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Secondary Ion Mass Spectrometry of Automotive Coating Systems

by Steven J. Simko, Steven L. Koberline, and Larry P. Hascak
Ford Research and Innovation Center

This article is the final installment in a series focusing on surface analysis techniques. Previous articles examined x-ray photoelectron spectroscopy and Auger electron spectroscopy. These complementary methods serve as valuable tools for resolving questions on the surface composition of solid materials in applications such as automotive paint systems.

INTRODUCTION

Secondary ion mass spectrometry (SIMS) is a specialized form of surface analysis that is used primarily to determine the elemental and chemical structure of solid materials. It is based on mass spectrometry, which is a family of techniques where elements, molecules, and molecular fragments are sorted based on their atomic/molecular weights. The technique employs a source to excite the material of interest into the gas phase with some portion of it as ionized species. The ions then pass through a mass filter which sorts them based on their mass-to-charge ratio. The resulting mass spectrum gives a representation of the elemental and/or molecular composition of the material of interest. Often, the list of molecular fragments in the spectrum can be pieced together to obtain a detailed understanding of the chemical structure of the material.

In SIMS, the excitation source consists of a vacuum chamber and an ion gun. Placing the sample in a vacuum keeps the surface clean and allows for easy transport of ions through the instrument. The ion gun produces a stream of ions, called primary ions, that illuminate the sample. As the primary ions reach the sample surface, they transfer energy to the atoms in the solid through elastic collisions in a process called a "collision cascade." A schematic diagram of this process is shown in Figure 1. Enough energy is transferred in the collision cascade to break chemical bonds and to displace atoms from their positions in the solid lattice. A small fraction of these atoms and molecular fragments obtain enough energy to escape the solid and enter the gas phase. Some of the ejected particles are electrically charged (ionized). These particles, called secondary ions, can be passed through a mass spectrometer to generate the SIMS spectrum of the solid.

Figure 1—Simplified illustration of the ion sputtering process.

A number of different ion sources and mass spectrometers are available for performing SIMS experiments which gives the analyst great flexibility in designing how the experiment is performed. The experimental set-up also influences the type of data that can be generated. The wide variety of SIMS instrumentation can be classified into two general categories, dynamic SIMS and static SIMS. Historically, the first SIMS instruments that were developed were dynamic SIMS systems designed to take advantage of the method's high sensitivity which can approach parts per billion (ppb) levels. This is achieved in part by employing a high flux of primary ions. During analysis, a crater is eroded into the solid, producing enough secondary ions to achieve high sensitivity. These instruments have evolved into sophisticated systems designed to measure ultra low concentrations, depth distributions (depth profiles), and lateral distributions (maps of elements). One of the main uses of dynamic SIMS is determining the distribution of dopants in semiconductor devices. This information is indispensable in tailoring the electrical properties of a device and is responsible in part for the dramatic improvements in semiconductor performance. However, the high primary ion fluxes employed in dynamic SIMS break most of the chemical bonds in the solid resulting in minimal structural and chemical information. Thus, dynamic SIMS has limited utility for studying coating systems which are often composed of organic materials.

This limitation was rectified in the late 1960s when Benninghoven introduced the concept of static SIMS. If the total flux of primary ions used in the experiment was held below a certain threshold, statistically each primary ion would interact with the solid in a region that was undamaged by a prior primary ion bombardment. Since these secondary ions had only suffered one collision cascade, they contained a higher percentage of molecular fragments that contained structural information about the materials in the solid. This threshold was dubbed the static limit (<5 x 10^12 ions/cm^2), and the technique static SIMS.

Because the flux of secondary ions that are generated in static SIMS is so low, a mass spectrometer with high efficiency is desirable to maintain adequate sensitivity. The type of spectrometer that has proven most useful for the static SIMS experiment is the time-of-flight (ToF) mass spectrometer. There are no signal-wasting slits in this spectrometer; instead, it relies on differences in flight time through the instrument to separate ions of different masses. Hence, a high percentage of the generated secondary ions is detected in this type of instrument. A schematic of the ToF spectrometer is shown in Figure 2. Note that the ion source generates a pulse of ions rather than a continuous stream. The arrival time of this primary ion pulse starts the time clock as this is the instant when secondary ions are generated. Secondary ions are accelerated to a constant kinetic energy using a grid held at a high electrical potential. They then pass through the long flight tube and hit the detector where the time clock is stopped. The arrival times of the secondary ions at the detector are determined by the simple kinetic energy equation:

\[ KE = \frac{1}{2} m v^2 \]

where KE is the kinetic energy the ion receives from the acceleration grid, m is the mass of the ion, and v is the final velocity the ion. If we substitute length of the flight tube (d) over flight time for velocity, this equation can be rearranged to:

\[ \text{dwell time} = \frac{d}{v} = \frac{\sqrt{2KE}}{m} \]

Hence, flight time is inversely proportional to the square root of the ion's mass. If ions take a short time to reach the detector and heavier ions take longer. The number of ions of a given mass are counted, resulting in an intensity at that mass. The resulting spectrum consists of a plot of intensity of ions as a function of mass. The rich collection of peaks in the resulting spectrum is representative of the composition of the solid and the elements are combined. The ability of ToF-SIMS to measure molecular fragments with high sensitivity makes it a popular choice for studying coating systems.

Table 1 lists some key characteristics of the ToF-SIMS experiment. Both positive and negative ions can be examined with this instrument. This increases the sensitivity of the technique as some materials produce high amounts of positive ions while others produce greater amounts of negative ions. The collision cascade only propagates a few monolayers into the solid so the technique is very...
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| Table 1 – Key Characteristics of the ToF-SIMS Experiment |
| ToF-SIMS Feature | Specification |
| Surface probe | Ion beam |
| Species detected | +/- ions |
| Analysis depth | Monolayers |
| Surface damage | Minimal |
| Detection limit | 1 ppm |
| Spatial resolution | 150 nm |
| Mass resolution | 9,000 |
| Analysis area | 1 or 50 mm² |
| Elements detected | All + isotopes |
| Quantification | Difficult |
| Molecular information | Fragments +/- 20K amu |

Surface sensitive. Operating in the static regime results in minimal surface damage, yet SIMS can be very sensitive with detection limits in the 1 ppm range. The primary ion beam can be focused to a small diameter resulting in a spatial resolution of 150 nm. This allows characterization of small localized areas and/or generation of elemental and molecular fragment maps with high spatial detail. In addition, modern instruments have a movable stage which allows for examination of relatively large areas (up to 50 mm²).

A great advantage of a ToF-SIMS instrument is that sample charging during analysis is not usually a serious problem, even when dealing with non-conducting samples such as paints and polymers. There are two reasons for this. First, since the primary ion source is pulsed, the duty cycle of the primary ions is very low. Typically, the primary ion beam is "off" for only nanoseconds each pulse, then the electron-los "wait" for milliseconds for all of the ions to reach the detector and be counted. Second, during this dead time while waiting for the ions to reach the detector, an electron flood gun can be used to direct a pulse of electrons onto the sample surface, which balances out the positive primary ions and greatly minimizes any sample charging.

Often ions of different elemental compositions will have the same nominal mass. This is illustrated in the comparison of low and high mass resolution spectra included in Figure 3. In this example, both aluminum (Al⁴⁺) and the hydrocarbon fragment C₂H₄⁺ are present. The low mass resolution spectrum, m/Δm = 300, shows only a broad featureless peak at mass 27. However, the high mass resolution spectrum at m/Δm = 8000 reveals two peaks separated by approximately 0.04 amu. Thus, the true masses of these two materials differ enough to allow for their peaks to be separated by operating the spectrometer at high mass resolution. In this example, the broad peak observed at mass 27 is actually composed of both aluminum (mass 26.9815) and the C₂H₄⁺ hydrocarbon fragment at mass 27.0239.

With SIMS analysis, all elements in the periodic table are detectable including hydrogen, which is a significant advantage over other surface analysis techniques. In addition, SIMS can identify different isotopes of a given element which allows for interesting and powerful labeling experiments. Quantification is difficult as concentrations rely on the ionization efficiency of the elements and fragments, a parameter that can vary by several orders of magnitude. However, with effort and the use of suitable SIMS standards, quantification of 10-20% is possible.

**ANALYSIS METHODS**

There is a lot of flexibility in how the SIMS instrument can be operated, which allows the analyst to tailor the experiment to the type of information that is needed. The simplest SIMS experiments is to obtain a spectrum from an area of interest on the surface of a material. Results are often compared to spectra obtained from the surrounding area and/or other samples. For example, Figure 4 shows two SIMS spectra obtained from an automotive paint system where the clearcoat does not completely wet out on the basecoat, causing a crater to form. The spectrum from outside the crater (Figure 4, bottom) exhibits numerous peaks that can be identified as mass fragments from polydimethylsiloxane (PDMS). Silicones are common contaminants that possess low surface energy. The presence of a low-surface energy contaminant will result in poor wetting of the subsequently applied paint layers. Only a few monolayers of PDMS will cause craters to form, so a surface sensitive analysis method such as SIMS is required to identify the presence of this material.

SIMS can also be used to generate chemical and elemental maps showing how elements and compounds are distributed laterally across the surface of a sample. This is accomplished by rastering the primary ion beam over the area of interest and tuning the mass spectrometer to pass only the selected masses of interest. Specific locations on the specimen where the material of interest is present result in a high SIMS signal when the beam is probing that location. The high signal is turned into a bright pixel on the SIMS map. The result is illustrated in Figure 5 which is a SIMS map of the PDMS fragment (mass 73) from one of the paint craters previously discussed. For comparison, the figure also contains an optical micrograph of the paint crater showing the one-to-one correspondence between the crater and the PDMS contaminant on this coating surface. The high SIMS signal is present throughout the crater bottom showing that the contaminant is uniformly distributed in this area. This result confirms that PDMS contamination was the root cause of poor clearcoat wetting and crater formation.

The collision cascade that is the basis for SIMS results in material being removed from the sample surface during the experiment. When a high flux of primary ions is employed, this results in erosion of a crater into the specimen. Measuring the intensity of elements that are ejected from the sample as a function of sputter time results in an elemental profile of the near surface region. The depth profile is useful for identifying how a solid might change in elemental composition from the top surface down into the...
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Figure 3—Comparison of low mass resolution (top) and high mass resolution (bottom) SIMS spectra of the mass 27 region of a coating specimen.
The high sensitivity of SIMS is an important advantage over other surface-sensitive analysis techniques which allows the experiment to be conducted in unique ways. For example, elemental mapping can be combined with sputter depth profiling to generate a three-dimensional image of the specimen. These images show the distributions of elements both laterally across the surface as well as a short depth into the specimen. The utility of generating three-dimensional maps will be demonstrated in the following Applications section by revealing how bake oxides can alter the surface chemistry of organic coatings during the cure process.

**APPLICATIONS OF SIMS TO PAINT TECHNOLOGY**

The ability to analyze insulating samples with high sensitivity and high spatial resolution makes SIMS an ideal method for characterizing paint and coating systems. In the Ford Research Lab, SIMS is routinely used to study and compare the extent of paint weathering and how stabilizing additives are distributed within the coating system. A few examples of these studies are highlighted as follows.

When a paint system is exposed to UV light or sunlight in an oxygen atmosphere, photooxidation occurs. Bonds are broken and atmospheric oxygen reacts with paint molecules to produce carbonyl, ester, alcohol, ketone, and other oxidized species. Because there already are significant amounts of oxygen incorporated in the paint system molecules (approximately 15% atom%), it is impossible to measure the photooxidation products directly with SIMS as any oxygen-containing fragments could be the result of either unstained paint molecules or photooxidation. However, by taking advantage of the ability of SIMS to separate and measure isotopes, the photooxidation products can be labeled with a unique isotope of oxygen, allowing direct measurement of the photooxidation products (see Figure 7). If the paint system is exposed to UV light in an atmosphere of oxygen-18, then oxygen-18 labeled photooxidation products will be created.

Figure 8 outlines the oxygen labeling experiment. A complete automotive paint system (clearcoat/basecoat/primer/electrocoat) is placed in an air-tight chamber fitted with a quartz-UV-transparent window. The chamber is evacuated and back-filled with a (3:2) mixture of oxygen-18 and nitrogen. The paint system is exposed to direct UV light (i.e., through the electrocoat) to UV light. Depending on the reactivity of the paint system, oxygen-18 can permeate into subsurface regions and possibly react with the different coating layers through photooxidation. After exposure, the paint sample is microtomed edge-on to produce a smooth cross-section allowing examination of all the paint layers by SIMS. During SIMS analysis, the primary ion beam is rastered across this smooth cross-section and the resulting secondary ions are detected. The photooxidation products are readily detected with SIMS by analyzing fragments that have unique masses due to the presence of the oxygen-18 isotope. Elemental and chemical fragment maps can be generated to reveal where photooxidation has occurred within the stack of layers forming the paint system.

The use of high-intensity artificial sunlight combined with the sensitivity of the SIMS allows for very short UV exposure times. This greatly accelerates the photooxidation process allowing coating systems to be evaluated in much less time than with conventional weathering tests. Several weeks of exposure in the oxygen-18 cell can produce photooxidation results that are equivalent to several years of exposure in Florida-based weathering experiments. These experiments have been shown to provide critical information to paint design engineers as they can be used to rapidly predict the weathering durability of paint formulations in development for future paint systems.

Figure 9 shows the results of a typical oxygen-18 weathering experiment. On the left side is the oxygen-18 map showing the location where photooxidation had occurred. On the right side is a corresponding oxygen-18 linescan which was generated by drawing a vertical line from the top of the map through to the bottom and then plotting the pixel count value at each linescan point. The oxygen-18 signal associated with the reactivity of each layer within the paint system can be readily identified. The two layers marked "stb" are an oxygen-18 reference standard that is sandwiched over the sample before microtoming. They serve as markers to delineate the location of the coating layers and to calibrate the intensity of the oxygen-18 signal. On the top of the clearcoat layer, a thin layer of surface oxidation is apparent. This thin layer is typically seen on the top clearcoat surface of all exposed paint systems and corresponds to the small amount of photooxidation that occurs on the unprotected paint surface. The remainder of the clearcoat layer shows only a small amount of photooxidation.

In this example, the top surface of the basecoat also shows a small amount of photooxidation indicated by the rise in the oxygen-18 signal at the surface of this layer. For the basecoat, this indicates that the light absorbing additives (UV additives) in the clearcoat are not completely dissolved in the material. An example of a SIMS depth profile is shown in Figure 6. The sample is a semi-conductor device with an aluminum surface film on top of a gallium-cadmium layer on a silicon nitride substrate. The elemental composition of each layer and the contaminants that are distributed within each can be observed in this plot. However, limited chemical or molecular information about the sample is presented in the profile due to the extensive damage caused by the impact of the primary ion beam. Thus, analogous to dynamic SIMS, this SIMS system is mentioned earlier, damage caused by extended exposure of the primary ion beam in sputter depth profiling also limits the utility of this technique for determining molecular or structural information as a function of depth in organic coating systems.
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When a paint system is exposed to UV light or sunlight in an oxygen atmosphere, photodegradation occurs. Bonds are broken and atmospheric oxygen reacts with paint molecules to produce carbonyl acids, alcohols, ketones, and other oxidized species. Because there already are significant amounts of oxygen incorporated in the paint system molecules, it is impossible to measure the photodegradation products directly with SIMS as any oxygen-containing fragments could be the result of either undisturbed paint molecules or photodegradation. However, by taking advantage of the ability of SIMS to separate and measure isotopes, the photodegradation products can be labeled with a unique isotope of oxygen, allowing direct measurement of the photodegradation products (see Figure 7).

If the paint system is exposed to UV light in an atmosphere of oxygen-18, then oxygen-18 labeled photodegradation products will be created. Figure 8 outlines the oxygen labeling experiment. A complete automotive paint system (clearcoat/basecoat/primer/electrocoat) is exposed in an air-tight chamber fitted with a quartz U/V transparent window. The chamber is evacuated and back-filled with a 3:2 mixture of oxygen-18 and oxygen-16 gas and nitrogen. The paint system is exposed top-down (i.e., through the clearcoat) to UV light. Depending on the reactivity of the paint system, oxygen-18 can permeate into subsurface regions and possibly react with the different coating layers through photodegradation. After exposure, the paint sample is microtomed edge-on to produce a smooth cross-section allowing examination of all the paint layers by SIMS. During SIMS analysis, the primary ion beam is rastered across this smooth cross-section and the resulting secondary ions are detected. The photodegradation products are readily detected with SIMS by analyzing fragments that have unique mass due to the presence of oxygen-18. Elemental and chemical fragment maps can be generated to reveal where photodegradation has occurred within the stack of layers forming the paint system.

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Much of the weathering performance of the paint systems included in the examples is governed by the additives that are incorporated into each layer to absorb light photons and prevent them from generating photooxidation reactions. Two important classes of these compounds are long wavelength (400–320 nm) ultraviolet light absorbers (UVA) and hindered amine light stabilizers (HALS), which are effective at preventing photooxidation reactions when incorporated into coatings at low concentrations, typically 1–2%.

The low concentration levels present a challenge for analyzing their presence and location within the coating system. However, the sensitivity and microanalysis capability of SIMS makes it an ideal technique for studying these coating additives.

The chemical formula and structure of two commonly used HALS additives, Tinuvin 123 (mw 738) and Tinuvin 292 (mw 509), are given in Figure 12. Despite their low concentration, these additives can yield a strong ToF-SIMS signal and can be readily detected. Figure 13 includes three spectra that illustrate how SIMS can identify the presence of Tinuvin 123 (mw 738) additive within a top mass spectrum. In Figure 13 shows the high mass portion of the mass spectrum from the surface of an automotive clearcoat containing no additives. The hydrocarbon peaks present at nearly every mass are from the clearcoat chemistry as well as from an adventitious carbon contamination layer on the surface. There are no additives peaks detected in this spectrum. The bottom spectrum contains the mass spectrum of a sample of pure liquid Tinuvin 123 acquired from a one-milimeter droplet deposited on a clean silicon wafer. The clearcoat spectrum shown in the middle spectrum contained a 2% Tinuvin 123 additive. Note that the SIMS data in this mass region is nearly identical to the pure Tinuvin 123 standard. From this data it was determined that the signal strength of the mass 608 peak of Tinuvin 123 in the clearcoat is strong enough to identify as little as 0.2 wt% of the additive in the paint system.

The high sensitivity of ToF-SIMS allows the mapping of these additives in order to track migration and longevity. An experiment was conducted in which a three-layer clearcoat test sample was generated, containing 4%, 2%, and 1% concentrations of Tinuvin 292 light stabilizer. Each layer was completely cured before the next layer was added to the stack. SIMS data were acquired immediately after this paint stack was constructed and again after one week of aging at room temperature in a laboratory environment. The peak at mass 507 was used to characterize the additive as it tracks one of the unique molecular ions for Tinuvin 292. The paint stack was microtomed edge on and then analyzed by ToF-SIMS. The results after one week of aging are shown in Figure 14. The three distinct Tinuvin...
This example illustrates how the oxygen-18 ToF-SIMS technique offers a rapid way to compare the weathering performance of “identical” coatings systems. The SIMS allows one to quickly identify minor differences in weathering that would not be easy to accomplish by any other analytical technique.

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The chemical formula and structure of two commonly used HALS additives, Tinuvin 123 (mw 738) and Tinuvin 292 (mw 509), are given in Figure 12. Despite their low concentration, these additives can yield a strong SIMS signal and can be readily detected. Figure 13 includes three spectra that illustrate how SIMS can identify the presence of the Tinuvin 123 (mw 738) additive within a top paint mass spectrum. In Figure 13 shows the high mass portion of the mass spectrum from the surface of an automotive clearcoat containing no additives. The hydrocarbon peaks present at nearly every mass are from the clearcoat chemistry as well as from an adventitious carbon contamination layer on the surface. There are no additive peaks detected in this spectrum. The bottom spectrum contains the mass spectrum of a sample of pure liquid Tinuvin 123 acquired from a one-nanometer droplet deposited on a clean silicon wafer. The clearcoat spectrum shown in the middle spectrum contained a 2% Tinuvin 123 additive. Note that the SIMS data in this mass region is nearly identical to the pure Tinuvin 123 standard. From this data it was determined that the signal strength of the mass 608 peak of Tinuvin 123 in the clearcoat is strong enough to identify as little as 0.2% of the additive in the paint system.

The high sensitivity of ToF-SIMS allows the mapping of these additives in order to track migration and longevity. An experiment was conducted in which a three-layer clearcoat test sample was generated, containing 4%, 2%, and 1% concentrations of Tinuvin 292 light stabilizer. Each layer was completely cured before the next layer was added to the stack. SIMS data were acquired immediately after this paint stack was constructed and again after one week of aging at room temperature in a laboratory environment. The peak at mass 507 was used to characterize the additive as it tracks one of the unique molecular ions for Tinuvin 292. The paint stack was microtomed edge on and then analyzed by ToF-SIMS. The results after one week of aging are shown in Figure 14. The three distinct Tinuvin
layers are still intact and show minimal dilution when compared to the unaged sample (not shown).

The same experiment was repeated, this time using a different HALS additive, Tinuvin 123, and four layers containing 4%, 2%, 1%, and 0% concentrations of the light stabilizer. The Tinuvin 123 pigment peak at 1660 was selected for mapping this compound as it was an intense peak in the spectrum and had no interfering contributions from the cleavage fragments (see Figure 13). The results from the freshly constructed paint stack (not shown) are similar to the Tinuvin 291 results discussed previously, with four distinct layers visible. However, compared to the Tinuvin 291 additive, the Tinuvin 123 shows extensive diffusion into adjacent layers after just one week of aging (see Figure 15). The signal profile exhibits a continuous gradient and the distinct layers are no longer discernable. The linescan plot clearly shows the extent of the additive migration. It is remarkable that just a change in alkyl end groups, or what might be considered a minor structural change in the Tinuvin molecule (see the chemical compositions in Figure 12), has such a large effect on the diffusion of the additive in the clearcoat. With this information, the Tinuvin additive can be tailored to the given application and designed to either enhance or retard its diffusion within a coating system.

A real example highlights how ToF-SIMS can be used to characterize chemistry induced in a paint coating during bake oven cure. It is known that water vapor and nitrogen oxides form in the combustion exhaust of gas fired bake ovens can react with the surface of a coating during cure.17, 18 For example, experiments revealed that nitrogen oxide radicals can react with and remove a crater-control additive from the surface of an epoxy-based electrocoat during cure. This chemistry did not occur when the epoxy was cured in an electric bake oven. In the example, the top clearcoat of an automotive paint system was cured either in an electric or gas fired oven in order to identify whether differences in surface chemistry would occur. These experiments were analyzed by ToF-SIMS three-dimensional depth profiling, which combines elemental mapping with sputter depth profiling to create a visual representation of where species exist within the near surface in the paint clearcoat. The three-dimensional maps in Figure 16 show the distribution of three different components after either gas or electric oven cure. View 1 includes a map of components A, B, and C, while View 2 removes component A from the map allowing visualization of the layers beneath. It can be seen that Component A forms a thin, uniform coating on both specimens. In contrast, component B forms a thick, uniform film on the panel baked in the electric oven but a thin, patchy layer on the panel baked in the gas-fired oven. This variation in the distribution of component B clarifies why adhesion performance differences were observed on panels baked in the different cure ovens. Based on these results, recommendations were made to specify the precise paint formulation to employ based on the type of bake oven used to cure the coating.

CONCLUSIONS

Previous articles in this journal19, 20 have shown that a ray photography system (XPS) and Auger electron spectroscopy (AES) can be useful surface analysis tools for characterizing materials and coatings. XPS is excellent for accurately determining the composition and chemical state of elements, while AES excels in measuring the integrity of conversion layers used to impede corrosion on metal substrates under coatings.

The great flexibility of ToF-SIMS completes this suite of surface analysis techniques. ToF-SIMS complements XPS and AES with the ability to yield molecular information with high sensitivity at high spatial resolution. The rich structural information provided by SIMS is unique in a surface analysis technique, and the wide variety of experiments that are available to SIMS is the ideal analysis method for studying a variety of coatings issues.

In automotive paint systems the technique can serve as a problem-solving tool to elucidate the presence of water in the coating, while at the same time serve as a premier research tool that can measure and quantify the migration of additives. It ability to measure solutes allows the analyst to perform interesting and powerful labeling experiments that can predict the longevity of coating systems. In the future, ToF-SIMS will serve well as an analysis tool and as a predictive tool to help design and formulate the next generation of coatings for a wide variety of industries and applications.

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References


AUTHORS

Steve J. Stas, Steven L. Kamberene, and Larry P. Haasl, Ford Research and Innovation Center, 2301 Village Rd., Dearborn, MI 48121; stasrn@ford.com.
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The same experiment was repeated, this time using a different HALS additive, Tinuvin 123, and four layers containing 4%, 2%, 1%, and 0% concentrations of the light stabilizer. The Tinuvin 123 fragment peak at 160°/min was selected for mapping this compound as it was an intense peak in the spectrum and had no interfering contributions from clearcoat fragments (see Figure 13). The results from the freshly constructed paint stack (not shown) are similar to the Tinuvin 129 results discussed previously, with four distinct layers visible. However, compared to the Tinuvin 292 additive, the Tinuvin 123 shows extensive diffusion into adjacent layers after just one week of aging (see Figure 15). The signal profile exhibits a continuous gradient and the distinct layers are no longer discernable. The line scans clearly shows the ex- tent of the additive migration, it is remarkable that just a change in aliphatic end groups, or what might be considered a minor structural change in the Tinuvin molecule (see the chemical compositions in Figure 12), has such a large effect on the diffusion of the additive in the clearcoat. With this information, the Tinuvin additive can be tailored to the given application and designed to either enhance or retard its diffusion within a coating system.

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The three-dimensional maps in Figure 16 show the distribution of three different components after either gas or electric oven cure. View 1 includes a map of components A, B, and C, while View 2 removes component A from the map allowing visualization of the layers beneath. It can be seen that Component A forms a thin, uniform coating on both specimens. In contrast, component B forms a thick, uniform film on the panel baked in the electric oven but a thin, patchy layer on the panel baked in the gas-fired oven. This variation in the distribution of component B clarified why adhesion performance differences were observed on panels baked in the different cure oven. Based on these results, recommendations were made to specify the precise paint formulation to employ based on the type of bake oven used to cure the coating.

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AUTHORS

Steven J. Stee. Steven L. Kaben, and Larry P. Haas. Ford Research and Innovation Center, 2301 Village Rd., Dearborn, MI 48121; steemillon@ford.com.