PHYSICAL ELECTRONICS
A DIVISION OF ULVAC-PHI

TOF-SIMS Characterization
Of Multi-Layer Paint coatings

Introduction

Over the last ten years much attention has been given to finding accelerated aging tests for predicting performance of new or improved exterior automotive coatings (Figure 1). For complete multi-layer coating system analysis, some success has been found in methods that require mechanical separation of layers prior to analysis. However, these methods are generally very laborious or specialized and require that analytical methods be applicable to small sample sizes and low concentrations. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) allows characterization of intact multi-layer coating systems. By imaging the molecular ion, or major ion fragments, TOF-SIMS provides direct information on the distribution of specific organic molecules. In addition, submicron spatial resolution can be achieved when imaging paint cross-sections via TOF-SIMS. Kaberline *et al.* have been able to determine the relative photo-oxidation resistance among the layers in a paint system. They used isotopic labeling and microtomed samples to monitor ^{18}0 uptake by TOF-SIMS.[1] Physical Electronics TOF-SIMS instruments have been optimized for organic imaging applications. The unique TRIFT mass spectrometer, with its large solid angle of collection, provides excellent imaging on rough insulating materials. In addition, secondary electron detection efficiency is very high, allowing pulsed SEM images to be acquired with the very low ion beam doses used in TOF-SIMS. This study demonstrates the use of TOF-SIMS for characterizing multi-layer coatings systems. The migration of additives among the coatings can be tracked, and as a result, the effects of weathering exposure on the system can be evaluated.

Experimental
Sample Description

Microtomed cross-section slices of three-layer coating systems were studied (Figure 2). The multi-layer system employs a thermoplastic olefin substrate composed of polypropylene and rubber. It is coated with a primer layer (adhesion promoter) approximately 6 μm thick based on a chlorinated polyolefin.

Figure 1. The automotive industry has a large interest in paint coatings.

A basecoat approximately 20 μm thick and clearcoat approximately 37 μm thick are deposited on top of the adhesion promoter. Both were composed of 2K polyester-acrylic polyurethane crosslinked with a biuret type HDI isocyanate adduct and cured at 121 C. The multi-layer system was studied before and after weathering conditions: identified as "unexposed" and "exposed" (three years, 5 south, Florida).
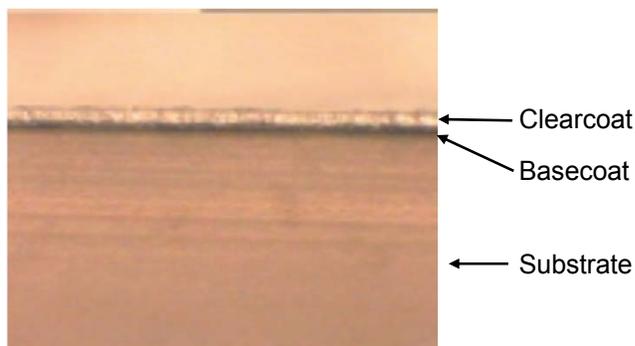

Figure 2. Optical microscopy view of a cross-sectioned multi-layer paint coating (field of view ~ 2 x 2 mm).

Clearcoat
Basecoat
Substrate

HALS and UVA type additives are used in both the clearcoat and basecoat (Figure 3). In the coating system studied here, different HALS additives are used in the basecoat and clearcoat. HALS 1 is a low molecular weight type put in the clearcoat (1% level by weight), whereas HALS 2 is a higher molecular weight type put in the basecoat (1%). The UVA is put in both the basecoat (3.5%) and the clearcoat (2%).

Instrumentation

The experiments were performed using a PHI *TRIFT II* TOF-SIMS instrument. During analysis, the instrument employed a 15 keV In^+ ion source. The 600 pA DC primary ion beam was pulsed at 11 kHz with a pulse width of 12 ns and rastered over a 200 x 200 µm area. A low energy electron beam was used for charge compensation.
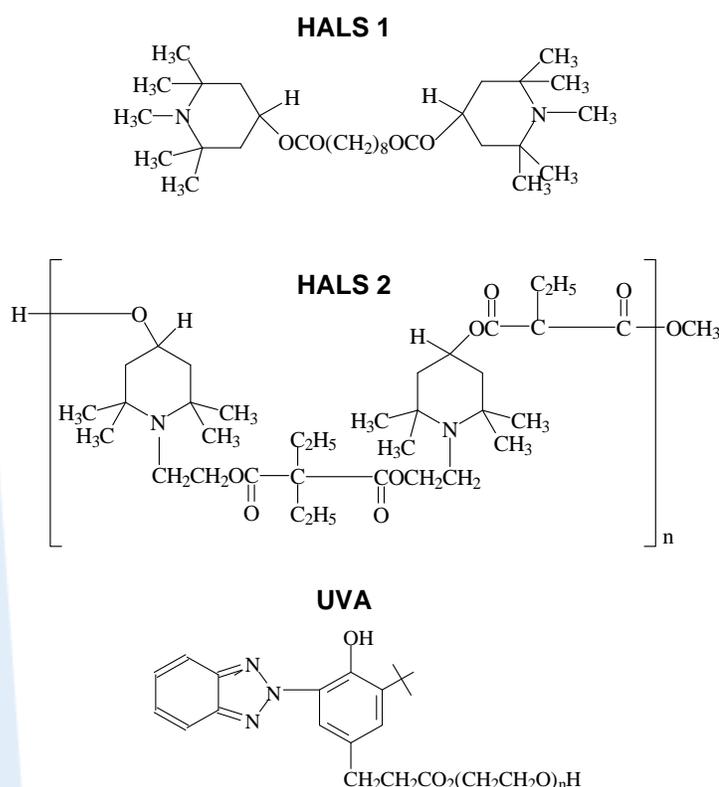
HALS 1

HALS 2

UVA

Figure 3. Molecular structures of the additives evaluated in this study.

Results
Characterization of Each Layer
in a Cross-Section

In the total ion image of the unexposed Coating System 1, the sample holder and the layers of the system are not very well distinguished. However, dramatic distinction of the layers can be observed by mapping components specific to the layers, and evaluating their location in the multi-layer system.

In Figure 4, each layer of the multi-layer system is visible (200 µm field of view): mapping of Cl^- (35 Da) identifies the layer of adhesion promoter; mapping of CNO^- (42 Da) demonstrates the region of polyurethane (clearcoat and basecoat layers); mapping of Mg^+ (23.9 Da) identifies the substrate and demonstrates talc is present as small particles (< 5 µm); mapping of Al^+ (26.9 Da) identifies the basecoat layer (which contains a potassium aluminum silicate) and distinguishes it from the clearcoat. Mass spectra can be extracted from each of the layers to evaluate chemical composition.

Evaluation of Additive Migration

The distribution of three additives was evaluated by TOF-SIMS. Each additive was analyzed as a pure compound to identify its molecular fragmentation pattern (Figure 5 shows an example for the positive spectrum of HALS 1). Table 1 lists the molecular fragments characteristic of each additive that were used for identifying their distribution in the multi-layer cross-sections.

The distributions of the unique molecular fragments from each of the additives were compared. Figure 6 shows a comparison of exposed and unexposed coating systems and the distribution of HALS 1. The 42 Da (CNO^-) peak shows the location of the clearcoat and basecoat regions. The 58 Da ($C_3H_8N^-$) signal shows HALS 1 to be mainly in the basecoat before weathering and more equally distributed in the basecoat and clearcoat after weathering.
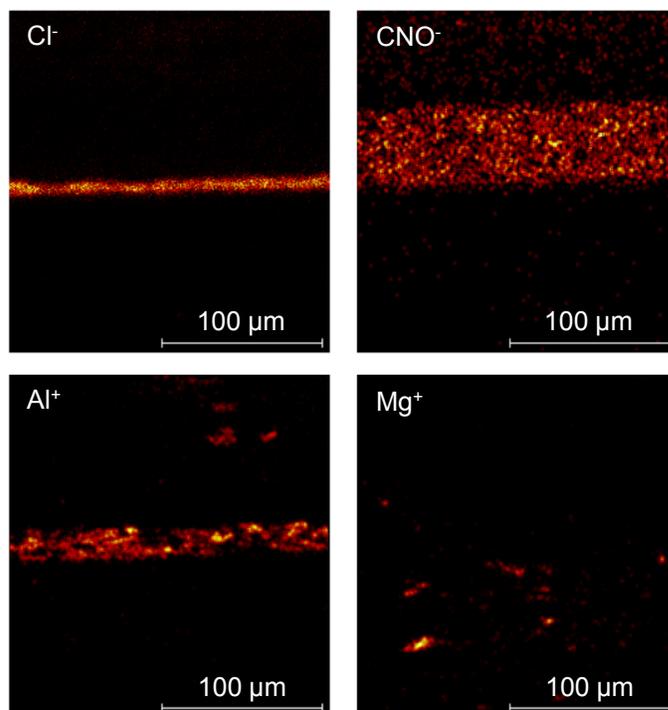

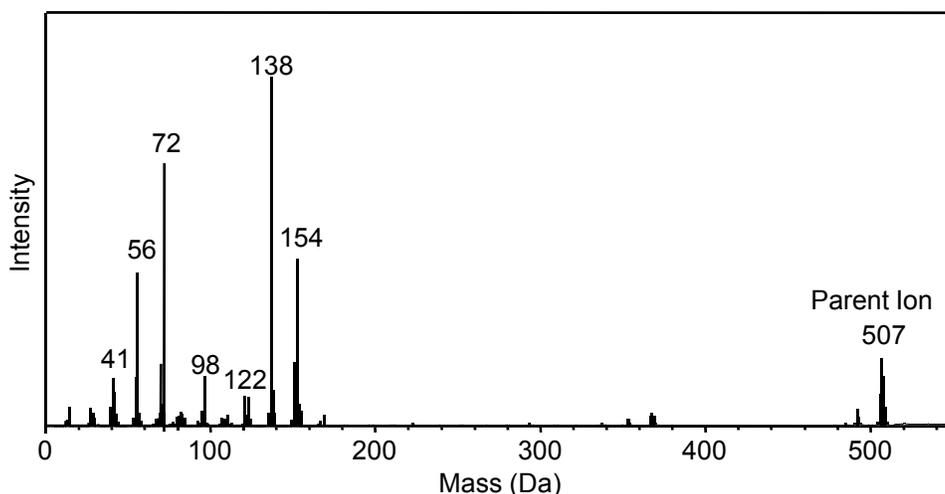*Figure 4. TOF-SIMS images of a multi-layer paint cross-section.*

Figure 5. Positive Mode TOF-SIMS reference spectrum of HALS-1. Characteristic peaks can be used for mapping the additive in multi-layer cross-sections.

Molecular fragments from the other additives were also mapped, and their distributions were evaluated. For the unexposed system, HALS 1 and UVA have a tendency to concentrate in the basecoat layer. On the other hand, HALS 2 appears to have moved freely out of the basecoat distributing itself equally between clearcoat and basecoat. Siloxane appears to equalize itself between basecoat and clearcoat (in all samples studied), even though it was present initially only in the clearcoat.

Each of the additives was also evaluated in the exposed system. The UVA does not migrate from the basecoat layer, although UVA migration into the primer and substrate has been observed in the past by other techniques. HALS 1 shows more peak intensity in the clearcoat layer relative to the unexposed sample (peaks have also been observed in basecoat for both samples) (Figure 6). Moreover, HALS 2 has migrated into the substrate, and also remains in the clearcoat and basecoat.
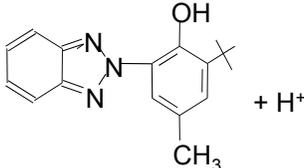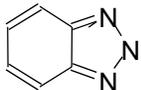
Additives Evaluated	Characteristic Fragments Used for Mapping	Chemical Species (best assignment, based on exact mass)
Hals 1	72 Da	$C_4H_{10}N^+$
	138 Da	$C_9H_{16}N^+$
	58 Da	$C_3H_8N^-$
	71 Da	$C_4H_9N^-$
UVA	280 Da	+ H$^+$
	118 Da	
Hals 2	70 Da	$C_4H_8N^+$
	84 Da	$C_5H_{10}N^+$

Table 1. Characteristic TOF-SIMS molecular fragments observed in additive reference spectra.

Conclusions

TOF-SIMS offers a new tool of significant benefit for tracking and characterizing coatings and additive distributions in high performance multi-layer coating systems. Results in this study offer new insights, indeed some surprises, for the particular systems evaluated. The results focus on qualitative tracking of additives; however, quantitative analysis is possible with standards as references. The impact of tracking all the additives simultaneously and *in situ* in cross-sections of a multi-layered paint film gives a value-added perspective to coating analysis.

Acknowledgements

Reference

[1] Kaberline, S.L.; Prater, T.J., deVries, J.E.; and Gerlock, J.L.; *Secondary Ion Mass Spectrometry (SIMS X)*; Benninghoven, A; Hagenhoff, B.; Werner, H.W., Eds.; Wiley: Chichester, UK, (1997) 969.
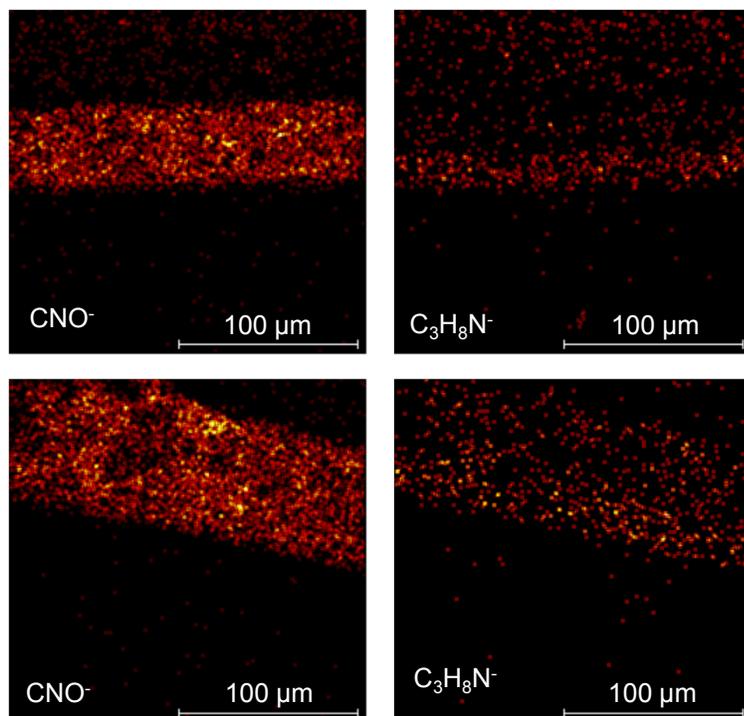
Figure 6. TOF-SIMS images which demonstrate HALS 1 (mapped with $C_3H_8N^-$) has migrated from the basecoat during exposure to both the basecoat and clearcoat (mapped with CNO^-). Images from the unexposed system are shown on top, and images from the exposed system are on the bottom. The exposed sample was rotated during sample mounting, producing a rotated TOF-SIMS image.