Chemical Depth Profiling of Automotive Coating Systems Using Slab Microtome Sectioning with IR/UV-VIS Spectroscopy and Optical Microscopy

Karlis Adamsons—DuPont Performance Coatings*

Chemical surface/near-surface analysis and depth profiling of high performance automotive coating systems can be done efficiently by commonly available infrared (IR), ultraviolet-visible (UV-VIS) and optical microscopy (OM) measurement technologies. The different stages of mass loss for acrylic/melamine-crosslinked clearcoats modeled after those used in high performance automotive coating systems were explored as a function of exposure time/conditions. Two approaches were used. Transmission mode IR experiments were conducted to monitor mass loss in isolated clearcoats. OM was used to monitor mass loss in clearcoats that are part of actual multilayered coating systems. UV-screener (UVA) permanence and interphase mixing (i.e., between clearcoat and basecoat layers) as well as general chemistry depth profiling studies of model acrylic/melamine-crosslinked and acrylic/melamine+silane-crosslinked clearcoats were done as a function of system preparation and exposure time/conditions. UVA depth profiles were obtained using slab microtomy sectioning co-planar to the surface, followed by solvent extraction and UV-VIS solution analysis to monitor UVA content as a function of section mass and thickness. General chemistry depth profiles were obtained using slab microtomy sectioning (as mentioned previously), followed by ATR (IR) analysis to monitor changes in the photooxidation index values and the spectral envelop in the 2600-3800 cm^{-1} range. The approaches described herein do not require expertise/equipment that is available to only a few, thus increasing the potential utility of such tools.

INTRODUCTION

Infrared (IR) and ultraviolet-visible (UV-VIS) based measurement technologies have been successfully applied in surface/near-surface analysis and depth profiling of high performance automotive coating systems.[1] Automotive finishes are typically multilayered and are applied over metal or plastic substrates, as shown in *Figure* 1. This report highlights recent success in understanding the chemistry, including factors like component concentration heterogeneity, segregation/stratification effects, interlayer mixing, and/or migration.[2-5] This, in turn, gives the product developer tools to determine factors such as ultraviolet light absorber/active hindered amine light stabilizer (UVA/HALS) effectiveness and permanence,[6-10] correlations between chemical composition changes and mechanical performance changes,[5,11,12] degradation mechanisms and associated kinetics,[13-17] and estimates of expected service lifetimes.[18-21] Effective design often requires a comprehensive understanding of a coating or coating system, from the chemical building blocks to overall customer driven system performance (*Figure* 2). Over recent years this chemical information has become essential to the creation of current/future products, allowing incorporation of state-of-the-art materials (i.e., crosslinkers, monomers, additives, catalysts) and allowing suppliers to take advantage of the newest in processing/manufacturing technologies. This understanding also permits controlled, customer-driven evolution of products with tailored chemical composition, physical properties, mechanical performance, and, of course, appearance characteristics.

This work evolved from a need to quickly and reliably assess the impact of climatic factors on automotive finishes.[22-25] The factors commonly studied include solar radiation (i.e., primarily UV wavelengths encountered outdoors), heat (i.e., surface or substrate temperatures, thermal expansion/contraction cycles), moisture (i.e., dew, rain, humidity), pollutants (i.e., acid rain, ozone, aerosols), biological (i.e., plant, insect, or animal residue), and wind (i.e., impact of airborne particulate matter over the long term). The studies involved acrylic polyol polymer based network chemistry, including those that are acrylic/

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*Marshall R&D Laboratory, Philadelphia, PA, 19146.

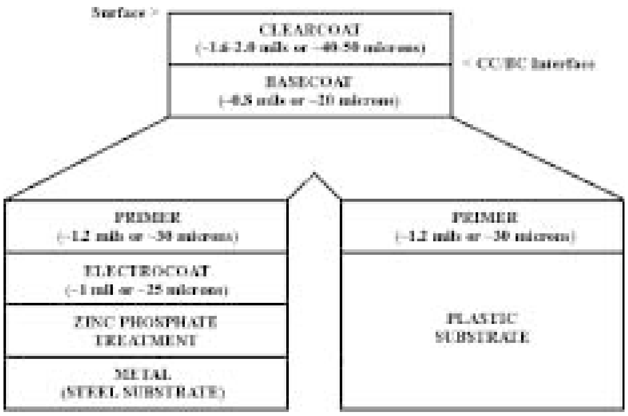

Figure 1—Automotive coating system cross-section. Left branch illustrates sequence of layers over a steel substrate. Right branch illustrates sequence of layers over a plastic substrate. Typical thickness ranges are given for each layer.

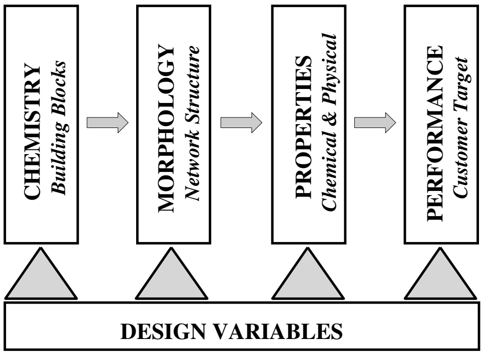

Figure 2—Levels of complexity in automotive coating system design. The most basic level includes chemical components with specific structure and functionality. The second level includes the three-dimensional arrangement of the components or "building blocks." The third level includes specific chemical or physical properties (i.e., surface chemistry, micro/macro-hardness, network density). The highest level includes targeted field (in-use) performance (i.e., scratch and mar characteristics, acid etch resistance, fracture resistance, appearance) in the context of expected service life.

melamine-crosslinked (*Figure* 3A) and acrylic/melamine-crosslinked/silane-crosslinked (*Figure* 3B).

Historically, the automotive industry, including coating system suppliers and car manufacturers (i.e., primary coating component/system consumers), has long relied on appearance-based measurements to monitor finish condition and durability. Measurements commonly used include gloss, distinctness of image (DOI), orange peel, haze, color, and visual inspection. A degradation (chemical bond/function change) cartoon of surface/near-surface acrylic/melamine-crosslinked or acrylic/melamine/silane-crosslinked networks is shown in *Figure* 4, suggesting the extent of cumulative change caused by the above climatic factors over a longer exposure time frame. The primary limitation in using appearance-based measurements is in the time required for significant (i.e., measurable and reproducible) changes to take place. [26-30] Years may be required for significant appearance changes to take place in typical outdoor environments. Although the time frame is somewhat reduced with various types of accelerated weathering/exposure, time frames are still typically on the scale of thousands of hours. The objective is to further reduce the time frame needed to determine service life performance, and to do so with high confidence. From the business standpoint focus must be on market opportunity, which can be relatively short in duration, perhaps a few years or less. Today's competitive

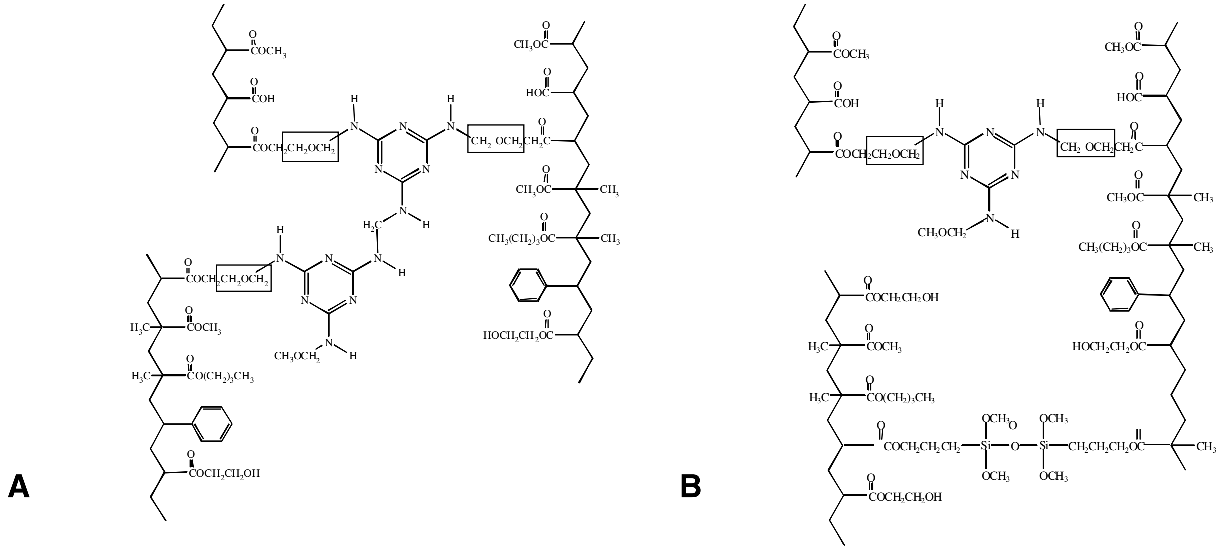

Figure 3—A. Exploded view of a typical acrylic melamine-crosslinked automotive clearcoat network. B. Exploded view of a typical acrylic melamine/silane-crosslinked automotive clearcoat network.

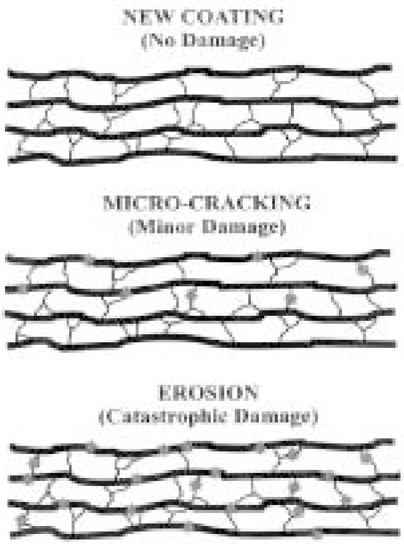

Figure 4—Degradation cartoon of surface/near-surface acrylic/melamine-crosslinked or acrylic/melamine+silane-crosslinked network through acrylic chain and/or melamine crosslink bond scission. Sequence illustrates: (top) a clearcoat recently cured with no detectable chain/bond scission; (middle) a clearcoat with minimal exposure to agents (causing hydrolysis or photooxidation) capable of some chain/bond scission; and (bottom) a clearcoat with extensive exposure to agents (causing hydrolysis and/or photooxidation) capable of catastrophic damage, including mass loss through erosion.

automotive finishes marketplace requires a continuous reduction in the product design/development cycle, forcing decisions to be made before all appearance testing is complete. Therefore, realizing this objective has become increasingly urgent.

Fortunately, changes in chemical composition/distribution, physical properties, and mechanical performance can often be monitored well before appearance-based changes are sufficient to be measured. The sequence of events (i.e., chemical composition changes) for degradation of a typical acrylic/melamine-crosslinked automotive system is illustrated in *Figure* 5. The time frame required for determining product durability or service life could be significantly reduced by taking advantage of nonappearance based measurements as illustrated in *Figures* 6A and B. The demand for decreased cycle time requires that the automotive finishes industry identify measurement technologies to take advantage of these other material and property changes in predicting the durability or service life. This report documents application of chemical measurement technologies that require moderate resource investment in hardware, software, expertise, and training, but that also provide detailed characterization of coating layer or system chemistry.

A variety of measurement technologies have been used for surface and interface analysis, as well as depth profiling, in the study of automotive original equipment manufacturer (OEM) and refinish coating systems.[1,2,31-33] The ability to obtain detailed chemical, physical, and/or mechanical information for a given layer, interface, or at a specific depth locus, will be increasingly important in designing future systems. Consumers are demanding products that have long-term durability with respect to appearance. In order to deliver such products, suppliers must, out of necessity, do the appropriate nonappearance-based characterization "homework."

The volume element referred to for surface/near-surface characterization is dependent on the measurement technology applied, but was typically within the first few microns of the surface. Depth profiling was top-down in the normal direction. Steps (i.e., increments) in a depth profile are, of course, a function of the sampling approach, but were on a scale of ~6-10 microns in work detailed herein.

EXPERIMENTAL

Materials

Two types of automotive clearcoat chemistry were studied, including: (a) acrylic polyol crosslinked with alkoxylated melamine formaldehyde resin, catalyzed with dodecyl-benzenesulfonic acid, and cured 30 min at 130°C; and (b) acrylic polyol crosslinked with alkoxylated melamine formaldehyde and silane resins, catalyzed with dodecylbenzene-sulfonic acid, and cured 30 min at 130°C. A standard solventborne black basecoat was used in producing the model automotive coating system samples.

Methods

Slab Microtoming: A Leica microtome model # Polycut E was used in all slab sectioning. The blade is Part

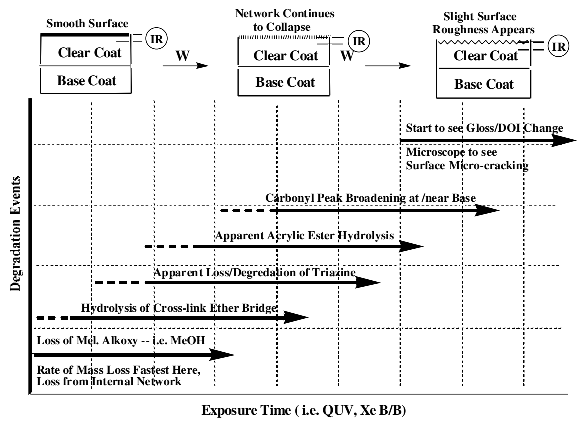

Figure 5—Timeline for acrylic/melamine-crosslinked automotive system degradation. The timeline cartoon is not drawn to scale, but rather depicts a typical sequence of events for this type of network. Note: Various chemical events can be monitored well in advance of appearance events becoming evident. All of these changes in chemistry can be readily monitored, especially by techniques that are surface/near-surface specific and/or through depth profiling. Also, mass loss due to migration and evaporation of volatiles from the bulk can be observed prior to detectable visual appearance changes.

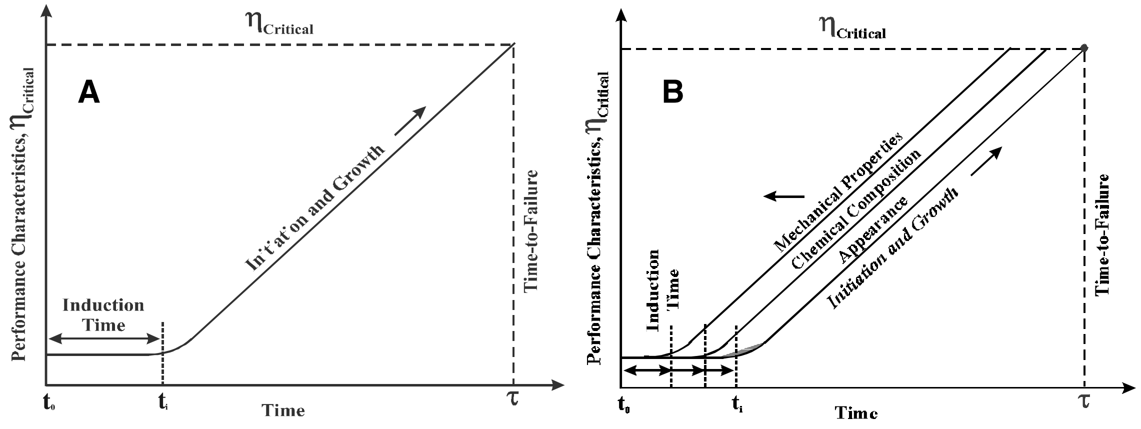

Figure 6—A. Performance characteristic(s) versus exposure time/conditions, including field use that leads to (as defined) product failure. $\eta_{critical}$ is the threshold beyond which coating system performance is no longer acceptable. τ is time-to-failure. B. Effective shift in $\eta_{critical}$ versus τ curves due to earlier detection of chemical composition or physical/mechanical properties resulting from the aforementioned exposure.

#021611739, 16 cm, D Profile Tungsten Carbide Knife, Helmut Patzig of Microscopical Optical Consulting Inc. Knife sharpening was done by Micro Data Tech, Newport, RI. The double-sided tape used to anchor the samples to the cutting block was Kapton Polyimide, Silicone Adhesive, two-sided CHR product # K100, 2 in. (~50 mm) wide from HR Carlson Inc., Greenwich CT.

The depth resolution is limited by the thickness of the slab-microtomed sections. Practical handling dictates use of sections ~6 µm or thicker. Automotive coating sections that are thinner than ~5-6 µm tend to shred while handling. Aging (i.e., photooxidation, hydrolysis) of the coatings tends to mechanically weaken the coatings even more, increasing handling difficulty.

ACCELERATED EXPOSURE: QUV FS-40 exposure uses a QUV weathering chamber manufactured by Q-Panel Company, Cleveland, OH. Protocol for exposure was the Surface Vehicle Standard, SAE J2020™, "Accelerated Exposure of Automotive Exterior Materials Using a Fluorescent UV and Condensation Apparatus." The bulb used was the FS-40 bulb, which has a spectral energy distribution with a high-energy UV component not present in natural sunlight. There have been recent shifts to using FS-340 and Xenon as light sources, both of which do not have a significant component below the 290 nm wavelength. For this work the FS-40 bulb was thought to be appropriate because of the extensive exposure database available. The cycle used was eight hours UV exposure at 70°C, followed by four hours condensation at 50°C.

Xe B/B exposure uses an Atlas Weather-ometer model Ci-65 (weathering chamber) manufactured by Atlas Electrical Devices Company, Chicago, IL. Protocol for exposure was the Surface Vehicle Standard, SAE J-1960 Jun-89™. A Xenon lamp with an inner/outer borosilicate filter set was used (0.45 W/m^2 at 340 nm), which has a spectral energy distribution similar to natural sunlight in the 270-650 nm range. The cycle used was two hours irradiation (including 40 min light alone, 20 min light with front specimen spray, and 60 min light alone) at 70°C and one hour dark (including back rack spray) at 38°C.

Infrared Analysis

Infrared (IR) analysis of general surface chemistry, and associated changes, was done either directly using an attenuated total reflectance (ATR) technique or by IR-microscopy in transmission-mode of a skived/microtomed section. Depth profiling of the general chemistry was done by ATR analysis of slab microtomed sections of a given coating layer or coating (i.e., multilayered) system. No additional sample preparation was required. An important advance in recent years has been the design and application of internal reflection elements (IREs) such as ZnSe which has a thin layer of diamond on the surface. Here the IRE effectively acts as if it is ZnSe, but with a much more durable surface. Under sufficient contact pressure the material opposite the diamond will deform to provide uniform surface contact, optimizing the quality of the resultant ATR spectrum. Depth profiling of additives, specifically benzotriazole-type UV-screeners, was done using UV-VIS spectroscopy (*Figure* 7). ATR mode analysis was done using a Nicolet Nexus 470 FT-IR ESP equipped

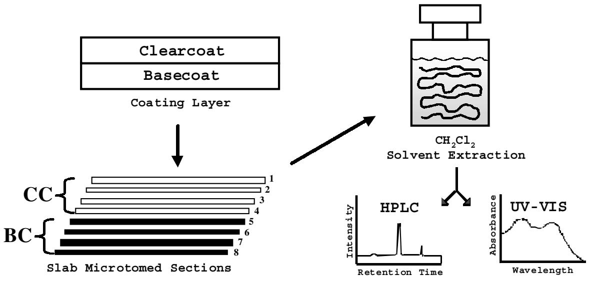

Figure 7—Depth profiling of UVA solvent extractable additives. Slab sections are typically prepared 6-10 µm thick. Methylene chloride (CH_2Cl_2) was used as extraction solvent for benzotriazole-based UV-screener additives. Chromatography (i.e., HPLC) and spectroscopy (UV-VIS) techniques were used to quantitate additive levels after normalizing to the weight (mass) of each slab microtomed section.

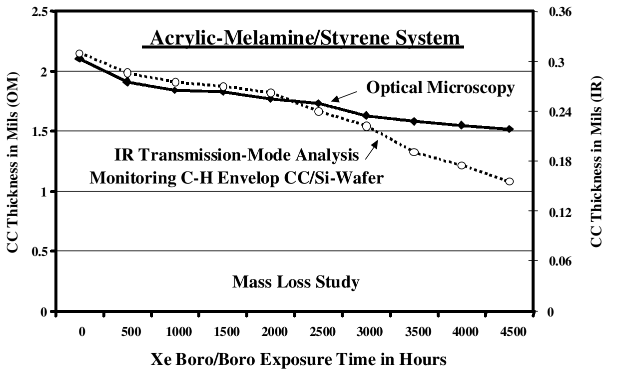

Figure 8A—Acrylic/melamine-crosslinked CC erosion as a function of Xenon boro/boro exposure time/conditions. Key: OM = optical microscopy used to measure CC thickness via cross-section; IR = infrared analysis using Si-wafer/CC to monitor CC thickness via C–H envelop area changes. Note 1 Mil (unit common to the coatings industry) = 25.4 µm.

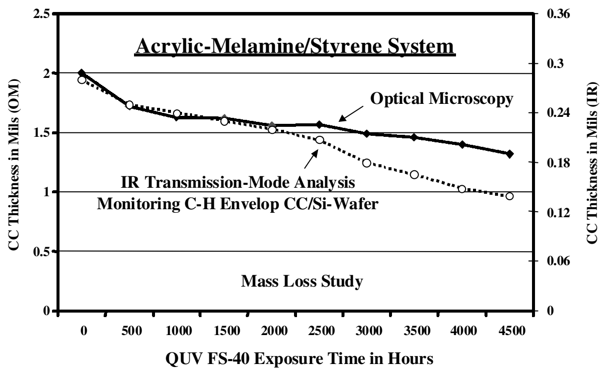

Figure 8B—Acrylic/melamine-crosslinked CC erosion as a function of QUV FS-40 lamp exposure time/conditions. Key: OM = optical microscopy used to measure CC thickness via cross-section; IR = infrared analysis using CC/Si-wafer to monitor CC thickness via C–H envelop (area) changes. Note 1 Mil = 25.4 µm.

with a Smart Dura SamplIR module. Transmission mode analysis was done using a Nicolet 20SXC FTIR spectrophotometer equipped with a standard sampling compartment.

Mass loss determinations of CC on Si-wafers (CC/Si-wafers) were done in transmission mode. CC was applied on Si-wafers by either drawdown or spin coating. The targeted thickness was in the 6-7 mm range. The samples are locked into an aluminum support allowing for accurate repositioning of samples after each QUV FS-40 or Xe B/B exposure period. The area under the methylenic (C–H) envelop in the ~2700-3700 cm^{-1} range is used to determine relative mass loss.

Ultraviolet-Visible (UV-VIS) Analysis

UV-VIS analysis of CH_2Cl_2 (solvent) extract solutions was done using an HP 8452A diode array spectrophotometer equipped with the UV-Visible ChemStation Rev. A.06.03 [48]. When 5 mL CH_2Cl_2 was used to extract a ~7-8 µm thick × 25 µm × 25 µm area slab section, the solutions were run without further dilution in a standard quartz 1 cm × 1 cm cell. A period of approximately one day was used to extract the UVA (benzotriazole type) molecules from the solvent swollen slab sections.

RESULTS AND DISCUSSION

Material loss determinations were done by both and optical microscopy (OM) techniques. *Figure* 8A shows the material loss for a CC subjected to Xe B/B exposure time/conditions. Both IR and OM techniques show similar rates of loss for a period of ~2500 hr. Note that IR analysis monitored a decrease in the area of the methylenic en-

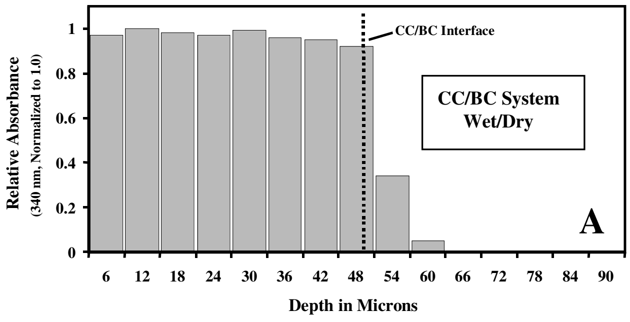

Figure 9A—UVA (benzotriazole type, Tinuvin® 384) distribution for an unexposed CC/BC solventborne system. The acrylic/melamine+ silane-crosslinked CC was formulated with standard UVA loading and the BC was formulated without UVA. The BC was fully cured prior to application of CC layer. Slab microtomy used to obtain ~6 µm thick sections followed by CH_2Cl_2 extraction. Note locus of sections is relative to the CC surface. Analysis by UV-VIS spectroscopy.

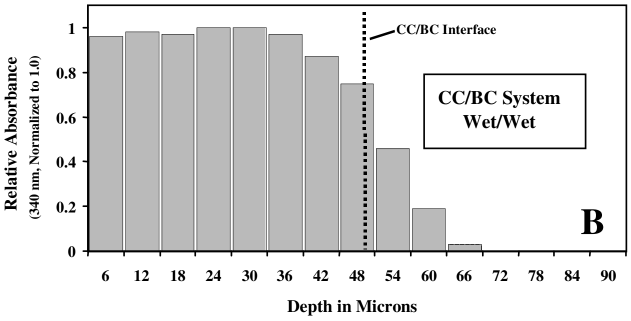

Figure 9B—UVA (benzotriazole type, Tinuvin® 384) distribution for an unexposed CC/BC solventborne system. The acrylic/melamine+ silane-crosslinked CC was formulated with standard UVA loading and the BC was formulated without UVA. The BC/CC bilayer was applied wet on wet as per industry practice. Slab microtomy used to obtain ~6 µm thick sections followed by CH_2Cl_2 extraction. Note locus of sections is relative to CC surface. Analysis by UV-VIS spectroscopy.

velop (i.e., mass loss via chemistry), while OM analysis monitored decrease in the physical thickness of the coating layer. During this period the material loss may be primarily due to loss of volatiles from the bulk. Over time the melamine crosslinker releases low molecular weight species such as methanol, butanol, and formaldehyde. Melamine and relatively low molecular weight acrylic oligomer species that, during cure, are not integrated into the network are also easily washed/extracted from the CC surfaces. It is observed that minimal changes in surface morphology occur up to this point. After ~2500 hr, the rate of CC material loss for the CC/Si-wafer appeared to be relatively greater. However, note that the starting thickness of the CC on the CC/Si-wafer sample is ~7 µm and that the CC on the coating system sample is ~50 µms. In both cases, surface morphology changes are becoming evident. The hypothesis is that mechanisms such as photooxidation and hydrolysis are continually causing microscopic network damage (*Figure* 4), but that it requires a threshold of cumulative damage to be reached before erosion is apparent. If one assumes that the rate of erosion is independent of CC thickness, then the fraction of material lost for the thinner sample will be significantly higher. *Figure* 8B shows material loss for a CC subjected to QUV FS-40 exposure time/conditions. Both IR and OM techniques show similar rates of material loss for a period of ~2000 hours. These results are analogous to those indicated for the aforementioned Xe B/B exposure study. The same explanations should also apply.

Depth profiling of CC/BC bilayers prepared wet (CC with standard commercial UVA loading) on dry (cured BC without UVA) and prepared wet (CC with standard commercial UVA loading) on wet (BC without UVA) highlights differences in UVA distribution. The wet-on-dry case (*Figure* 9A) shows some migration/mixing of UVA into the previously cured BC layer, but is significant only in the top ~6-12 µm of the BC. This is not unexpected since some swelling of the top of the BC by solvents from the applied CC will occur, allowing local migration/mixing of UVA. The wet-on-wet case (*Figure* 9B) shows more pronounced migration/mixing of UVA into the uncured BC layer, and thus UVA is observed in the top ~12-18 µm of the BC following coating system cure. Note that, due to the thickness of the microtomed sections, there is a low probability of slicing exactly along the CC/BC interface. Thus, some of the UVA associated with the BC (particularly in *Figure* 9A) resulted from the crudeness of the slices. OM was used to determine the approximate locus (i.e., depth) of the CC/BC interface in these studies.

Due to the material loss encountered in longer term Xe B/B and QUV FS-40 type exposures, there are, of course, correspondingly fewer slab microtomed sections observed for aged CCs. When changes in chemical composition or mechanical performance are reported, particularly for coatings subjected to > 2000-2500 hr under these exposure conditions, it should be done in the context of physical loss (or erosion) of material previously at the surface. For example, *Figure* 10A shows a UVA depth profile for an acrylic/melamine-crosslinked CC prior to such exposures. *Figure* 10B shows a UVA depth profile for the same CC taken from a full coating system (i.e., CC/BC/Primer/E-coat/Steel-substrate) subjected to 5000 hr QUV FS-40 exposure. Note the apparent reduction in the overall CC thickness.

Chemical depth profiles can be used effectively for determining UVA permanence over time as a function of weathering or exposure conditions. A comparison between depth profiles shown in *Figures* 10A and 10B can provide information as to the level of UVA protection at a

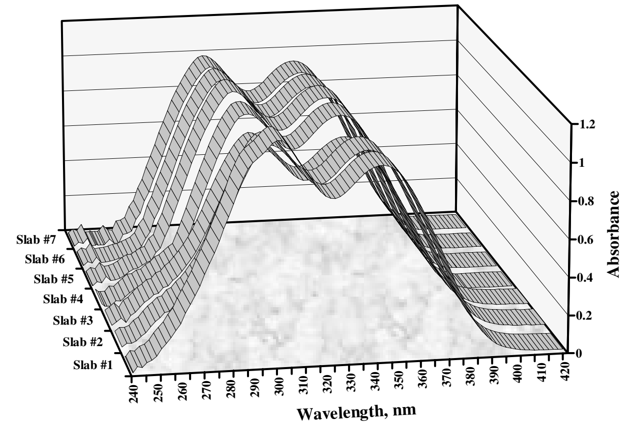

Figure 10A—UVA depth profile for an acrylic/melamine-crosslinked CC prior to exposure. Application is wet (CC) on dry (cured BC). UV-VIS spectra obtained using an HP 8452A diode array spectrophotometer equipped with UV-Visible ChemStation Rev. A.06.03 (48). Slab microtomy sampling used to obtain ~8 µm thick sections at ~25 µm × 25 µm area. Extraction overnight in 5 mL CH_2Cl_2. UV-VIS spectra were normalized to corresponding section weights.

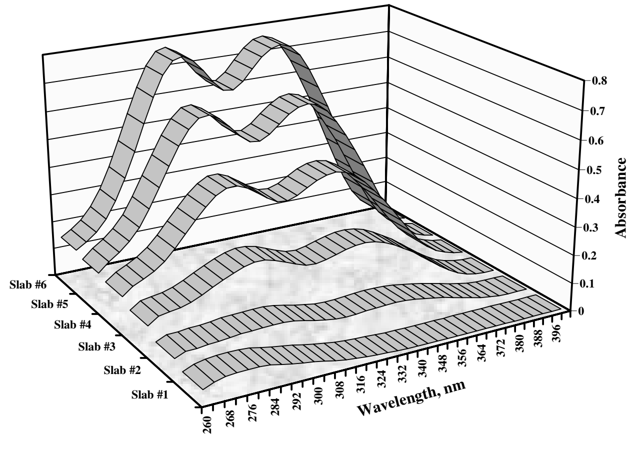

Figure 10B—UVA depth profile for an acrylic/melamine-crosslinked CC after long-term 5000 hr QUV FS-40 exposure. Application is wet (CC) on dry (cured BC). UV-VIS spectra obtained using an HP 8452A diode array spectrophotometer equipped with UV-Visible ChemStation Rev. A.06.03 (48). Slab microtomy sampling used to obtain ~7 µm thick sections at ~25 µm × 25 µm area. Extraction overnight in 5 mL CH_2Cl_2. UV-VIS spectra were normalized to the corresponding section weights.

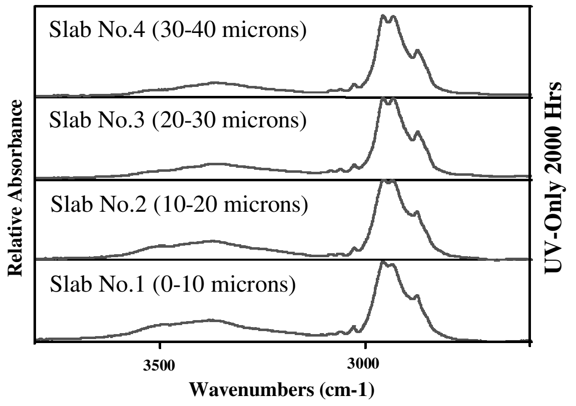

Figure 11A—UV-only (QUV cabinet) 2000 hr exposure depth profile for top 40 µms of clearcoat layer containing acrylic polyol with melamine crosslinking. ATR (IR) spectra obtained from each slab microtomed section. Spectral region displayed 2600-3800 cm^{-1}, highlighting methylenic (–CH) and hydroxy/amine/carboxylic acid (–OH, –NH, –COOH) envelops.

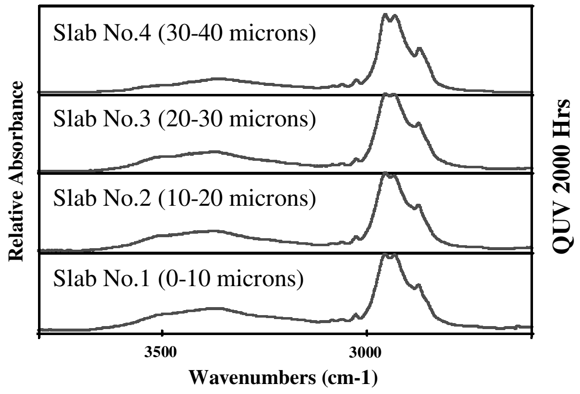

Figure 11B—QUV UVA-340 (QUV cabinet) 2000 hr exposure depth profile for top 40 mms of clearcoat layer containing acrylic polyol with melamine crosslinking. ATR (IR) spectra obtained from each slab microtomed section. Spectral region displayed 2600-3800 cm^{-1}, highlighting changes in the methylenic (–CH) and hydroxy/amine/carboxylic acid (–OH, –NH, –COOH) envelops.

specific locus (i.e., surface ~7-8 µm thick section) or net UVA content in a specific coating system layer (i.e., clearcoat). If one assumes that the durability of a coating at a given locus is a function of the UVA concentration, then such information may allow some degree of confidence in durability prediction. Appropriate separation techniques, including chromatography (i.e., HPLC) or spectrometry (i.e., potassium ionization of desorbed species MS, GPC with electrospray MS), should permit identification or characterization of the degradation species. This work is currently in progress. Another type of information obtained from depth profiling of these coating systems is extent of melamine crosslinker or acrylic chain incorporation. Evidence for a gradient of the more surface-active species resulting during cure can be observed in *Figure* 10A in the ~250-290 nm range. Soft ionization of desorbed species (K^+IDS) MS analysis of CH_2Cl_2 extract solutions indicates that standard cure conditions (30 min at 265°F) result in a gradient of primarily melamine species. The highest level of extractable melamine species is found at/near the surface. Note the presence of a slightly elevated UVA concentration in the first section relative to deeper sections. Over a longer period of time (5000 hr QUV FS-40) the amount of extractable UVA results in the depth profile shown in *Figure* 10B. Although not currently determined, factors such as physical migration and chemical degradation may account for the overall concentration and depth profile.

General chemistry depth profiles were obtained by ATR (IR) analysis of slab microtomed sections. *Figure* 11A illustrates the changes in the ~2600-3800 cm^{-1} range as a function of depth and 2000 hr UV-only (QUV cabinet with UVA-340 lamp, but no water/humidity) exposure. *Figure* 11B illustrates the changes in the same range as a function of depth and 2000 hr QUV (UVA-340 lamp and water/humidity; standard SAE J2020™ cycle conditions) exposure. Note the somewhat subtle increase in the relative intensity of the [–OH,–NH,–COOH] envelop when water/humidity is a factor during the exposure cycle. This result is consistent with an increase in hydrolysis. Also, the changes are evident at a deeper level into the CC, but are not uniform throughout. This suggests that water migration/penetration into the CC is controlled by the network chemistry, indicating a more hydrophobic environment at deeper levels.

Chemical depth profiles have been determined top-down by other less commonly available measurement technologies,[1] including photoacoustic spectroscopy (PAS), UV-VIS confocal imaging, Raman confocal imaging, variable-angle ATR, and dynamic SIMS. Chemical depth profiles have also been determined via cross-section by other less commonly available measurement technologies,[1] including UV-VIS microscopy, Raman microprobe, and ToF-SIMS. In addition, the latter analyses have been successfully used in creation of species or function specific chemical (i.e., component distribution) maps, with select applications reported on exposed automotive coating systems.

Surface and depth profile characterization tools such as those described allow developers of automotive coating systems an intimate look at chemical composition and component distribution/redistribution. Studies are underway to determine correlation between the chemistry and mechanical performance, all of which tend to be early indicators of impending appearance and in-use changes. Since chemical changes can be monitored long before appearance changes are observed, tools to document chemistry and to follow chemical changes have great potential in predicting service life performance. The measurement technologies and sampling techniques described increases the efficiency of gathering such chemical information, regardless of locus. Databasing and data-mining tools are also being developed, which will permit rapid and effective use of this chemical information in rapid evolution of future products.

SUMMARY

General chemical composition and extractable additive (benzotriazole-type UV-screener) distribution in automotive coating systems have been effectively determined with the experiments described. Knowledge of the CC chemistry at a given locus and/or CC layer thickness changes (i.e., CC mass loss by IR analysis) as a function of exposure time/conditions provides a better understanding of the inherent species migration and degradation processes, as well as the associated kinetics. Chemical depth profiling also provides a more detailed understanding of the relationships between chemical composition (i.e., functionality and/or distribution) to product performance (i.e., chemical, physical, mechanical, and appearance properties). These relationships are becoming ever more important in designing future products, since original equipment (car/truck) manufacturers are now demanding coating systems that have longer-term durability with respect to appearance, while maintaining their chemical resistance and mechanical performance properties. The hope is that the sampling techniques and measurement technologies described here will provide researchers and product developers insight into the application of these tools in addressing their own material characterization needs.

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