N90-25529

SATELLITE MATERIAL CONTAMINANT OPTICAL PROPERTIES*

B. E. Wood, W. T. Bertrand, B. L. Seiber, and E. L. Kiech
Calspan Corporation Corporation/AEDC Operations
Arnold Engineering Development Center,
Arnold AFB, TN 37389

Capt. P. M. Falco
Air Force Wright Research and Development Center,
Wright-Patterson AFB, OH

and
Capt. J. D. Holt
Arnold Engineering Development Center, Arnold AFB, TN 37389

ABSTRACT

The Air Force Wright Research and Development Center and the Arnold Engineering Development Center are continuing a program for measuring optical effects of satellite material outgassing products on cryo-optic surfaces. This paper presents infrared (4000 to 700 cm^{-1}) transmittance data for contaminant films condensed on a 77 K geranium window. From the transmittance data, the contaminant film refractive and absorptive indices (n, k) were derived using an analytical thin-film interference model with a nonlinear least-squares algorithm. To date 19 materials have been studied with the optical contants determined for 13 of those. The materials include adhesives, paints, composites, films, and lubricants. This program is continuing and properties for other materials will be available in the future.

INTRODUCTION

Contamination control and prediction are becoming increasingly important as satellite applications become more sophisticated and anticipated satellite lifetimes are extended. A satellite mission can be terminated due to a cryogenically cooled optical system or sensor becoming contaminated. A spacecraft designer must predict effects of this contamination with a very limited amount of data. The Air Force Wright Research and Development Center (AFWRDC) is sponsoring a program to determine and predict effects of satellite material outgassing products on critical surfaces. This is being carried out through an experimental-analytical study of the optical properties of contaminants originating from satellite materials.

Infrared transmittance measurements of contaminants condensed from satellite material outgassing products have begun in the AEDC 2- by 3-ft chamber. The materials being investigated were heated to 125°C under vacuum and the outgassed products were frozen as thin films on a 77 K germanium window. A scanning Michelson-type interferometer was used to measure the transmittance over the 4000 to 450 cm^{-1} wavenumber range. These data were input into the TRNLIN computer code which was based on thin film interference with a germanium window as substrate. Using this program, the refractive (n) and absorptive (k) indices of the contaminant films were determined. Once determined, these n and k values can be used to calculate the transmittance or reflectance of other optical components contaminated with the outgassing products of the same satellite material and for any film thickness or radiation incidence angle. This is demonstrated through the use of another program, CALCRT, which can be used for calculating transmittances and/or reflectances of substrates with contaminant films present.

EXPERIMENTAL APPARATUS

Infrared transmittance measurements were made of satellite material outgassing contamination products on cryogenic surfaces in the AEDC 2- by 3-ft chamber (Fig. 1). The pumping system consisted of a turbomolecular pump with a mechanical forepump and a liquid nitrogen (LN_2) cooled chamber liner. The turbopump and the cryopanels were necessary to provide a near-contaminant-free vacuum. Base pressures before contamination deposition were generally in the mid-10^{-7}-torr range.

The outgassing products for contaminating the sample surface were generated using an effusion cell. It had a cylindrical aluminum body 8.89 cm (3.5 in.) long with an internal diameter of 4.45 cm (1.75 in.) The material to be analyzed was placed in the closed end of the effusion cell. Heating elements covered the outside cylinder surface, and the temperature of the cell was thermostatically controlled to 125°C. The evolved gases exited through the open end aperture, which was 3.81 cm (1.5 in.) in diameter.

The substrate surface on which the contaminants were deposited was a germanium window 6.99 cm (2.75 in.) square and was 4 mm (0.157 in.) thick. It was mounted in the center of the chamber and was cooled to near 77 K with a constant flow of LN_2. Germanium was picked for the deposition surface because it has good thermal conductance and a flat transmittance of 47 to 48percent over the 700 to 4000 cm^{-1} (2.5- to 14-μm) range. The mass flux deposited on the germanium was monitored using a quartz crystal microbalance (QCM) mounted adjacent to it. The QCM was also cooled with LN_2.

A commercial Michelson-type interferometer (See Fig. 1) was utilized in making infrared transmittance measurements of the deposited contaminant film on the germanium window. The interferometrically modulated infrared beam was collimated and passed through a KBr window on the vacuum chamber port,

*The research reported herein was sponsored by the Air Force Wright Research and Development Center (AFWRDC) and performed by the Arnold Engineering Development Center (AEDC), Air Force Systems Command. Work and analysis for this research were done by personnel of Calspan Corporation/AEDC Division, operating contractor for the AEDC aerospace flight dynamics facilities. Further reproduction is authorized to satisfy needs of the U.S. Government.

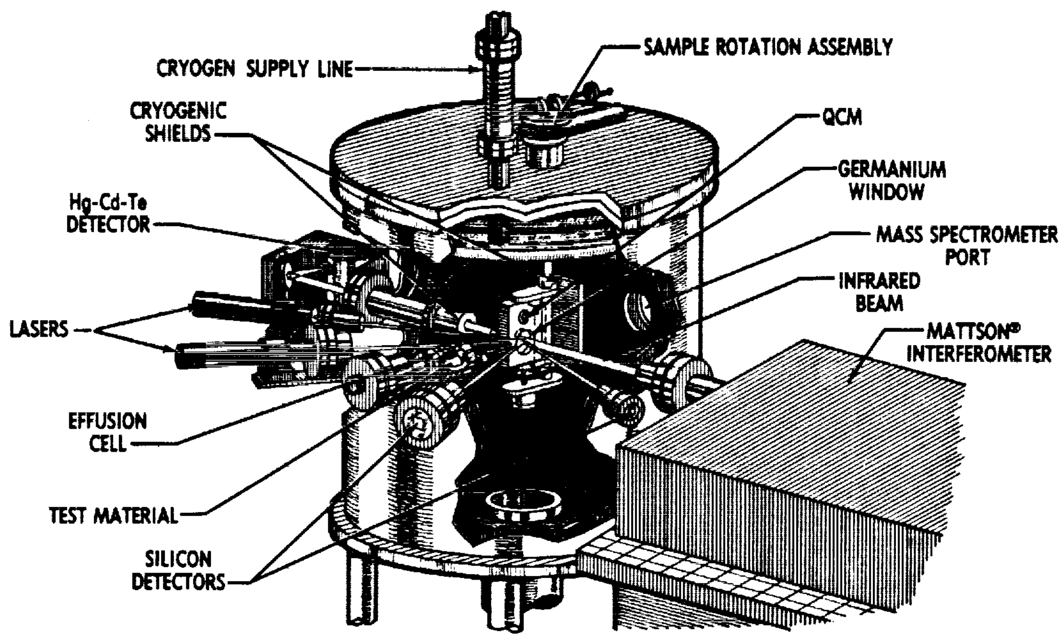

Fig. 1 Schematic of 2- by 3-ft cryogenic optics degradation chamber.

through the germanium window, through another KBr window on the opposite side of the chamber, and finally to detector optics and the Hg-Cd-Te detector. The wavenumber/wavelength range sensed was from 4000 to 450 cm^{-1} (2 to 22 μm). Typically, 32 scans were co-added for both the sample and reference measurements with a resolution of 2 cm^{-1}. A reference measurement was made before each sample measurement. Transmittance data were initially stored on the system hard disk and later transferred to flexible disks.

A list of some of the materials studied is given in Table I along with the condensed film properties measured. These include the refractive index at the He-Ne laser wavelength, film density, mass of material heated to 125°C, the total mass loss in percent (TML), and the maximum film thickness measured. The n's, k's column indicates whether or not the contaminant film was thick enough to determine the infrared n's and k's. Adhesives, paints, films, and graphite composites comprised the materials investigated. The adhesives were prepared by pouring them into an aluminum foil boat which was 3 by 1.5 by 1.5 in. (7.62 by 3.81 by 3.81 cm) and allowing them to cure. The empty aluminum foil boat was outgassed at 125°C for 24 hr prior to installation of the material. The paints were applied to aluminum foil strips and allowed to dry for the vendor-recommended time. All materials investigated were preconditioned by placing them in a 50-percent (±5 percent) relative humidity cell for 24 hr prior to installation in the chamber.

Table I. Materials investigated in AEDC 2 by 3 optical properties chamber

Material	Ref.Index .6328 μm	n's, k's Infrared	density, g/cc	Mass, grams	TML %	Thickness, microns
RTV-732	1.44	yes	0.69	21.	4.53	2.75
DC93-500	1.44	yes	0.57	66.5806	.09	~1.3
DC6-1104	1.46	yes	0.80	109.7	--	9.28
Solithane	--	no	--	38.531	.20	~ 0.85
Kapton	1.21	yes	0.91	124.6644	1.26	3.59
S13G/LO	1.34	yes	1.11	53.4544	.16	2.96
RTV-566	1.43	yes	0.86	97.9884	.57	8.49
RTV-560	1.42	yes	0.9	78.0342	2.00	7.41
Mylar	1.28	yes	1.07	123.0593	.13	1.25
FEP teflon	--	no	--	142.7436	.01	~0.25
Stycast 2850	--	no	--	113.4790	.02	~0.37
Epoxi-patch	-	no	--	89.6960	.01	~0.25
Crest 7450	1.32	yes	0.94	93.0990	.35	11.24
AS4/PEEK	--	no	--	82.9237	.03	0.25
AS4/J2	1.32	yes	0.85	110.7016	.24	3.01
EP30LI	1.32	yes	0.75	102.1996	.12	~1.5
AS4/PPS	--	no	--	93.1507	.03	--
Chemglaze Z306	1.45	yes	1.03	6.7162	2.07	~1.82
Chemglaze A276	1.47	yes	1.00	14.9695	4.80	~10.7

EXPERIMENTAL TECHNIQUES

In order to make accurate n, k measurements, the transmittance must be measured for carefully determined film thicknesses. The thin film interference technique provides an excellent method for calculating these discrete thicknesses. This technique has been described previously[1,2] and will only be reviewed here. As a thin film forms on a reflecting substrate the intensity of a reflected beam of radiation (such as from a laser) will vary sinusoidally. From thin interference equations, the maxima and minima locations can be used to accurately calculate the film thickness at these maxima-minima locations.[1] In order to make these calculations, the film refractive index, n, must be known for the incident radiation wavelength. To determine n, two He-Ne laser beams were incident on the germanium window at two angles (24.0 and 67.5 deg). The reflected beams were detected with silicon solar cells. Interference maxima were observed on a strip chart recorder as the contaminant film deposited. The refractive index at 0.6328 μm was determined from the interference patterns by using the fringe (interference maxima or minima) counting technique described in Refs. 1 and 2. Knowing the refractive index at 0.6328 μm, the film thicknesses for the reflected interference maxima and minima were calculated from the thin film interference equation,

$$t = m\lambda / 2n\left(1 - \frac{\sin^2\theta}{n^2}\right)^{0.5}$$

where t = film thickness (μm), λ = wavelength (μm), n = real part of refractive index at wavelength λ, θ = incidence angle (deg), and m = order of interference where m = 1,2,3, etc. for maxima, and 1/2, 3/2, 5/2 etc. for minima. The refractive indices determined at the wavelength of 0.6328 μm are shown in Table 1 for outgassing products of the materials analyzed. Knowing the film thickness and the mass condensed (determined using the QCM), the film density also was calculated.

CRYOGENIC CONTAMINATION CHAMBER EXPERIMENTAL PROCEDURES

After the sample material had been preconditioned, it was inserted in the effusion cell and installed in the 2- by 3-ft chamber. The centers of the germanium window and the QCM were aligned equidistant from the effusion cell centerline so that the two surfaces would see the same flux rate. Pumpdown of the chamber then began. After the pressure had reached 10^{-5} torr, LN_2 cooling of the chamber liner, germanium window, and QCM began. Both QCM and germanium window reached thermal equilibrium before measurements began. At this point the chamber pressure was in the mid-to-high 10^{-7}-torr range. An initial germanium transmittance measurement was made to insure the window was clean. The effusion cell warmup to 125°C began and the laser-solar cell outputs were observed with time on a strip chart recorder. Outgassed components were condensed on the germanium window and the QCM. As the outgassed products condensed on the germanium window, the thin film interference caused the laser-solar cell outputs to exhibit sinusoidally varying signals. Deposition continued until the first interference minimum (quarter wavelength) was reached. The transmittance of the germanium window with the deposited film was then measured. The QCM change in frequency with time was also recorded during contaminant deposition.

Once the transmittance measurements were completed, the germanium was rotated back into the original deposition position, and the film buildup and transmittance measurements continued. This procedure was repeated for as many thicknesses as could be obtained before the deposition rate decreased to a minimal value. For some materials, films up to 25 interference maxima thick were obtained, whereas for others only 1 to 2 were observed. Transmittance measurements were made for as many thicknesses as possible to maximize the accuracy of the n,k calculations. In some cases transmittance measurements were made during warmup of the germanium window. This helped to determine the temperature where individual contaminant species were re-evaporated and to aid in their identification.[2] The total mass loss percentage (TML) was determined by dividing the mass lost due to outgassing for 24 hr (at 125°C under vacuum) by the original mass.

EXPERIMENTAL DATA

All of the materials listed in Table 1 have been analyzed. In some instances, not enough contaminant was obtained to determine the infrared n's and k's. Generally, film thicknesses of about 1.5 μm or greater were required for optical properties determination. Examples of the infrared transmittance data obtained are shown in Figs. 2 through 4 for Mylar® film (5 mil), AS4/J2 thermoplastic composite, and Chemglaze® Z306 black paint, respectively. These figures show the infrared transmittance of the 77 K germanium window with three film thicknesses of contaminant condensed as material outgassing products. Infrared transmittance spectra for contaminant films from some of the other materials studied are reported in Ref. 2.

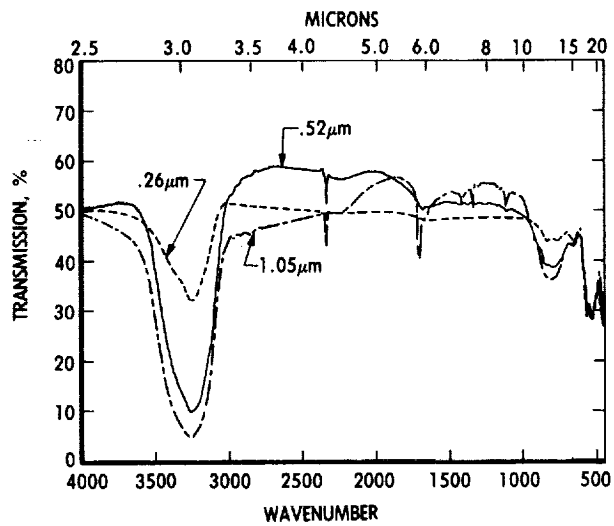

Fig. 2. Transmittance of condensed Mylar components–0.26, 0.52, and 1.05 μm thick.

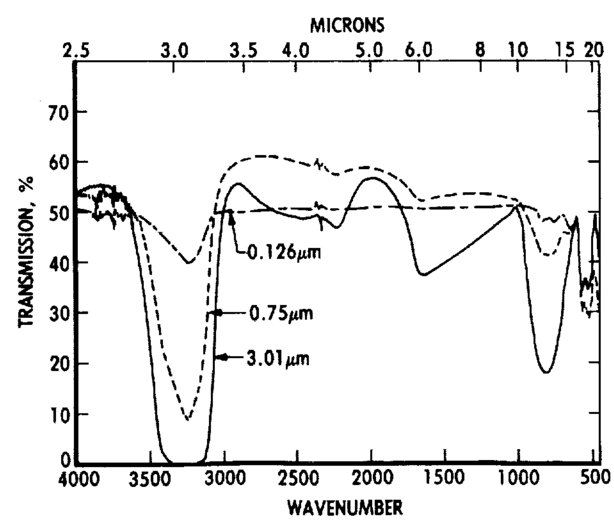

Fig. 3. Transmittance of condensed AS4/J2 thermoplastic composite components 0.126, 0.75, and 3.01 μm thick.

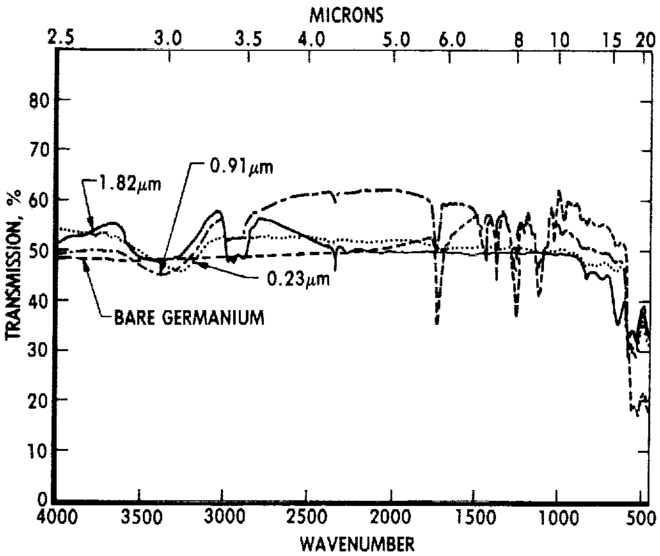

Fig. 4. Transmittance of condensed Chemglaze Z306 components 0.23, 0.91, 1nd 1.82 μm thick.

Fig. 2 shows the infrared transmittance of the germanium window with condensed Mylar contaminant films of 0.26, 0.52, and 1.05 μm. (Bare germanium transmits about 49 percent between 4000 and 700 cm^{-1}.) The major identifiable component outgassed from Mylar is water as evidenced by the broad strong absorption band (See Fig. 2) centered near 3300 cm^{-1}. A trace of CO_2 shows up as the thin spike located at 2340 cm^{-1}. For the 1.05-μm-thick film, several weak bands show up between 900 and 1500 cm^{-1}, which are probably due to hydrocarbons. Total mass loss (TML) was found to be 0.13 percent.

For the AS4/J2 composite material, condensed outgassing products of 0.126, 0.75, and 3.01 μm produced transmittance spectra shown in Fig. 4. The spectra show a strong resemblance to that observed for Mylar. Water vapor again was the dominant species outgassed with even less CO_2 observed than for the Mylar. The water bands are more pronounced as thicker contaminant films were obtained for the composite materi..l than for Mylar. The absorption band locations 3300, 2250, 1600, and 800 cm^{-1} are all due to water. There was no evidence of other outgassed species other than the previously mentioned trace of CO_2. The TML found for AS4/J2 was 0.24 percent.

For Chemglaze Z306 (Fig. 4), transmittance spectra of films 0.23, 0.91, and 1.82 μm are shown. The painted samples were allowed to dry for 7 days prior to the measurements. The outgassing species appear to be predominantly hydrocarbons, with some water and a trace of CO_2. The hydrocarbons are identified by the bands near 3000 cm^{-1} and several between 1800 and 800 cm^{-1}. The TML observed was 2.07 percent.

The housekeeping data were monitored and stored by a computer. A typical set of data included the QCM parameters (frequency, mass, mass rate, and temperature), the laser-solar cell outputs, the effusion cell temperature, and the germanium window temperature. Typical plots of these parameters are contained in Ref. 2.

OPTICAL PROPERTIES DETERMINATION

Most contaminant problems encountered in space involve contaminant thicknesses of a few micrometers or less. Therefore, thin film interference equations are generally used to predict contaminant effects on the reflectance or transmittance of an optical element. These calculations require knowledge of the optical properties of the contaminant film, the refractive and absorptive indices, n and k. They are components of the more general expression for the complex refractive index given by $n^* = n - ik$. In order to determine the complex refractive index of the thin, solid-contaminant films, an analytical model called TRNLIN has been developed.[3,4] The model uses the expressions given in Ref. 5 for thin film transmittance and reflectance. The model assumes the germanium window is a thick film, and all interference occurs within the thin contaminant film. The expressions derived were for the normal transmittance of a thin film on a nonabsorbing substrate, which accurately represents the experimental conditions under which the transmittance measurements were made. Transmittance values of the germanium window with known contaminant film thicknesses were input into the TRNLIN program. The program uses a nonlinear least-squares convergence routine for determining n and k. The n's and k's were determined at every 2 cm^{-1} in the range from 700 to 4000 cm^{-1}. The refractive and absorptive indices determined from the transmittance data are shown in Figs. 5 through 7 for Mylar film, AS4/J2 thermoplastic composite, and Chemglaze Z306 black paint, respectively. The refractive indices are shown at the top with the absorptive indices directly below.

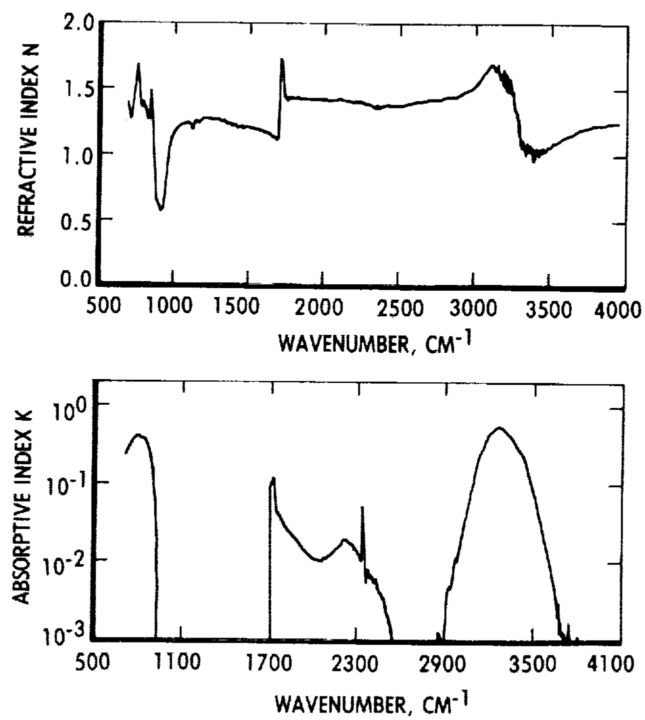

Fig. 5. Refractive and absorptive indices for Mylar film (5 mil) outgassing products.

The standard deviations for each wavenumber were calculated as part of the TRNLIN program. They generally varied with wavenumber, but for the most part were on the order of 0.01 for the refractive index and 0.001 for the absorptive index. Tabulated n, k data for all of the materials discussed will eventually be included in an AFWRC data base.

TRANSMITTANCE AND REFLECTANCE CALCULATIONS USING CALCRT

To realize the maximum utility of the n,k data generated from the experimental and analytical studies, a computer program, CALCRT was developed. CALCRT, written in FORTRAN IV, calculates the transmittances and reflectances for a radiation

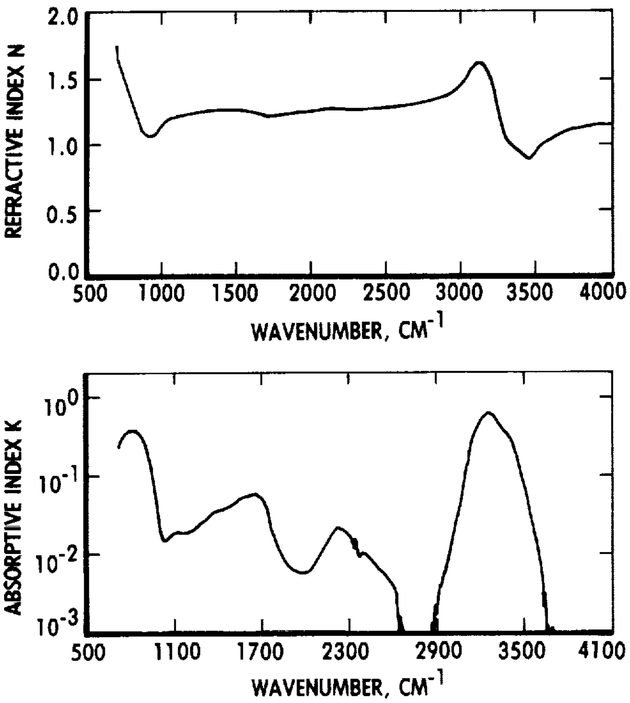

Fig. 6. Refractive and absorptive indices for AS4/J2 thermoplastic composite outgassing products.

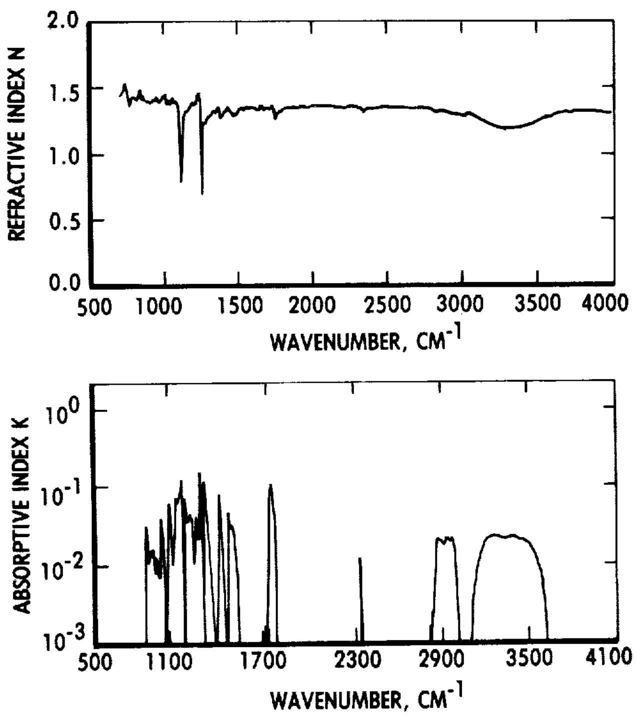

Fig. 7. Refractive and absorptive indices for Chemglaze Z306 outgassing products.

beam that strikes a film and substrate system which has planar interfaces that are, ideally, infinite in extent. The film and substrate are sandwiched between semi-infinite vacuums, and the refractive indices on each side of the filmsubstrate are identically equal to one.

The user must supply the optical constants and thicknesses of the film and substrate, and the incidence angle of the beam. The user must choose either an output format that gives the reflectances and transmittances as functions of wavenumber or wavelength at a constant film thickness, or an output format that displays the transmittances and reflectances versus film thickness at a constant wavenumber or wavelength.

To show how CALCRT can be used, an example of transmittance versus wavenumber was calculated using the n's and k's previously determined for Chemglaze Z306 material. Figure 8 shows curves of transmittance versus wavenumber for a 1.82-µm-thick contaminant film. The two curves overplotted are the actual measured spectral transmittance and the calculated transmittance curve based on the n's and k's determined. As seen in Fig. 8, there is excellent agreement between the experimental and calculated curves. Differences of about 3 percent were the largest seen.

CALCRT was also used to calculate the transmittance dependence on film thickness. An example is shown in Fig. 9 for contaminant films deposited from the outgassing products of a composite material AS4/J2, which is a thermoplastic. The three curves shown are for (top to bottom) 2000, 800, and 3250 cm^{-1}. The corresponding n,k values used for the calculations are also given in Fig. 9. There is relatively little absorption observed for 2000 cm^{-1} (k = 0.0061) and only the interference phenomena is seen superimposed on the germanium transmittance. For the 3250 cm^{-1} curve, however, the strong absorption index (k = 0.597) reduces the film-substrate transmittance to near zero for a film thickness of approximately 1.5-µm thick. (The high absorption index at 3250 cm^{-1} is typical of films containing water). The middle curve (for 800 cm^{-1}) is for a region where there is medium absorption (k = 0.394) and represents the location of another water absorption band (See Fig. 3). The solid curves show the analytical results calculated using CALCRT and the derived n's and k's, whereas the symbols denote the actual experimental values. As can be seen in Fig. 9, the analytical and experimental results agree very well. The important point that should be re-emphasized about the n's and k's of contaminant films is that, once determined, they can be used to calculate transmittances and reflectances for any desired film thickness, incidence angle, or substrate (provided the substrate refractive index is known).

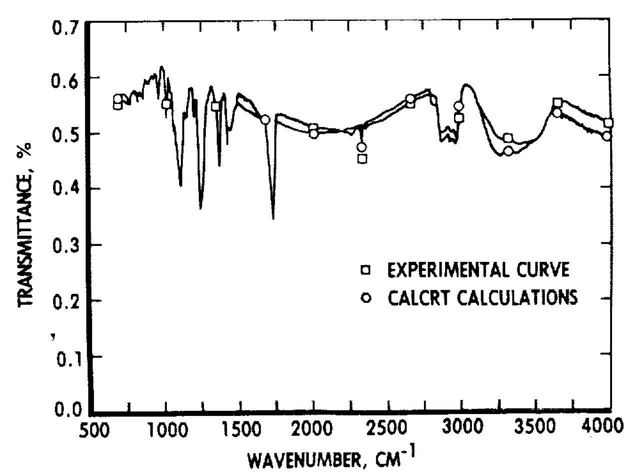

Fig. 8. Transmittance versus wavenumber for experimental measurement and CALCRT calculations for a 1.82-µm-thick Chemglaze Z306 outgassing films for 2000, 800, and 3250 cm^{-1}.

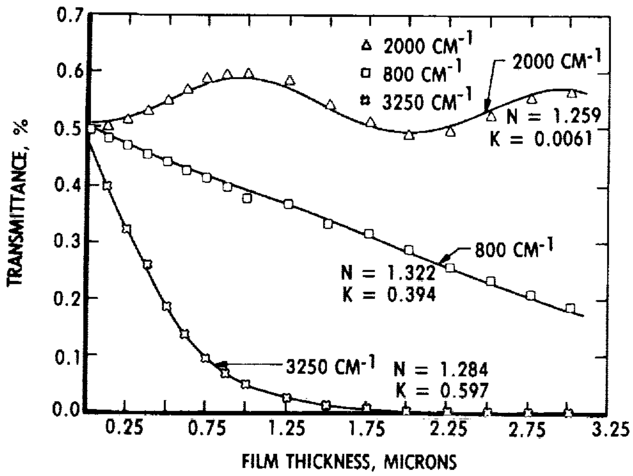

Fig. 9. Comparison of calculated and experimental transmittance values versus film thickness for AS4/J2 outgassing products contaminant films for 2000, 800, and 3250 cm-1.

SUMMARY

The Air Force Wright Research and Development Center (AFWRDC) and the Arnold Engineering Development Center (AEDC) have initiated a program for measuring contaminant surface effects of satellite material outgassing products on cryo-optic surfaces. The complex refractive index components, n and k, of thin contaminant films condensed on a cryogenic surface, were determined from experimental infrared transmittance measurements for the wavenumber range from 4000 to 700 cm-1. The materials studied were heated to 125°C and outgassing products were condensed on a 77 K germanium window. From the infrared spectra, outgassing components can be identified by absorption band locations. Water, CO_2, hydrocarbons, and silicones are easily identified. The n's and k's were determined using a thin film interference analytical model and a nonlinear least-squares algorithm. Infrared transmittance data and the n's and k's determined, are presented for 5-mil-thick Mylar film, AS4/J2 composite material, and Chemglaze Z306 black paint. These are only 3 of approximately 20 materials which have been investigated. For information on other materials, see Ref. 2.

A computer program, CALCRT, has been written which calculates the transmittance and reflectance values for the following parameters: substrate refractive index and thickness, contaminant refractive index and film thickness, incidence angle, wavenumber, and wavelength. This provides a potential optical property user with the program for utilizing the n's and k's generated for the materials mentioned previously.

REFERENCES

1. Wood, B. E. and Smith, A. M., "Infrared Reflectance of Condensed Gas Films," *AIAA Progress in Astronautics and Aeronautics: Thermophysics and Thermal Control*, Vol. 65, Ed. Raymond Viskanta, 1979, pp. 22-38.

2. Wood, B. E., Bertrand, W. T., Bryson, R. J., Seiber, B. L., Falco, P. M., and Cull, R. A., "Surface Effects of Satellite Material Outgassing Products," *Journal of Thermophysics and Heat Transfer*, Vol. 2, No. 4, October 1988, pp. 289-295.

3. Wood, B. E. and Roux, J. A.,"Infrared Optical Properties of Thin H_2O, NH_3, and CO_2 Cryofilms," *Journal of the Optical Society of America*, Vol. 72, No. 6, June 1982, pp. 720-728.

4 Wood, B. E. and Roux, J. A., "Infrared Optical Properties of Thin CO, NO, CH_4, HCl, N_2O, O_2, N_2, and Ar Cryofilms," *Progress in Astronautics and Aeronautics, Spacecraft Contamination: Sources and Prevention*, Vol. 91, Ed. J. A. Roux and T. D. McCay, 1984, pp. 139-161.

5. Heavens, O. S., *Optical Properties of Thin Films*, Dover Publications, Inc., New York, 1965.