Final Report

submitted to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER, ALABAMA 35812

March 22, 1999

for Grant NAG8 - 1071

entitled

# Surface Characterization and Contamination

by

Gary L. Workman Ph.D.
Principal Investigator

In-line Process Control Laboratory
Center for Automation & Robotics
University of Alabama in Huntsville
Huntsville, Alabama 35899

# INTRODUCTION

Nondestructive characterization of surface contamination can play an extremely important role in improving quality in manufacturing processes. This area of interest led to the formation of a Surface Contamination Analysis Team (SCAT) at Marshall Space Flight Center, which is primarily concerned with critical bondlines and has provided the major focus for activites under this grant. In addition, determining minute levels of contamination on emerging aerospace systems fabricated from composites has also been an area of interest for which the methods being presented here can be used. Important considerations for the inspection methodologies are good sensitivity, large area coverage, robustness, portability and ease of use for normal production personnel. In parallel with the evaluation of detection methods, considerable effort has been made to developing good, uniform contamination films to use as calibration standards. This activity within itself has presented unique challenges. The development of NIR methods for detecting and identifying contaminants has been in progress for several years. Cooperative efforts between the University, NASA, and Thiokol Corporation has shown some useful results for implementation in both laboratory and on-line procedures.

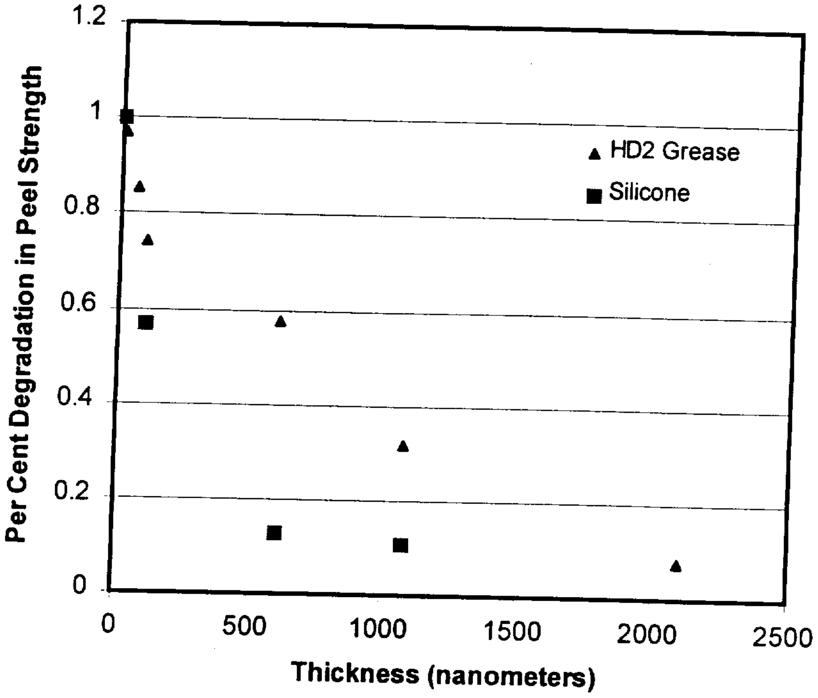


**Figure 1.** This chart shows the relationship between bond integrity and level of contamination for silicone and HD2 grease.[1]

The problem being worked for the solid rocket motor production activity is addressed in that a number of debonding agents exist within the manufacturing area for the aerospace systems, some intentional and some unintention. Silicones, hand creams, and similar types of materials can inadverdently end up on a critical bonding surface. Studies at MSFC show that bonding strength degrades significantly with these types of contaminats. For example Conoco HD2 grease is used as a moisture barrier/rust inhibitor in storing SRM's at the manufacturing facility. Silicone is used in many other operations within the plant. Inadverdent occurance of these materials prior to bonding can provide the results shown in figure 1 above. Methods to detect and recognize the contaminating material is critical to maintaining high quality production of these very expensive components.

## NEAR INFRARED SPECTROMETRY

NIR spectrometry offers unique capabilities for detection and identification of contaminants on aerospace flight hardware and other critical surfaces, either stand-alone or in conjunction with other inspection processes. Multivariate analysis methodologies provide the most useful approach to performing the quantitative analysis for the NIR spectral domain. Much progress has been made in understanding spectral features observed from surface films with optical fiber probes, yet the interpretation of spectral features on surfaces continues to be the major challenge for this spectrometric tool. Simple prediction models of contaminant concentration are easily accomplished in most cases. However, frequently the complexity of the interactions due to thin film reflection/absorption phenomena still requires some chemical and physical knowledge about the surface being analyzed. In these cases, considerable expertise may still be required to sort through the spectral features obtained, to pick out the significant features and determine the origin of these features.

Several instruments were used in this work; however an older Guided Wave 260 grating spectrophotometer provided all the experimental data. Newer instruments under consideration include systems based on Fourier Transform methodology and acousto-optic devices. The fiber transmission capability works well for production environment in that the probe and the spectrometer can be a distance apart. In general, optical fiber NIR spectrometry is a very flexible analytical tool which provides a number of challenges for accurate surface analysis.

In the spectral region in which this work has been performed, 1.0 - 2.5 microns, -OH stretching vibrations are the major peaks observed for species which result from hydrolysis or hydration. These spectral bands represent the second harmonic or combination bands of features normally observed in the mid-IR using FTIR or other infra-red instruments. In most cases, -CH stretching vibrations are also observed in this region as combination bands. This observation, for example, allows us to easily differentiate between HD2 and silicone greases.

The procedures followed in obtaining spectral data and performing the analysis were fairly consistent. Once a series of NIR spectra were obtained from the experiments described in this report, a variety of of chemometric techniques were employed to isolate significant spectral features as factors using either Principal Component Analysis (PCA) or Partial Least Squares (PLS) techniques. Optical fiber spectral scans performed with the Guided Wave 260 were normally run at the highest resolution to provide better results with the chemometric modeling, thereby requiring relatively long scan times.

Typically spectra are recorded in units of watts and transformed into absorbance using the relationship:

$$A = \log \frac{I_{sample}}{I_{ref}} \qquad 1)$$

Much work was spent in the beginning of the research to determine what reference surfaces to use for calculating absorbances. The major problem that arises in the analysis of organic contaminants on surfaces is the occurrence of specular reflection from the contaminant, causing $I_{ref}$ to be greater than $I_{sample.}$ When a spectral feature goes negative; i.e. $I < I_{ref}$ then most matrix multiplication techniques are not applicable. In practice, a negative absorbance is undefined, which means that the reference is not valid. Several reference surfaces used in this work include an aluminum or gold mirror; i.e. totally or specular reflecting; barium sulfate i.e., diffuse reflecting, and native surfaces such as D6AC steel or aluminum alloys.

Continuing work has provided the opportunity to apply the capabilities of optical fiber NIR techniques to the following cases:

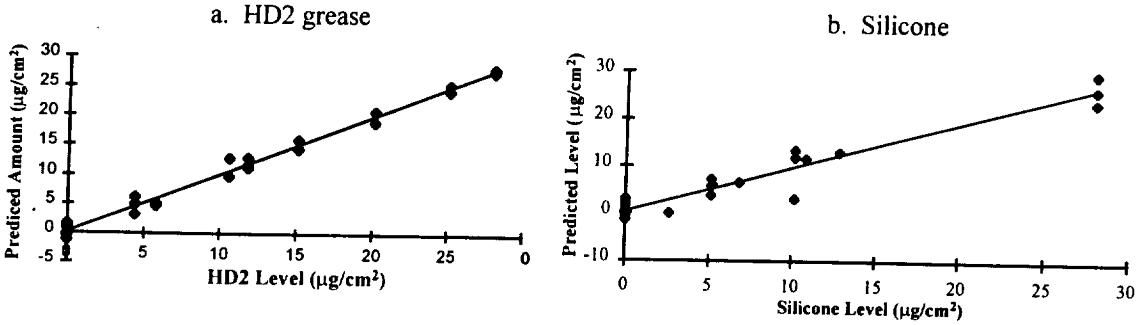
- Single component films of HD2 and silicone grease on D6AC steel and 7075 aluminum
- Mixtures of HD2 and silicone films on D6AC steel and 7075 aluminum
- D6AC steel, 7075 Aluminum and Lithium Aluminum plates in controlled temperature and humidity environments for extended periods of time.

The primary results of these observations was been to show that NIR spectrometry using PLS analysis is able to:

- Discriminate between HD2 and silicone greases in single or mixed applications, both qualitatively and quantitatively.

- Detect the various water/hydroxide species that occur on both D6AC steel and aluminum alloy surfaces under variable humidity and temperature conditions.
- Detect levels of contamination by tape residues used in the manufacturing operations of the RSRM.

The results of two different types of experiments are reported here. The first experiment reported here is concerned with the quantitative identification of HD2 and silicone films on D6AC steel and 7075 Aluminum. Since the manufacturing facilities for SRM's provide a number of opportunities for either of these two materials to occur on a critical bonding surface, an inspection technique to confirm surface cleanliness needs to be able to quantify these contaminants. A set of D6AC and aluminum 7075 panels were vapor degreased and grit blasted; contaminated at six levels with either HD2 or silicone or a combination of both. NIR spectra of the panels obtained and analyzed with PLS are shown in figure 2 above. Note that the sensitivity obtained is in the range 1 to 2 μg/cm$^2$.


a. HD2 grease

b. Silicone

**Figure 2.** Calibration curve for HD2 and silicone contaminants on D6AC Steel

In the final sequence of experiments reported here, the residues of adhesives from four different tapes used by Thiokol in their manufacturing process were studied to determine if they could be quantitatively identified using an NIR method. In various stages before bonding it is necessary for the manufacturer to use adhesive tapes in order to complete an assembly. When the adhesive tape is removed from the assembly, an adhesive residue can be left behind. It is this residue which needs to be removed before proceeding onto bonding operations. A method is thus needed to inspect the surface and provide information of any adhesive residue is remaining and if possible how much and which type of residue remains.

Spectra were collected from the samples of residue that remain on a bonding surface after tape has been applied, then removed and the adhesive cleaned from the surface with solvent. The residues from four different tapes currently used by Thiokol were extracted using 1,1,1 Trichloroethane as a solvent. The four tapes studied, and their occurrence in the manufacturing process, are:

1) Teflon tape, a tape used in the grit blast process;
2) P mask, a masking tape used in the painting operation;
3) B mask, a masking tape used in the grit blast process;
4) Vinyl tape, a tape used in the cleaning operations.

The residues were sprayed concurrently on large aluminum plates and witness foils. The gravimetric weights were determined for the witness foils from which conclusions about the levels on plates were deduced. Each residue was applied in two distinct levels of contamination, yielding eight contaminated levels, two for each type of contaminant. A blank panel was also measured. The PLS analysis confirmed that the tape residues from the four potential contaminants could be quantitatively identified in the NIR. The close similarity of the chemistry for the adhesives, for example a common plasticizer such as a phthalate was present in each residue, made the differentiation among the four a little more difficult; however, the PLS model did a good job of differentiating between the tape residues.

After determining that the tape residues were quantifiable, another experiment was performed to determine the amount of residue after performing normal cleaning operations with solvent. The tapes were adhered to the substrates, aged for a period of ten days, after which, the tapes were then removed from the substrates. Spectral data was then collected from the surface of each substrate which remained after the tape was peeled off. Four measurements were taken for each sample, providing a cluster of four data points for each type of sample. The substrates were then cleaned with 1,1,1 trichlorethane to simulate the cleaning process used presently in the manufacturing of SRM parts and spectra were then repeated for the post cleaned substrates. The total number of spectra taken, including blanks, was 60.

**Table 1.** Amount of tape residue measured by NIR before and after wiping with solvent.

| Residue | Vinyl Tape | Teflon Tape | B-Masking Tape | P-Masking Tape |
|---|---|---|---|---|
| Pre-wipe | 16.83 | 15.0 | 15.9 | 19.2 |
| Post-wipe | 6.0 | 4.1 | 9.9 | 8.8 |

The spectral data was analyzed by looking at the variation of the absorption which occurred on the surfaces of the substrates due to the presence of the residues after removing the tape and after cleaning with solvent. The results given in table 2. above show that the cleaning process does not remove all of the tape residue, leaving a thin film which may be detrimental to the required bonding process. The plots show the measured amounts for all 60 measurements acquired before and after cleaning. Note that the chemometric regression shows for each plot only the amount of each residue for that plate. The cluster of points near 0.0 is either a blank or an indication that that that specific tape residue isn't on the plate.

## VARIABLE ANLE SPECTROSCOPIC ELLIPSOMETRY

Ellipsometry provides a very sensitive method for characterizing films on smooth surfaces. The method is based upon measurement of the polarization of light reflected from the surfaces under inspection and provides the ability to obtain the optical constants, n (refractive index) and k(extinction coefficient) as well as film thickness. The measurements of the changes in polarization allows one to obtain the Fresnel reflection coefficients for the interfaces in the light passing from medium 1, through film 2, and then reflecting off substrate 3 through the well known relations:

$$R_p = \frac{r_{12}^p + r_{23}^p + \exp[-4\pi i n_2 \cos(\phi_2 d_2 / \lambda)]}{1 + r_{12}^p r_{23}^p + \exp[-4\pi i n_2 \cos(\phi_2 d_2 / \lambda)]} \qquad 2)$$

$$R_s = \frac{r_{12}^s + r_{23}^s + \exp[-4\pi i n_2 \cos(\phi_2 d_2 / \lambda)]}{1 + r_{12}^s r_{23}^s + \exp[-4\pi i n_2 \cos(\phi_2 d_2 / \lambda)]} \qquad 3)$$

where $r_{12}^p$ , $r_{23}^p$ are the coefficients of reflection polarized parallel to the plane of incidence and

$r_{12}^s$, $r_{23}^s$ are the coefficients polarized perpendicular to the plane of incidence.

The ratio of the Rp and Rs is used to define $\Psi$ and $\Delta$ , i.e. $\rho = \frac{R^p}{R^s} = \tan\Psi e^{i\Delta}$. In this representation the changes in polarization are given in terms of an amplitude ($\Psi$) and a phase component ($\Delta$), which provides an extremely sensitive measurement for characterizing multilayer films. A major advantage of this approach is that specular reflection off contaminating films does not affect the measurement. Only variation in polarization is used to extract film thickness. These relations hold for each wavelength used to make the measurements. Earlier ellipsometry instrumentation provided light sources for one specific wavelength and one specific angle of incidence, making it difficult to solve for n and k for multilayer films.

Newer approaches use a broad spectral source and monochromator arrangement to obtain measurements over a broad spectrum. For instance the J.A. Woolam VASE® instrument used in this laboratory provides n and k values for the spectral region from 300 nm to 1700 nm and allows for varying the angle of incidence.

This capability allows one to characterize the n or k values for specific film types to reduce ambiguity in interpretation of the film constituents and thicknesses.

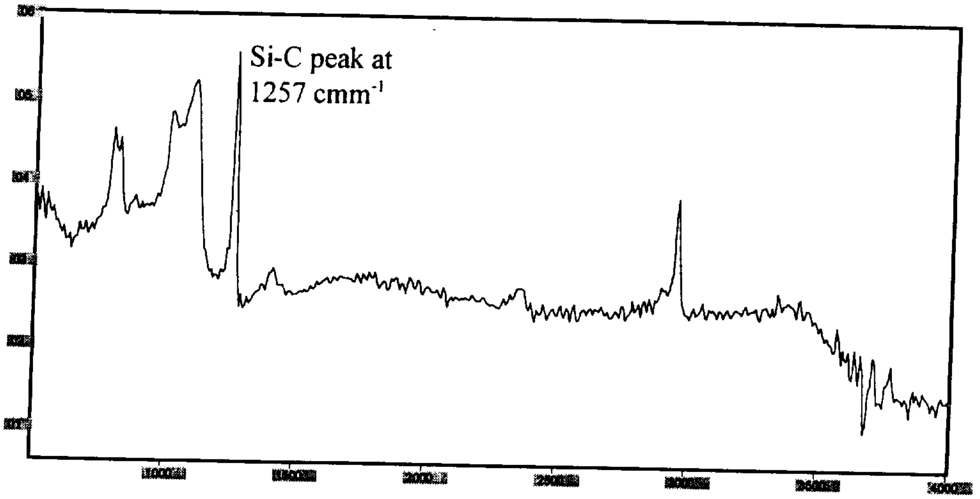
Characterization of contaminating films on optical surfaces has been carried out routinely in this laboratory using the VASE instrument. Applying this methodology to bonding surfaces for solid rocket motors has been less successful due the rough surfaces (relatively speaking) found on D6AC steel and aluminum alloys used for those systems. The surfaces are prepared for bonding by grit blasting, thus creating very rough surfaces. The instrumentation is not very portable and still remains a laboratory instrument. To date the primary application for VASE has been characterizing space optics prior to being assembled in flight hardware and in analyzing optics returned from space to characterize contaminating sources.

## FOURIER TRANFORM INFRARED METHODS

Methodology in the spectral range 400 - 5000 $cm^{-1}$ has also been applied to the detection and identification of organic contaminants on critical bonding surfaces using a portable FTIR instrument developed specifically for the surface inspection by Surface Optics Inc. The unit is portable, lightweight and collects the light from a 5 $mm^2$ spot to provide a spectrum of the surface. The SC-400 is extremely sensitive due to the large aperture optics and easy to operate. The complex interactions of the reflected light from the contaminant surface still occurs for the mid-IR spectra; however, the molecular absorption coefficients are much larger than those obtained in the NIR. Quantitative methods are very straight-forward for single contaminant detection, allowing the use of one or two peaks for determining contamination levels.. Films in the range from 100 nm to 100 micrometers may be characterized with this instrument.

The recorded spectra using the FTIR system is shown in figure 7 below. Note the strong Si-C peak at 1257 $cm^{-1}$ which allows for straight-forward quantification of contaminant levels above 2 $mg/ft^2$. Below that level interactions with surface oxides begins to interfere with the peak definition and quantitative analysis becomes more difficult.

Figure 7. FTIR spectrum of silicone grease on D6AC steel



· Absorbance / Wavenumber (cm-1)
File # 9 : PLATE3-1
13.94 mg ft² Silicone Grease -background at 50 scans; 16cm⁻¹ resolution

Paged Y-Zoom CURSO
12/18/97 2:05 PM Res=16 cm-

## ULTRAVIOLET FLUORESCENCE METHOD

The newest system to be evaluated for detection and identification of contaminants is the UV Fluorescence Surface Contamination Detection System developed by SAIC for the NASA Solid Propulsion Integrity Program(SPIP). The system has been designed to pulse spectrally filtered ultrviolet light on the surface to be inspected and record low levels images of fluorescence from a contaminated surface. The system uses a liquid crystal tuned filter, which allows the users to select any spectral band between 400 and 720 nm, for observing the fluorescing contaminants under computer control. This approach allows for optimization of the detectivity for specific contaminants by providing selectivity of the illuminating spectral band and the fluorescent band. Since all potentially contaminating species do not fluoresce under the same bandwidth conditions, this feature provides a useful parameter to work with. The sensitivity of detection is about 1 $\mu g/cm^2$ and is able to work in daylight conditions.

SAIC has demonstrated the system to other aerospace manufacturing groups in other SPIP activities; however, the UV Fluorescence system to be used by the SCAT Team was not set up for evaluation prior to the writing of this paper.

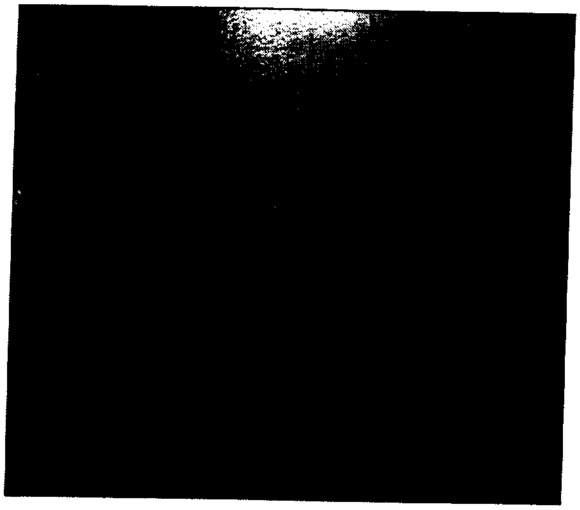
# THERMOGRAPHY NONDESTRUCTIVE EVALUATION

Another method which was evaluated during th elatter part of the grant was infrared thermography or Thermal Imaging. Inclusion of this method broadened the range of inspection tools to include a more traditional NDE tool and provided the capability for locating manufacturing and service related defects in advanced aerosapce structrures, including composites. As an example of applying this method, a composite fuel tank of the low cost booster technology propulsion system was inspected using the Amber Radiance 1 thermal camera (25 mm lens) running under EchoTherm 32 software. The TWI Flash system with hood extension was used to thermally load the tank's exterior surface. The regions inspected include the bellyband, the aft skirt attachment zone and leak spots. Typical results are:

1. Bellyband

Few indications were observed across the belly band region. Most prominent was the zone labelled B17. The thermal imaging results can then provide a more in-depth, but destructive, inspection of the inner layers of the composite structure. A debonded condition is the most likely suspect.

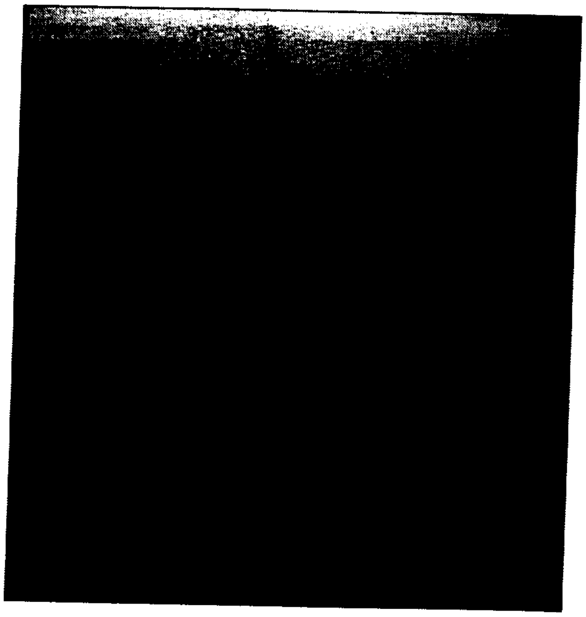
Figure 8. Thrmal image of belly band region of low cost booster



2. Skirt to Dome Attachment

This region was marked by regions of varying thermal properties as the two structures were joined in this region. As shown in the region marked Skirt18, the gradations in properties is quite evident. Since other areas in this region did not show as much gradation, there is a possibility of bonding problems here.

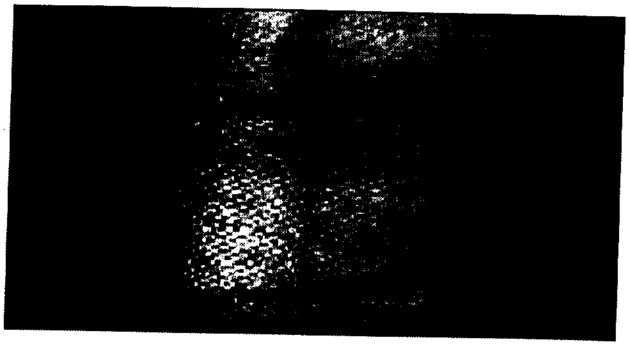
Figure 9. Thrmal image of the aft skirt to dome region of low cost booster



3. Leak Spots

Leak spots showed up as temperature gradations across the area under inspections as shown by the region labelled leak spot 6.

Figure 10. Thrmal image of leak spot region of low cost booster



## SUMMARY

The capabilities of several inspection tools for monitoring the presence of contaminants on critical bonding surfaces have shown to be supplemental in that more than one method is required for complete confidence in the results. NIR spectrometry can provide a useful tool for quantifying a variety of contamination conditions, if calibration models can be developed. The use of thermal imaging also braoadedns the range of surface inspection tools and allows one to probe benearth the surface for defects for a number of structural materials.

## ACKNOWLEDGMENTS

We all express our thanks to Dr. William Arendale, Mr. Charles Hughes and Mr. Wayne Thompson for performing many of the experiments and Ms. Yadilett Garlington for assistance in performing the NIR analyses reported here.. Assistance of the SCAT team at Marshall Space Flight Center in performing many of these experiments is greatly appreciated, particularly Mr. Billy Nerren and DeWitt Burns who managed the Scat Team efforts and Dr. Sam Russell who provided support for the thermal imaging activities.. Also in performing many of the thermal imaging experiments, thanks go to Mr. James Walker and Matt Lansing of UAH. Various phases of this work have been performed under grant NAG-1071, contract NAS8-38609, D.O. 83 and Thiokol Contract #3MR029.