Y-12

OAK RIDGE Y-12 PLANT

LOCKHEED MARTIN

MANAGED BY
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

UCN-13672 (26 8-95)

Y/DZ-2507/R1
Preprint

CONF-9708172--

Diffuse Reflectance FTIR of Stains on Grit Blasted Metals

G. L. Powell
R. L. Hallman, Jr.
R. L. Cox

Oak Ridge Centers for Manufacturing Technologies

RECEIVED

JUL 21 1998

OSTI

Date of Issue: August 9, 1997

Preprint for submission to the proceedings of:

11th International Conference on
Fourier Transform Spectroscopy
Athens, Georgia
August 10-15, 1997

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Prepared by the
Oak Ridge Y-12 Plant
Oak Ridge, Tennessee 37831
managed by
Lockheed Martin Energy Systems, Inc.
for the
U. S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

COPYRIGHT NOTICE

The submitted manuscript has been authored by a contractor of the U.S. Government under contract DE-AC05-84OR21400. Accordingly, the U.S. Government retains a paid-up, nonexclusive, irrevocable, worldwide license to publish or reproduce the published form of this contribution, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, or allow others to do so, for U.S. Government purposes.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Diffuse Reflectance FTIR of Stains on Grit Blasted Metals

G. L. Powell, R. L. Hallman, Jr., and R. L. Cox

Oak Ridge Centers for Manufacturing Technologies, P. O. Box 2009, Oak Ridge, TN 37831-8096*

Diffuse reflectance mid-infrared Fourier transform (DRIFT) spectroscopy has been applied to the detection of oil contamination on grit-blasted metals. The object of this application is to detect and discriminate between silicone and hydrocarbon oil contamination at levels approaching 10 mg m^{-2} . A portable FTIR spectrometer with dedicated diffuse reflectance optics was developed for this purpose. Using translation devices positioned by instructions from the spectrometer operating system, images of macroscopic substrates were produced with millimeter spatial resolution. The pixels that comprise an image are each a full mid-infrared spectrum with excellent signal-to-noise, each determined as individual files and uniquely saved to disc. Reduced spectra amplitudes, based on peak height, area, or other chemometric techniques, mapped as a function of the spatial coordinates of the pixel are used to display the image. This paper demonstrates the application of the technique to the analysis of stains on grit-blasted metals, including the calibration of the method, the inspection of substrates, and the migration of oil contamination.

INTRODUCTION

The detection of oil contamination on grit-blasted metals, the arch-typical surfaces for bonding where there exists bond strength requirements, requires that silicone and hydrocarbon oil contamination be detected and discriminated at levels approaching 10 mg m^{-2} . For this purpose, a portable FTIR spectrometer with dedicated diffuse reflectance optics was developed through a collaboration between Lockheed Martin Energy Systems, Inc., National Aeronautics and Space Administration Marshall Space Flight Center, and Surface Optics Corporation. The instrument is used to inspect the interior walls of solid rocket motor cases after grit-blasting and cleaning, and prior to the application of a primer. This instrument has been coupled with translation devices positioned by instructions from the spectrometer operating system to produce images of macroscopic substrates with millimeter spatial resolution and unlimited substrate size. Preliminary work in this area has been reported.^{1,2} This paper describes the application of general purpose spectral acquisition and data analysis techniques for producing images to the analysis of stains on grit-blasted metals including the calibration of the method, the inspection of substrates, and the migration of oil contamination on surfaces.

EXPERIMENTAL

The diffuse reflectance spectra were obtained using an SOC-400 Surface Inspection Machine/Infrared², a portable FTIR spectrometer with dedicated diffuse reflectance optics and sensitivities to efficient light scattering media approaching 1×10^{-4} absorbance units in one minute using

a deuterated triglycerol sulfate detector and KBr windows and beam splitter. This instrument was coupled with linear translation devices (3 orthogonal 0.3 m travel VELMEX Unislides using an NF90 serial controller) positioned by instructions through serial communications from the MIDAC/GRAMS/32 operating system. The spectrometer was mounted such that the diffuse reflectance optics looked down on the specimen that was moved in the horizontal plane during mapping. The vertical Unislide manually located the plane of the substrate at the focal point of the diffuse reflectance optics.

The software for spectral collection and mapping was an Array Basic program that initially loaded a complete set of operational parameters and mapping grid, constructed a file list for building a GRAMS multifile sorted for optimum image conversion, and produced a text file containing the mapping parameters. The program then collected an individual spectrum with calibration and typically coadded 48 scans. The specimen was advanced the predetermined distance in the +X direction and another spectrum taken with the file name numerically incremented. Thus individual spectra were taken with appropriate calibration and with each spectrum saved as a closed file to protect against loss of data during power outages or other system crashes. This is important since the system typically collects 500 to 10,000 spectra per day, depending on wavenumber resolution and number of coadded scans, and often requires several days to collect a spectral map. The mapping motion is to move along the X direction the predetermined distance at predetermined step lengths, take one step in the Y direction, and then move in the opposite X direction resulting in the same amount of time for each step. At the end of data collection, the software constructed a GRAMS Multifile from the individual files using the file list that sorted the spectra as though all spectra had been collected in the +X direction. A second Array Basic program operated on this GRAMS

*Managed for the U. S. Department of Energy by Lockheed Martin Energy Systems, Inc. under Contract No. DE-AC05-84OR21400.

Multifile to read baseline corrected peak heights and areas as well as to pick values from the spectra and constructed other GRAMS Multifiles representing these reduced spectra as a course in the X direction.

Figure 1 demonstrates this mapping process and also demonstrates the spatial resolution of the SOC 400. A total of 2601 spectra were obtained from a 5-mm by 5-mm area on a grit-blasted gold substrate at 0.1-mm steps. In the center of this area two 0.1-mm diameter mono-filament fishing (Stren) lines formed a cross with the Y direction being parallel to the light entering the SOC 400's barrel ellipse. The amplitude in Fig. 1 is the peak height of the mono-filament line at 1675 cm^{-1} after linear baseline correction at 3800 cm^{-1} and 2000 cm^{-1} , each averaged over 50 cm^{-1} . The zigzag texture in the Y direction is the reversible whiplash ($\sim 0.1\text{-mm}$) of the positioning device.

FIGURE 1. Reduced spectral image of 0.1-mm crossed filaments showing the spatial resolution of the SOC 400 as a GRAMS/32 Multifile.

The white region on each side of Fig. 1 marks the spatial resolution functions for the SOC 400 when crossing a linear boundary. This data, along with the spatial response function previously reported for the Z direction, demonstrates that the SOC 400 has a 2-mm diameter sphere in front of the focal point that is very robust with respect to sensitivity tolerance with respect to the sample position.

The stained grit-blasted steel substrates evaluated in this work consisted of two specimens of D6AC steel 112-mm by 112-mm by 12-mm step-plate contamination specimens prepared by the method of Booth³ and provided by NASA-MSFC. The clean metal substrates were repeatedly masked with a witness foil and sprayed with non-volatile solutes in a volatile solvent to produce contamination steps on these plates that were 19-mm wide with each step more contaminated than the last by 108 mg m^{-2} . The two contaminants provided were a paraffin wax, chosen because it deposited as a solid and did not migrate, as well as being a very simple hydrocarbon, and (2) CRC

silicone, because it was a simple silicone and deposited as a liquid that wet the substrate surface. A grit-blasted gold specimen 75-mm by 75-mm by 0.5-mm was also prepared using a technique previously described¹. This gold specimen was contaminated by placing a drop of Dow Corning DC-200 Silicone Oil (5cs.) at the center of this specimen using a microliter syringe while the specimen was being weighed with 0.01 mg resolution. The 0.70 mg of silicone oil spread rapidly and spectral mapping was begun 4 hrs. later.

The spectra were obtained at 16 cm^{-1} resolution using 48 coadded scans determined in absorbance units (a. u.). The steel specimens were mapped at increments of 2.5-mm resulting in a 44 X 44 pixel image. The gold specimens were mapped at 2.0-mm increments resulting in a 48 X 48 pixel image. The spectral reduction routine executed a linear baseline correction based on the average values over the range of 2700 cm^{-1} to 2725 cm^{-1} and 3150 cm^{-1} to 3175 cm^{-1} , constructed reduced spectral maps based on the peak height for the aliphatic C-H bands near 2920 cm^{-1} and 2960 cm^{-1} (aliphatic hydrocarbons and silicones), and aromatic C-H bands near 3020 cm^{-1} (polystyrene and other plastics). Reduced spectral maps were also produced using a linear baseline correction of the average values over the range of 2025 cm^{-1} to 2050 cm^{-1} and 3550 cm^{-1} to 3775 cm^{-1} , using the average value over 3375 cm^{-1} to 3400 cm^{-1} to detect O-H bands (fingerprints), and the peak height near 1260 cm^{-1} relative to the adjacent minima to detect the Si-C band (silicones). These peak height values were also stored as text in a table with the mapping coordinates and time.

RESULTS AND DISCUSSION

Figure 2 compares the first three contamination steps on a paraffin contaminated D6AC steel step-plate in terms of the main aliphatic and aromatic C-H bands. That the two bands represented either the paraffin or polystyrene was confirmed by inspection of the full individual infrared spectra. The "clean" step in the absence of polystyrene residue or particles, had an average value of $0.0002\text{ a. u.} \pm 0.0004\text{ a. u.}$. This positive (greater than zero) bias results from comparing a maximum value for a peak height with an average value for the baseline and effectively measures the half width of the baseline noise. The first contamination step at 108 mg m^{-2} was at the $0.017\text{ a. u.} \pm 0.005\text{ a. u.}$ level, where the variability was probably due to real contamination variations due to the contamination deposited as "splats" of millimeter or less size visible to the unaided eye. Analysis of a line map across the steps indicated a linear calibration factor of $3.6\text{ g m}^{-2}\text{ a.u.}^{-1}$ or detection limits below 2 mg m^{-2} ($\sim 2\text{ nm}$ film thickness). Previously reported work using safflower oil indicated a calibration factor twice that large (i.e., half the sensitivity), probably because the calibration is peak height determined and the safflower oil C-H bands are much less sharp. A calibration based on band area would probably bring the

FIGURE 2. Reduced spectral maps (as GRAMS/32 hidden line 3-D displays) of a D6AC step-plate based on the main aliphatic (left) and aromatic (right) C-H bands. The step-plate was clamped at the corners with polystyrene contacts and some polystyrene dust migrated onto the rest of the step-plate since there is a one-to-one correspondence between the spikes in the aliphatic and aromatic C-H spectral maps. The high peak at the far end of the 0.06 a. u. step was due to a fingerprint.

two calibration factors into better agreement. The safflower oil spread as a liquid, but oxidatively cured to a solid film at $\sim 1.7 \text{ g m}^{-2}$.

Figure 3 shows a step-plate map of the Si-C band on CRC silicone step-plate contamination standard. Note that, like the safflower oil, the silicone oil migrated, but unlike the safflower oil, it was not chemically fixed. The silicone oil not only migrated to erase the steps, but migrated off the front surface of the plate and also concentrated in the polystyrene at the edges. Thus, the silicone contaminated

FIGURE 3. Reduced spectral map of a CRC silicone step-plate based on the peak height Si-C band on the silicone. The Y abscissa has been trimmed on each end so that the polystyrene effects at the corners do not distract from the observation of the silicone behavior. The spikes along the Y direction at the extreme X values represent silicone absorbed on the polystyrene.

step-plate was of little use in establishing quantitative limits and calibration factors. On the other hand the silicone did not migrate onto the first (clean) step, but rather migrated only where the spray process wet the substrate. The clean step region had an average peak height value of $0.0001 \text{ a. u.} \pm 0.0002 \text{ a. u.}$

Finding a contaminant that will wet the substrate, be applicable at levels near 100 mg m^{-2} , and be fixed sufficiently well to yield quantitative information led back to the oil drop spreading experiment¹. Gold was used because it was capable of achieving constant weight at the 0.01 mg level sufficiently long to weigh a microliter of oil. The object was to allow the oil to migrate, but as it migrated, to map it over a region that included all the oil stain so that integration over the spectral map of the spot would yield a calibration factor. Figure 4 shows spectral maps taken of a DC 200 Silicone (5 cs.) stain taken over several days. Integration of these maps for 0.70 mg of silicone yielded calibration factors of 6.4 g m^{-2} for the highest concentration (first day after application) and 10.4 g m^{-2} for the map taken on the third day, and 12.2 g m^{-2} for the map taken on the sixth day. On the sixth day the stain was no longer visible to the unaided eye.

CONCLUSIONS

Diffuse reflectance mid-infrared Fourier transform (DRIFT) spectroscopy is capable of qualitatively and quantitatively detecting oil contamination on grit-blasted metals at levels below 10 mg m^{-2} . DRIFT measurements also give considerable insight into the processes associated with oils on metals, many of which are very complex. Portable DRIFT spectrometers with dedicated diffuse reflectance optics are capable of this task and of extending

the task to manufacturing applications. Spatial mapping enhances this capability by using visual contrast to optimize reference spectra and decisions related to chemometric analysis.

REFERENCES

1. G. L. Powell, T. E. Barber, M. Marrero-Rivera, D. M. Williams, N. R. Smyrl, and J. T. Neu, *Mikrochim. Acta [Suppl.]* 14, 655 (1997).
2. G. L. Powell, T. E. Barber, and J. T. Neu, "Diffuse Reflectance Mid-Infrared Spectroscopy as a Tool for the Identification of Surface Contamination on Sandblasted Metals," Aerospace Environmental Technology Conference, NASA Conference Publication, A. F. Whitaker, ed., MSFC, Alabama, (1996) in press.
3. R. E. Boothe, "Standardization of Surface Contamination Analysis Systems," Aerospace Environmental Technology Conference, NASA Conference Publication 3298, A. F. Whitaker, ed., MFSC, Alabama, 517-524 (1995).

FIGURE 4. Images of the spread of a 0.7 mg silicone oil drop applied to a clean sandblasted gold surface based on the 1265 cm^{-1} silicone (Si-C) absorption band. Elapsed time: Upper map-first day, Middle map-third day, Lower map-sixth day.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the staff of Surface Optics Corporation, San Diego, CA for their diligence in developing this DRIFT spectrometer and to B. H. Nerren of NASA, MSFC, AL for his efforts to develop this technology and for providing the D6AC step-plate calibration specimens.

Distribution

International Symposium on Fourier Transform Spectroscopy University of Georgia

Dr. J. A. de Haseth (2)

Oak Ridge National Laboratory

R. C. Cox

Oak Ridge Y-12 Plant

R. L. Hallman, Jr.

G. L. Powell

P. E. McKenzie/W. E. Smith

Y-12 Central Files / DOE-OSTI (3)