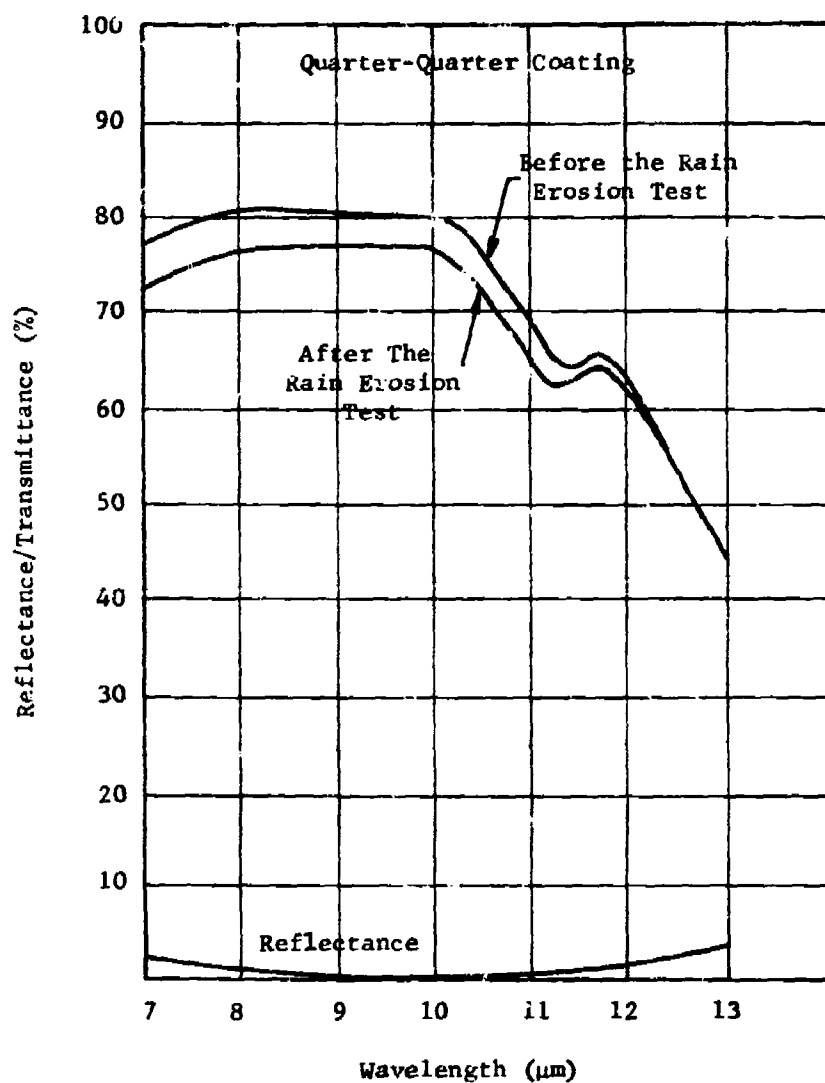
Rain Erosion Test Parameter: 1 Inch/Hour Rainfall, 1.9mm Drop Size, Impact Velocity 470 mph, Impact Angle 90°, Exposure Time 20 Minutes.

Figure 4-10: Transmission Before and After Rain Erosion Testing of ZnS Piece (AFML #10221) Coated on One Side with (ZnSe/LaF₃/ZnS/LaF₃). Reflectance of the Coating is Also Given.



Rain Erosion Test Parameter: 1 Inch/Hour Rainfall, 1.8mm Drop Size, Impact Velocity 470 mph, Impact Angle 90°, Exposure Time 20 Minutes.

Figure 4-11. Transmission Before and After Rain Erosion Testing of ZnS Piece (AFML #10222) Coated on One Side with $(\text{ZnSe/CeF}_3/\text{ZnSe/CeF}_3)$. Reflectance of the Coating is Also Given.



Rain Erosion Test Parameter: 1 Inch/Hour Rainfall, 1.8mm Drop Size, Impact Velocity 470 mph, Impact Angle 90° , Exposure Time 20 Minutes.

Figure 4-12. Transmission Before and After Rain Erosion Testing of ZnS Piece (AFML #10225) Coated on One Side with $(\text{ZnSe}/\text{YF}_3/\text{ZnSe}/\text{YF}_3)$. Reflectance of the Coating is Also Given.

coating removal was observed. A comparison between Figure 4-9 and AFML data on transmission losses of uncoated substrates indicated that losses were due to damage in the substrates.

4.2.3 Visible/NIR/IR Coatings

Large transmission losses were observed in visible, near-infrared and infrared for $(\text{ZnSe}/\text{ThF}_4)^5\text{MgF}_2$, $(\text{ZnSe}/\text{ThF}_4)^5$, and $(\text{ZnSe}/\text{ThF}_4)^5\text{CeF}_3$ coatings as indicated by Figures 4-13 through 4-18. Absence of peaks in the visible transmission curves of these coatings after the rain erosion test indicates that many coatings layers have been removed during testing. This is consistent with our conclusion from rain erosion test data discussed in Appendix A, paragraph A3.

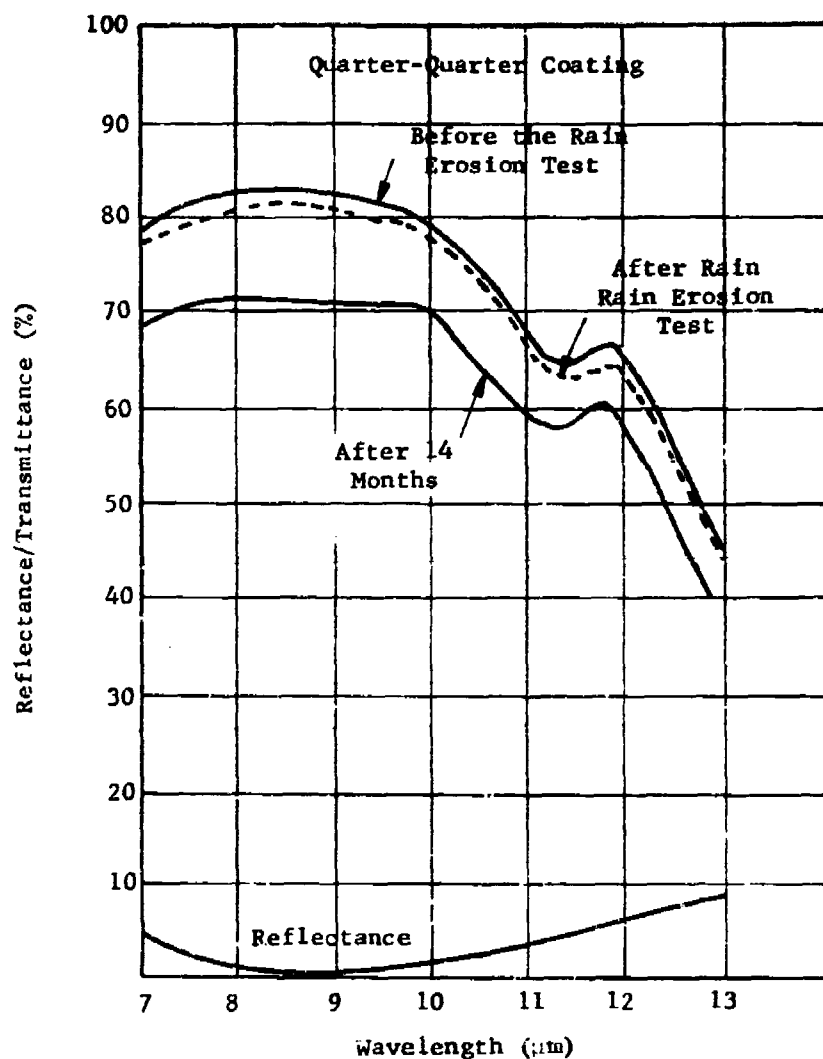
The transmission losses in $(\text{ZnSe}/\text{YF}_3)^5$ coatings were small in infrared, as indicated by Figure 4-19. No coating removal was observed on these coatings. The presence of the peaks in the visible/NIR transmission curve (Figure 4-20) after the rain erosion test also suggests no removal of coating. The transmission losses were due to cracks in the substrate. Thus, $(\text{ZnSe}/\text{YF}_3)^5$ multi-layer design is an acceptable rain erosion resistant visible/NIR/IR coating.

4.3 DURABILITY TFSTS

Durability tests were performed at Perkin-Elmer and the results are summarized below.

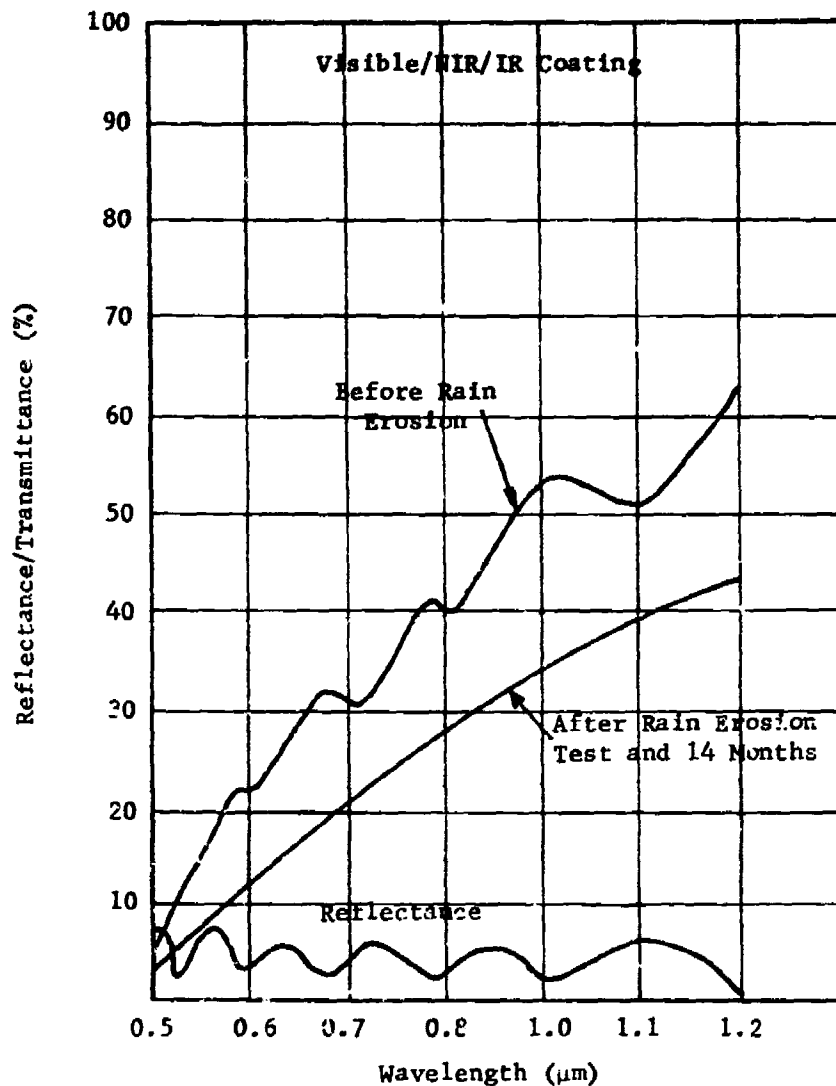
4.3.1 Infrared Coatings

- a) Double Layer Coatings: All the double layer coatings except ZnSe/NdF_3 passed adhesion, hardness, abrasion, solubility, salt fog and 24-hour humidity tests per MIL-C-675A. The ZnSe/NdF_3 coating passed adhesion, hardness and abrasion tests but failed the 24-hour humidity test. This coating was not tested for either solubility or salt fog. ZnSe/YF_3 , ZnSe/LaF_3 and ZnSe/CeF_3 also passed an extended salt fog test of 5 days and a humidity test of 10-days duration.



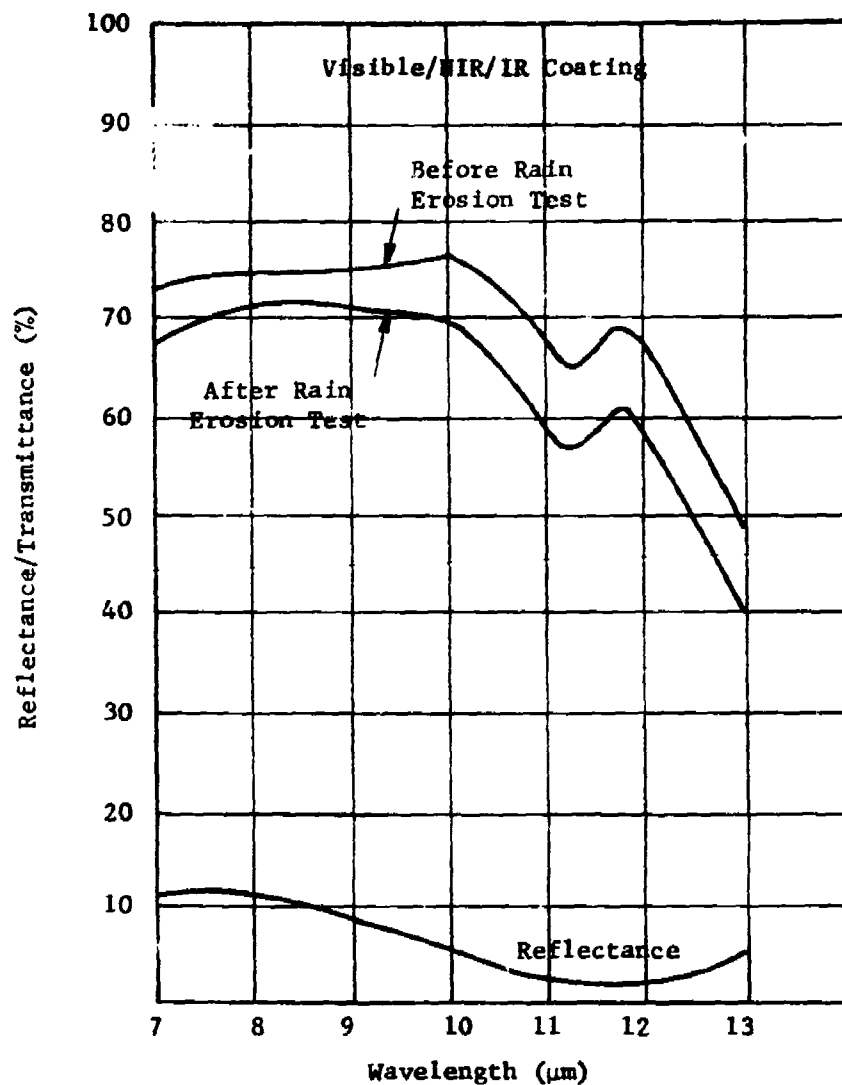
Rain Erosion Test Parameter: 1 Inch/Hour Rainfall, 1.8mm Drop Size, Impact Velocity 470 mph, Impact Angle 90°, Exposure Time 20 Minutes.

Figure 4-13. Infrared Transmission Before and After Rain Erosion Testing of ZnS Piece (AFML #9167) Coated on One Side with $(\text{ZnSe/ThF}_4)\text{MgF}_2$. Reflectance of the Coating is Also Given.



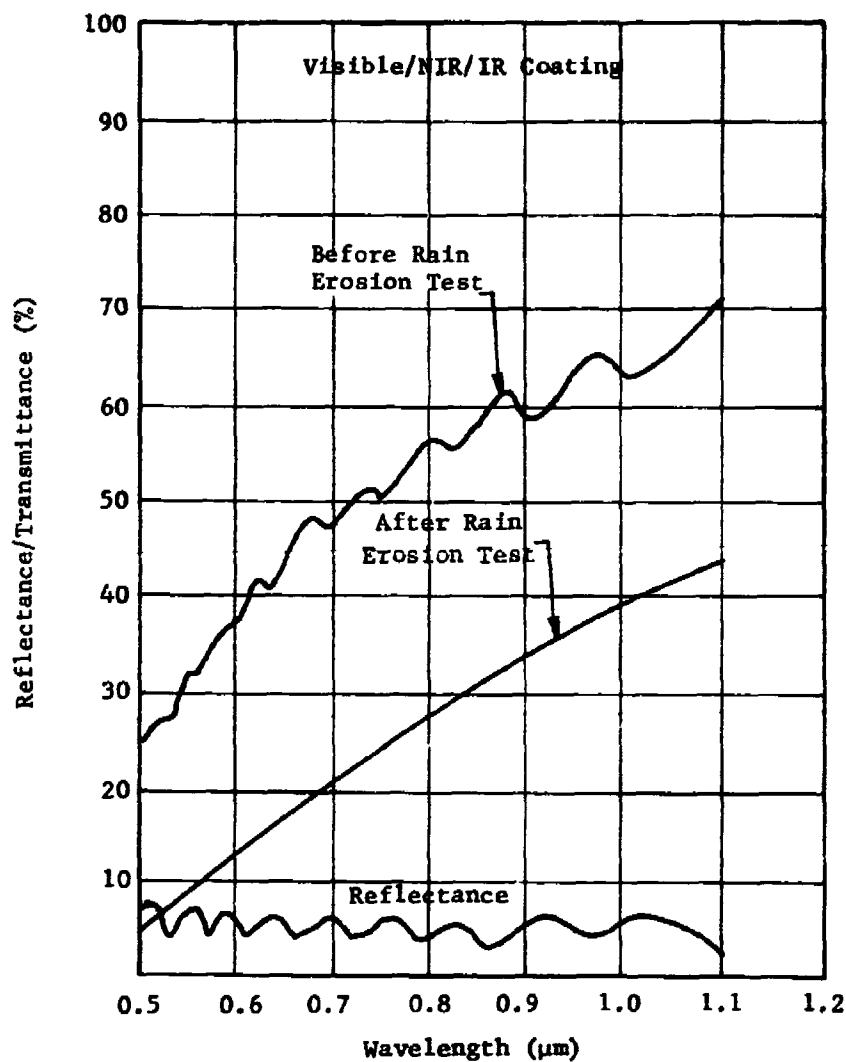
Rain Erosion Test Parameter: 1 Inch/Hour Rainfall, 1.8mm Drop Size, Impact Velocity 470 mph, Impact Angle 90°, Exposure Time 20 Minutes.

Figure 4-14. Visible Transmission Before and After Rain Erosion Testing₅ of ZnS Piece (AFML #9167) Coated on One Side with (ZnSe/ThF₄)₅MgF₂. Reflectance of the Coating is Also Given.



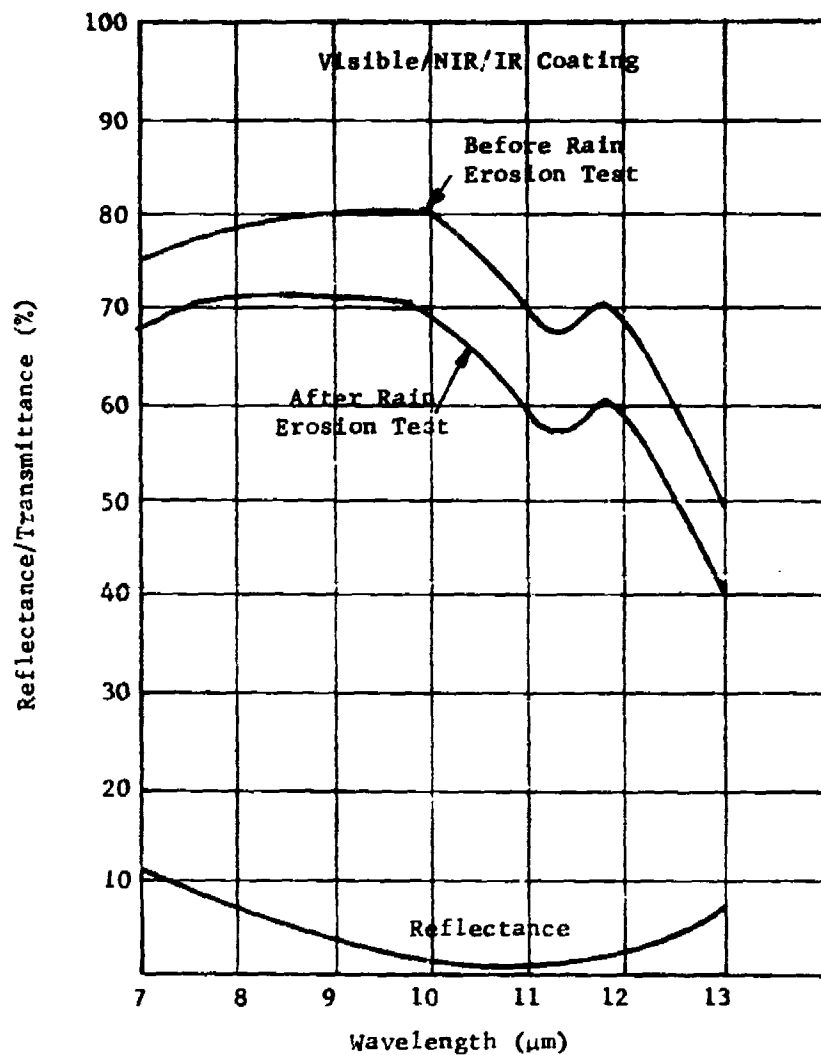
Rain Erosion Test Parameter: 1 Inch/Hour Rainfall, 1.8mm Drop Size, Impact Velocity 470 mph, Impact Angle 90°, Exposure Time 20 Minutes.

Figure 4-15. Infrared Transmission Before and After Rain Erosion Testing of ZnS Piece (AFML #9169) Coated on One Side with $(\text{ZnSe}/\text{ThF}_4)$. Reflectance of the Coating is Also Given.



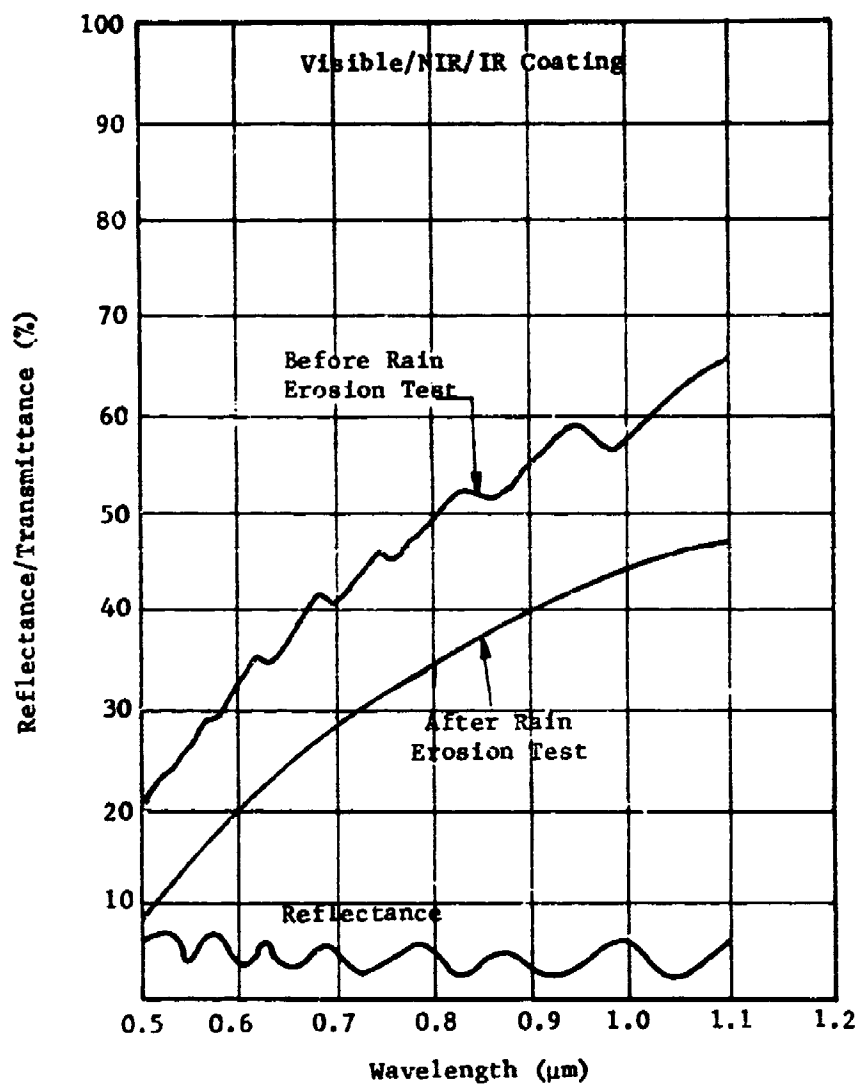
Rain Erosion Test Parameter: 1 Inch/Hour Rainfall, 1.8mm Drop Size, Impact Velocity 470 mph, Impact Angle 90°, Exposure Time 20 Minutes.

Figure 4-16. Visible Transmission Before and After Rain Erosion Testing₅ of ZnS Piece (AFML #9169) Coated on One Side with $(\text{ZnSe}/\text{ThF}_4)$. Reflectance of the Coating is Also Given.



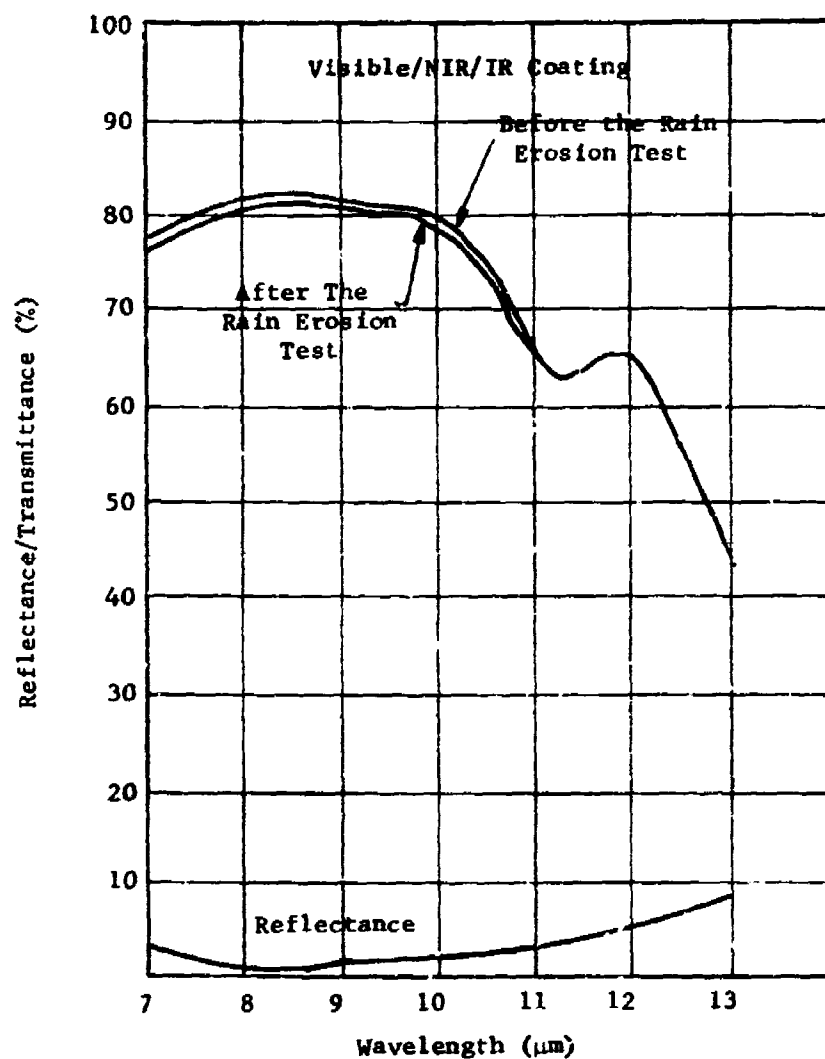
Rain Erosion Parameter: 1 Inch/Hour Rainfall, 1.8mm Drop Size, Impact Velocity 470 mph, Impact Angle 90°, Exposure Time 20 Minutes.

Figure 4-17. Infrared Transmission Before and After Rain Erosion Testing of ZnS Piece (AFML #9171) Coated on One Side with $(\text{ZnSe}/\text{ThF}_4)^{\text{CeF}_3}$. Reflectance of the Coating is Also Given.



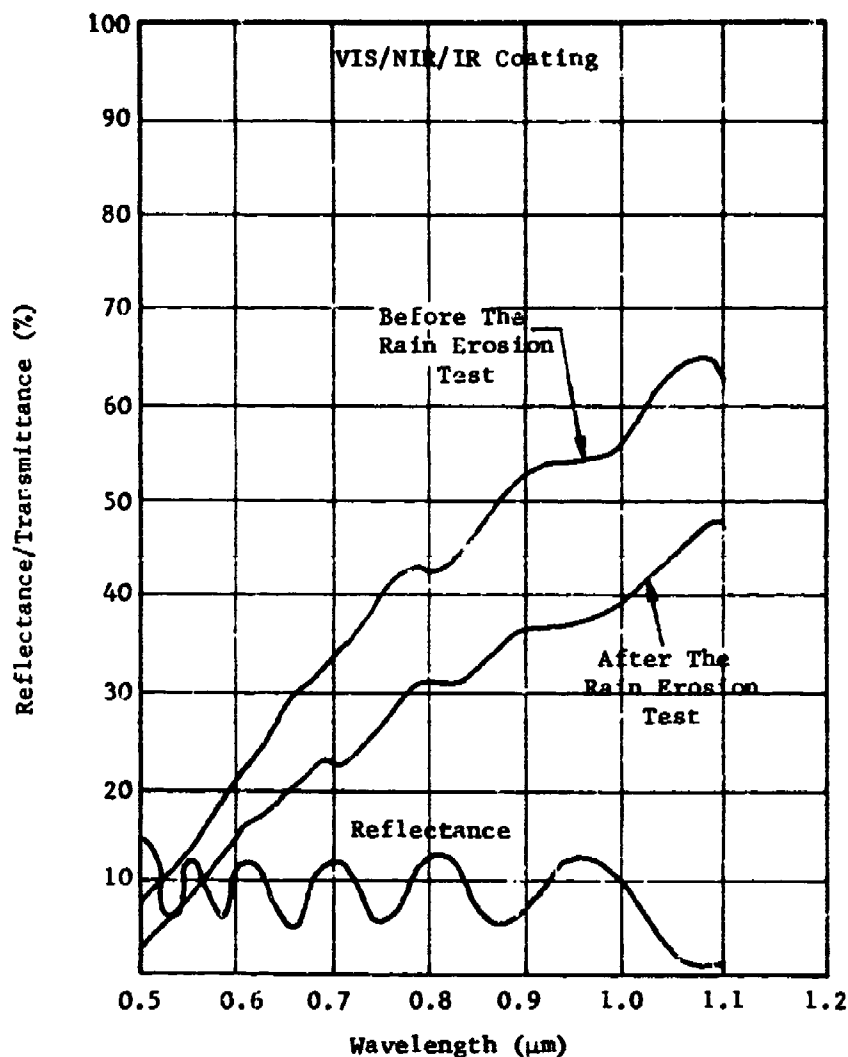
Rain Erosion Parameter: 1 Inch/Hour Rainfall, 1.8mm Drop Size, Impact Velocity 470 mph, Impact Angle 90°, Exposure Time 20 Minutes.

Figure 4-18. Visible Transmission Before and After Rain Erosion Testing₅ of ZnS Piece (AFML #9171) Coated on One Side with $(\text{ZnSe}/\text{ThF}_4)_5 \text{CeF}_3$. Reflectance of the Coating is Also Given.



Rain Erosion Test Parameter: 1 Inch/Hour Rainfall, 1.8mm Drop Size, Impact Velocity 470 mph, Impact Angle 90°, Exposure Time 20 Minutes.

Figure 4-19. Infrared Transmission Before and After Rain Erosion Testing of ZnS Piece (AFML #10226) Coated on One Side with $(\text{ZnSe}/\text{YF}_3)$. Reflectance of the Coating is Also Given.



Rain Erosion Test Parameter: 1 Inch/Hour Rainfall, 1.8mm Drop Size, Impact Velocity 470 mph, Impact Angle 90°, Exposure Time 20 Minutes.

Figure 4-20. Visible Transmission Before and After Rain Erosion Testing of ZnS Piece (ARML #10226) Coated on One Side with $(\text{ZnSe/YF}_3)_5$. Reflectance of the Coating is Also Given.

b) Quarter-Quarter Coatings: All the quarter-quarter coatings passed the adhesion, hardness, abrasion, solubility, salt fog and 24 hour humidity test per MIL-C-675A. $\text{ZnSe/YF}_3/\text{ZnSe/YF}_3$ and $\text{ZnSe/ThF}_4/\text{ZnSe/ThF}_4/\text{CeF}_3$ coatings were also tested for an extended salt fog test of 5 days. Both of the coatings passed this test. $\text{ZnSe/ThF}_3/\text{ZnSe/ThF}_4/\text{CeF}_3$ coatings were also tested for the 10 day humidity test and dust (fine sand) test per MIL-STD-810C and successfully passed the test.

4.3.2 Visible/NIR/IR Coatings

All of the visible coatings passed adhesion, hardness, abrasion and 24 hour humidity tests. Only $(\text{ZnSe/YF}_3)^5$ coatings were tested for salt fog and solubility. This coating passed both these tests.

4.4 SUMMARY OF RESULTS

Eight different coatings passed the various rain erosion tests. The transmission losses on the coated substrates were comparable with transmission losses on the uncoated substrates. In other words, the transmission losses were mainly due to cracks in the substrate produced by the impact of the drop and not due to any degradation of coatings. The coating designs which passed the rain erosion tests are given below. All of the coatings were deposited at 375°C and were post annealed at 200°C in dry nitrogen flow for 2 hours.

Type of Design	Coating Designs
Double-Layer	ZnSe/YF_3
	ZnSe/LaF_3
	ZnSe/CeF_3
Quarter-Quarter	$\text{ZnSe/YF}_3/\text{ZnSe/YF}_3$
	$\text{ZnSe/LaF}_3/\text{ZnSe/LaF}_3$
	$\text{ZnSe/CeF}_3/\text{ZnSe/LaF}_3$
	$\text{ZnSe/ThF}_4/\text{ZnSe/ThF}_4/\text{CeF}_3$
Visible/NIR/IR	$(\text{ZnSe/YF}_3)^5$

None of the coatings met the reflectivity requirement of $\leq 1\%$ at all wavelengths between 8-12 μm for infrared coatings and between 0.5 to 0.9, 1.06 and between 8-12 μm for Visible/NIR/IR coatings. However, two quarter-quarter coatings ($\text{ZnSe/YF}_3/\text{ZnSe/YF}_3$ and $\text{ZnSe/LaF}_3/\text{ZnSe/LaF}_3$) came close to meeting the requirement. Table 4-1 shows the maximum and average reflectivities of all the rain erosion resistant coatings. In general, quarter-quarter coatings have better reflectivities because of their broad band nature. The Visible/NIR/IR coating also did not meet the requirement. The coating has a reflectivity of less than 2% at 1.06 μm . The visible reflectivity is high. It is believed that the coating can be optimized for better reflectivity provided the visible properties of YF_3 can be accurately established.

Table 4-2 summarizes the rain erosion data on these coatings. Table 4-3 summarizes the data on durabilities of these coatings. All of the eight coatings met all the durability requirements of the program.

TABLE 4-1. REFLECTIVITIES OF RAIN EROSION COATINGS

COATING DESIGN	WAVELENGTH RANGE (μm)	REFLECTIVITIES %		COMMENTS
		MAX.	AV.	
ZnSe/YF ₃	8 to 12	3.5	1.5	-
ZnSe/LaF ₃	8 to 12	4.5	2.7	Could be Optimized
ZnSe/CeF ₃	8 to 12	3.5	2.0	-
ZnSe/YF ₃ /ZnSe/YF ₃	8 to 12	1.5	0.7	-
ZnSe/LaF ₃ /ZnSe/LaF ₃	8 to 12	1.5	0.9	-
ZnSe/CeF ₃ /ZnSe/CeF ₃	8 to 12	2.0%	1.3%	-
ZnSe/ThF ₄ /ZnSe/ThF ₄ /CoF ₃	8 to 12	2.5	1.6	Could be Optimized
(ZnSe/YF ₃) ⁵	0.5 to 0.9	16%	8.0%	Could be Optimized
	1.06	2.0%	-	
	8 to 12	4.5	2.0%	

TABLE 4-2. SUMMARY OF RAIN EROSION TEST DATA

COATING DESIGN	RAIN EROSION TEST #	TRANSMISSION LOSS	COMMENTS
ZnSe/YF ₃	1	2.5%	No Coating Removal
ZnSe/LaF ₃	1	2.5%	No Coating Removal
ZnSe/CeF ₃	1	3%	No Coating Removal
ZnSe/YF ₃ /ZnSe/YF ₃	1	4.0%	No Coating Removal
ZnSe/LaF ₃ /ZnSe/LaF ₃	1	2.5%	No Coating Removal
ZnSe/CeF ₃ /ZnSe/CeF ₃	1	1%	No Coating Removal
ZnSe/ThF ₄ /ZnSe/ThF ₄ /CeF ₃	1	3%	No Coating Removal
	2	4.0%	No Coating Removal
	3	6.5%	No Coating Removal
(ZnSe/YF ₃) ⁵	1	1.5%	No Coating Removal

Test 1: 1 inch/hour, 1.8mm drop size, 470 mph, 90° impact angle, 20 minutes exposure time.

Test 2: 1 inch/hour, 1.8mm drop size, 575 mph, 90° impact angle, 5 minutes exposure time.

Test 3: .4 inch/hour, .7mm drop size, 682 mph, 90° impact angle, 1 minute exposure time.

TABLE 4-3. DURABILITIES OF RAIN EROSION COATINGS

Coating Design	Adhesion MIL-C-675	Hardness MIL-C-675	Abrasion MIL-C-675	24 Hr. Humidity MIL-C-675	24 Hr. Salt Fog MIL-C-675	Solubility MIL-C-675	5 Day Salt Fog	10 Day Humidity MIL-STD-810C
ZnSe/YF ₃	Passed	Passed	Passed	Passed	Passed	Passed	Passed	Passed
ZnSe/LaF ₃	Passed	Passed	Passed	Passed	Passed	Passed	Passed	Passed
ZnSe/CeF ₃	Passed	Passed	Passed	Passed	Passed	Passed	Passed	Passed
ZnSe/YF ₃ /ZnSe/YF ₃	Passed	Passed	Passed	Passed	Passed	Passed	Passed	Not Tested
ZnSe/LaF ₃ /ZnSe/LaF ₃	Passed	Passed	Passed	Passed	Passed	Passed	Not Tested	Not Tested
ZnSe/CeF ₃ /ZnSe/CeF ₃	Passed	Passed	Passed	Passed	Passed	Passed	Not Tested	Not Tested
ZnSe/ThF ₄ /ZnSe/ThF ₄ /CeF ₃ (ZnSe/YF ₃) ⁵	Passed	Passed	Passed	Passed	Passed	Passed	Passed	Passed
	Passed	Passed	Passed	Passed	Passed	Passed	Not Tested	Not Tested

SECTION V

COATING FABRICATION OF LARGE WINDOW SAMPLES

5.1 INTRODUCTION

This section first describes the selection process of a coating design. The coating fabrication process and optical and mechanical properties of the coating selected from the eight designs mentioned previously are discussed in the following paragraphs.

5.2 SELECTION OF COATING DESIGN

In all, there were eight coatings which passed the rain erosion test. The primary program requirement of low reflectivity over the whole 8 to 12 μ m band automatically reduces the choice to four quarter-quarter coatings: (a) ZnSe/YF₃/ZnSe/YF₃, (b) ZnSe/LaF₃/ZnSe/LaF₃, (c) ZnSe/CeF₃/ZnSe/CeF₃, and (d) ZnSe/ThF₄/ZnSe/ThF₄/CeF₃. Double layer and Visible/NIR/IR coatings are eliminated as candidate designs because they are not broad enough for the whole 8 to 12 μ m. Also, optical properties of LaF₃ and YF₃ are neither well documented nor well known and their long term mechanical properties also are not well known. Therefore, the coating designs utilizing these materials were not chosen. This reduces the choice to two coatings, namely ZnSe/CeF₃/ZnSe/CeF₃ and ZnSe/ThF₄/ZnSe/ThF₄/CeF₃. Since ThF₄ has a lower refractive index than CeF₃, theoretically ZnSe/ThF₄/ZnSe/ThF₄/CeF₃ should give better AR coating than ZnSe/CeF₃/ZnSe/CeF₃. In addition, ZnSe/ThF₄/ZnSe/ThF₄/CeF₃ coatings have passed three different rain erosion tests and have also passed extended salt fog and humidity tests. Therefore, this coating was selected for coating fabrication of large windows.

In summary, the ZnSe/ThF₄/ZnSe/ThF₄/CeF₃ coating was chosen over other coatings for the following reasons.

- o Perkin-Elmer's extensive experience in depositing ZnSe, ThF₄ and CeF₃ materials at 375°C in comparison to LaF₃ and YF₃.

- o Proven ability of such coatings to pass more than one type of rain erosion test.
- o Perkin-Elmer's extensive experience in fabricating ZnSe/ThF₄ coatings with CeF₃ protective overcoat on large windows of up to 14" in size with good uniformity.
- o Known ability to pass salt fog and humidity tests for extended periods.
- o Broad nature of coating in comparison to double layer coatings.

5.3 DEPOSITION PROCESS

Both of the large windows were coated at the same time in a 56" coating chamber, previously described in Section 3.3. ZnSe and ThF₄ were deposited from a platinum boat. CeF₃ was deposited from an electron gun. The substrate temperature was 360°C and the evaporation pressure was 3×10^{-6} torr. After removal from the chamber, the window samples were post annealed at 200°C for 2 hours in a dry nitrogen gas atmosphere.

5.4 OPTICAL AND MECHANICAL PROPERTIES

Since the coating put on the large window samples is an infrared coating, only optical properties in the infrared region are presented in this section. Figure 5-1 shows the transmission curve of one of the large window samples, before and after coating, between the 2.5 μ m to 20 μ m wavelength range. The reflectance curve of this optimized coating is shown in Figure 5-2. The average reflectance of the coating in the 8 to 12 μ m wavelength band is 0.95%, and maximum reflectance is 1.9%. This is in comparison to theoretical values of 0.45% average and 0.81% maximum reflectance. The discrepancy between the theoretically predicted values and the experimentally measured values is due to dispersion in the film. The theoretical model does not take into account the dispersion process of coating materials. The achieved transmittance and reflectance values of the infrared coating are summarized in Table 5-1 together with the theoretically predicted values. The small discrepancies are due to dispersion in coating materials. Figure 5-3 compares the transmittance of a 0.2" thick coated ZnS piece measured at 20°C and 200°C. Comparison of this figure with Figure 4-3 indicates no appreciable transmission losses in coating due to heat.

The coating passed the following durability tests per program requirement:

Adherence per MIL-C-675

Hardness per MIL-C-675

Abrasion per MIL-C-675

24 Hour Humidity per MIL-C-675

24 Hour Salt Fog per MIL-C-675

Solubility per MIL-C-675

In addition, the coating also passed the following tests:

10 Day Humidity per MIL-STD-810C

Dust (Fine Sand) per MIL-STD-810C

5 Day Salt Fog Test

The Nomarski micrograph of this coating before and after rain erosion tests are shown in Figure 5-4. No coating removal was observed except at ring cracks in the ZnS, where some chipping was noted when the coating was viewed through the microscope at 157X.

TABLE 5-1. REFLECTANCE AND TRANSMITTANCE VALUES OF AR COATING ON 2" x 2" x 1/2" ZnS WINDOW SAMPLE

Wavelength λ (μ m)	REFLECTANCE (%)		TRANSMITTANCE (%)	
	Theoretical	Measured	Theoretical	Measured
8	0.74	1.9	95	93
9	0.73	1.7	90	88
10	0.46	0.6	88	87
11	0.25	0.1	57	57
12	0.27	0.5	56	55

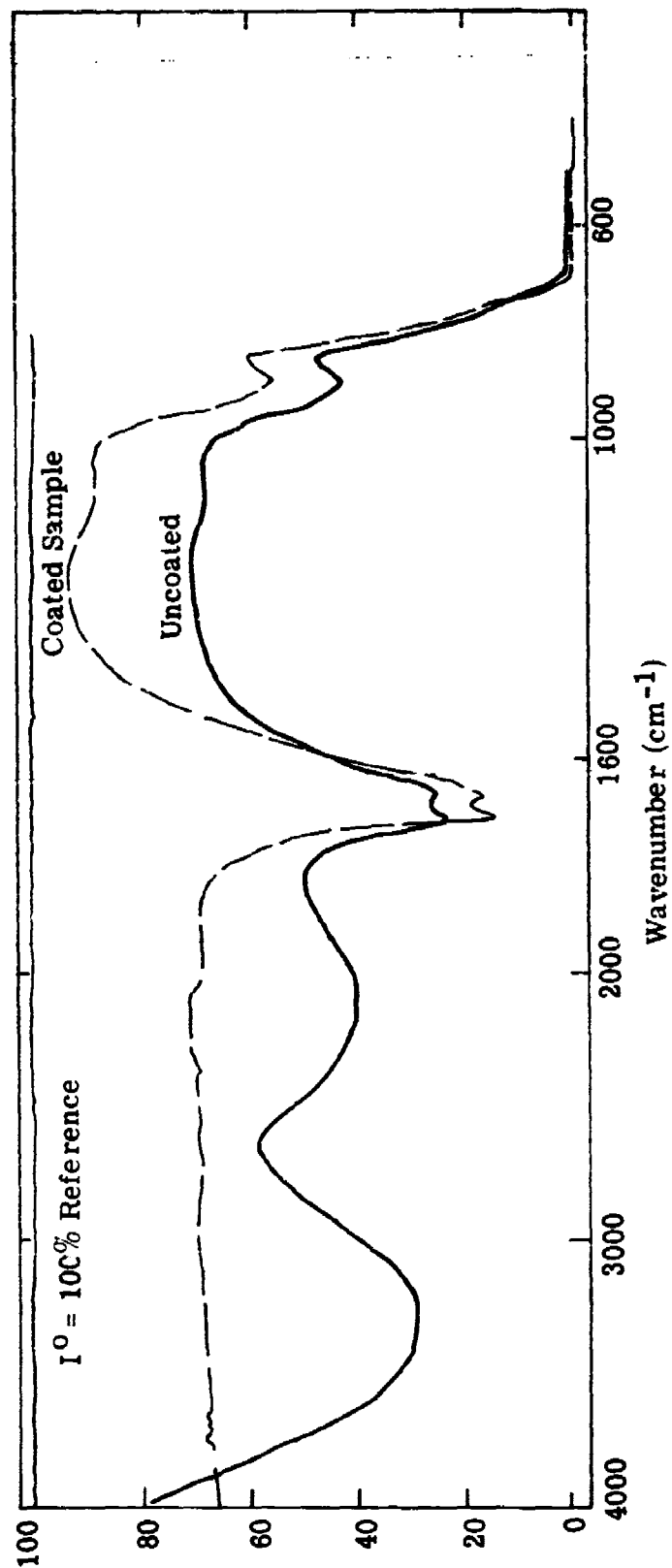


Figure 5-1. Transmission of 2" x 2" x 0.5" Window Sample
Before and After Coating on the Sides

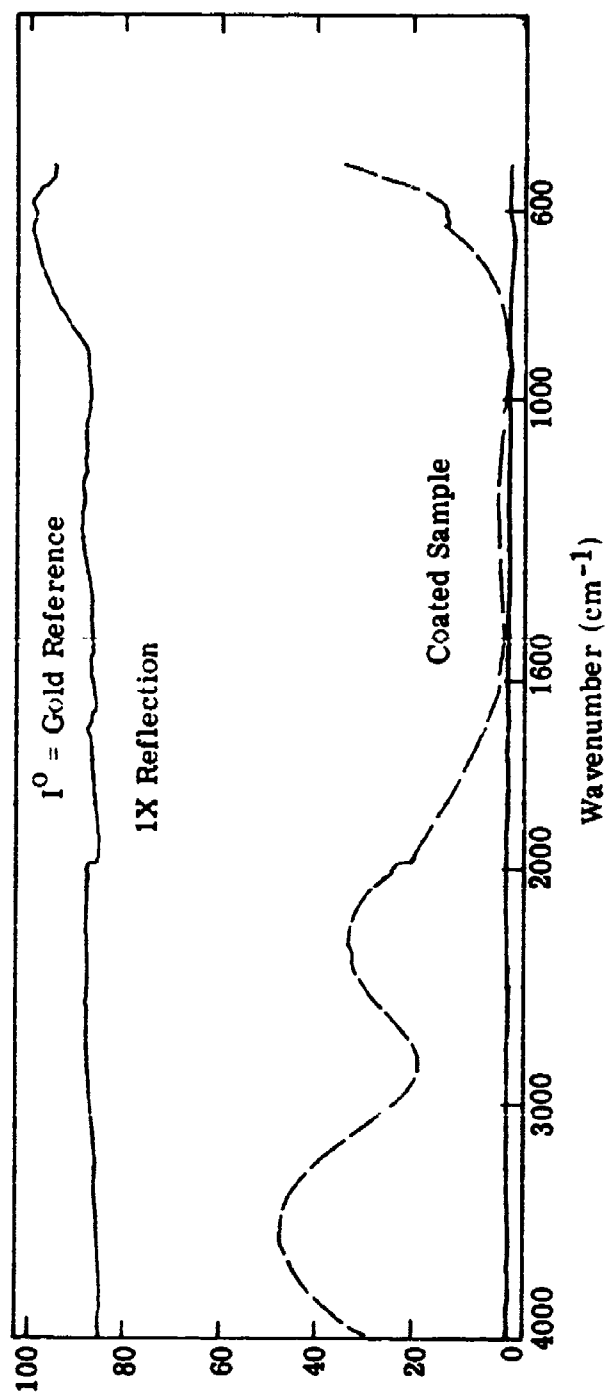
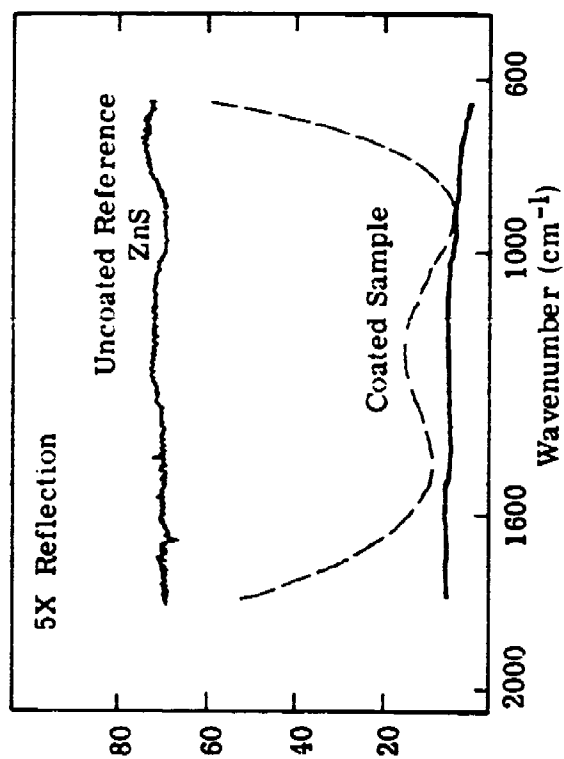


Figure 5-2. Reflectance of the Coating

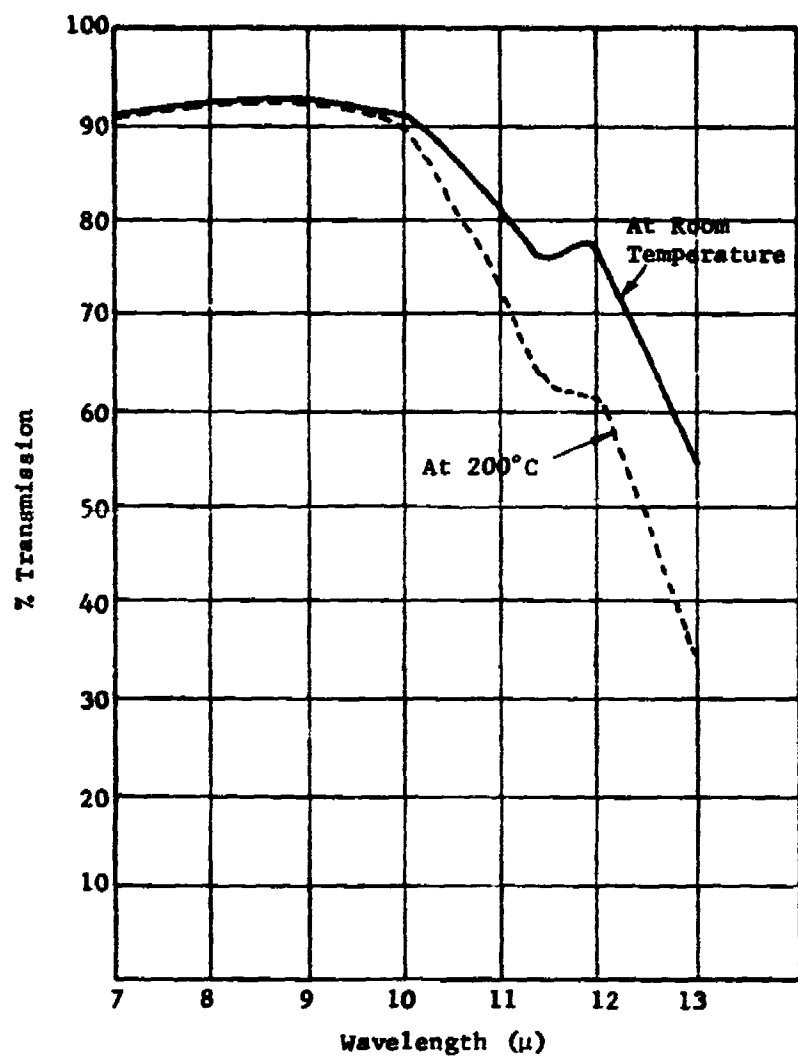


Figure 5-3. Transmittance of 0.2" Coated ZnS Piece at Room Temperature and 200°C



a. Before Rain Erosion



b. After Rain Erosion Test 1



c. After Rain Erosion Test 2



d. After Rain Erosion Test 3

Figure 5-4. Nomarski Micrograph of Coated Substrate Before and After Rain Erosion Test. (Magnification = 157X)

SECTION VI

CONCLUSIONS AND RECOMMENDATIONS

Prior to this program, the rain erosion resistant optical coatings consisting of ZnSe/NdF_3 proved to be unsatisfactory. This was primarily due to the decomposition of NdF_3 . In view of the problems associated with NdF_3 , this program addressed the issue of alternate coating materials and coating designs and fabrication technique to produce rain erosion resistant coatings. As a result of this development effort, eight rain erosion resistant antireflection coatings on ZnS IR window test samples have been successfully demonstrated under various rain environment conditions with small transmission losses. These transmission losses were found to be due to cracks in ZnS substrates produced by the rain drop impact.

One of these eight coating designs, $\text{ZnSe}/\text{ThF}_4/\text{ZnSe}/\text{ThF}_4/\text{CeF}_3$, was chosen for the coating of the two large ZnS window samples. These coated large window samples have met the durability requirements and have been shipped to the Air Force for further testing (MTF, etc.).

The other conclusions based on this coating development program are that the rain erosion resistant coatings on ZnS substrates can be achieved by conducting the coating fabrication at elevated substrate temperatures ($\sim 375^\circ\text{C}$). A post-coating annealing at 200°C in a dry nitrogen atmosphere was also needed to produce the required coatings. Additionally, substrates with surface quality of 60/40 scratch-to-dig ratios and 40Å to 80Å rms roughness did not affect the performance of the coatings.

The average reflectance of the final coating design was less than 1% from 8 to 12μm. The maximum reflectance was 2% compared to 1% required by the program. The visible reflectance was much higher than 1% as required by the program.

In view of the above results, it is recommended that the visible transmittance of $(\text{ZnSe}/\text{YF}_3)^n$ (n being number of groups) should be optimized. This optimization would require detailed study of the optical properties of YF_3 .

Future investigations into increasing the transmittance in the visible, the transmittance in the 10 to 12 μ , also need to be initiated. AR coating on composite windows may well be the solution for this. ZnS/ZnSe composite windows have been developed by the Raytheon Company. The rain erosion resistant AR coating on the ZnS side of the window (exterior surface in the aircraft) and a normal AR coating on the ZnSe side (interior surface in the aircraft) may prove to be rain erosion resistant and highly transmitting. AR coatings should also be developed on Si/ZnSe composite windows, on which encouraging results have been obtained in the rain erosion testing.

REFERENCES

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2. A. Herpin, Compt. rend. 225, 182 (1947).
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4. H. Schroeder, Z. Angew. Phys. 3, 53 (1951).
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APPENDIX A

THE RAIN EROSION TEST DATA

A.1 INTRODUCTION

Coated window samples of ZnS (1.5" x 0.5" x 0.2") were delivered to AFML. Most of the rain erosion testing was conducted by AFWAL/MLBE. Some samples were tested at Bell Aerospace TEXTRON. The rain erosion test variables were:

- o Rainfall Rate
- o Diameter of Rain Drop
- o Drop Impact Velocity
- o Impact Angle
- o Exposure Time

The program goal was to withstand a rainfall of 1 inch/hour with an average rain-drop diameter of 1.8mm and impact velocity of 470 mph at a 90° impact angle for a minimum exposure time of 20 minutes. Results of the rain erosion testing were submitted to Perkin-Elmer by AFWAL/MLBE in the following sections:

A.2 INFRARED COATINGS

Major results of the rain erosion testing can be summarized and interpreted as follows:

A.2.1 Double Layer Coatings

The rain erosion test data for double layer coatings is presented in Tables A-1 and A-2. The results can be summarized and interpreted as follows:

- o ZnS/NdF₃ coatings (AFML Numbers 9021, 9022, 9024, 9025 and 9026) passed the rain erosion test but a large transmission loss was observed. To investigate this loss, the coating on sample 9021 was polished off and the substrate was measured for transmission. The transmission loss at 10μm, due to cracks and fractures produced by impingement, was only 3%. This large transmission drop was then attributed to the degradation of the NdF₃ coating.

TABLE A-1. RAIN EROSION DATA - 1 INCH/HOUR SIMULATED RAINFALL, 1.8mm DROP SIZE

Specimen ID# APNL	P.E.	Coating Design (Inner Layer First)	Rain Erosion Parameters			Transmission Loss at 10µm	Comments
			Impact Velocity (mph)	Impact Angle (Degrees)	Exposure Time (Minutes)		
9021	8-001	ZnSe/NdF ₃	470	90	20	14%	Ring cracks in the coating and the substrate, essentially no coating removal.
9022	8-002	ZnSe/NdF ₃	470	90	20	14%	Same as 9021.
9023	8-003	ZnSe/NdF ₃	470	78	30	14%	Same as 9021.
9024	8-004	ZnSe/NdF ₃	470	78	20	14%	Same as 9021.
9025	8-005	ZnSe/NdF ₃	470	90	20	14%	Same as 9021.
9026	8-006	ZnSe/NdF ₃	470	90	20	14%	Same as 9021.
9122	15-01	*ZnSe/NdF ₃ /CeF ₃	470	90	20	11%	No Coating Removal.
9123	15-02	*ZnSe/NdF ₃ /CeF ₃	470	90	20	11.5%	No Coating Removal.
9124	15-03	*ZnSe/NdF ₃ /CeF ₃	470	90	20	--	Specimen Broken. No Coating Removal.
9125	15-04	*ZnSe/NdF ₃ /CeF ₃	470	90	20	11.5%	No Coating Removal.
9126	15-05	ZnSe/NdF ₃ /CeF ₃	470	90	20	10.05%	No Coating Removal.
9127	15-06	ZnSe/NdF ₃ /CeF ₃	470	90	20	7.5%	Removal of at Least Top Layer in Center of Specimen. About 20% Layer Removed.

*Substrate surface roughness 60-80A

*Substrate surface roughness 40-60A

TABLE A-2. RAIN EROSION DATA * NCII/HOUR SIMULATED RAINFALL, 1.8mm DROP SIZE

Specimen ID# AFML P.E.	Coating Design (Inner Layer First)	Rain Erosion Parameters			Transmission Loss at 10um	Comments
		Impact Velocity (mph)	Impact Angle (degrees)	Exposure Time (Minutes)		
9556 22-01	*ZnSe/CeF ₃	470	90	20	5%	Small areas of coating removal distributed uniformly over surface. About 10% coating removed.
9557 22-02	*ZnSe/CeF ₃	470	90	20	5%	Same as 9556.
9558 22-03	*ZnSe/CeF ₃	470	90	20	4%	Small areas of coating removed. Less than 5% of coating removal.
9559 22-04	*ZnSe/CeF ₃	470	90	20	3%	Similar to 9558.
9560 22-05	*ZnSe/CeF ₃	470	90	20	3%	Similar to 9558.
9561 22-06	*ZnSe/CeF ₃	470	90	20	3%	Similar to 9558. Shallow straight cracks associated with flaws introduced by previous coating tests.

*Samples not post-annealed.

Microscopic examination revealed the formation of a powder-like compound believed to be some complex compound formed by the chemical reaction of NdF_3 with water.

- o To avoid the chemical reaction of NdF_3 with water, the NdF_3 was protected by CeF_3 . These coatings (AFML Numbers 9122, 9123, 9124, 9125, 9126 and 9127) passed the rain erosion test but, again, a large transmission was observed. It was believed that water went through the CeF_3 layer and converted the NdF_3 to a complex compound. The transmission loss was not as high as in the bare NdF_3 coating because the CeF_3 layer remains the same.
- o The results on Samples 9122, 9123, 9124 and 9125 also indicated that variations in surface roughness values from $40\text{\AA}$ to $80\text{\AA}$ do not effect the performance of the coatings.
- o Comparison of Samples 9556, 9557, 9558, 9559, 9560 and 9561 with 9606 and 9607 indicates that post annealing plays an important role for rain erosion resistance. ZnSe/CeF_3 coatings that weren't post annealed failed the rain erosion test, whereas post annealed similar coatings passed the rain erosion test. In both cases, the transmission loss was appreciably small in comparison to coatings containing NdF_3 . This suggests that these coatings are not chemically attacked by water.
- o In addition to ZnSe/CeF_3 coatings, ZnSe/YF_3 (AFML Numbers 9602 and 9603) and ZnSe/LaF_3 (AFML Numbers 9604 and 9605) also passed rain erosion tests with a maximum transmission loss of 2.5%. All of these coatings were post annealed in dry nitrogen gas at 200°C for 2 hours.

A.2.2 Quarter-Quarter Coatings

The rain erosion test data for quarter-quarter coatings is presented in Tables A-3 and A-4. The results can be summarized as follows.

- o All the quarter-quarter coatings submitted to AFML passed the rain erosion test.
- o Quarter-quarter coatings with CeF_3 as a protective overcoat were tested under various rain erosion test parameters. Samples 9953

TABLE A-3. RAIN EROSION DATA - 1 INCH/HOUR SIMULATED RAINFALL, 1.8mm DROP SIZE

Specimen ID# AFML P.E.	Coating Design (Inner Layer First)	Rain Erosion Parameters			Transmission Loss at 10µm	Comments
		Impact Velocity (mph)	Impact Angle (Degrees)	Exposure Time (Minutes)		
9602 25-01	ZnSe/YF ₃	470	90	20	2.5%	No coating removal visible. Very few 20µm diameter areas of removal generally associ- ated with pits in ZnS at cracks seen at 250X.
9603 25-02	ZnSe/YF ₃	470	90	20	2%	Same as 9602.
9604 30-03	ZnSe/LaF ₃	470	90	20	2.5%	No coating removal visible. Very few small areas of re- moval generally associated with pits in ZnS at cracks seen at 250X. Maximum diameter of areas in 20µm.
9605 30-04	ZnSe/LaF ₃	470	90	20	-	Specimen broken. Same com- ments about coatings as for 9604.
9606 31-05	ZnSe/CeF ₃	470	90	20	3%	No coating removal visible. Very few small areas of re- moval at pits in ZnS at cracks seen at 250X. Maxi- mum diameter of areas is 30µm.
9607 31-06	ZnSe/CeF ₃	470	90	20	2%	Same as 9606.

TABLE A-4. RAIN EROSION DATA - 1 INCH/HOUR SIMULATED RAINFALL, 1.8 mm DROP SIZE

Specimen ID# AFML P.E.		Coating Design (Inner Layer First) (ZnSe/ThF ₄) ² CeF ₃	Rain Erosion Parameters				Transmission Loss at 10 μm	Comments
			Impact Velocity (mph)	Impact Angle (Degrees)	Exposure Time (Minutes)			
9953	51-01		470	90	20		3%	No coating removal. (Very slight removal microscopically visi- ble along some ring cracks).
9954	51-02	(ZnSe/ThF ₄) ² CeF ₃	470	90	20		2%	Same as 9953
9955	51-03	(ZnSe/ThF ₄) ² CeF ₃	575	90	5		4%	No coating removal except for slight re- moval visible micro- scopically along ring cracks.
9956	51-04	(ZnSe/ThF ₄) ² CeF ₃	575	90	5		2.5%	Same as 9955
9957	51-05	(ZnSe/ThF ₄) ² CeF ₃ *	470	90	2		-	Sample broke into pieces
9958	51-06	(ZnSe/ThF ₄) ² CeF ₃	682	90	1		6.5%	No coating removal except for slight re- moval visible micro- scopically along ring cracks.

*Tested under 1 cm/hour simulated rainfall and 0.7mm drop size.

and 9955 were tested at 470 mph for 20 minutes. These samples passed the rain erosion test with a maximum transmission loss of 3% at $10\mu\text{m}$. Samples 9955 and 9556 were tested at 575 mph for 5 minutes and passed the rain erosion test with a maximum transmission loss of 4% at $10\mu\text{m}$. Samples 9957 and 9958 were tested at Bell Aerospace. Sample 9957 broke into pieces in 2 minutes while tested at 470 mph. It is possible that breakage may have taken place due to the process used for cutting the samples in order to fit them in Bell Aerospace rotating arm fixtures. Sample 9958 was tested in 0.7mm diameter and 1cm/hour rainfield at 602 mph drop impact velocity for 90 seconds and passed the test. The transmission loss in the first 30 seconds was 2%. Additional 30 seconds caused the transmission to drop another 4% at $10\mu\text{m}$. No coating removal (except some chopping at cracks) occurred for additional 30 seconds (total 90 seconds) even though transmission could not be measured due to breakage of the substrate into pieces. The percentage of transmittance versus exposure time was about the same for the coated specimen as the uncoated Raytheon Zinc sulfide standard. The photomicrographs showed that the appearance of the ring fracture damage on both materials was quite different. Etching revealed that the grain size of the coated specimen was one-half that of the uncoated specimen.

- o Quarter-quarter coatings containing ZnSe and LaF_3 (AFML Numbers 10220 and 10221) were tested on 470 mph, 90° impact angle for 20 minutes. The coatings passed the rain erosion test with a maximum transmission loss of 2.5% at $10\mu\text{m}$.
- o Quarter-quarter coatings containing ZnSe and CeF_3 (AFML Numbers 10222 and 10223) also passed the rain erosion test (470 mph, 90° impact angle, exposure time 20 minutes). The maximum transmission loss for these coatings was 1.5% at $10\mu\text{m}$.
- o Quarter-quarter coatings contain ZnSe and YF_3 (AFML Numbers 10224 and 10225) also passed the rain erosion test (470 mph,

90° impact angle, exposure time 20 minutes). The maximum transmission loss for these coatings was 4% at 10 μ m.

A.3 VISIBLE/NIR/IR COATINGS

The rain erosion test data for Visible/NIR/IR coatings is presented in Table A-5. The results can be summarized and interpreted as follows.

- o (ZnSe/ThF₄)⁵ MgF₂ coatings (AFML Numbers 9167 and 9168) were tested for rain erosion (470 mph, 90° impact angle, exposure time 20 minutes). The removal of coating was observed along the ring cracks on the surface. The coating removal just after the test was less than 5%. Subsequently, more coating removal was observed with time. It is believed that at least one or more layers came off within a period of 14 months. This coating removal is believed to be due to stress build-up in the multilayer systems.
- o (ZnSe/ThF₄)⁵ coatings (AFML Numbers 9168 and 9169) appear to pass the rain erosion test (470 mph, 90° impact angle, exposure time 20 minutes), but lost transmission by 8.5% at 10 μ m. Total thickness measurement of the coating at Perkin-Elmer indicated the complete removal (by TENCOR α -step profiler) of more than one layer. This removal of layers (not visually observed) was responsible for loss in transmission. It is again believed that the stress build-up in the multilayer system caused the removal of layers.
- o (ZnSe/ThF₄)⁵ CeF₃ coatings (AFML numbers 9171, 9172, 10228, 10229, 10230 and 10231) failed the rain erosion test. On some samples the coating even flaked off before the rain erosion test. Comparison of sample 9171 with 10231 indicates that flaking is not due to a bad coating run, but to stress build up in the multilayer system.
- o (ZnSe/YF₃)⁵ coatings (AFML Numbers 10226 and 10227) passed the rain erosion test (470 mph, 90° impact angle, exposure time 20 minutes) with a transmission loss of 1.5% at 10 μ m. This suggests that ZnSe and YF₃ have opposite stress and the net stress is significantly smaller as compared to ZnSe and ThF₄.

TABLE A-5. RAIN EROSION DATA - 1 INCH/HOUR SIMULATED RAINFALL, 1.8 mm DROP SIZE

Specimen ID# AFML	P.E.	Coating Design (Inner Layer First)	Rain Erosion Parameter			Transmission Loss at 10 μ m	Comments
			Impact Velocity (mph)	Impact Angle (Degrees)	Exposure Time (Minutes)		
9167	16-01	(ZnSe/ThF ₄) ⁵ /MgF ₂	470	90	20	2.5%	Removal of coating along ring cracks on surface <5% coating removal.
9168	16-02	(ZnSe/ThF ₄) ⁵ /MgF ₂	470	90	20	1%	Same as 9168
9169	17-03	(ZnSe/ThF ₄) ⁵	470	90	20	-	Specimen broken. No coating removal.
9170	17-04	(ZnSe/ThF ₄) ⁵	470	90	20	9.0%	No coating removal.
9171	18-05	(ZnSe/ThF ₄) ⁵ CeF ₃	470	90	20	-	Specimen broken. CeF ₃ layer removed. No removal of lower layers
9172	18-06	(ZnSe/ThF ₄) ⁵ CeF ₃	470	90	20	7%	CeF ₃ flaking off before rain exposure.
10226	66-01	(ZnSe/YF ₃) ⁵	470	90	20	1.5%	Specimen cracked. CeF ₃ layer removed.
10227	66-02	(ZnSe/YF ₃) ⁵	470	90	20	-	No coating removal.
10228	67-03	(ZnS ₂ /ThF ₄) ⁵ CeF ₃	470	90	20	-	Specimen broken. No coating removal.
10229	67-04	(ZnSe/ThF ₄) ⁵ CeF ₃	470	90	20	6%	Specimen broken. About 25-50% of coating removed.
10230	67-05	(ZnSe/ThF ₄) ⁵ CeF ₃	470	90	20	-	About 60-70% of coating removal.
10231	67-06	(ZnSe/ThF ₄) ⁵ CeF ₃	470	90	20	-	Not run.
							Not run. Coating flaking off before exposure to rain.

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