Surface Analysis Applications in Automotive Paint Operations

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INTRODUCTION

Solid materials interact with the environment at their surface. Properties such as adhesion, corrosion, and weathering are all "surface" phenomena. As a result, the elemental and chemical composition at the surface is often different than the bulk of the solid. This has led to the development of a host of techniques for studying the surface composition of solid materials. Of these techniques, three main instruments have evolved: X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS).[1-3] Together, these complementary methods can be used to resolve the majority of the technical questions that concern the surface chemistry of solid materials.

The development of these techniques has been pushed by the rapid growth of the microelectronics field.[4] Surface phenomena and measurements were critical to the growth of the integrated circuit (IC) industry throughout the 1970s and 1980s, and the growth in popularity and improvements in performance of these techniques paralleled the growth in ICs. This rapid improvement in performance has benefitted other technologies that rely on surface chemistry and measurements such as the coatings industry. In the Ford Research laboratory, all three techniques are employed to study various coating technology issues in the automotive industry. In general, however, the concepts discussed here are applicable to all coatings areas. This introduction is the first in a series of articles that will describe the operation of each technique with examples of their use in studying automotive coating systems.

XPS uses X-rays to probe the sample surface, and measures the energy of photoelectrons that are ejected during the process. AES focuses a narrow beam of electrons onto a conducting sample, and measures the energy of near surface Auger electrons that are emitted. SIMS probes the surface with a focused ion beam, and determines the mass distribution of electrically charged atoms and molecules that are ejected.

All three surface analysis techniques are performed in an ultra-high vacuum (UHV) environment. UHV is a convenient way to keep samples clean and allows for efficient movement of energetic particles to and from the sample. At a pressure of $1x10^{-6}$ torr, it only takes one second for one monolayer of gas molecules to hit the solid surface.[5] Practical experiments require vacuum levels several orders of magnitude lower. This environment imposes constraints on the type of samples that can be examined. First, the specimens must be vacuum compatible. Volatile materials will evaporate in UHV, altering the specimen surface. For example, low molecular weight hydrocarbons can cause wetting and adhesion problems for organic coatings leading to crater defects in the film. Unfortunately, these contaminants cannot be identified with these techniques as the contaminants evaporate when introduced into the vac-

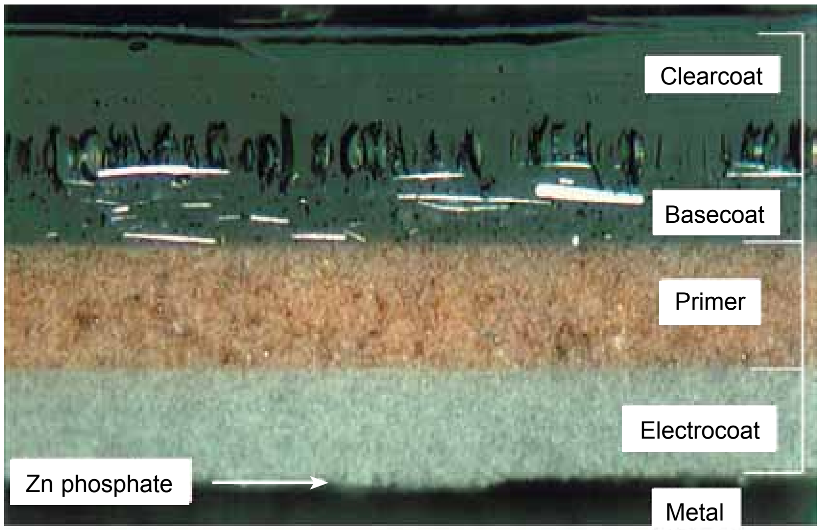

Figure 1—Typical automotive coating system for a metal substrate.

uum. Second, the specimen must be stable when exposed to high energy radiation. Electrons (AES), X-rays, (XPS), and ions (SIMS) can change the composition of fragile materials.[6,7] Finally, specimens must be small enough to fit into the vacuum chamber. Load locks used to move specimens from air into UHV are only a few inches in diameter, constraining samples to that size.

Automotive paint systems consist of several organic and inorganic coatings carefully designed to provide the appearance and corrosion protection that customers demand. A cross section image of a typical coating system for a metal substrate is shown in *Figure* 1. In this system, zinc metal, zinc phosphate, and electrocoat layers are added for corrosion protection, a primer layer is added for leveling and adhesion, a basecoat is added for color, and a final clearcoat is added for appearance and durability. This system provides a wide range of surface and interface chemistries that require multiple techniques to fully characterize. AES is commonly employed for characterization of the metal substrates and their interactions with the first coating layer, the pretreatment film. XPS has proved useful for evaluating chemical changes at interphase regions at adjoining layers, and the interfaces between layers that determine adhesion. SIMS produces detailed information and has high sensitivity to components of the paint system that are present in low concentrations. This method is ideal for studying paint weathering and migration of additives between layers. Together, these methods provide a powerful suite of tools to characterize most of the technological issues that this system presents.

The first surface analysis technique, X-ray photoelectron spectroscopy, will be detailed in the February 2011 issue of CoatingsTech.

References

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