Analytical Series

X-ray Photoelectron Spectroscopy as an Analysis Tool for Coatings

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This article is the second in a series focusing on surface analysis techniques for studying the surface composition of solid materials in automotive paint operations. The first, published in the January 2011 issue of CoatingsTech *(Vol. 8, No. 1, pp 46–47) provided an overview of three techniques that will be covered in the series. Upcoming articles will detail Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS). Together, these complementary methods can be used to resolve the majority of the technical questions that concern the surface chemistry of solid materials.*

X-ray photoelectron spectroscopy (XPS) is the most commonly used surface analysis technique. The XPS instrument is relatively simple to operate, and for most samples, data interpretation is easy and straightforward. It can accurately measure the composition and determine the chemical state of elements on the surface of a material. Recent developments have allowed the technique to evolve from a static spot analysis method to that of a legitimate small-spot microprobe machine. The technique is extremely surface sensitive, probing only the top 50 Å or less of a material. For this reason, the chemical information gathered is well suited for predicting adhesion characteristics, as well as diagnosing contaminants responsible for inducing adhesion failures in adhesives, paints, and coatings in general. This technology review will demonstrate how XPS can provide useful information to the coatings industry by measuring the chemistry of a material surface, and also by probing into a material using angle resolve depth profiling, sputter depth profiling, and ultra-low-angle microtomy.

INTRODUCTION

X-ray photoelectron spectroscopy is a quantitative analysis tool for measuring surface chemistry. The technique can determine both the composition and chemical state, or, commonly, the oxidation state, of elements at the surface of a material. The principal of operation is based on the photoelectric effect, where photoelectrons are ejected from core electron orbitals of an element contained in a surface that has been impinged with X-ray electromagnetic radiation. Although the impinging X-rays can penetrate to a micrometer depth in the sample surface, the resultant photoelectrons have a short mean-free path, and can escape to be detected and measured from a depth of only a few nanometers. For this reason, the technique is extremely surface sensitive. As a result, the chemical information gathered is well suited for predicting adhesion characteristics, as well as diagnosing contaminants responsible for inducing adhesion failures in adhesives, paints, and coatings in general. This sensitivity requires careful material handling to reduce the chance of inducing contaminants that may interfere with the true desired surface measurement. For instance, with analysis by XPS, the grease from a fingerprint, which can leave a visible mark on a water glass, will easily mask the chemistry of the underlying material.

In addition to contamination that can result from handling, the analyst also must be aware of the confounding nature of adventitious contaminants. Although not necessarily a problem with organic materials, these carbon-based organics coat surfaces that have been exposed to the atmosphere. This is especially true for metal substrates that have a high affinity for

adsorbing carbon. It is important to note that these contaminants are not observed with other surface techniques such as scanning electron microscopy, where chemistry is measured at a micrometer scale two or three orders of magnitude deeper into the surface than what is probed by X-ray photoelectron spectroscopy.

This article illustrates the types of chemical information that can be measured by XPS, with examples regarding bonding in organic coatings and surface treatments to enhance the bonding of coatings. It then details how different depth profiling analysis techniques can be used with XPS to measure material composition as a function of depth from nanometers to microns deep into a substrate.

THEORY

The invention of X-ray photoelectron spectroscopy is attributed to Kai Siegbahn who worked at the University of Uppsala, Sweden, in the 1960s.[1] Instruments manufactured for commercial use became available in the 1970s. These first generation instruments utilized non-monochromatic Mg Kα X-ray flood sources with an intrinsic energy width around 0.70 eV.

Current generation instruments have advanced to monochromatic Al Kα X-ray sources. The schematic diagram in *Figure* 1 depicts how XPS is accomplished using monochromatic X-rays. X-ray radiation from an energized aluminum anode is diffracted off the (1010) lattice face of a precisely bent disc of crystalline quart. The resultant beam has a wavelength of 0.83386 nm, corresponding to an energy of 1486.7 eV. Monochromatic Al Kα X-rays, generated in this manner, have an energy width of about 0.25 eV, considerably narrower than that of the conventional flood source. This results in markedly better spectral resolution, translated from a significant reduction in the peak widths of the photoelectron lines radiating during spectroscopy. Photoelectrons generated from the X-rays are then focused by lenses and filtered by energy using a hemispherical analyzer, and counted by a detector, typically a channeltron for conventional spectroscopy, or alternatively a micro-channel plate, or a position sensitive detector (PSD) that provides for spatial resolution required for imaging. The kinetic energy *(KE)* of the ejected photoelectron that is detected and measured relates to binding by the equation:

$$KE = h\nu - BE - \Phi_s$$

where $h\nu$ is the energy of the incident photon, *BE* is the binding energy of the electron in the atomic orbital, and Φ_s is the spectrometer work function.

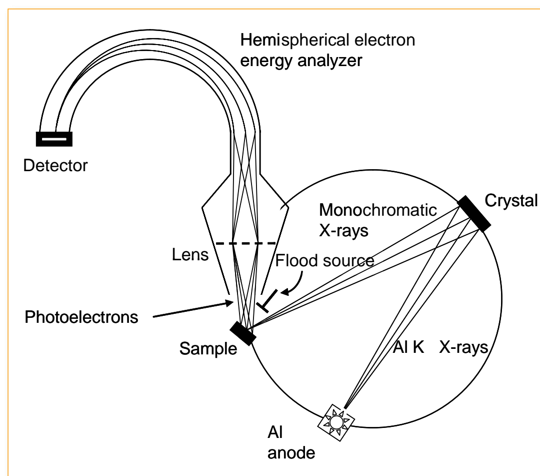


Figure 1—Schematic diagram of X-ray photoelectron spectrometer.

Further specifics relating to spectroscopy and advancements in XPS are beyond the scope of this article. Details relating to the experimental principles of XPS, including spectroscopy, detection, line and chemical state identification, and data interpretation can be obtained from handbooks on X-ray photoelectron spectroscopy.[2,3]

CHEMICAL INFORMATION

The high surface sensitivity (1 or 2 nm) of XPS makes it ideal for measuring chemistries that dictate adhesion properties. This is because the technique probes only the very top surface of a material where functional groups that participate in chemical bonding are present. As a consequence, the surface composition measured is often different than what is measured for the bulk material. This can be due to the presence of surface active additives formulated to enhance bonding, low-molecular-weight additives with low surface energy needed to control surface rheology, or simply to interactions of the material with the atmospheric environment leading to oxidation, hydration, or deposition of adventitious carbon-based contaminants. This is especially true for metals, which exhibit a high attraction for adventitious contaminants. However, with organic polymers such as plastics and paints, this is usually not the case. For instance, the surface of a "clean" iron metal may contain as much as 30 to 40% carbon, due to the fact that iron has a high affinity for adsorption of organics from the atmosphere. On the other hand, in this laboratory, we have measured the surface of pure polypropylene to contain less than 1% of adventitious contaminants. This article focuses on XPS measurements of polymeric materials, and as such, the XPS compositions determined should reflect what is close to the "true" surface chemistry

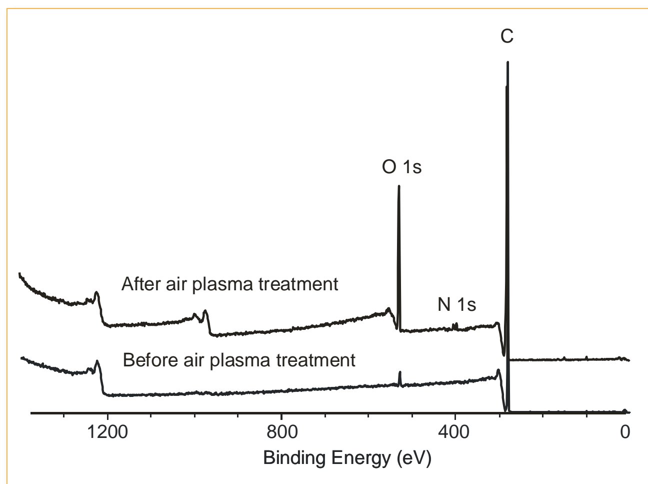


Figure 2—XPS survey spectra of polypropylene before and after treatment by air plasma.

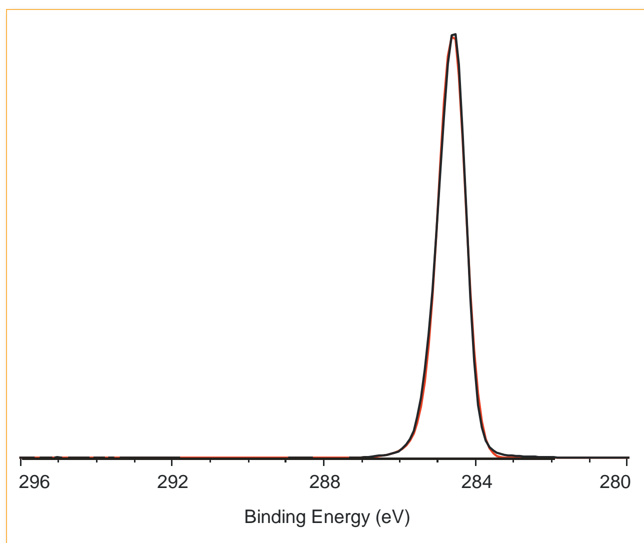


Figure 3—XPS C 1s core level spectrum of polypropylene.

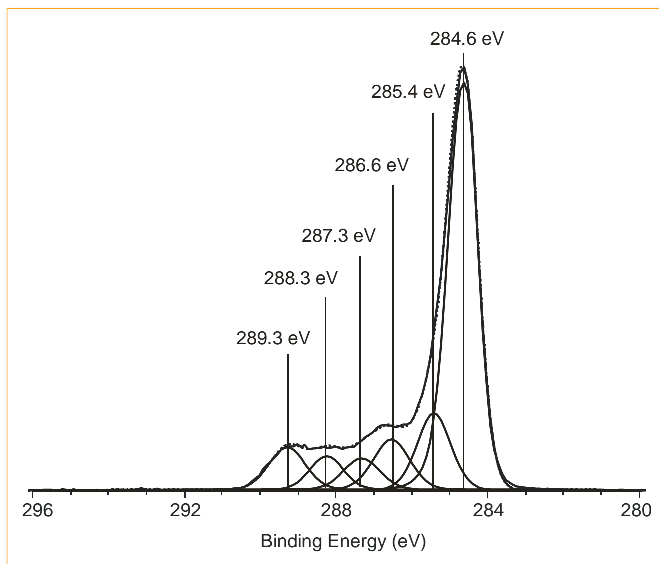


Figure 4—XPS C 1s core level spectrum of polypropylene after treatment by air plasma.

of the material, and not those highly affected by atmospheric contaminants.

The first example demonstrates the fundamental types of chemical information that is measured by XPS. Energetic surface treatment techniques such as UV/ozone, corona, flame, and plasma can be used to remove surface contaminants and functionalize the surface of materials to enhance adhesion of applied coatings. In this case, XPS was used to characterize the surface of polypropylene before and after exposure to an air plasma surface treatment.

Elemental Composition

The most basic information gathered through XPS is surface elemental composition. *Figure* 2 shows XPS survey spectra acquired from polypropylene before and after treatment with air plasma. The initial spectrum reveals mostly carbon, with a trace of oxygen. Polypropylene is purely an olefinic hydrocarbon, and should contain only carbon. However, XPS analysis of the surface reveals both oxygen (2.1%) and carbon. In this case, the oxygen can be attributed to either surface oxidation or, quite possibly, to the existence of mold release agents. After oxidation with air plasma treatment, the surface of the polypropylene increased in oxygen concentration from 2.1 to 18.0%. In addition to the expected increase in oxygen, nitrogen (2.6%) was also observed, formed by radical reactions during excitation by the highly energetic air plasma.

In practice, this basic elemental data measured by XPS can be extremely useful for correlating the amount of surface oxidation that would take place for a given dosage of air plasma treatment. In a designed experiment, the oxygen uptake could be used as the response (output), whereas the inputs variables would be factors that control the plasma dosage, such as power, speed, and distance of treatment.

Chemical State

More detailed chemical state information can be obtained through XPS by high resolution core level data. In this case, oxidation states of carbon created by air plasma oxidative treatment are revealed. *Figures* 3 and 4 show XPS C 1s core level spectra of polypropylene before and after treatment, respectively. Initially, the peak envelope mainly contains a single state of carbon, referenced as aliphatic or olefinic carbon, at a binding energy of 284.6 eV. A slight tail on the higher binding energy side of the envelope is attributed to a small amount of carbon oxidation, consistent with the oxygen observed in the initial survey spectrum (*Figure* 2). After treatment, additional states of carbon are revealed, as identified in *Table* 1. Species

Table 1—Species Identified in XPS C 1s Core Level Spectrum (*Figure* 4) on the Surface of Polypropylene after Treatment by Air Plasma

Species	Observed Binding Energy (eV)
Aliphatic	284.6
Carbon bonded to nitrogen	285.4
Alcohol / ether	286.6
Ketone / aldehyde	287.3
Carboxyl	288.3
Carbonate	289.3

Table 2—XPS Survey Spectra from Interfacially Failed Surfaces of Weak Bonding Model Automotive Paint System

Paint Interface	Elemental Composition—Atomic Percent			
	C	O	N	S
Interfacial Basecoat	80.3	15.4	3.4	0.9
Interfacial Primer	82.2	13.1	3.2	1.5

that contain exchangeable hydrogen, such as alcohols, are the essential functional groups that form strong and resilient covalent bond linkages with crosslinking agents in applied coatings.

ANALYSIS METHODS

XPS is commonly used to determine the presence of surface additives that promote adhesion, as well as the presence of contaminants or reactive chemical species that can impede adhesion.[4,5] *Figure* 5 shows an XPS survey spectrum acquired from the surface of a model melamine crosslinked polyacrylate automotive paint system. The elemental composition is composed mostly of carbon, oxygen, and nitrogen, which is consistent with what would be expected for an amine crosslinked polyol. However, in addition, silicon was observed. The silicon is present in an additive that segregates to the surface during bake out to promote adhesion. There is a precise amount of this additive needed to promote adhesion, beyond which excess material will coat the surface and instead act as a weak boundary layer. In this case, XPS is an ideal technique for monitoring the process and determining the optimal amount of additive needed in the paint formulation for promoting adhesion.

On the other hand, chemistries can take place that are detrimental to adhesion. *Figure* 6 shows an image acquired from two model automotive paint systems subjected to the scribe and crosshatch tape pull test.[5] Paint system *A* exhibited a substantial amount of paint loss, while paint system *B* remained essentially intact. The paint loss on the poor adhering system *A* occurred between the basecoat and primer paint layers. *Table* 2 includes results from XPS analysis acquired on the interfacially failed surfaces. The amounts of carbon, oxygen, and nitrogen are consistent with what would be expected for composition of the paint systems. What is unexpected is the presence of sulfur. Further definition of the chemistry was accomplished through high resolution acquisition at the N 1s core level (*Figure* 7). The spectrum reveals nitrogen to be mainly in two chemical states. The lower binding energy peak at 399.8 eV is due to nitrogen present either as an amine or amide (urethane). The prominent higher binding energy peak is attributed to an ammonium salt. In fact, the actual chemical state of nitrogen is an amine sulfate. In this case, the XPS analysis shows that weak bonding in paint system *A* can be attributed to the presence of salt that forms a weak boundary layer at the primer/basecoat bonding interface.

DEPTH PROFILING TECHNIQUES

Besides measuring chemistry at the surface, XPS can also be used to measure the composition of a material as a function of depth. Three methods in which this can be accomplished are: (1) angle resolve, (2) sputter depth profiling, and (3) mechanical microtoming.

Angle Resolve Depth Profiling

Angle resolve depth profiling, commonly referred to as ARXPS, or angle resolve x-ray photoelectron spectroscopy, is a nondestructive method that is able to discern subtle differences in chemistry at the topmost atomic layers of a surface.

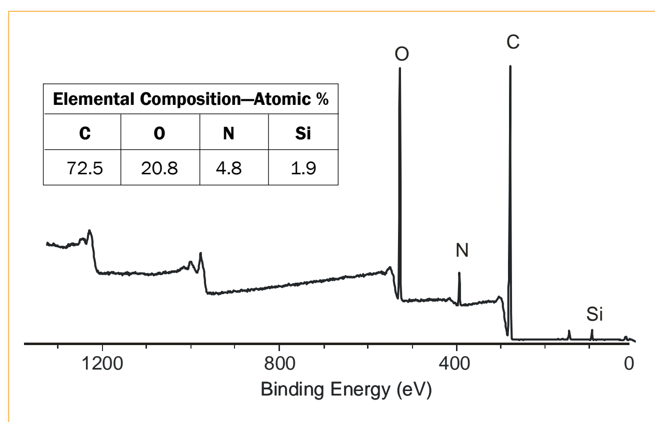


Figure 5—XPS survey spectrum revealing elemental composition of the top surface of automotive clearcoat paint.

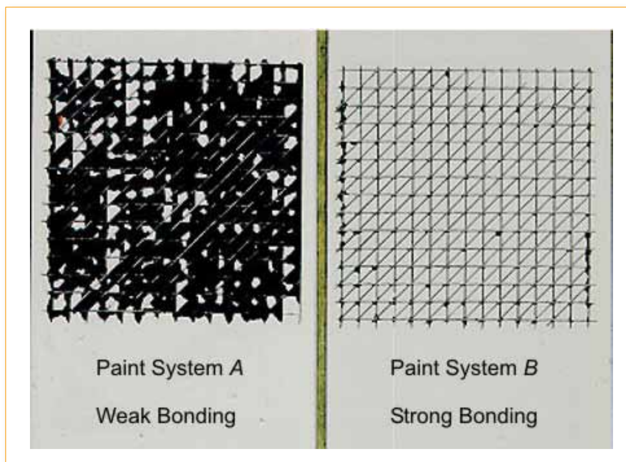


Figure 6—Model automotive paint systems *A* and *B* exhibiting weak and strong adhesion results according to the scribe and cross-hatch tape-pull test.

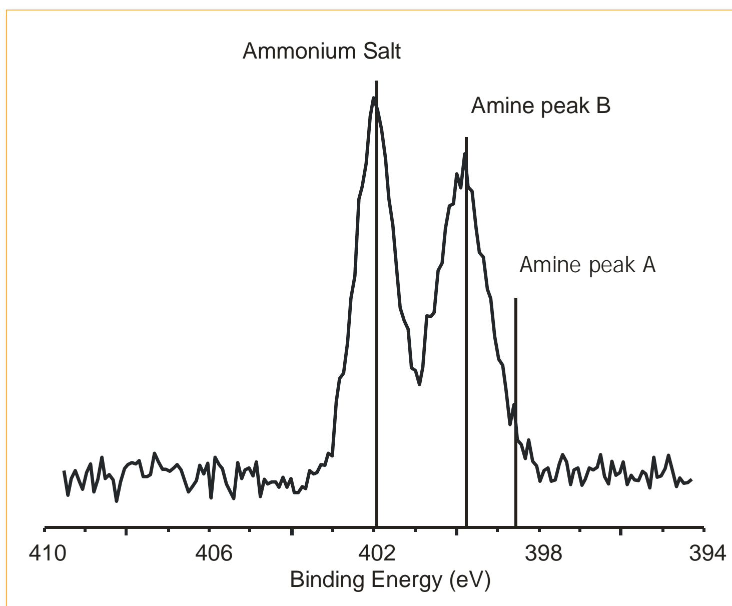


Figure 7—XPS N 1s core level spectrum acquired from the interfacially failed primer interface of a weak bonding model automotive paint system *A*.

Figure 8 illustrates how this technique works. With the sample positioned normal to the detector, or at a 0° takeoff angle, photoelectrons have the most direct path through the sample to the detector, and thus are able to be measured at the full sample escape depth. The sample can then be rotated to a shallow takeoff angle to the detector. In this case, per the same escape depth, the photoelectrons analyzed travel a shallow angled path. As a consequence, photoelectrons from only the topmost atomic layers are able to escape the sample and be detected. For the example in *Figure* 8, much of the bulk material is sampled at the 0° takeoff angle, while a higher percentage of the photoelectrons measured would emanate from the overlayer at the shallower 45° takeoff angle.

If a material contains no overlayer, and is instead homogenous throughout, the same elemental composition is measured at each takeoff angle. Thus, with ARXPS, the spectroscopist is able to determine the degree to which a composition of elements measured is either intermingled or segregated and layered at the surface of a material. *Figure* 9 shows XPS C 1s core level spectra acquired from an electrocoat paint at 0° and 45° takeoff angles. The spectra clearly reveal a higher concentration of ether at the surface measured at the shallower 45° angle. In this case, the electrocoat contains a low-surface-energy polyethylene oxide crater-control additive that segregates to the surface of the paint.

Nondestructive ARXPS can be a valuable tool for measuring thin films on metals, surface segregation in polymers, the amount and depth that surface treatments impart on metals and polymers, as well as clarifying the presence of contaminants on a surface that would disrupt bonding. The integrity of the analysis is affected by the flatness of the surface of the material analyzed. The technique becomes less accurate with increased surface roughness, as the spectroscopy becomes less discriminating with varied takeoff angles. However, if the sample surface is flat, and escape depths are well defined, the technique can be used to quantify the thickness of an overlayer. A simplified relationship, the Hill equation,[6] quantifies the layer thickness *t* by:

$$\ln\left[1+\frac{I_o\rho_s\lambda_s}{I_s\rho_o\lambda_o}\right]=\frac{t}{\lambda_o\cos\theta}$$

where I_o and I_s are the ratio of peak intensities, λ_o and λ_s are the photoelectron escape depths at a given kinetic energy, and ρ_o and ρ_s are the atomic densities of the overlayer and substrate, respectively, while θ is the emission angle of the photoelectron to the detector. In practice, a plot of the left side of the equation vs. $1/(\lambda_o \cos\theta)$ for various takeoff angles will yield the slope *t*, the overlayer thickness. More complex equations are available for defining layer thicknesses where surface and bulk intermixed, and also for systems where multiple thin and well-defined layers are present,[7] with the caveat that the probe depth limitation is around 4 nm.

Sputter Depth Profiling

Materials that possess an overlayer thickness greater than the photoelectron escape depth will not allow photoelectrons generated from the underlying material to escape to the surface and be detected. In this case, ARXPS cannot be utilized to measure layer thickness, and destructive methods such as sputter depth profiling need to be employed to determine chemical composition as

a function of depth. The method entails using ion etching to physically abrade through the sample surface. Argon is commonly used for sputter depth profiling in XPS, as it is similarly used with Auger electron spectroscopy or time-of-flight mass spectrometry techniques. With XPS, however, it is necessary to sputter relatively larger craters a few millimeters in diameter to accommodate the larger size of the X-ray beam, typically on the order of a few hundred microns in diameter.

Figure 10 gives an argon sputter depth profile generated from a silicon oxide layer on aluminum, formed by air plasma polymerization of hexamethyldisiloxane. For this profile, which plots atomic composition against sputter time, argon etching was performed at 30-sec cycles with data collection in between. The profile reveals that the initial carbon measured was removed after the first 30-sec etch cycle, indicating that this carbon is not native to the layer, but instead is an adventitious contaminant. Silicon and oxygen are removed after 400 to 500 sec of sputtering, followed by a second layer of mixed aluminum and silicon oxides removed between 600 to 800 sec of sputtering. The remaining plot shows continued removal of aluminum oxide as the profile nears the bulk of aluminum metal. The actual thickness of the oxide layer can be determined by calibrating sputter rate against a standard of known oxide overlayer thickness. The argon sputter depth profile revealed information regarding both the thickness of the silicon oxide overlayer, as well as details of the physics of the deposition process through the discovery of a mixed Si–Al metal oxide underlayer.

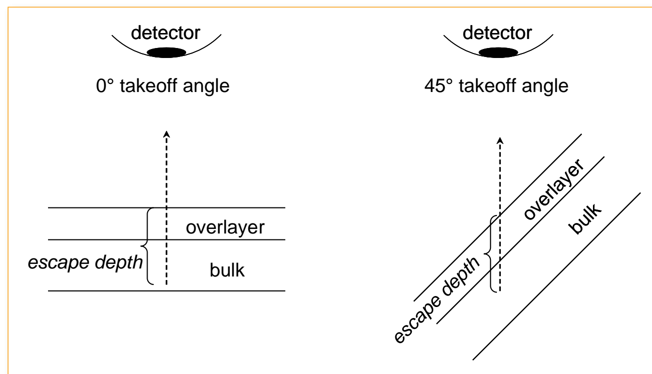


Figure 8—Photoelectron escape depth from a material with an overlayer at 0° and 45° takeoff angles.

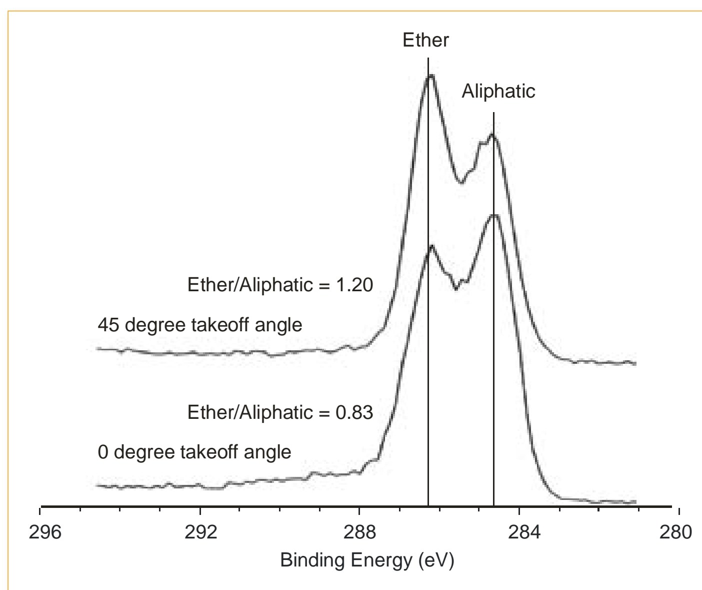


Figure 9—C 1s core level spectra acquired using ARXPS of electrocoat paint at 0° and 45° takeoff angles.

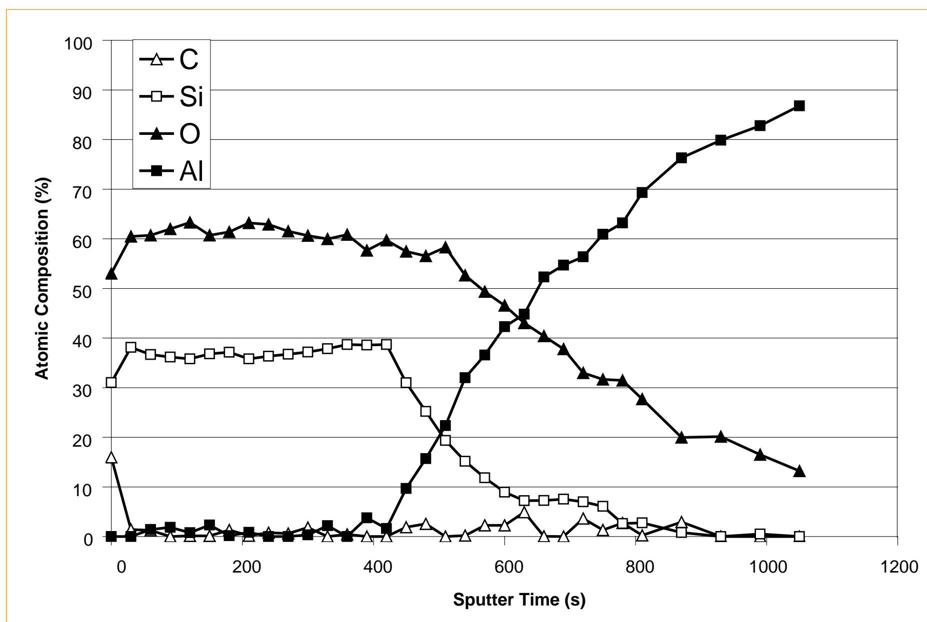


Figure 10—XPS argon sputter depth profile of a silicon oxide layer on aluminum containing a native oxide layer.

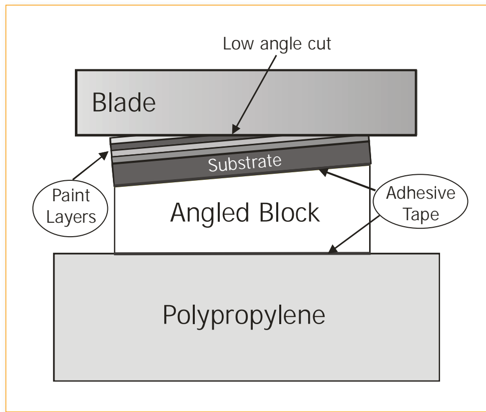


Figure 11—Diagram of ultra-low-angle microtoming apparatus.

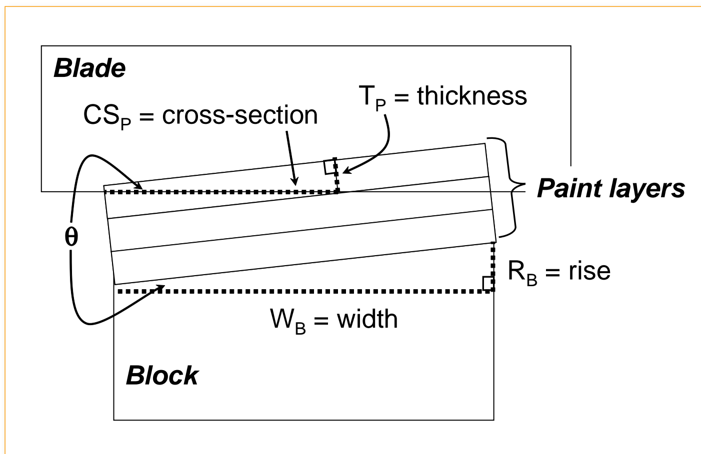


Figure 12—Diagram relating rise and width of block to cross-sectional magnification of microtomed paint layer.

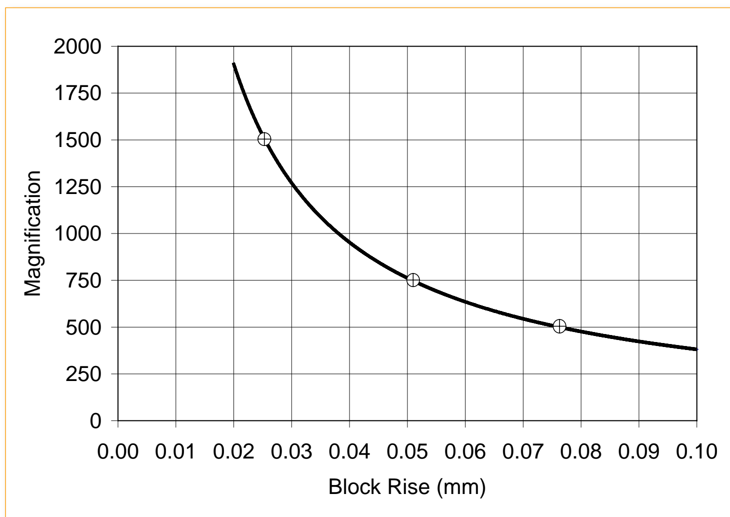


Figure 13—Cross-sectional magnification related to the rise at one edge of a 38.1 mm wide block. The three marked areas relate block rises that would translate to magnifications of 500x, 750x, and 1500x.

Ultra-Low-Angle Microtomy

Cross-hatch tape pull testing can be used to expose chemistries at weak bonding interfaces of multi-layered paint systems. When a paint system bonds well, though, it is not possible to force a fracture failure in a controlled manner at a specific bonding interface. In practice, this would be highly desirable since it would be advantageous to gather information at the bonding interfaces of both good and poor bonding paint systems to compare chemistries. To this end, a novel microtoming method, ultra-low-angle microtomy (ULAM), has been developed that can resolve material composition as a function of depth.[8,9] The method is capable of exposing layers and bonding interphases between layers with high precision. Conventional microtoming is accomplished at a 90° diagonal cross-section to the layered material. Deviations from this angle allow for slight magnification of the exposed layers, but still require µm scale high-spatial-resolution techniques such as time-of-flight mass spectroscopy to resolve features. However, a device known as a sled or sliding microtome[10] allows a layered material to be fixed in-parallel to a wide cutting blade. In this manner, layers are removed sequentially. Slightly tilting the sample angle from parallel allows the layers to be exposed at high magnification. Since its inception, ULAM has been utilized to characterize coating composition as a function of depth,[11-14] determine the chemistry of adhesion at buried interfaces,[15-18] as well as measure the migration of additives in and between layers in paint systems.[19,20]

A diagram of the ULAM apparatus is shown in *Figure* 11. A polypropylene block, mounted onto a moveable sample stage, is first cut level with the blade to ensure parallelism. A multi-layered paint sample is then attached to an angular steel block, and the block to the planed polypropylene, using double-sided tape. The sloped angular block is fabricated having one side raised so as to angle a cut across the layered paint system and expose a magnified cross-sectional area.

The diagram in *Figure* 12 is used to derive how the angle of the block translates into a calculated cross-sectional magnification of a paint layer. Angle θ relates the rise of the block per a given width, and also relates the exposed cross-sectional width of a microtomed paint layer for a given layer thickness. For the angled block,

$$\tan(\theta) = \frac{R_B}{W_B}$$

where R_B is the raised distance (rise) of one edge of the block, and W_B is the block width. For the paint layer,

$$\sin(\theta) = \frac{T_P}{CS_P}$$

where T_P is the paint layer thickness, and CS_P is the width of the exposed layer after microtoming. Tan(θ) = sin(θ), to within 99% accuracy, for angles of θ less than 8°. The block angles (θ) used for microtoming paint layers in this study were quite small, ranging from 0.0382 to 0.114°. Thus, the block slope and microtome magnification can be related as:

$$\frac{CS_P}{T_P} \cong \frac{W_B}{R_B},$$

and the microtoming magnification can be calculated for a given angled block simply by the width divided by the rise, or W_B / R_B.

Figure 13 graphs magnifications that would be realized for a block of a width of 38.1 mm with a raised edge varying from 0.02 to 0.10 mm. For instance, blocks fabricated with one side raised 0.0254, 0.0508, and 0.0762 mm will result in calculated cross-sectional magnifications (W_B / R_B) of 1500x (38.1/0.0254), 750x (38.1/0.0508), and 500x (38.1/0.0762), respectively. For reference, these magnifications are marked on the curve in *Figure* 10.

During microtoming, paint layers are mounted with the high edge of the block orthogonal to the cutting blade so that layers are exposed parallel to the direction of the cutting stroke, thus minimizing the effect of cross-contamination due to smearing of surface layers.

A cross-sectional image of an OEM automotive multi-layered paint system microtomed at a magnification 500x is shown in *Figure* 14. The paint layers visible consist of clearcoat (C), basecoat (B), primer (P), and electrocoat (E). The approximate thickness of the primer layer calculated from this image is 10 mm ÷ 500 or 20 µm. Interphase regions are clearly discernable at the basecoat/primer and primer/electrocoat interface, but not at the clearcoat/basecoat interface (applied wet-on-wet). XPS elemental surface compositions measured at the paint layer and interphase regions after ULAM are given in *Table* 3. These results reveal a segregation of Na at the primer/electrocoat interphase region, and a slight enrichment of S at the basecoat/primer interphase.

In a final example, ULAM is used to compare the bonding chemistries of the model automotive paint systems exhibiting good and poor adhesion that were shown in *Figure* 6. *Figure* 15 shows the results of a highly magnified (1500x) ULAM cross-section of the model automotive paint system *B* in *Figure* 6 that exhibited good intercoat adhesion according to the cross-hatch tape-pull test. The paint layers exposed in the image are basecoat and primer, and a basecoat/primer interphase region is revealed in detail. The width of this layer exposed by microtoming (*Figure* 15) was measured at 3.5 mm; thus, the true thickness of this interphase region in the paint system is calculated to be 2.3 µm (3.5 mm ÷ 1500). This thickness is quite substantial, as it amounts to about 12% (2.3 µm ÷ 20 µm x 100) of the total thickness of the primer layer.

Figure 14—Cross-sectional image of an OEM automotive multi-layered paint system microtomed at magnification 500x.

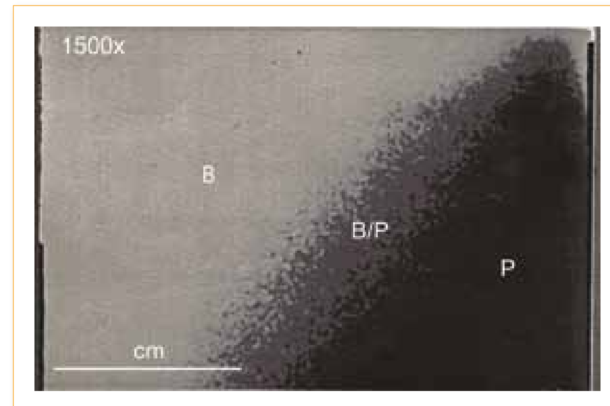


Figure 15—Cross-sectional image of a model automotive multi-layered paint system microtomed at magnification 1500x.

Table 3—XPS Surface Data from the Paint Layer and Interphase Regions of an Automotive Multi-layered Paint System following Ultra-Low-Angle Microtoming at 500x

Layer	Elemental Composition—Atomic Percent							
	C	O	N	S	Ba	Na	Zn	Si
Basecoat	67.8	23.9	4.9	0.7	0.2	1.3	0.2	1.1
Basecoat/primer interphase	72.8	20.1	4.7	1.0	0.6	0.5	0.3	--
Primer	73.1	20.6	4.6	0.8	0.8	--	--	0.1
Primer/electrocoat interphase	71.8	21.6	3.7	0.3	0.1	0.9	0.2	1.5
Electrocoat	68.9	24.1	3.8	0.4	0.2	0.2	0.4	2.1

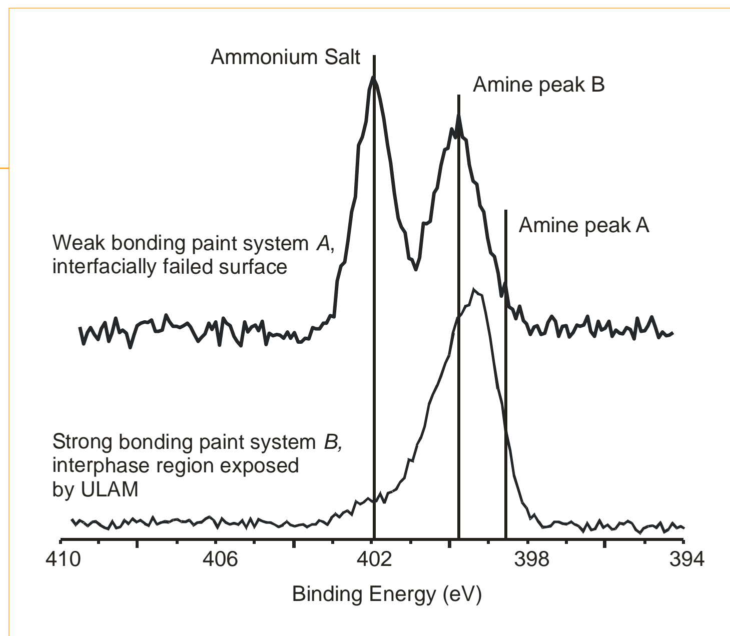


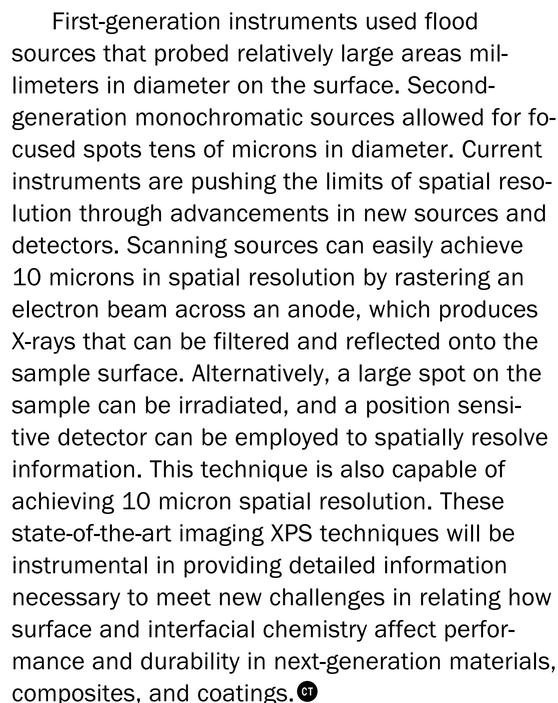
Figure 16—XPS N 1s core level spectra from the primer/electrocoat interphase region exposed by ULAM of a strong bonding paint system B compared to that of interfacially failed primer surface of weak bonding paint system *A*.

It was revealed though nitrogen chemistry (*Figure* 7) that the poor adhesion exhibited by paint system *A* was caused by formation of an amine salt that created a weak boundary layer at the basecoat/primer interface. A direct comparison to this chemistry can be made by acquiring XPS data at the basecoat/primer interphase region of the good bonding paint system *B* exposed by ULAM. This comparison is shown in *Figure* 16. The N 1s core level shows that only a small amount of ammonium salt was formed at the basecoat/primer interphase region of paint system *B*. The majority of the nitrogen here is instead attributed to amine species that would couple to form strong covalent bonds between the paint layers.

The comparison of bonding chemistries of paint systems *A* and *B* would not have been possible to make by normal stressing of the paint layers, since a controlled bond failure would only occur in the weak system. Bond failure cannot be induced at a specific bonding interface between paint layers of a strong bonding system, as it will instead fracture uncontrollably and randomly throughout the paint stack. However, by utilizing ULAM, it is possible to accurately expose any bonding interphase region and thus allow for spectroscopy and chemical characterization that otherwise would not be attainable.

SUMMARY

X-ray photoelectron spectroscopy is a useful tool for characterizing the surface of a material. The high surface sensitivity of the technique makes it ideal for identifying chemistries that promote adhesion and contaminants that impede adhesion. XPS can accurately measure all elementals of the periodic table but hydrogen, and can identify oxidation states, or chemical states, of the elements as well. Besides measuring the chemistry at the top surface, nondestructive ARXPS, sputter depth profiling, and ULAM techniques can be employed to probe the chemistry deeper into a material.



First-generation instruments used flood sources that probed relatively large areas millimeters in diameter on the surface. Second-generation monochromatic sources allowed for focused spots tens of microns in diameter. Current instruments are pushing the limits of spatial resolution through advancements in new sources and detectors. Scanning sources can easily achieve 10 microns in spatial resolution by rastering an electron beam across an anode, which produces X-rays that can be filtered and reflected onto the sample surface. Alternatively, a large spot on the sample can be irradiated, and a position sensitive detector can be employed to spatially resolve information. This technique is also capable of achieving 10 micron spatial resolution. These state-of-the-art imaging XPS techniques will be instrumental in providing detailed information necessary to meet new challenges in relating how surface and interfacial chemistry affect performance and durability in next-generation materials, composites, and coatings.

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