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SURFACE INSPECTION USING FTIR SPECTROSCOPY

G. L. Powell
Oak Ridge Y-12 Plant,* Martin Marietta Energy Systems, Inc.
Oak Ridge, Tennessee 37831-8096

N. R. Smyrl, D. M. Williams, and H. M. Meyers, III
Oak Ridge Y-12 Plant,* Martin Marietta Energy Systems, Inc.
Oak Ridge, Tennessee 37831

T. E. Barber and M. Marrero-Rivera
Oak Ridge Institute for Science and Education
Oak Ridge, Tennessee 37831

ABSTRACT

The use of reflectance Fourier transform infrared (FTIR) spectroscopy as a tool for surface inspection is described. Laboratory instruments and portable instruments can support remote sensing probes that can map chemical contaminants on surfaces with detection limits under the best of conditions in the sub-nanometer range, i.e.. near absolute cleanliness, excellent performance in the sub-micrometer range, and useful performance for films tens of microns thick. Examples of discovering and quantifying contamination such as mineral oils and greases, vegetable oils, and silicone oils on aluminum foil, galvanized sheet steel, smooth aluminum tubing, and sandblasted 7075 aluminum alloy and D6AC steel. The ability to map in time and space the distribution of oil stains on metals is demonstrated. Techniques associated with quantitatively applying oils to metals, subsequently verifying the application, and non-linear relationships between reflectance and the quantity oil are described.

INTRODUCTION

Reflectance Fourier transform infrared (FTIR) spectroscopes are powerful techniques for materials characterization and surface analysis provided the spectrometer can address the appropriate location on a specimen under conditions for which the resulting measurement is meaningful(1). The spectra obtained over the energy range of 400 to 5000 cm^{-1} (wavelength range of 2 to 25 μm) contains information that directly correlates qualitatively and quantitatively to chemical functional groups, and that can be read like a book by most chemist. Reflectance techniques include external or specular, internal, and diffuse reflection. In collaboration with Harrick Scientific, Inc., a system of remote sampling terminals individually dedicated to each of these reflectance techniques, along with the means for multiplexing these terminals, was developed for use with FTIR spectrometers to obtain spectra from the surfaces of large flat or convex objects in ambient air or in environmental chambers with sufficient ease that meaningful statistical comparisons of spectra obtained from many locations on an object or from many objects can be made (2). Capabilities for gas analysis and emission analysis were also integrated into the system. External reflectance is done at 75° with an externally operated KRS-5 wire-grid polarizer. Internal reflectance uses a 45° single-reflection ZnSe element with p-polarized light, and diffuse reflection uses a barrel ellipse. The system, attached to a BIO-RAD FTS-60 FTIR spectrometer, also includes the capability to perform the above functions in controlled environments, i.e., cells and glove boxes, facilities for mapping surfaces, i.e., obtaining spectra from measured coordinates on a specimen, a 1-m path high-throughput gas-cell, and a spare port. The key design features of these sensors are maximum light recovery from the specimen, maximum signal-to-noise (sensitivity) for a given spectrum, no limitation on specimen size, high specimen throughput rate, and convenience. A portable surface inspection

instrument, consisting of a barrel ellipse diffuse reflectance sampling terminal attached to a MIDAC Illuminator FTIR spectrometer configured for 12-Vdc operation and minimum size (200 mm by 200 mm by 600 mm) and weight (13 kg) has also been developed. Internal reflectance spectroscopy is being heavily exploited by the chemical industry for process monitoring of organic liquids, requires intimate contact with the specimen, and has a strong potential for bulk and surface analysis of soft, organic materials. External and diffuse reflectance are methods for analyzing the surfaces of solids and their potential in process monitoring and inspection is just beginning to be recognized. This paper describes the application of external and diffuse reflectance optics to practical inspection processes on metals of practical importance. Qualitative and quantitative determination of surface contamination is demonstrated and discussed. Criteria are presented that are consistent with current state-of-the-art FTIR spectrometry for a practical, hand-held FTIR surface inspection machine and the technical support necessary for its implementation.

EXTERNAL REFLECTANCE

External reflectance is simply the reflection of light by a mirror in which light passes through films on the mirror surface. Grazing angle 75° reflectance from relatively flat metal objects is the most sensitive method of surface analysis, with p-polarized light (light oscillating normal to the sample surface) being absorbed by surface species and s-polarized light (light oscillating in the plane of the surface) not being absorbed by surface species. Specular reflectance is normally considered to be a method for analyzing mirror finishes, but in the mid-infrared region (λ = ~10 μm), quite a number of very practical surfaces pass for mirrors. High-quality, front-surface, gold mirrors are used as the reference spectra, requiring a separate reference for each polarization. These mirrors are prepared by degreasing with a household spray cleaners containing detergents and 2-butoxyethanol grease cutters followed by a deionized water rinse, a 1-ks soak in concentrated sulfuric acid, another thorough deionized water rinse, and a rapid drying in a nitrogen stream. Calibration is done using aluminum foil, which is weighed, wiped uniformly with an oil, thoroughly wiped with dry tissue to remove all excess oil, and reweighed. Such treatment leaves behind typically 150 mg m^{-2} (~ 150 nm film, 14 mg ft^{-2}) of residue, which is easily weighed on foil specimens of 0.1 m^2 area and yields spectra of good quality. Many spectra (typically 12) can be obtained from one calibration specimen to give reasonable statistics to the calibration measurement. Calibrations were performed using DC-200 (5 cps) silicone (dimethoxy silane), corn oil, (polyunsaturated triglyceride) and a commercial light mineral oil (aliphatic hydrocarbon). Table 1 shows the results of these calibrations.

Table 1. Calibration values for oil stains on aluminum foil.

Oil	Band	Calibration Factors	Standard Deviation
DC-200 5 cps	2965 cm^{-1}	2.694 g m^{-2} (a.u.)$^{-1}$	2960 nm (a.u.)$^{-1}$ 13%
DC-200 5 cps	1265 cm^{-1}	1.536 g m^{-2} (a.u.)$^{-1}$	1688 nm (a.u.)$^{-1}$ 17%
Mineral Oil	2925 cm^{-1}	1.491 g m^{-2} (a.u.)$^{-1}$	1373 nm (a.u.)$^{-1}$ 13%
Corn Oil	2925 cm^{-1}	1.324 g m^{-2} (a.u.)$^{-1}$	1218 nm (a.u.)$^{-1}$ 19%
Corn Oil	1750 cm^{-1}	1.490 g m^{-2} (a.u.)$^{-1}$	1371 nm (a.u.)$^{-1}$ 27%

The noise level of the system is typically 0.0002 a.u. near 2900 cm^{-1}, so that the presence of hydrocarbons at the nanometer film thickness level (1 mg m^{-2}) can be detected with certainty. Aluminum foil, as taken from the roll, shows no detectable hydrocarbon bands at the 0.0002 a.u. level. At this noise level, the sulfuric acid cleaning process appears to be equivalent to sputter cleaning of the gold mirrors immediately before obtaining the reference spectra. Angle-resolved electron spectroscopy for chemical analysis (ESCA) generally supports the observations that the 1-nm hydrocarbon film, as determined by the preceding calibration, left behind by the cleaning described above is equivalent to 1 nm of carbon residue

supporting the general assumption that the calibration can be linearly extrapolated to lower concentrations.

Galvanized sheet steel specimens (0.3 m by 0.3 m) were exposed to a variety of greases, paints, and oils, was hammered, and then a 0.1 m region near the center of each specimen was cleaned using a carbon dioxide pellet blaster. They were evaluated for residual contamination using 75° specular reflectance mid-infrared spectroscopy. Figure 1 shows the p-, s-, and p- minus s-polarization spectra for this galvanized sheet metal in new condition, degreased with a spray cleaner, and thoroughly rinsed with water. The absorption bands for zinc oxide (1100 cm⁻¹) and sorbed water (1600 cm⁻¹ and 3400 cm⁻¹) are obvious. A trace of water vapor (near 1600 cm⁻¹ and 3800 cm⁻¹) can be seen in the p- and s-polarization spectra. Since this water vapor is in the spectrometer and not on the specimen surface, it occurs equally in both spectra and disappears in the difference spectra.
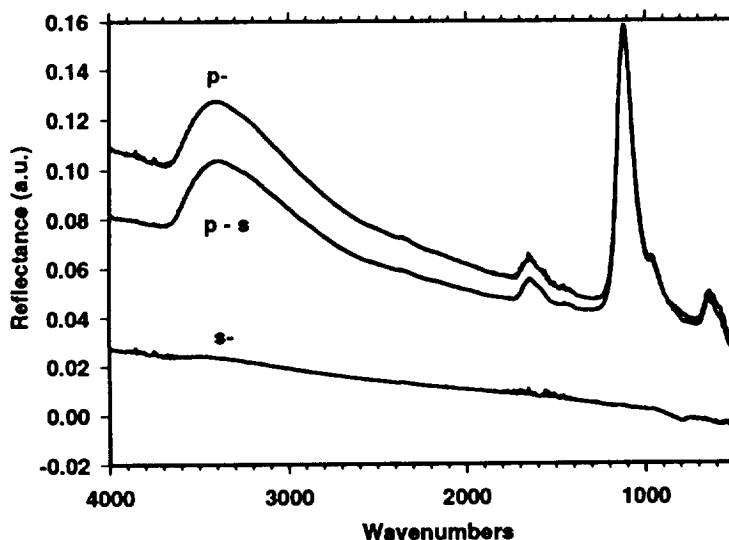

Figure 1. The polarization dependent, 75° specular reflectance spectra for galvanized steel sheet referenced to a gold mirror.
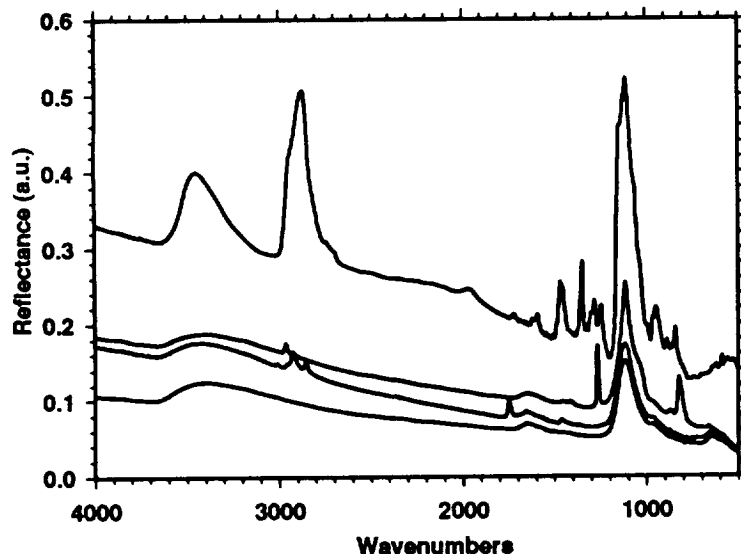

Figure 2. Typical p-polarized 75° specular reflectance spectra for contamination on galvanized steel sheet referenced a cleaned gold mirror. Bottom-to-top: cleaned, corn oil stain, silicone grease, orange felt-tip pen mark.

Figure 2 shows typical p-polarization spectra of galvanized sheet metal having ink, silicone, and corn oil stains with the as-cleaned metal. The carbon dioxide pellet blasting cleaned these specimens to an effective hydrocarbon film of 3 to 5 mg m⁻², with the exception of two specimens that had a silicone-based, high-temperature lubricant that indicated 8 and 18 mg m⁻² as silicone. On the peripheral region of these specimens, where the carbon dioxide blaster did not clean, silicone levels as high 118 mg m⁻² were detected. The hammered surfaces were not as reflective as the original metal and resulted in a decrease in the signal to noise that translated into a lower level of detection of 1 mg m⁻².

Another study involved the analysis of a 25-mm-diam by 1.45-m-long aluminum tube that was suspected of being contaminated with some unknown film. The axis of the rod was aligned with the direction of the infrared beam, and the resulting spectra identified the contaminant

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as a silicone oil. The rod was then repositioned such that many spectra were taken along the surface of the rod to map the contamination along the rod. Figure 3 compares a spectrum from the rod to spectra of Dow-Corning silicone vacuum grease (high-viscosity), DC-200 silicone temperature bath fluid (low-viscosity), and fused silica (solid, spectra 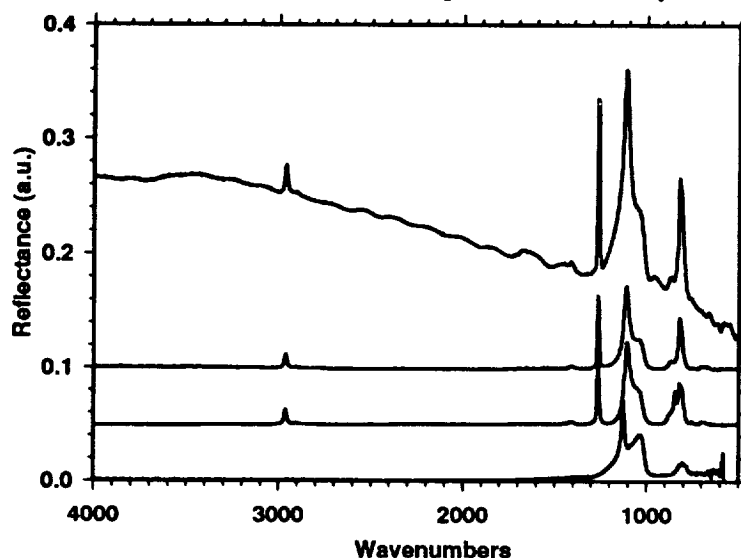determined by internal reflectance). Figure 3 demonstrates the simple relationship between chemical functional groups and the infrared absorption spectra. The infrared spectra of the silicone oils are very similar to fused silica ($O-Si-O$ polymer) with additional bands corresponding to CH_3 (2965 cm^{-1}) and to $Si-C$ bonds (1265 cm^{-1}). Subtle differences around the 800 cm^{-1} distinguish the grease from the light oil. Based on 19 measurements along the rod, the absorbance from the 2965 cm^{-1} band was 0.0182 a.u. (49 mg m^{-2}, σ=0.0048 a.u.) and the 1265 cm^{-1} band was 0.0499 a.u. (77 mg m^{-2}, σ=0.0184 a.u.) with no values observed to be less than 29 mg m^{-2}.

Figure 3. A comparison of external reflectance spectra from an aluminum rod with silicone greases on gold mirrors. Bottom-to-top: fused silica (by internal reflectance), DC-200 (5 cs), vacuum grease, aluminum tube.

Ratios of the methyl band (2965 cm^{-1}) to the Si-C band (1265 cm^{-1}) indicates that the silicone is not DC-200 (5 cps) and this is supported by the lack of structure near 850 cm^{-1}. Thus, the conclusion that the silicone is similar to Dow Corning high vacuum grease. Others studies have been carried out on aluminum and aluminum alloys with good results. For these systems, the reflectance spectra indicate not only the presence of contaminants, but also bands from surface oxides and other reflective losses, perhaps from surface texture, that seem to be strongly dependent on the cleaning agent.

DIFFUSE REFLECTANCE

In the strictest sense, diffuse reflectance refers to light which is simultaneously absorbed and scattered in a generally transparent medium. Paper is an example of a diffuse scatterer. The absorbance relationship used for external reflectance of thin films discussed above is simply first-order absorption of light in a film as a function of concentration and thickness of the film leading to a logarithmic relationship between light lost and concentration/film thickness. For a true diffuse reflector, differential equations for first order light scattering and first order adsorption are solved simultaneously to yield the Kubelka-Munk relationship. The optics required for diffuse reflectance is such that only light diffusely scattered is directed to the detector and specularly reflected light is rejected from the detector, a process that is optimized by the barrel ellipse. For the analysis of textured metal surfaces, for which sandblasted metal surfaces and graphite cloth are two common examples, diffuse reflectance optics are used to collect light that is specularly reflected in random directions. For the examples to follow, the light scattering process will be specular reflectance from randomly oriented micromirrors for which diffuse reflectance optics works very well. This approach has a significant loss of sensitivity relative to grazing angle external reflectance because the effective light path, determined by the angle of incidence and of reflection, through the film is shorter by a factor of 3 or 4, and because p- and s-polarizations cannot be separated. The s-polarized light contributes to the total light intensity, but not to reflective losses, lowering the sensitivity by a factor of 2. For cleanliness, more sensitivity is always desirable, however,

the 10,000:1 or greater signal-to-noise is retained and losses in the high sensitivity, low detection limit are converted to good performance for thick films. For example the resin (tens of microns thick) on the outer surface of most graphite-resin composites (graphite cloth) is ideally suited for cure and heat damage inspection using diffuse reflectance optics. The barrel ellipse remote sensor is an imminently practical way to passively look down on a host of surfaces, without demanding too much knowledge of either the surface or the light scattering processes, to reveal a rich world of chemistry. As with most aspects of analytical chemistry, there remains the task of providing standards of known composition with which to calibrate the method.

Marshal Space Flight Center provided several 6 by 6-in. plates of sandblasted 7075 aluminum alloy and D6AC steel specimens that had been sprayed with grease contaminants (Conoco HD-2 grease, Kaydol oil, and CRC silicone grease) dissolved in a volatile solvent. Aluminum foil masks were used to form 1-in. wide concentration steps on these plates and the masks were subsequently weighed to determine the quantity of grease deposited. Contamination levels varied from a clean first step to levels as high as ~35 mg ft^{-2}. These plates were analyzed using a barrel ellipse mapping station supported by a BIO-RAD FTS-60 FTIR spectrometer by obtaining spectra at 0.1-in. intervals along a line normal to the steps near the center of the plate. Spectra were taken using sandblasted gold as a reference, and once verified to be as clean as the gold the reference was changed to the clean step on the plate. Each spectrum consisted of 256 coadded scans at 16 cm^{-1} resolution and 4 times zero-filling.

The results for the 7075 aluminum alloy in terms of the most sensitive peak heights for these contaminates are shown in Figure 4. The HD-2 grease was present on the plate as steps, but the lighter Kaydol oil at all but the lowest concentrations migrated to erase the steps. For Kaydol, the 5 to 6 in. step was not the maximum contamination level because this oil migrated off the edge of the plate. The higher
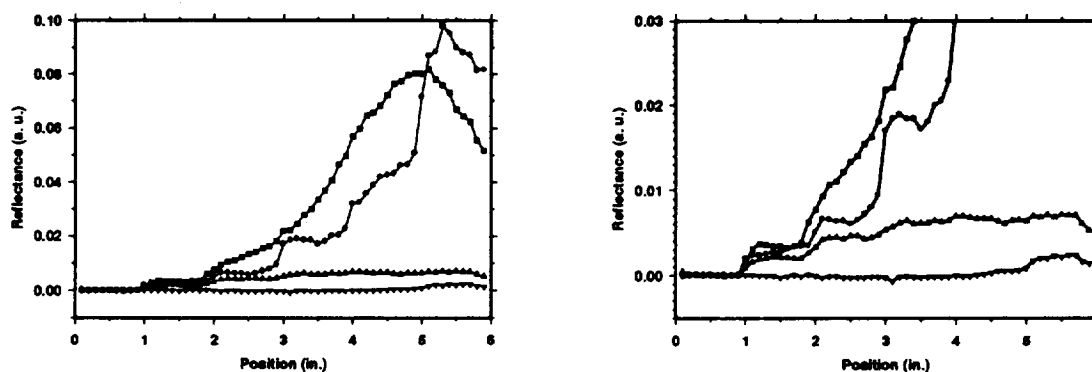

Figure 4. Absorbance measurements on 7075 aluminum alloy based on the 2925 cm^{-1} band for HD-2 and Kaydol and 1265 cm^{-1} for the silicone. Squares - Kaydol, Circles - HD-2, Up-triangles - silicone, Down triangles - 3010 cm^{-1} baseline.

dose silicone levels appear to be in distinguishable. The D6AC steel plates responded similarly, but with less sensitivity. Figure 5 gives the average step level and standard deviations for the data for both types of plates using the log-linear format because the sensitivity appears to decrease superlinearly with decreasing dose. Spectral manipulation techniques in FTIR spectroscopy are very powerful tools that allow one to average all the spectra taken in a region to improve the signal-to-noise and thus the sensitivity for detecting surface contamination. Figure 6 shows the average of spectrum for each step for the 7075 aluminum alloy plate and similar data for silicone on D6AC steel, the plate with the lowest detectability limits on the basis of both dose and substrate. For the six plates, the only step on which the presence of the contaminant could not be detected and distinguished from the other two contaminants was the lowest step (1.5 mg ft^{-2} CRC silicone) on the D6AC steel plate. The spectra of HD-2 grease and the Kaydol are very similar, i.e., both are aliphatic hydrocarbons with the dominant C-H stretching band at 2925 cm^{-1} and bending modes near 1400 cm^{-1}, with the exception that HD-2 grease contains a carbonate additive to
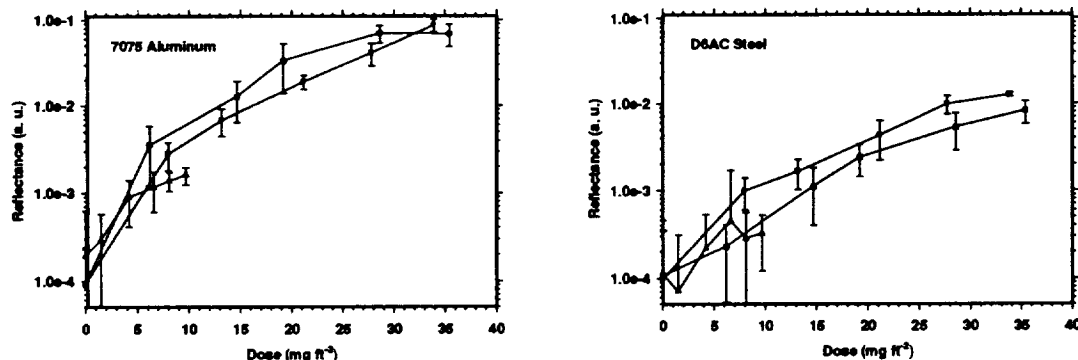
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Figure 5. Average absorbance measurements as a function of dose on 7075 aluminum alloy (left) and D6AC steel (right) based on the 2925 cm⁻¹ band for HD-2 and Kaydol and 1265 cm⁻¹ band for the silicone. Squares - Kaydol, Circles - HD-2, Up-triangles - silicone.
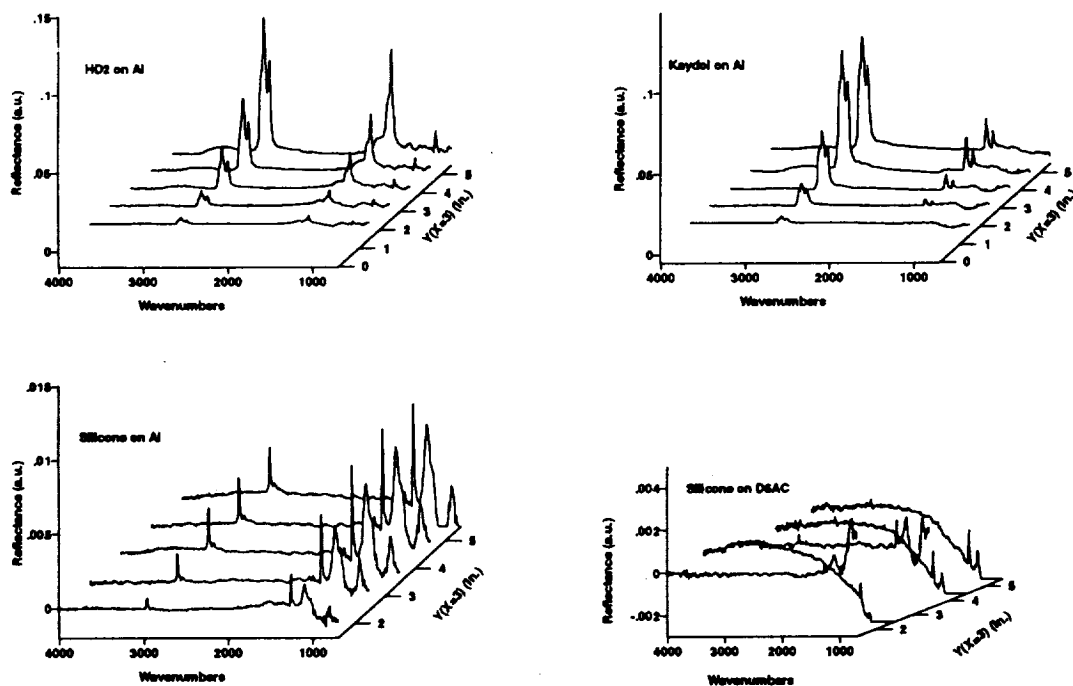

Figure 6. Reflectance spectra from 7075 aluminum alloy and D6AC steel. Each spectrum is located at its average step position and each spectrum is the average ten spectra taken on that step.

control pH that obscures the C-H bending modes and makes for a clear distinction between the two contaminants. The silicone spectra were described in the previous section of this paper.

The behavior of various common contaminants on sandblasted aluminum plates (3-in. by 3-in. by 0.04-in.) have been further explored using a mechanically rastered air brush to apply the contaminant as a dilute solution in acetone through a mask that allows a 0.3-in. diam. spot to be contaminated to relatively high levels of ~1 g ft⁻². The dose was controlled by the composition and quantity of the acetone solution being sprayed. Mapping techniques were then applied to measure a contamination profile across the specimen. These profiles were repeated at time intervals to monitor the spread of the oil across the plate. Once the spread of the oil had stabilized, the spot could be mapped in

two dimensions. One major difficulty was moisture sorption on the plate that produced a weight gain comparable to the applied oil. Another difficulty was that many oils spread very fast. The early time profiles were measured using the Harrick/MIDAC Inspector located near the hood where the spraying was carried out because of its superior data collection speed. Once the stain stabilized, the operation was transferred to the barrel ellipse mapping station supported by a BIO-RAD FTS-60 FTIR spectrometer because of better sensitivity near 3000 cm⁻¹. Figure 7 shows the short term response of the 2925 cm⁻¹ band for the mineral oil as it spread over the aluminum plate and diminished in intensity. Weight gain measurements indicated that a maximum of 1.5 mg of oil had been deposited on the plate. As shown in Figure 8, this spread continued at a diminishing rate for several weeks forming a stain with an abrupt
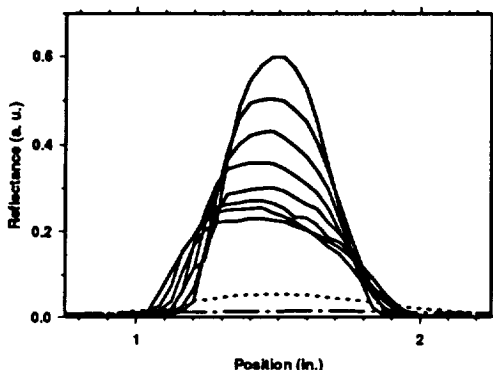

Figure 7. The short term spread of light mineral oil over sandblasted aluminum alloy based on the reflectance response of the 2925 cm⁻¹ band. Solid curves taken at 0.04-in. steps at 30-min. intervals starting 10-min. after spraying. Dotted curve - 24 hr. after spraying. Dot - dash curve - 8 d. after spraying.
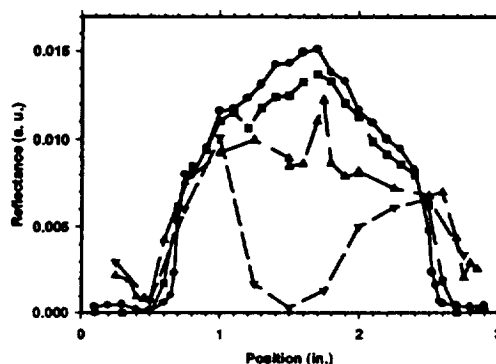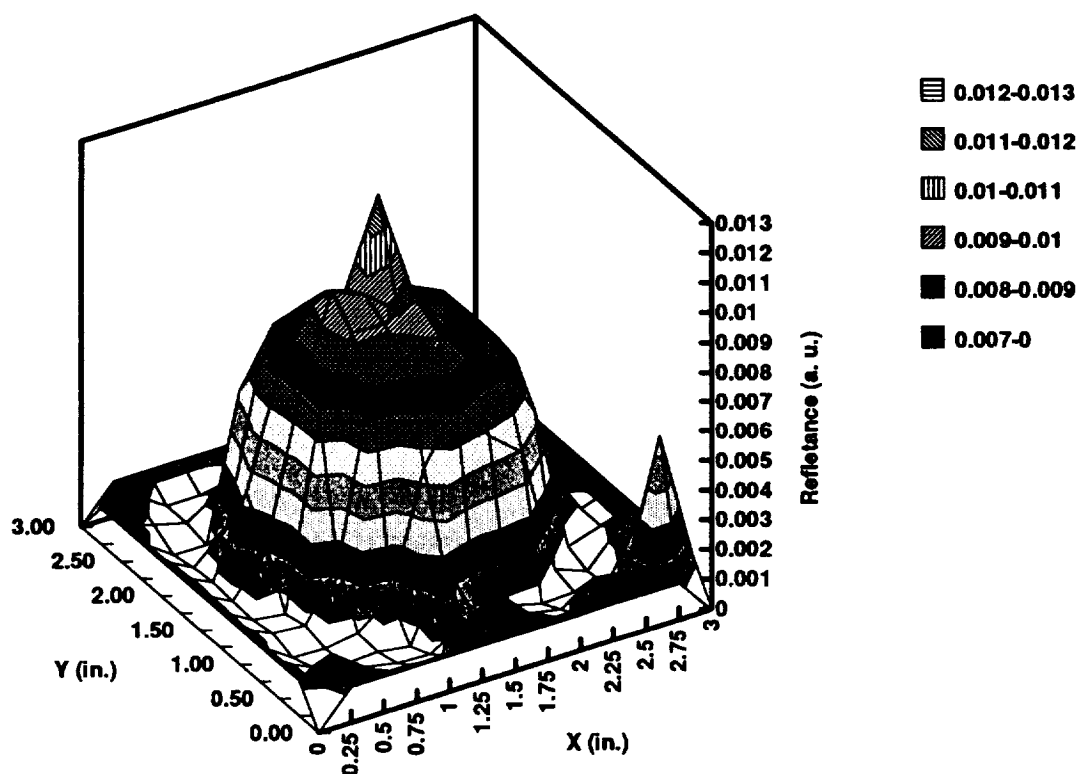
Figure 8. The long term spread of light mineral oil over sandblasted aluminum alloy based on the reflectance response of the 2925 cm⁻¹ band. Circles - 8 d. after spraying, Squares - 15 d. after spraying, up-triangles - 6 wk. after spraying, down triangle - 7 wk. after spraying and spot extraction of the oil with freon.

edge. After 6 weeks, the stain was mapped in both dimensions of the surface and the resulting definition of the stain is given in Figure 9. In a further effort to quantify the amount of stain on the aluminum plate, an extraction method was devised to remove the oil from a well defined area of the plate. A mini-conflat straight union, consisting of a 3-in. long by 0.75-in. diam. tube, was closed at one end with a blank flange and copper gasket. The opposite end was clamped to the oil stained plate with a viton O-ring sealing the assembly that was filled with freon. The system was shaken and the freon was recovered. The plate was remapped yielding the lower curve in Figure 8 and the entire process was repeated. The freon from the second extraction was analyzed by transmission infrared absorption spectroscopy against a calibration curve developed from the original mineral oil and indicated that 50 µg of oil had been extracted. This corresponded to a net change of 0.00226 a.u. in² or a calibration factor of 22 mg a.u.⁻¹ in⁻². The stain described in Figure 9 has a total volume of 0.0245 a.u. in² that indicates a mineral oil content of 0.54 mg spread over 0.02 ft² indicating a contamination level in the stained region of 26 mg ft⁻² giving this aluminum plate sample a calibration factor similar to that observed for the D6AC steel. This is approximately one-third of the weight gain during the original spraying operation that may have overestimated the oil quantity by as much as a factor of two due to moisture absorption. There is also the possibility that some of the oil may have evaporated. Spray experiments with docosene-1 $(CH_3(CH_2)_{18}CH_3)$ indicates that this hydrocarbon does not spread from where it is deposited, octadecene-1 $(CH_3(CH_2)_{16}CH_3)$ spreads in a manner similar to the light mineral oil used for this study, and hexadecene-1 $(CH_3(CH_2)_{14}CH_3)$ evaporates. The large decrease in the reflectance values during the spreading of the oil is generally consistent with the increase in area of the stain, i.e., and increase by approximately a factor of 40.

0.012-0.013
0.011-0.012
0.01-0.011
0.009-0.01
0.008-0.009
0.007-0

0.013
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0.004
0.003
0.002
0.001
0

Reflectance (a. u.)

3.00
2.50
2.00
1.50
1.00
0.50
0.00
Y (in.)

0 0.25 0.5 0.75 1 1.25 1.5 1.75 2 2.25 2.5 2.75 3
X (in.)

DISCUSSION

Reflectance mid-infrared Fourier transform spectroscopy is a very powerful tool for determining the surface cleanliness of metals, particularly when remote sensing hardware is used so that there is minimum perturbation of the materials being analyzed and large numbers of analyses can be made. The large sample capability is critical both for mapping capability and for the passive nature of the analysis. Obtaining a cleanliness determination from metal parts is demanding, but not as demanding having the parts unaffected by the experience. External reflection at grazing incidence with p-polarized light on smooth metal surfaces yields the best detection limits. Diffuse reflectance optics offers an extremely practical approach to a host of real surfaces that are neither smooth or well understood. Computerized data processing of FTIR spectroscopic data has been around for a quarter century. Much progress has been made in the last two years in developing software to match the great and growing potential of microcomputers, particularly in the areas of speed and decreasing size and cost. A practical portable FTIR surface analyzer has been fielded. Smaller, more rugged, and more sensitive instruments operating at near real time speeds will soon be available. The potential for imparting intelligence to these inspection machines is tremendous.

The surfaces to be analyzed, however, are infinitely variable and diverse with complex processes related to the fundamental manner with which particular contaminants interact with particular surfaces in relation to how light interacts with a particular surface and a particular contaminant. Apparent nonlinear calibration curves, and migration and fractionation of the contaminant over time are possible explanations

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for some of the above observations. Experimental technique is very demanding for the preparation of calibration standards, reference materials, and corroboration of calibration standards. But these techniques are no more demanding than the handling of very clean materials before, during, and after the analysis. Though these machines may be trained to recognize contaminants, mixtures of contaminants, and give forth a quantitative number, at the 10 mg ft^{-2} contamination level the distinction between the spectra of an aliphatic hydrocarbon, a triglyceride, and a silicone is as plain as the nose on your face.

ACKNOWLEDGMENTS

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