AN EVALUATION OF REFLECTANCE-ABSORPTION INFRA RED SPECTROSCOPY FOR IN SITU INVESTIGATION OF ORGANIC COATINGS ON CORRODED METALS

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Introduction

Reflection-Absorption Infrared Spectroscopy (RAIRS) along with Attenuated Total Reflectance Spectroscopy (ATR) has been widely used as characterization and monitoring tools that can be used to evaluate the effectiveness of coatings on metal(2). Increasingly, these techniques are being applied to test coatings for cultural property metals of, such as outdoor bronze monuments (2). The advantage is that thin films of a few nanometers thickness can carry out an in-depth characterization of the bulk coating to the metal surface analyzing changes in the chemical bonds.

This work evaluates the application of RAIRS to investigate Paraloid®-B-72 and Poligen® ES 91009® coatings of variable thickness on corroded iron and copper alloy coupons under the auspices of the EC project PREMET. Furthermore, it highlights a simple FTIR system which, Spectrum GX DS (2), can be adapted to carry out reflectance measurements coupling with a reflectance accessory (IR, 2.5 μm band integrated on a relative low cost. Such apparatus makes it attractive for conservation research, since most Conservation facilities, such as ours have a simple FTIR system.

For an accurate interpretation of the spectra throughout the coating layers, the following properties are significant: thickness and uniformity of the coating, smoothness of the surface, and the nature of the metal surface. In conservation research, the effectiveness of coatings often needs to be evaluated on corroded metals which are far from being considered as ideal cases.

The Reflection-Absorption FTIR Technique

IR beam geometry during the reflectance-absorption technique

In a typical reflection-absorption FTIR experiment the infra red beam impinges on the coating at a specific angle of incidence. Part of the beam is reflected and at the same moment, this beam is reflected on the coating surface (specular reflection). Another part is transmitted inside the film, accordingly reflects on the metal surface, re-transmits and finally, exits the metal surface. This is the absorption part of the RAIRS technique, recording the average information throughout the beam path. Both beam paths are detected within the different experiment: different physical information is recorded in each case, along with the chemical information of the involved materials.

Beam polarization and reflection

Polarization of the electrical IR component can be either parallel (p-polarized) or perpendicular (s-polarized) to the plane normal of incidence (transverse electric field).

Reflectance spectroscopy: Thin or thick films?

This question illustrates the geometrical aspects of a coating, basically controlled by the film application technique. The effectiveness of metal protection, as well as the chemical information acquired spectroscopically is dependent on the film thickness, as the contribution spectral features of the coating surface and the metal surface. In general, the behavior of polymeric coating chains and their functional groups with the metal surface is dependent on the film thickness, as this controls reactive species through the small path of a few nanometers, as it records orientational phenomena of polymeric chains towards the metal surface. Orientation is recorded on thicker films, as chains tend to be more "random", away from the metal surface.

Physical information can be dominant in IR reflectance in thick films, where anomalous dispersion of refractive index is important. This results in numerous distortions of the recorded chemical peaks, depending on the optical properties of the investigated medium (i.e. metal, coating). The film thickness, surface smoothness, IR beam polarization and the angle of incidence. Predicting these distortions can lead to a spectrum with "pure" chemical information.

Paraloid®-B-72 Transmittance and RAIR spectra

Transmittance spectra

The carbonyl band and the methyl/methylene stretch are marked by anisotropic alternation of organic coatings.

Reliable absorbance measurements of bands v(C=O) and v(CH2) of Paraloid B 872 can be taken for films up to 8-9 μm whereas linearizing in absorbance vs. thickness is obeyed.

Kramers-Kronig Transformation

Application of the Kramers-Kronig algorithm transforms the distorted spectral line (1, 2) to an absorption spectrum of the film (1, 4).

Poligen®-ES91009 RAIR spectra

Poligen® ES91009 is sold commercially by BASF and reported to be a "water emulsion prepared from polyethylene wax". FTIR spectra actually show hydration-like structure as well as carbonyl and functional groups. RAIRS spectra of a film cast from water emulsion on a smooth surface (S Ilawer, metal, bronze, iron) both show carbonyl ion functionality depending upon the water content of the film.

Poligen®-ES91009 on bronze and iron

Significant changes were observed in reflectance mode of Poligen films. Most notably the sharp decrease of the original 1535 cm\(^{-1}\) carbonylate band, the increase of the 1700 cm\(^{-1}\) carbonyl acid and the formation of a new band at 1605 cm\(^{-1}\) (only on bronze), possibly due to a copper-coordinated carbonylate phase. These features were correlated with those in model coupons incorporating the same coatings materials with controlled thicknesses and surface glossiness. Thus, our examination of infra-red RAIRS bands for the coated copper coupons & bronze is entirely attributed to chemical changes.

Reflectance spectra: angle of incidence

The carbonyl overtone and reflectance IR bands exhibit distorted line shapes and saturation (very high absorbance that does not obey Beer’s law), as is common the case in thick films. Band line shapes can be optimized choosing Brewer’s angle (55°) for reflectance spectra as angle incidence angle.

pFTIR on corrosion products on iron coated with Paraloid +benzotriazole-based corrosion inhibitor

Paraloid B72 spectra are here recorded in micro-scale resolution. The quality of spectra varies between coatings. Common peaks are also detected.

Conclusions

1. Typical spectra of protective coatings on metal surfaces generally involves non-ideal films of high, non-uniform thickness on non-optimal surfaces. RAIRS spectra in these cases suffer from band distortions due to anomalous dispersion of refractive index and/or saturation due to high absorbances that fall out of the Beer law regime.

2. In films of low-medium thickness, both the transmitted and reflected beam reach the detector. Optimization involves use of the suitable polarizing angle and angle of incidence, which can eliminate the above problems. Use of p-polarized beam at Brewer’s angle, and film thickness where linearity in absorbance is obeyed, results in good spectra quality, in which all features carry entirely chemical information.

3. In cases of films so thick, that the transmitted beam is almost zero (because it is fully absorbed in the medium), or with metal surface is so rough that the transmitted beam is poorly reflected, the specular reflectance beam becomes important. In these cases the Kramers-Kronig transformation renders a spectral line that corresponds to an absorption spectrum.

References

